

RESEARCH ARTICLE | AUGUST 28 2025

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J. Chem. Phys. 163, 084313 (2025)

<https://doi.org/10.1063/5.0280381>



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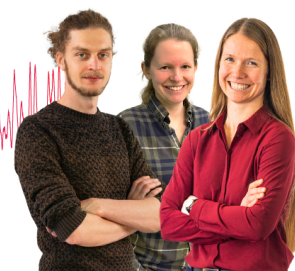
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Cite as: J. Chem. Phys. 163, 084313 (2025); doi: 10.1063/5.0280381

Submitted: 12 May 2025 • Accepted: 31 July 2025 •

Published Online: 28 August 2025



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ABSTRACT

Interatomic Coulombic electron capture (ICEC) is an environment-mediated process in which a free electron attaches to a species by transferring excess energy to a neighbor. While previous theoretical investigations assumed fixed nuclei, recent studies indicate that nuclear dynamics significantly influences the ICEC process. In this work, we incorporate the vibrational motion into an analytical model of the ICEC cross section, including both energy and electron transfer. To validate this approach, we compare the results to the adiabatic-nuclei approximation based on fixed-nuclei *ab initio* R-matrix calculations. We apply our theory to the helium–neon dimer, which is ideal for studying diverse dynamical effects. We show that while vibrational dynamics can slightly reduce ICEC efficiency, ICEC remains dominant over photorecombination and can trigger dimer dissociation. Accounting for the nuclear motion also enables to describe the broadening of the electron spectrum and enables evaluation of temperature-dependent cross sections—capabilities beyond the reach of fixed-nuclei approaches.

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I. INTRODUCTION

The capture of free electrons by atoms, ions, molecules, and quantum dots is a fundamental process with wide-ranging implications in both basic and applied sciences. It plays a key role in astrophysics and plasma physics, where it influences stellar processes and ionized gases.^{1,2} Furthermore, electron capture is critical for understanding electrochemical and photochemical reactions, impacting biological systems³ and solid-state technologies.⁴

One such electron capture mechanism is the interparticle Coulombic electron capture (ICEC) that occurs exclusively in systems embedded within an environment.⁵ In ICEC, a free electron is captured by an electron acceptor (A), which in this work will be a cation, while the excess energy is transferred via Coulomb

interaction to a neighboring electron donor (D), leading to the ionization of D,

$$e_k^- + A + D \rightarrow A^- + D^+ + e_{k'}^-. \quad (1)$$

This environment-mediated coupling significantly enhances the probability of electron capture across various systems, as shown in theoretical studies.^{6,7} A detailed overview of the mechanism and its theoretical basis can be found in Ref. 8.

In most earlier studies, theoretical approaches to investigate ICEC have assumed static nuclei, neglecting the influence of nuclear dynamics.⁸ However, recent results⁹ reveal that nuclear motion, particularly vibrational dynamics, can substantially affect the efficiency and outcome of the process. Findings for related processes, such as

resonant two-center photoionization¹⁰ and two-center dielectronic recombination,¹¹ further support the importance of nuclear motion in interparticle electron capture. These findings highlight the necessity of incorporating nuclear dynamics into ICEC models to achieve a more complete theoretical understanding.

In this work, we extend the previous analytical energy and electron transfer model^{6,12} of ICEC by explicitly incorporating the relative nuclear motion between the interacting partners, providing intuitive insights grounded in the physical characteristics of the individual systems. We apply this approach to the positively charged helium–neon dimer and benchmark our results against the adiabatic-nuclei approximation based on fixed-nuclei *ab initio* R-matrix calculations, which offer a rigorous quantum mechanical treatment of ICEC as a scattering process.^{13,14} Using both approaches, we assess the impact of nuclear dynamics on ICEC and aim to provide theoretical guidance for future experimental efforts.

This paper is organized as follows: we first establish the theoretical framework in Sec. II, incorporating nuclear degrees of freedom into the analytical model of ICEC. In Sec. III, we describe the approximations taken to include nuclear dynamics into the R-matrix approach. Section IV describes the physical parameters of our example of a weakly bound system, the positively charged helium–neon dimer. Section V outlines the computational details. The results for the ICEC cross sections of the helium–neon dimer are discussed in Sec. VI. Finally, we summarize our findings and their implications in Sec. VII. We use atomic units ($\hbar = m_e = e = 1$) throughout this paper, unless explicitly mentioned otherwise.

II. NUCLEAR DYNAMICS IN THE ANALYTICAL ENERGY AND ELECTRON TRANSFER MODEL OF ICEC

From a scattering theory perspective, ICEC is a multichannel inelastic process in which an incoming electron interacts with a target.^{6,15} It is characterized by a cross section that quantifies its probability for a given electron energy. Our goal is to derive an approximation to the ICEC cross section that includes nuclear dynamics.

We consider the process in Eq. (1), where an electron is captured by an electron acceptor A and a neighboring electron donor D emits an electron. Both species can be atoms, molecules, or ions. The corresponding differential cross section is

$$\frac{d\sigma}{d\Omega_{k'}} = \frac{1}{(2\pi)^2} \frac{k'}{k} |M|^2, \quad (2)$$

where $\Omega_{k'}$ is the solid angle of the outgoing electron and M is the transition matrix element,^{6,15} in our case between two vibronic states Ψ_α accounting for the vibrational dynamics between A and D. We describe the vibronic states as a single term of the Born–Huang expansion,^{16,17}

$$|\Psi_\alpha(\mathbf{r}, R)\rangle = |\phi_\alpha(\mathbf{r}; R)\rangle |v_\alpha(R)\rangle, \quad (3)$$

where ϕ_α is the electronic wave function, v_α is the nuclear wave function, $\mathbf{r}$ are the electronic coordinates, and R is the distance between the centers of mass of A and D.

As shown in Ref. 12, the antisymmetry of the electronic wave function leads to two distinct contributions to M ,¹⁵

$$M(\mathbf{k}' \leftarrow \mathbf{k}) = M_{\text{el}}(\mathbf{k}' \leftarrow \mathbf{k}, e_k^- = e_{k'}^-) + M_{\text{en}}(\mathbf{k}' \leftarrow \mathbf{k}, e_k^- \neq e_{k'}^-). \quad (4)$$

The electron transfer term, M_{el} , assumes the incoming and outgoing electrons are the same and describes direct scattering accompanied by electron relocation from donor to acceptor. The energy transfer term, M_{en} , involves capture of the incoming electron by A, with excess energy transferred to D, which emits an electron.

These two mechanisms dominate at different distances between the two particles: electron transfer requires short-range interactions, while energy transfer remains effective even at larger separations.¹⁸ In the following, we focus on incorporating nuclear dynamics into the energy transfer contribution before turning to electron transfer.

A. Energy transfer contribution to ICEC

For the energy transfer contribution M_{en} , we extend the derivation from Refs. 5 and 6, incorporating the necessary modifications to account for nuclear motion. Here, we treat the process as events taking place separately on A and D, linked by the energy transfer via first order of perturbation theory. This approach is referred to as “asymptotic” or “virtual photon” approximation in the literature.⁸ We will see that this enables us to express the cross section in terms of physical parameters of A and D,^{5,6} which can be found in the literature or obtained from experiments.

We begin by approximating the initial (*i*) and final (*f*) electronic wave functions as products of the individual states of A and D,

$$\begin{aligned} |\phi_i\rangle &= |\phi_{A,k}\rangle |\phi_D\rangle, \\ |\phi_f\rangle &= |\phi_{A-}\rangle |\phi_{D^+,k'}\rangle, \end{aligned} \quad (5)$$

where the energy-normalized state $\phi_{A,k}$ ($\phi_{D^+,k'}$) describes A (D^+) together with the incoming (outgoing) electron of momentum $\mathbf{k}$ ($\mathbf{k}'$).⁵ This is justified if A and D are far enough away from each other and the electronic interaction between them can be assumed to be weak.

By using Eqs. (5) and (3) and employing the Born–Oppenheimer approximation, the transition matrix element within the first order of perturbation theory for a single initial and final state is

$$M_{\text{en}} = \langle v_f | \langle \phi_{A-} | \langle \phi_{D^+,k'} | \hat{V} | \phi_{A,k} \rangle | \phi_D \rangle | v_i \rangle, \quad (6)$$

where $\hat{V}$ is the Coulomb interaction between the charges of the two systems and v_i (v_f) is the nuclear wave function of the initial (final) state according to Eq. (3).

For sufficiently large distance R between A and D, we expand $\hat{V}$ in a Taylor series around R and retain the leading term that yields a non-zero contribution to the transition matrix element M_{en} . This term corresponds to the dipole–dipole interaction of the two charge densities,

$$\hat{V}_{\mu\mu} = \frac{1}{R^3} (\hat{\mu}_A \cdot \hat{\mu}_D - 3 (\mathbf{u}_R \cdot \hat{\mu}_A) (\mathbf{u}_R \cdot \hat{\mu}_D)), \quad (7)$$

where $\mathbf{u}_R$ is the unit vector pointing from A into the direction of D. As the electronic dipole moment operators $\hat{\mu}_A$ and $\hat{\mu}_D$ of A and D are independent of R , we can separate the integration over electronic and nuclear coordinates.

Substituting Eqs. (6) and (7) into Eq. (2) yields the differential cross section in the lowest-order approximation for the energy transfer contribution to ICEC,

$$\frac{d\sigma}{d\Omega_{\mathbf{k}'}} = \frac{1}{(2\pi)^2} \frac{k'}{k} \left| \left[\boldsymbol{\mu}_A \cdot \boldsymbol{\mu}_D - 3 (\mathbf{u}_R \cdot \boldsymbol{\mu}_A) (\mathbf{u}_R \cdot \boldsymbol{\mu}_D) \right] \langle v_f | R^{-3} | v_i \rangle \right|^2, \quad (8)$$

where $\boldsymbol{\mu}_A = \langle \phi_A^- | \hat{\boldsymbol{\mu}}_A | \phi_{A,k} \rangle$ and $\boldsymbol{\mu}_D = \langle \phi_{D^+} | \hat{\boldsymbol{\mu}}_D | \phi_D \rangle$ are the electronic transition dipole moments. To obtain the total cross section, Eq. (8) is integrated over the solid angle $\Omega_{\mathbf{k}'}$ of the outgoing electron and averaged over the incoming electron angle $\Omega_{\mathbf{k}}$. To facilitate this integration, one expands the plane waves in the initial and final states in terms of spherical waves.^{5,19}

The dipole transition moments involved in the process can be related to the corresponding photorecombination (PR) and photoionization (PI) cross sections. The PR cross section of the electron acceptor A is given by¹⁹

$$\sigma_A^{\text{PR}}(\varepsilon) = \frac{4\pi^2 \omega^3}{3c^3 k^2} |\boldsymbol{\mu}_A|^2, \quad (9)$$

where c is the speed of light and ε is the kinetic energy of the incoming electron, corresponding to momentum k . The quantity ω is the energy of the emitted photon, corresponding here to the excess energy of the electron capture. Its value is given by the sum of ε and the electron attachment energy of A, which is equal to the ionization potential of A^- , IP_{A^-} .

Similarly, the PI cross section for the electron donor D is¹⁹

$$\sigma_D^{\text{PI}}(\omega') = \frac{4\pi^2 \omega'^3}{3c^3 k^2} |\boldsymbol{\mu}_D|^2, \quad (10)$$

where ω' corresponds to the energy available to ionize D. The difference of ω' and ω is $\Delta\omega_{fi} = E_f - E_i$, where E_i (E_f) is the energy of the initial (final) vibrational state of the dimer. As a result, the kinetic energy of the outgoing electron is

$$\varepsilon' = \omega - \Delta\omega_{fi} - \text{IP}_D, \quad (11)$$

where IP_D is the ionization potential of the electron donor D.

Using these two expressions, we arrive at an approximation to the energy-transfer contribution to the ICEC cross section for the transition from vibrational state $|v_i\rangle$ of AD to vibrational state $|v_f\rangle$ of A^-D^+ ,

$$\sigma(k, v_i \rightarrow v_f) = \frac{3c^4}{4\pi} \frac{\sigma_A^{\text{PR}}(\varepsilon) \sigma_D^{\text{PI}}(\omega - \Delta\omega_{fi})}{\omega^3 (\omega - \Delta\omega_{fi})} \left| \langle v_f | R^{-3} | v_i \rangle \right|^2. \quad (12)$$

Having established a working expression for the energy transfer contribution to ICEC, we now turn our attention to the electron transfer mechanism.

B. Electron transfer contribution to ICEC

For the electron transfer contribution M_{el} , we extend the derivation from Ref. 12, modifying to account for nuclear motion, analogously to Sec. II A. In this approach, the overlap of the electronic wave functions is not neglected, but instead approximated by the overlap of two Gaussians.^{12,20–22}

In the electron transfer contribution, we assume that we can distinguish the scattering electron from the bound electrons of

(AD). We further assume that we can treat the interaction of the continuum electron and the target as a simple interaction of charge distributions, neglecting electron correlation. We can then write our initial and final electronic states as

$$\begin{aligned} |\phi_i\rangle &= |\phi_{\text{AD}}\rangle |\mathbf{k}+\rangle, \\ |\phi_f\rangle &= |\phi_{A^-D^+}\rangle |\mathbf{k}'-\rangle, \end{aligned} \quad (13)$$

where ϕ_{AD} ($\phi_{A^-D^+}$) is the electronic wave function of the dimer and $\mathbf{k}$ ($\mathbf{k}'$) is the initial (final) momentum vector of the continuum electron. We denote with + (−) the incoming (outgoing) scattering state,¹⁵ where the continuum electron scatters off of AD (A^-D^+).

Although we do not consider the electrons of A and D as distinguishable, the electron correlation between them can still be treated as a perturbation. Applying Eqs. (3) and (13) within the Born–Oppenheimer approximation, the transition matrix element at first order of perturbation theory for a single initial and final state is given by

$$M_{\text{el}} = \langle v_f | \langle \mathbf{k}'- | \langle \phi_{A^-D^+} | \hat{V} | \phi_{\text{AD}} \rangle | \mathbf{k}+ \rangle | v_i \rangle, \quad (14)$$

where $\hat{V}$ is the Coulomb interaction between electrons situated on A (including the incoming electron) and on D, and now, ϕ neglects the correlation between electrons on A and D as the zero-order wave function.

We can again apply the multipole expansion to $\hat{V}$ [cf. Eq. (7)], but the lowest contributing order is now the R^{-1} term, as we assume the wavefunctions of A and D to have a nonzero overlap. We obtain the transition matrix element as

$$M_{\text{el}} = \left\langle v_f \left| \frac{\langle \phi_{A^-D^+} | \phi_{\text{AD}} \rangle \langle \mathbf{k}'- | \mathbf{k}+ \rangle}{R} \right| v_i \right\rangle. \quad (15)$$

Assuming a single Slater determinant for the initial and final electronic states of the dimer, the overlap $\langle \phi_{A^-D^+} | \phi_{\text{AD}} \rangle$ reduces to the product of the virtual orbital of A, which accepts an electron, ϕ_A^A , and the orbital of D, which donates said electron, ϕ_D^D . Approximating these two orbitals as Gaussians of widths a_A and a_D results in the following expression for the overlap:¹²

$$S_{\text{AD}}(R) = \langle \phi_A^A | \phi_D^D \rangle = \left(\frac{a_A a_D}{a_A^2 + a_D^2} \right)^{3/2} \exp \left(-\frac{R^2}{2(a_A^2 + a_D^2)} \right). \quad (16)$$

Note that the true overlap of the two orbitals can vanish due to their symmetries.

Now, let us gather the results for the approximation to the differential cross section of the electron transfer path of ICEC by substituting Eq. (15) into Eq. (2),

$$\frac{d\sigma}{d\Omega_{\mathbf{k}'}} = \frac{1}{(2\pi)^2} \frac{k'}{k} \left| \left\langle v_f \left| \frac{S_{\text{AD}}(\mathbf{k}' - \mathbf{k}+)}{R} \right| v_i \right\rangle \right|^2. \quad (17)$$

To obtain the total cross section σ , we integrate Eq. (17) over the solid angle $\Omega_{\mathbf{k}'}$ of the outgoing electron. The angular dependence enters only through the overlap of the incoming and outgoing scattering states, $\langle \mathbf{k}' - \mathbf{k}+ \rangle$. Assuming the potential of the dimer can be

approximated by its spherical component, we employ a partial wave expansion of the scattering states,¹⁵ leading to

$$\langle \mathbf{k}' - |\mathbf{k}+ \rangle = \frac{1}{2\pi^2 k k'} \int_0^\infty dr \sum_{\ell=0}^\infty (2\ell+1) \psi_{\ell\mathbf{k}'}^-(r, R) \times \psi_{\ell\mathbf{k}}^+(r, R) P_\ell(\hat{\mathbf{k}}' \cdot \hat{\mathbf{k}}), \quad (18)$$

where the hat denotes unit vectors, $\psi^\pm$ are the radial incoming and outgoing scattering wave functions, and P_ℓ is the Legendre polynomial. The angular parts of this expansion—the Legendre polynomials—do not depend on R , hence we can carry out the integration over $\Omega_{\mathbf{k}'}$. If we then define

$$J_\ell := \int_0^\infty dr \psi_{\ell\mathbf{k}'}^-(r, R) \psi_{\ell\mathbf{k}}^+(r, R), \quad (19)$$

the total cross section reads

$$\sigma_{\text{el}} = 32\pi \frac{1}{\sqrt{\varepsilon^3 \varepsilon'}} \sum_{\ell=0}^\infty (2\ell+1) \left| \langle v_f | S_{\text{AD}} J_\ell R^{-1} | v_i \rangle \right|^2, \quad (20)$$

where $\varepsilon(\varepsilon')$ is the kinetic energy of the incoming (outgoing) electron. Note that compared to Ref. 12, the integral defining J_ℓ is not squared and that we cannot simplify the absolute square further due to the integration over R .

We further assume an exponential decrease in J_ℓ squared, as in Ref. 12,

$$J_\ell^2 \approx C \exp\left(-\frac{\ell(\ell+1)}{K_{\text{AV}}^2}\right), \quad (21)$$

where we defined $K_{\text{AV}}^2 = (a_{\text{A}} + R)^2 \varepsilon + (a_{\text{D}} + R)^2 \varepsilon'$, and an ad hoc dependence of C on $\varepsilon' - \varepsilon$,

$$C \approx \bar{C} \exp\left(-\frac{|\varepsilon' - \varepsilon|}{d}\right), \quad (22)$$

where $\bar{C}$ and d are fitting parameters taken from Ref. 12.

With both the energy and electron transfer contributions established for a single vibrational transition, let us summarize the results.

C. Final considerations of the analytical energy and electron transfer model

In our model, the total ICEC cross section is given by the sum of energy and electron transfer contributions,

$$\sigma = \sigma_{\text{en}} + \sigma_{\text{el}}, \quad (23)$$

with expressions provided in Eqs. (12) and (20), respectively. Although these mechanisms could, in principle, interfere, their transition amplitudes are only comparable over a narrow range of R .¹² Since the integration spans all internuclear distances, their direct interference contributes only marginally and an incoherent sum of cross sections is appropriate.

So far, we have considered only a single vibrational transition. In practice, ICEC involves transitions to multiple bound and

dissociative final states. For the former, we sum over all final vibrational states v_f , and for the latter, we integrate over the dissociation energy E ,

$$\sigma(k, v_i) = \sum_f \sigma(k, v_i \rightarrow v_f) + \int_{E=0}^{E_{\text{max}}} \frac{d\sigma}{dE}(k, v_i \rightarrow E) dE, \quad (24)$$

where $E_{\text{max}} = \omega - \text{IP}_{\text{D}} + E_i$ is the maximum dissociation energy allowed by energy conservation, corresponding to the limit of $\varepsilon' = 0$.

To account for a thermal population in the initial state, we average over initial vibrational states using a Boltzmann distribution, which introduces temperature dependence,

$$\sigma(k, T) = \frac{1}{\sum_i e^{-E_i/(k_B T)}} \sum_i e^{-E_i/(k_B T)} \sigma(k, v_i), \quad (25)$$

where E_i is the energy of vibrational state v_i , T is the thermodynamic temperature, and k_B is the Boltzmann constant. This temperature dependence is a key feature of our model, made possible by explicitly including nuclear motion.

With this theoretical foundation, we now turn to the R-matrix approach.

III. NUCLEAR DYNAMICS IN THE R-MATRIX APPROACH

We aim to compare the results of the semi-empirical model introduced in Sec. II with a more rigorous approach. We calculate the cross section for the vibronic transitions using an approximation building upon the fixed-nuclei scattering T-matrix. We evaluate this T-matrix using the *ab initio* R-matrix method,^{23,24} which is well suited for low-energy electron–molecule scattering calculations. The fixed-nuclei cross section is given in terms of the T-matrix as²⁴

$$\sigma_{i \rightarrow f}(\varepsilon; R) = \frac{\pi}{k^2} \sum_{lm'l'm'} |T_{ilm \rightarrow f'l'm'}(\varepsilon, \varepsilon'; R)|^2, \quad (26)$$

where l, m (l', m') denote all the contributing partial waves of the incoming (outgoing) electron.

We employ the adiabatic-nuclei (AN) approximation²⁵ to compute the vibrationally resolved scattering cross section. In this approach, the vibrational scattering matrix is constructed as follows:

$$T_{iv_i \rightarrow f v_f}(\varepsilon, \varepsilon') = \langle v_f | T_{i \rightarrow f}(\varepsilon, \varepsilon'; R) | v_i \rangle_R, \quad (27)$$

The incoming ε and the outgoing ε' electron energies in the vibrationally resolved picture are related by the conservation of energy [an equivalent of Eq. (11)],

$$\varepsilon + \mathcal{E}_i^{v_i} = \varepsilon' + \mathcal{E}_f^{v_f}, \quad (28)$$

where $\mathcal{E}_i^{v_i}$ ($\mathcal{E}_f^{v_f}$) is the energy of the initial (final) vibronic state. If we define the energy reference as the energy of the final electronic state in the limit of large R , then $\mathcal{E}_f^{v_f} = E_f$. The approximation utilizes the fixed-nuclei on-shell T-matrix, $T_{i \rightarrow j}(\varepsilon, \varepsilon'; R)$, where the incoming ε and the outgoing ε' electron energies are related by the R -dependent conservation of energy,

$$\varepsilon + E_i(R) = \varepsilon' + E_f(R), \quad (29)$$

where $E_i(R)$ [$E_f(R)$] is the potential energy curve of the initial (final) electronic state. This means that $\tilde{\epsilon}' \neq \epsilon'$, i.e., the cross section for a vibronic transition at given outgoing electron energy ϵ' is calculated from fixed-nuclei data corresponding to a different, in fact R -dependent, outgoing energy $\tilde{\epsilon}'$. This is because the AN approximation does not take the energy of the vibrational states into account. Nevertheless, it has been used successfully for vibrational,²⁶ rotational,²⁷ and electronic²⁸ excitations and it is valid for electron energies larger than the corresponding excitation thresholds.²⁵

In ICEC, dissociation in the final state can be prominent, making the adiabatic-nuclei approximation invalid in a larger range of electron energies above the ICEC threshold. To remedy this, we use the energy-balanced adiabatic-nuclei (EBAN) approximation introduced for calculating electron impact dissociation of H_2 in Ref. 29. In this approximation, we use

$$T_{iv_i \rightarrow f v_f}(\epsilon, \epsilon') = \langle v_f | T_{i \rightarrow f}(\tilde{\epsilon}, \epsilon'; R) | v_i \rangle_R, \quad (30)$$

instead of Eq. (27), and

$$\tilde{\epsilon} + E_i(R) = \epsilon' + E_f(R), \quad (31)$$

instead of Eq. (29). In this variant, the vibronic outgoing electron energy coincides with the fixed-nuclei outgoing electron energy, and the non-equivalence is transferred to the incoming electron energies.

So far, we have not specified whether the vibrational states are bound or dissociative. In our study, the initial vibrational states are going to be bound, and in the final state, we consider both bound and dissociative ones. For the bound-bound transitions, Eq. (26) can be readily applied, replacing i by iv_i and f by fv_f . For bound-dissociative transitions, a similar formula holds

$$\frac{d\sigma_{iv_i \rightarrow f v_E}(\epsilon)}{d\epsilon'} = \frac{\pi}{k^2} \sum_{lm'l'm'} |T_{iv_i lm \rightarrow f v_E l' m'}(\epsilon, \epsilon')|^2, \quad (32)$$

provided that the dissociative states v_E are energy-normalized.^{29,30} We note that for dissociative states, the vibrational energy E_f equals the kinetic energy release (KER).

The dissociative character of the final states also hints at why, in Eq. (30), we should use the correct outgoing electron energy instead of the incoming electron energy. In our case, the fixed-nuclei incoming electron energy $\tilde{\epsilon}$ differs from the correct one, ϵ , on the energy scale of the dissociation threshold of the initial electronic state. If we took the correct incoming electron energy, the fixed-nuclei outgoing energy would have differed from the correct one on the scale of the dissociation energy. This discrepancy varies for different ϵ' with a fixed ϵ and is severe when most of the energy is released as KER and the outgoing electron is slow. For the ICEC scenarios which correspond to electronic deexcitation, we have to use AN because EBAN introduces an unphysical threshold. An illustration and more detailed discussion of the AN and EBAN cross sections can be found in the [supplementary material](#). Let us also note that for very low incoming electron energy, both AN and EBAN break down. Further work is necessary to properly understand how their performance compares, perhaps by an analytically or numerically exactly solvable model.

With both the analytical model and the R-matrix approach in place, let us introduce the physical system we shall investigate.

TABLE I. Parameters of the surfaces X, A, and B from Ref. 31: equilibrium distance R_e , dissociation energy D_e , harmonic vibrational frequency ω_e , and electronic energy E at equilibrium. The last column denotes corresponding asymptotic ($R \rightarrow \infty$) states.

State	R_e (Å)	D_e (cm ⁻¹)	ω_e (cm ⁻¹)	E (a.u.)	Asymptotics
X $^2\Sigma^+$	1.43	5200	911	-130.943 49	He + Ne ⁺ ($2p_z^{-1}$)
A $^2\Pi_{1/2}$	2.42	283	152	-130.921 76	He + Ne ⁺ ($2p_{x/y}^{-1}$)
B $^2\Sigma^+$	2.66	343	152	-130.807 54	He ⁺ ($1s^{-1}$) + Ne

IV. THE SYSTEM STUDIED: (HeNe)⁺

In the previous sections, we introduced two approaches for calculating vibrationally resolved ICEC cross sections. Section II presented an analytical model extended to include nuclear dynamics, accounting for both energy and electron transfer mechanisms. In Sec. III, we built upon the *ab initio* fixed-nuclei R-matrix results and included the nuclear dynamics using the AN or EBAN approximation, referred to as the R-matrix. We apply both methods to the (HeNe)⁺ dimer as an example of a weakly bound system.

To contextualize the calculations, we begin with the structural and electronic properties of (HeNe)⁺. Neon and helium have ionization potentials of 21.56 and 24.59 eV, respectively. Energy conservation implies that when He⁺ captures an electron, the electron affinity is sufficient to ionize neon. In contrast, electron capture by Ne⁺ requires additional kinetic energy.

Vibrational dynamics are described using Morse potentials for the three lowest electronic states, offering analytic solutions. Parameters from Ref. 31 are used and listed in Table I. Without loss of generality, we assume the dimer is aligned along the z axis. The ground state X asymptotically corresponds to HeNe⁺ ($2p_z^{-1}$), with

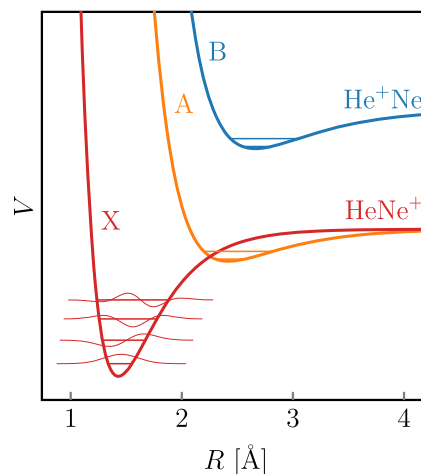


FIG. 1. Schematic potential energy surfaces X, A, and B corresponding to the three lowest electronic states of (HeNe)⁺. For ease of comparison, surfaces A and B are multiplied by 4 and B is shifted down by 2.5 eV. The figure is taken from E. M. Jahr and J. Šenk (2025). "Influence of vibrational motion and temperature on Interatomic Coulombic electron capture - Figures," Figshare. <https://doi.org/10.6084/m9.figshare.28883378.v2>.³² Copyright 2025 Author(s), licensed under a Creative Commons Attribution 4.0 License.

the charge localized on neon, also noted in the last column of Table I. The first excited state A—not to be confused with the electron acceptor—corresponds to $\text{HeNe}^+(2p_{x/y}^{-1})$, sharing the same asymptotic energy as X. The second excited state B, $\text{He}^+(1s^{-1})\text{Ne}$, is the first with the charge on helium.

This system provides an excellent platform for studying a wide range of vibrational effects, as it features potential energy surfaces with distinct characteristics. The excited states A and B are shallower and shifted toward larger internuclear distances compared to X (see Fig. 1), providing a diverse range of conditions found in different physical systems.

V. COMPUTATIONAL DETAILS

In this section, we outline the computational framework used to model ICEC in the $(\text{HeNe})^+$ dimer. We first describe the numerical implementation of the analytical model, followed by the details of the R-matrix calculations.

A. The analytical energy and electron transfer model

To implement the model, we require (i) atomic photoionization cross sections for the energy transfer term in Eq. (12), (ii) Gaussian widths for the electron transfer term in Eq. (20), and (iii) vibrational states of the dimer. The implementation³³ was carried out in Python using the mpmath module,³⁴ which supports confluent hypergeometric functions with complex arguments—necessary for the dissociative Morse states adopted from Ref. 35.

Photoionization cross sections for He and Ne were taken from Ref. 36. Since the three degenerate $2p$ orbitals in Ne contribute equally under an isotropic field approximation,¹⁹ we divide the total cross section by three: $\sigma_{2p_\ell}^{\text{PI}} = \sigma^{\text{PI}}/3$.

For the electron transfer contribution, we follow Ref. 12, using Gaussian widths in Eq. (16) based on covalent radii³⁷ scaled by $\alpha = 1.6$. Electron transfer efficiency depends on orbital orientation: in the ground electronic state (X), the $2p_z$ orbital of Ne^+ aligns with the interatomic axis and facilitates the transfer. In the excited A state, the perpendicular $2p_{x/y}$ orbital results in negligible overlap with He's s -orbital, suppressing electron transfer. Consequently, we include electron transfer only in X to B and B to X transitions and restrict A to B and B to A transitions to the energy transfer mechanism.

We use the analytical bound and dissociative solutions of the Morse potential from Ref. 35. Dissociative states are discretized and normalized within a finite box, $R \in (0, 10 \text{ \AA}]$. All but the highest bound vibrational state of each electronic state remain well confined within this range. We, therefore, exclude the highest initial bound state due to unreliable overlap with dissociative states in the finite box; this is justified at low temperatures where its population is negligible. Final vibrational states are not restricted, as long as only bound initial states are considered—excluding the highest initial state. Energy-normalized dissociative cross sections are obtained by multiplying the corresponding cross sections from box-normalized dissociative states of energy E_f with the density of states, $\rho(E_f) = 2/|E_{f+1} - E_{f-1}|$.

Unless stated otherwise, we assume the dimer starts in the vibrational ground state of the initial electronic state and sum over all final vibrational states. For fixed-nuclei calculations, the ICEC

cross section is evaluated at the equilibrium distance R_e of the initial electronic state.

B. The R-matrix approach

We employed the fixed-nuclei R-matrix method as implemented in the UKRmol+ suite.³⁸ Molecular orbitals for the scattering calculations were obtained using the MOLPRO^{39–41} implementation of the Hartree–Fock method applied to the HeNe system, with the cc-pVDZ basis set. Continuum orbitals were constructed using a radial GTO basis optimized for an R-matrix radius of $a = 13a_0$, as provided in the UKRmol+scripts release,⁴² and included partial waves up to angular momentum $l = 6$.

As the target orbitals of the scattering model, we used the $1s$ orbital of Ne as frozen and the $2s$, $2p$, and $3p$ orbitals of Ne and the $1s$ and $2s$ orbitals of He as active. We included four target states into the scattering calculations, as only those are energetically accessible in the investigated region of scattering energies. The R-matrix was propagated to $r_{\text{af}} = 80a_0$.

We performed the fixed-nuclei R-matrix calculations for interatomic distances ranging from $R = 1.5a_0$ to $R = 9.5a_0$ with a step of $\Delta R = 0.5a_0$. To evaluate the dissociative states, we use the sine discrete variable representation (DVR)⁴³ in the confinement box $R \in (0, 10 \text{ \AA}]$ with 3000 grid points.

We use the AN approximation for the transitions B to X and B to A and the EBAN approximation for the transitions X to B and A to B. The R -integral in Eqs. (27) and (30) for AN and EBAN, respectively, is facilitated using a composite 10-point Gauss–Legendre quadrature.^{44,45} Because the dissociative states in the energy range studied can oscillate with high frequencies, it is necessary to interpolate the fixed-nuclei T-matrices because performing the *ab initio* calculations on such a dense grid would be excessively computationally demanding. In the region of energies that we investigate, there are no resonances and the T-matrix elements are smooth both in energy and in R . The cubic spline interpolation⁴⁶ is used. The R -quadrature is carried out over the extent of the DVR box. For obtaining the T-matrix values outside the range of the fixed-nuclei calculations, we used linear extrapolation for $R < 1.5a_0$ and $1/R^3$ extrapolation for $R > 9.5a_0$ motivated by the form of the asymptotic approximation⁶ to fixed-nuclei ICEC cross sections that is valid in this range. The implementation is available at Ref. 47.

With the computational framework in place, we proceed to analyze the ICEC cross sections for the $(\text{HeNe})^+$ dimer.

VI. RESULTS AND DISCUSSION

In this section, we present the computed ICEC cross sections for the $(\text{HeNe})^+$ dimer, examining how vibrational motion affects the efficiency of electron capture. We compare results from the analytical model⁴⁸ and the R-matrix approach,⁴⁹ highlighting key trends and deviations.

We begin by discussing the energy transfer and electron transfer contributions to ICEC in Sec. VI A. In Sec. VI B, we investigate the total cross section for ICEC from the ground vibrational state and compare to the transitions from the excited vibrational states. Then, we present the temperature-dependent ICEC cross section in Sec. VI C. Last but not the least, we investigate the spectrum of the outgoing electron for a fixed incoming electron energy in Sec. VI D.

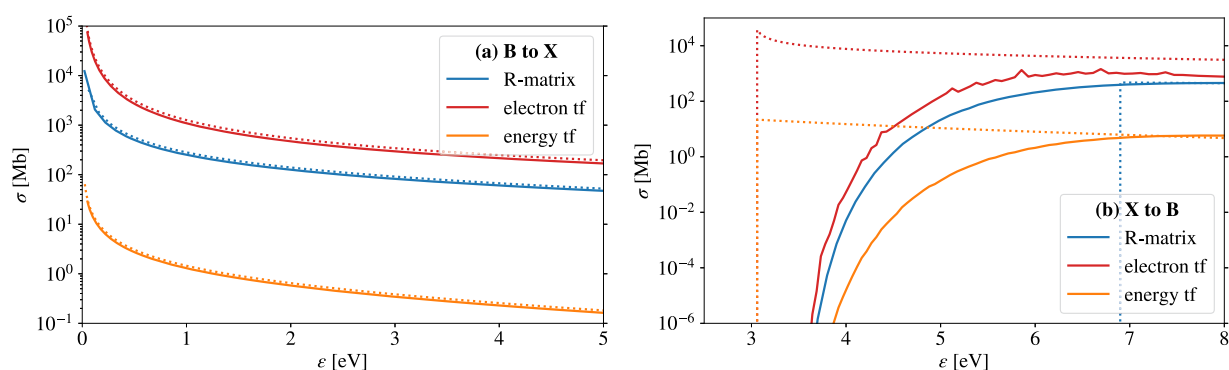


FIG. 2. ICEC cross section vs incoming electron energy ϵ for $\nu_i = 0$ from energy transfer (orange), electron transfer (red), and R-matrix (blue). The solid lines indicate nuclear dynamics; the dotted lines indicate fixed-nuclei results. The fixed-nuclei model uses asymptotic energies while R-matrix considers a vertical transition at R_0 , resulting in different thresholds for X to B. The figure is taken from E. M. Jahr and J. Šenk (2025). "Influence of vibrational motion and temperature on Interatomic Coulombic electron capture - Figures," Figshare. <https://doi.org/10.6084/m9.figshare.28883378.v2>.³² Copyright 2025 Author(s), licensed under a Creative Commons Attribution 4.0 License.

A. Energy vs electron transfer for B to X and X to B

The analytical model, introduced in Sec. II, includes both energy and electron transfer contributions to ICEC. While energy transfer applies to all transitions, electron transfer is only relevant

when the state X is involved (see Sec. V A). We, therefore, focus on the B to X and X to B transitions in this chapter.

Figure 2 shows the corresponding ICEC cross sections as a function of the incoming electron energy. The electron transfer contribution (red) dominates over energy transfer (orange) by three

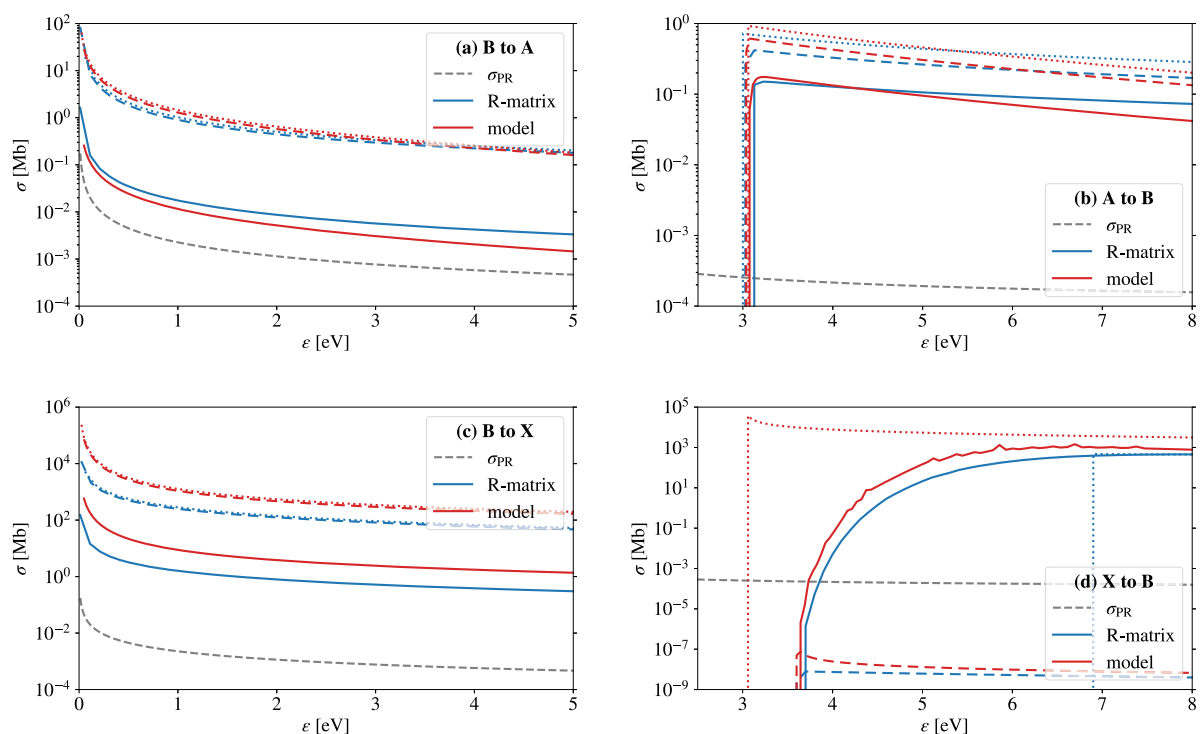


FIG. 3. ICEC cross section vs incoming electron energy ϵ for $\nu_i = 0$. Left panel: electron captured by He^+ ; right panel: captured by Ne^+ . R-matrix (blue) and model (red) results: the solid lines represent bound-dissociative, the dashed lines represent bound-bound transitions, and the dotted lines represent fixed-nuclei results. In panels (a) and (c), the dotted and dashed lines nearly coincide. The dashed gray lines represent photorecombination cross sections on the capturing atom. The figure is taken from E. M. Jahr and J. Šenk (2025). "Influence of vibrational motion and temperature on Interatomic Coulombic electron capture - Figures," Figshare. <https://doi.org/10.6084/m9.figshare.28883378.v2>.³² Copyright 2025 Author(s), licensed under a Creative Commons Attribution 4.0 License.

orders of magnitude, making it the primary mechanism for these transitions. This dominance stems from the electron transfer being strongly favored at short interatomic distances around R_e .¹² Despite their magnitude difference, both contributions show similar trends with increasing kinetic energy ϵ .

We compare the analytical model to the R-matrix results (blue), which include both energy and electron transfer contributions. While all curves exhibit the same overall trend, the analytical model is roughly a factor of three larger than the R-matrix results. This discrepancy stems from the electron transfer term, which is exaggerated due to parameter choices in the Gaussian description of the electronic distributions for the $(\text{HeNe})^+$ system.¹²

From here on, we include both energy and electron transfer contributions in the model for the X to B and B to X transitions. We now turn to comparing the total cross section with vibrationally resolved and fixed-nuclei results.

B. Total cross section

Figure 3 presents ICEC cross sections for all electronically distinct processes, comparing the analytical model, the R-matrix, and fixed-nuclei results. Across all cases, the model agrees with the R-matrix approach within an order of magnitude, consistent with the comparisons discussed in Sec. VI A.

Threshold energies differ between channels. When He^+ captures the electron (left panels), the process can occur at zero incoming electron energy due to the high electron affinity of He^+ . For the reverse process (right panels), the incoming electron has to supply an energy of 3–4 eV to make ICEC possible.

The relative importance of bound-bound (b–b) and bound-dissociative (b–d) transitions varies by channel. For B to X and B to A (left panels), b–b transitions dominate by about two orders of magnitude, driven by large overlaps between the ground vibrational state of B and bound states of X or A. For A to B, b–b transitions still dominate but only marginally.

In contrast, the X to B process is dominated by b–d transitions—by up to ten orders of magnitude. The suppression of the b–b transitions arises from minimal overlap between the ground state of X and the bound states of B due to the shift in equilibrium distance R , as shown in Fig. 1. The same holds even for low-energy

dissociative states but the overlap grows with increasing KER (the energy of the dissociative state), as the turning point moves to smaller R . With larger kinetic energy ϵ , more dissociative states are accessible, enhancing the total cross section. Once the relevant dissociative states are fully accessible, the cross section saturates and eventually decreases due to the kinetic energy dependence.

Comparison with fixed-nuclei results calculated at the equilibrium distance of the initial electronic state (dotted lines) reveals the impact of nuclear dynamics. For transitions B to A, B to X, and A to B, the fixed-nuclei cross sections are comparable with the dominant b–b or b–d contribution. For A to B, the agreement in magnitude is within a factor of two across the full energy range.

The X to B transition, however, shows a significant discrepancy in threshold between the fixed-nuclei and vibrationally resolved cross sections. This stems from different energy conservation assumptions: the fixed-nuclei model (dotted red) uses asymptotic energy conservation, $\epsilon' = \epsilon + \text{IP}_A - \text{IP}_B$,⁶ leading to a threshold energy of 3.02 eV for X to B, while the fixed-nuclei R-matrix (dotted blue) uses vertical transitions at R_e , shown in Eq. (29), corresponding to 6.9 eV. Both the model and R-matrix approaches for including nuclear dynamics instead conserve the vibronic energy, Eq. (11), yielding a more gradual onset of the cross section.

In all cases, the dominant ICEC cross section—whether b–b or b–d—surpasses the photorecombination cross section of the capturing ion by at least three orders of magnitude. For the X to B transition, the enhancement reaches up to six orders of magnitude, highlighting the efficiency of ICEC and its significant role in environments where low-energy electrons and weakly bound systems are present.

C. Temperature dependence

To model ICEC realistically, the thermal population of initial vibrational states must be considered. Unlike fixed-nuclei methods, our approach includes vibrational averaging via a Boltzmann distribution, introducing temperature dependence into the cross sections, as outlined in Sec. II C.

We show in Fig. 4 how the ICEC cross section for $(\text{HeNe})^+$ changes with increasing incoming electron energy for different temperatures. For the B to X, A to B, and B to A transitions, increasing

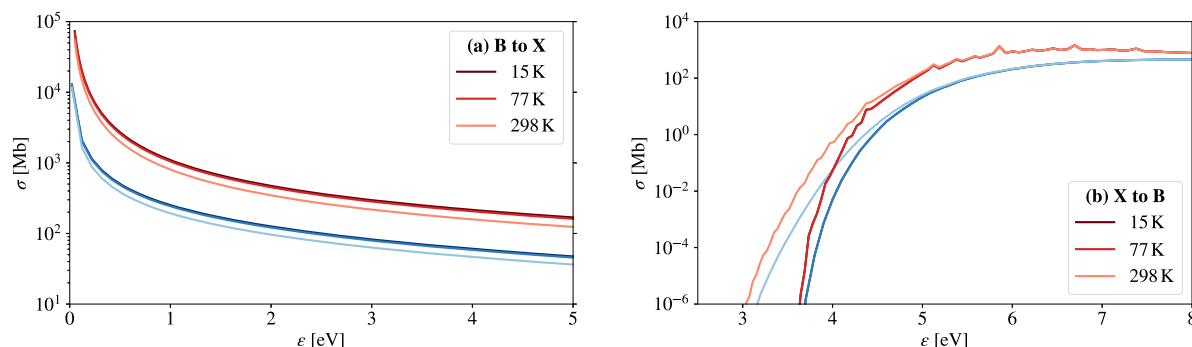


FIG. 4. Temperature-dependent ICEC cross section vs incoming electron energy ϵ . Shades of blue: the R-matrix; shades of red: the model. Lighter shades correspond to higher temperatures. The curves for $T = 15$ and 77 K coincide in the right panel. The figure is taken from E. M. Jahr and J. Šenk (2025). "Influence of vibrational motion and temperature on Interatomic Coulombic electron capture - Figures," Figshare. <https://doi.org/10.6084/m9.figshare.28883378.v2>.³² Copyright 2025 Author(s), licensed under a Creative Commons Attribution 4.0 License.

the temperature to $T = 298$ K results in a reduction in the total cross section. For instance, in the B to X transition (panel 4a), the asymptotic model predicts a decrease of up to a factor of 1.4 when comparing 298 K (orange) with 15 K (red). This trend is also observed in the R-matrix calculations (blue). The decrease stems from significant population of excited vibrational states at higher temperatures and for these transitions, excited initial states yield lower cross sections. A detailed analysis of this vibrational-state dependence is provided in the [supplementary material](#).

In contrast, the X to B transition [panel Fig. 4(b)] exhibits the opposite behavior. At low incoming electron energies, the cross section increases with temperature. This enhancement is due to the strong contribution from higher initial vibrational states, which, in this case, produce substantially larger cross sections in the low-energy regime due to lowering the threshold and enhancing the overlap between initial and final vibrational wave functions. More details can be found in the [supplementary material](#). At higher electron energies, where the dependence on the initial vibrational state becomes weaker, the temperature effect diminishes and the cross section remains nearly unchanged.

Moreover, for X to B, we observe a lowering of the ICEC threshold with increasing temperature. This is a direct consequence of the reduced threshold energies associated with vibrationally excited

initial states, which begin to dominate the vibrational average at higher temperatures.

D. Spectrum

Nuclear dynamics significantly impacts the spectrum of the outgoing electron in ICEC. At fixed incident electron energy, the spectrum features discrete peaks from bound-bound transitions and a continuum from bound-dissociative transitions.

Figure 5 presents the outgoing electron energy spectra for all ICEC processes considered, assuming initial ground vibrational states. We use $\varepsilon = 1$ eV (He^+ as acceptor) and $\varepsilon = 5$ eV (Ne^+ as acceptor). The line part of the spectrum denotes bound-bound transitions, with the signal of the highest outgoing electron energy corresponding to the ground vibrational final state; the continuous curves represent bound-dissociative contributions. Energy conservation links the outgoing electron energy to the final vibrational state, shown in the secondary x axis at the top of the plots. Spectra are truncated below $10^{-3} \times \sigma_{\text{PR}}$ due to experimental irrelevance.

For A to B, B to A, and B to X, bound-dissociative cross sections decrease with increasing KER, often with modulations. This behavior persists for higher initial vibrational states (see the [supplementary material](#)). For X to B, by contrast, the

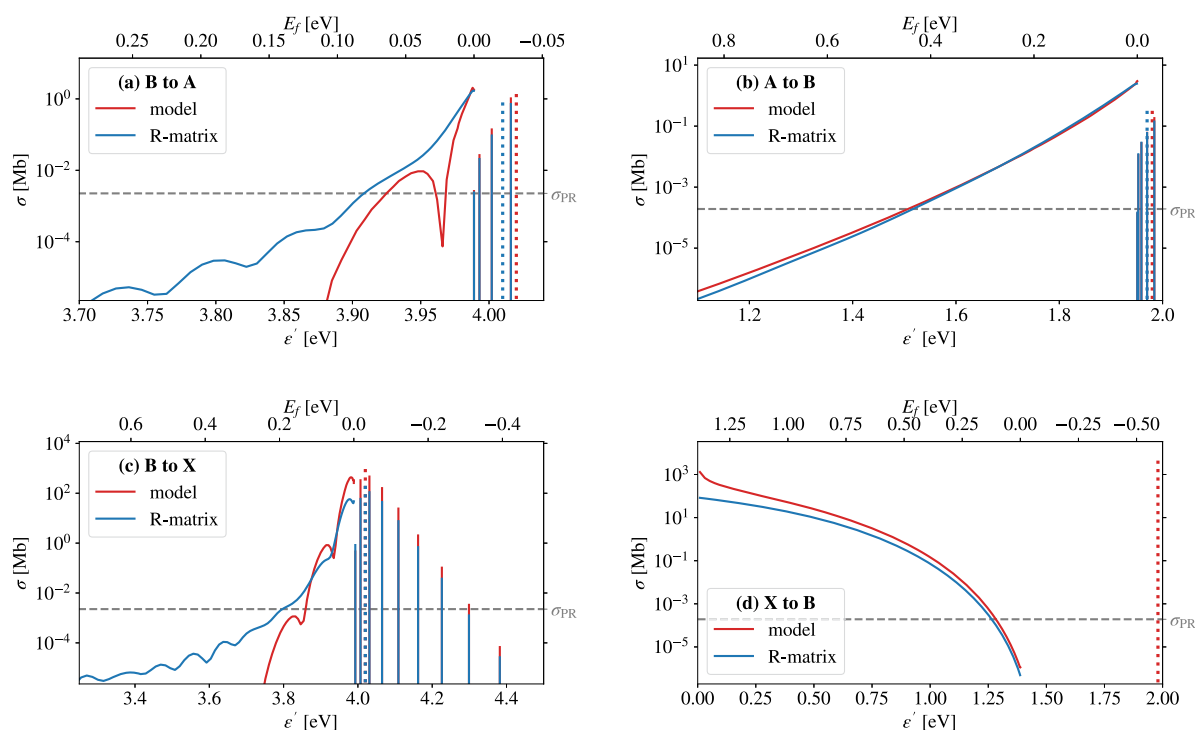


FIG. 5. ICEC cross section vs outgoing electron energy ε' for $v_i = 0$. Each panel shows a different electronic ICEC process: left for He^+ ($\varepsilon = 5$ eV), right for Ne^+ ($\varepsilon = 1$ eV). The line spectrum denotes bound-bound transitions and the solid curves represent bound-dissociative differential cross sections in Mb eV^{-1} ; see Eqs. (24) and (32). R-matrix (blue), model (red), photorecombination reference (dashed gray), and fixed-nuclei data (dotted line spectrum) are included. In panel (d), the fixed-nuclei ICEC channel is closed for the R-matrix result and, therefore, not represented. The figure is taken from E. M. Jahr and J. Šenk (2025). "Influence of vibrational motion and temperature on Interatomic Coulombic electron capture - Figures," Figshare. <https://doi.org/10.6084/m9.figshare.28883378.v2>.³² Copyright 2025 Author(s), licensed under a Creative Commons Attribution 4.0 License.

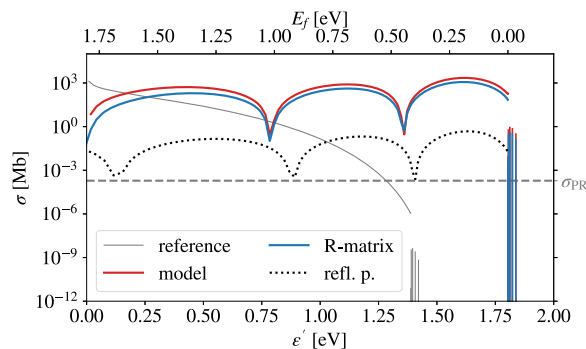


FIG. 6. ICEC cross section vs outgoing electron energy ϵ' for X to B. Ne^+ captures the incident electron with a kinetic energy of $\epsilon = 5$ eV. The initial vibrational state is $\nu_i = 5$. The dotted curve represents the reflection principle prediction of the cross section. The reference (gray curve) shows the model data for $\nu_i = 0$ [i.e., from panel Fig. 5(d)]. The blue and red lines are as in Fig. 5. The figure is taken from E. M. Jahr and J. Šenk (2025). "Influence of vibrational motion and temperature on Interatomic Coulombic electron capture - Figures," Figshare. <https://doi.org/10.6084/m9.figshare.28883378.v2>.³² Copyright 2025 Author(s), licensed under a Creative Commons Attribution 4.0 License.

bound–dissociative cross section increases rapidly with KER. Higher ν_i introduce modulations, with an increasing number of minima.

Note that in Fig. 5(d) (X to B), the discrepancy between the energy conservations discussed in Sec. VI B manifests in the fixed-nuclei ICEC channel being closed for the R-matrix approach and open for the analytical model. The fixed-nuclei R-matrix result is, therefore, not represented in this spectrum.

Figure 6 compares X to B spectra for $\nu_i = 0$ and $\nu_i = 5$. Three key differences arise: (i) the entire spectrum for $\nu_i = 5$ is shifted by ~ 0.4 eV due to the initial vibrational energy difference; (ii) bound–bound cross sections increase by eight orders of magnitude for $\nu_i = 5$, due to enhanced overlap with final bound states at larger R ; and (iii) the dissociative spectrum for $\nu_i = 5$ shows multiple peaks and valleys, in contrast to the monotonic shape for $\nu_i = 0$.

This structure can be qualitatively explained using the reflection principle.⁵⁰ By projecting the initial vibrational state's density, weighted by the electron transfer interaction $\propto \exp(-cR^2)/R^2$, Eqs. (16) and (20), we reproduce the overall shape and nodal structure of the cross section. However, the predicted peak positions are systematically shifted to higher ϵ' , likely due to the approximation of the final-state potential by its linear component at the turning point within the reflection principle approximation.

Finally, we compare the analytical model and the R-matrix results. Overall, the model cross sections agree well with the R-matrix results—both in magnitude and qualitative behavior. They show consistent trends and magnitudes for the bound–bound spectra and similarly capture the shape of the bound–continuum transitions. The largest discrepancies occur in bound–dissociative transitions with He^+ as electron acceptor: the model predicts more pronounced oscillations and shows a faster decay with increasing KER compared to the R-matrix results. These differences likely arise from limitations of the model, including the neglect of higher-order multipole terms and interference between energy and electron transfer mechanisms. The reliability of the R-matrix approach, on the

other hand, is affected by the use of the AN approximation in B to X and B to A, which becomes less accurate at higher KER.

VII. CONCLUSION

We have presented a comprehensive theoretical investigation of how nuclear motion influences the ICEC cross section in the positively charged helium–neon dimer—an example of a weakly bound system. In our approach, we incorporate vibrational dynamics into an analytical model of ICEC, including both the energy and electron transfer mechanisms in terms of a semi-empirical model. To validate the model, we implemented an approximation based on fixed-nuclei *ab initio* R-matrix results, finding agreement within an order of magnitude. Beyond this quantitative agreement, the model also reproduces the qualitative behavior and offers valuable interpretative insight.

Our results demonstrate that including nuclear motion and temperature dependence leads to important modifications of the ICEC cross sections. These include changes in threshold position, threshold behavior, energy dependence, outgoing electron energy, and overall magnitude. When the neon cation captures the incoming electron, the cross section rises near the threshold and is predominantly followed by dissociation at higher electron energies—tendency that becomes even more pronounced at elevated temperatures. In contrast, electron capture by the helium cation favors bound–bound transitions, with slightly reduced cross sections observed at lower temperatures. We find that electron transfer dominates the cross section, as the bound vibrational states are localized in the short-range region where the asymptotic energy-transfer approximation breaks down. Although nuclear motion can slightly reduce the total cross section compared to fixed-nuclei calculations at equilibrium geometries, ICEC remains several orders of magnitude more efficient in the helium–neon dimer than photorecombination, reinforcing its physical relevance.

It is important to note that, although we treat the electronic states X and A as distinct within our theoretical framework, such separation may not be feasible experimentally due to limited resolution, which could obscure individual contributions. In addition, while our treatment neglects molecular rotations, their inclusion would introduce further fine structure in the bound–bound transitions. However, resolving this substructure would be experimentally challenging, as the energy splitting between rotational states within the same vibrational level is minimal.

The influence of nuclear dynamics on ICEC has important implications for both theoretical modeling and experimental detection. Our results highlight the need for including this dynamics into ICEC descriptions, particularly in molecular and weakly bound systems.

SUPPLEMENTARY MATERIAL

The [supplementary material](#) provides the ICEC cross sections for higher initial vibrational states, which underlie the temperature dependence discussed in Sec. VI C. We further show the cross sections for different temperatures for all electronic transitions, as well as the spectra for higher initial vibrational states. We also show a comparison of the AN and EBAN cross sections in two example cases.

ACKNOWLEDGMENTS

We acknowledge the DFG-ANR for providing financial support through the QD4ICEC project. The corresponding Grant Nos. are FA 1989/1-1 and ANR-22-CE92-0071-01. E.F. and E.M.J. acknowledge the Zentrum für Frankophone Welten at the University of Tübingen for a travel grant; furthermore, E.F. acknowledges funding by LISA⁺ at the University of Tübingen. J.P.D. acknowledges financial support from the COST Action CA18212–Molecular Dynamics in the GAS phase (MD-GAS), supported by COST (European Cooperation in Science and Technology).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Elena M. Jahr: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (lead); Software (lead); Visualization (equal); Writing – original draft (equal); Writing – review & editing (supporting). **Jan Šenk:** Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (supporting); Software (supporting); Visualization (equal); Writing – original draft (equal); Writing – review & editing (supporting). **Jan P. Drennhaus:** Methodology (supporting); Writing – review & editing (supporting). **Přemysl Kolorenč:** Methodology (equal); Supervision (supporting); Writing – review & editing (equal). **Nicolas Sisourat:** Conceptualization (lead); Funding acquisition (equal); Methodology (equal); Project administration (equal); Supervision (equal); Writing – review & editing (equal). **Elke Fasshauer:** Conceptualization (lead); Funding acquisition (equal); Methodology (lead); Project administration (equal); Supervision (equal); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are openly available and cited at the appropriate locations within this paper.

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Many-body quantum dynamics with MCTDH-X

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Abstract

The lecture notes on “Many-body Quantum Dynamics with MCTDH-X”, adapted from the 2023 Heidelberg MCTDH Summer School, provide an in-depth exploration of the Multiconfigurational Time-Dependent Hartree approach for indistinguishable particles. They serve as a comprehensive guide for understanding and utilizing the MCTDH-X software for both bosonic and fermionic systems. The tutorial begins with an introduction to the MCTDH-X software, highlighting its capability to handle various quantum systems, including those with internal degrees of freedom and long-range interactions. The theoretical foundation is then laid out on how to solve the time-dependent and time-independent Schrödinger equations for many-body systems. The workflow section provides practical instructions on setting up and executing simulations using MCTDH-X. Detailed benchmarks against exact solutions are presented, showcasing the accuracy and reliability of the software in ground-state and dynamic simulations. The notes then delve into the dynamics of quantum systems, covering relaxation processes, time evolution, and the analysis of propagation for both bosonic and fermionic particles. The discussion includes the interpretation of various physical quantities such as energy, density distributions, and orbital occupations. Advanced features of MCTDH-X are also explored in the last section, including the calculation of correlation functions and the creation of visualizations through video tutorials. The notes conclude with a Linux/UNIX command cheat sheet, facilitating ease of use for users operating the software on different systems. Overall, these lecture notes provide a valuable resource for researchers and students in the field of quantum dynamics, offering both theoretical insights and practical guidance on the use of MCTDH-X for studying complex many-body systems.



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Published by the SciPost Foundation.

Received 2024-08-08

Accepted 2025-02-10

Published 2025-03-26

doi:[10.21468/SciPostPhysLectNotes.94](https://doi.org/10.21468/SciPostPhysLectNotes.94)



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Preamble

This tutorial assumes that you have a working copy of the MCTDH-X software running on your local system or on your supercomputing cluster. MCTDH-X can be run both on a Linux environment and Mac OS. The open-source software MCTDH-X can be downloaded from <https://gitlab.com/the-mctdh-x-repository/mctdh-x-releases> and instructions on how to install MCTDH-X can be found in the respective folder `documentation/Installation_guide` in the repository. Additional details about the MCTDH-X software are available on the <http://ultracold.org> website. Details of the MCTDH-X theory, the MCTDH-X code, and the software manual are all located in the ‘DOCUMENTATION’ section. This tutorial is based mainly on Refs. [1–3]. In this tutorial you will learn how to execute basic calculations with MCTDH-X for both bosons and fermions, extract observables, and plot the results.

1 Introduction

The time-dependent many-body Schrödinger equation (TDSE) and its time independent counterpart (TISE) are fundamental equations at the heart of many different fields of science: quantum chemistry, condensed matter physics, and atomic and molecular physics to cite a few. The TDSE describes the dynamics of quantum particles under the influence of their kinetic energy, external potentials, and many-body interactions, whereas the TISE describes the properties of their stationary states. Exact solutions to the TDSE exist only for model systems, like the time-dependent harmonic interaction model [1, 2, 4, 5]. To obtain solutions to the TISE and TDSE, numerical methods as well as their implementation in software are therefore indispensable. One such software is MCTDH-X. MCTDH-X implements the MultiConfigurational Time-Dependent Hartree (MCTDH) approach for indistinguishable quantum particles: bosons [6, 7, 54–57] and fermions [2, 8–14, 57].

In the MCTDH approach, the equations of motions for bosons and fermions can be formulated in a unified manner to enable the description of correlated wavefunctions. This is in stark contrast to mean-field treatments (e.g. Gross-Pitaevskii equation for bosonic systems or Hartree-Fock for fermionic systems) which completely neglect correlations. Furthermore, because the method relies on a time-dependent variational principle, MCTDH-X naturally captures any time dependence present in the parameters of the system.

The current version of MCTDH-X is able to deal with indistinguishable particles with internal degrees of freedom like bosonic spinor condensates [6] (calculations for fermions with spin are currently being developed), indistinguishable particles placed in a high-finesse optical cavity [15–22], indistinguishable particles with short-range [23–31], long-range (e.g. dipolar or regularized Coulomb potentials) interactions [32–36, 36–41, 41–45], quantum particles in complex, often time-dependent potentials [46–51], Hubbard lattice models [52], and has even been interfaced with machine learning [53]. In this tutorial, though, we will restrict to the simplest case of bosons and fermions without additional degrees of freedom. First, we will obtain ground state properties of interacting systems that can be solved exactly. We will systematically compare the numerical convergence of MCTDH-X to the exact solutions. Then, we will use MCTDH-X to simulate and visualize the dynamics of interacting bosons and fermions.

1.1 Structure of the MCTDH-X software

1.1.1 The theory in a nutshell

The objective of the MCTDH-X software is to numerically solve the TISE or TDSE for a given many-body Hamiltonian and to analyze the computed solutions. This general Hamiltonian describes N interacting, indistinguishable bosons or fermions subject to a one-body potential, and has the form

$$H = \sum_{i=1}^N \left[-\frac{1}{2} \partial_{\mathbf{x}_i}^2 + V(\mathbf{x}_i; t) \right] + \sum_{i < j}^N W(\mathbf{x}_i, \mathbf{x}_j; t), \quad (1)$$

that can be either explicitly dependent on time or not. Here, $\mathbf{x}_i$ is the coordinate of the i -th particle, $-\frac{1}{2} \partial_{\mathbf{x}}^2$ is the kinetic energy operator, $V(\mathbf{x}; t)$ is a general, possibly time-dependent, one-body potential and $W(\mathbf{x}, \mathbf{x}'; t)$ is a general, possibly time-dependent interparticle interaction operator. All the quantities are given in dimensionless units. In MCTDH-X, the length scale L can be chosen to appropriately represent the physical problem; the corresponding time and energy scales are then determined as $mL^2/\hbar$ and $\hbar^2/(mL^2)$, respectively. For example, in the presence of a harmonic confinement potential, a natural choice for the length scale is the inverse of the harmonic trapping frequency ω , i.e. $L = \sqrt{\hbar/(m\omega)}$. On the other hand, and for

chemical purposes, if the length scale is chosen to be one Bohr radius, the results are given in atomic units.

The TISE corresponding to the Hamiltonian of Eq. (1) is

$$H|\Psi_E\rangle = E|\Psi_E\rangle, \quad (2)$$

while the TDSE is

$$H|\Psi(t)\rangle = i\partial_t|\Psi(t)\rangle. \quad (3)$$

Note that H in the TISE needs to be a time-independent Hamiltonian. In Eq. (2), $|\Psi_E\rangle$ is an eigenstate of H with eigenvalue (energy) E . $|\Psi(t)\rangle$ stands for the solution of the TDSE at time t .

The MCTDH-X theory [57,58] uses an ansatz for the wavefunction that is a time-dependent superposition of time-dependent many-body basis functions:

$$\begin{aligned} |\Psi(t)\rangle &= \sum_{\vec{n}} C_{\vec{n}}(t) |\vec{n}; t\rangle, \quad \vec{n} = (n_1, \dots, n_M)^T, \\ |\vec{n}; t\rangle &= \mathcal{N} \prod_{i=1}^M [\hat{b}_i^\dagger(t)]^{n_i} |\text{vac}\rangle, \quad \phi_j(\mathbf{x}; t) = \langle \mathbf{x} | \hat{b}_j(t) | 0 \rangle. \end{aligned} \quad (4)$$

Here, the $C_{\vec{n}}(t)$ are referred to as coefficients, the $|\vec{n}; t\rangle$ as configurations, and the normalization factor is $\mathcal{N} = \frac{1}{\sqrt{\prod_{i=1}^M n_i!}}$ for bosons and $\mathcal{N} = 1$ for fermions. Each configuration is a fully symmetric or fully anti-symmetric many-body basis state built from M orthonormal time-dependent single-particle functions, known as *orbitals*, $\{\phi_k(\mathbf{x}, t); k = 1, \dots, M\}$. For bosons, the symmetrized configuration state corresponds to a permanent, whereas for fermions the antisymmetrized state is a Slater determinant. To fully specify the solution of the TISE or TDSE, the MCTDH-X software computes and stores the coefficients $C_{\vec{n}}(t)$ and the orbitals $\{\phi_k(\mathbf{x}, t); k = 1, \dots, M\}$ at times t that are specified by the user. The set of equations of motion for the parameters in Eq. (4) comprises a coupled set of first-order differential equations for time-dependent coefficients $C_{\vec{n}}(t)$ and non-linear integro-differential equations for the orbitals $\phi_j(\mathbf{x}; t)$. The MCTDH-X software integrates these equations of motion either in imaginary time (for time-independent Hamiltonians) to obtain the many-body ground-state wavefunction [59], or in real time to perform full-time propagation.

1.1.2 Quantities of interest

Once the coefficients $C_{\vec{n}}(t)$ and the orbitals $\phi_k(\mathbf{x}, t)$ are computed, the MCTDH-X software can analyze the solution and calculate several quantities of interest. In this tutorial, we will mainly be interested in the total system energy

$$E = \langle \Psi | H | \Psi \rangle, \quad (5)$$

the real-space density distribution

$$\rho(\mathbf{x}) = \langle \Psi | \hat{\Psi}^\dagger(\mathbf{x}) \hat{\Psi}(\mathbf{x}) | \Psi \rangle / N, \quad (6)$$

and the Glauber one-body and two-body correlation functions

$$g^{(1)}(\mathbf{x}, \mathbf{x}') = \frac{\langle \Psi | \hat{\Psi}^\dagger(\mathbf{x}) \hat{\Psi}(\mathbf{x}') | \Psi \rangle}{N \sqrt{\rho(\mathbf{x}) \rho(\mathbf{x}')}}, \quad (7)$$

$$g^{(2)}(\mathbf{x}, \mathbf{x}') = \frac{\langle \Psi | \hat{\Psi}^\dagger(\mathbf{x}) \hat{\Psi}^\dagger(\mathbf{x}') \hat{\Psi}(\mathbf{x}') \hat{\Psi}(\mathbf{x}) | \Psi \rangle}{N^2 \rho(\mathbf{x}) \rho(\mathbf{x}')}, \quad (8)$$

where $\hat{\Psi}^\dagger(\mathbf{x})$ and $\hat{\Psi}(\mathbf{x})$ are creation and annihilation operators for a particle at position $\mathbf{x}$. We will also discuss the occupation of the orbitals for both ground-state and real-time calculations, which give information about numerical convergence and many-body character of the system. These notions are best expressed via the natural orbitals $\phi_i^{(\text{NO})}$ and the orbital occupations ρ_i , which are the eigenfunctions and eigenvalues of the reduced one-body density matrix, defined as

$$\rho^{(1)}(\mathbf{x}, \mathbf{x}') = \frac{1}{N} \langle \Psi | \hat{\Psi}^\dagger(\mathbf{x}') \hat{\Psi}(\mathbf{x}) | \Psi \rangle = \sum_i \rho_i \phi_i^{(\text{NO}),*}(\mathbf{x}') \phi_i^{(\text{NO})}(\mathbf{x}). \quad (9)$$

In chemistry, these orbitals are called natural atomic orbitals. They are often optimized to maximize occupation numbers, resulting in natural bond orbitals (NBOs). For the latter, the local block eigenfunctions on one atomic center phenomenologically correspond to a lone-pair, while the block eigenfunctions involving two atomic centers correspond to a bond giving rise to the chemist's Lewis structure picture. They are natural in the sense of Löwdin [60], having optimal convergence properties for the description of the electron density.

For bosons, if the eigenvalues are dominated by a single contribution close to unity, the state is well-described by a single coherent single-particle wavefunction. This is often denoted as a Gross-Pitaevskii mean-field description. For fermions, because of the Pauli principle, there must be at least N separate contributions to the eigenvalues. If the contribution from the additional natural orbitals is negligible, the system is well-captured by a mean-field Hartree-Fock description. In our indexing convention, the natural orbitals are ranked in order of decreasing occupation, i.e. $\rho_1 \geq \dots \geq \rho_M$.

We remark that the capabilities of MCTDH-X extend to the calculation of more quantities not discussed in these lecture notes, such as momentum-space densities and momentum-space correlation functions, single-shot images, full distribution functions, variances, autocorrelation functions, many-body overlaps, many-body entropies, and cavity order parameters [3].

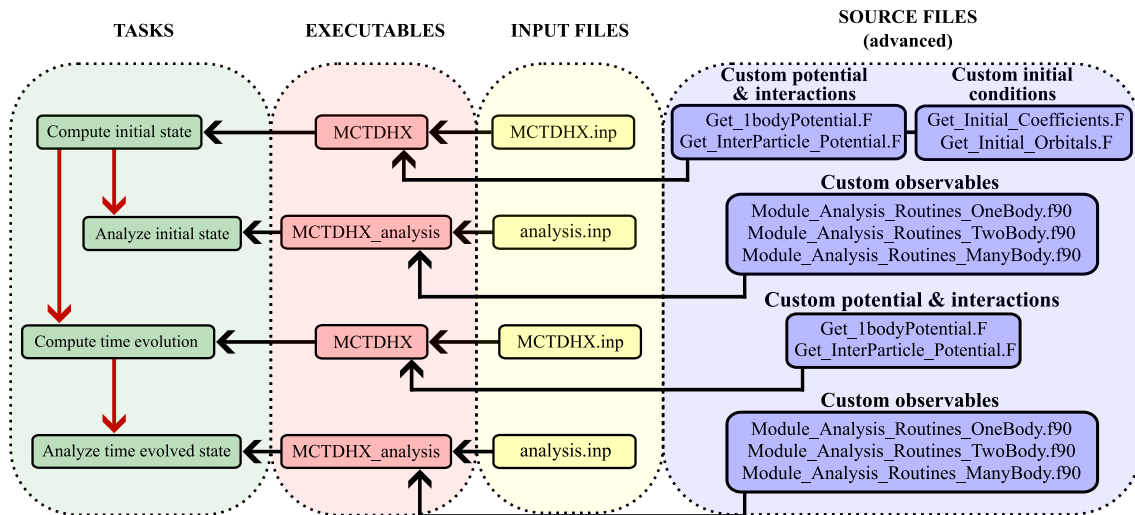


Figure 1: Workflow of the MCTDH-X software. The red arrows indicate the task workflow. The black arrows indicate the setup workflow: first change source files to define custom potential, interactions, initial conditions, and observables (optional), then set up input files, then run executables. In this tutorial, we focus only on the yellow, red, and green parts of the workflow.

2 Workflow

The MCTDH-X software consists of two main programs:

1. The main program, `MCTDHX_gcc`, computes the numerical solution of the TISE or TDSE.
2. The analysis program, `MCTDHX_analysis_gcc`, analyzes the found solution to calculate derived observables such as correlations, single-shot images, etc.

To set up a numerical task, the user modifies and chooses the parameters via the text input file `MCTDHX.inp`. If one is interested in the energetics and in the behavior of the real-space density, running the main program is sufficient. A detailed description of the available options is given in the manual [61] of the MCTDH-X software. Here and in the following, we use the verbatim font to refer to code, including executable commands, files, statements, and variables.

The workflow and structure of the MCTDH-X software follows naturally from its main objectives to determine a numerical solution to the TISE or the TDSE and then to extract desired quantities of interest from the solution. This workflow can be summarized in the following steps, which are also visualized in Fig. 1.

1. **Determine the initial state.** Compute the ground state of some Hamiltonian $\hat{H}$ by running `MCTDHX_gcc` and configuring the numerical task (“relaxation mode”, Hamiltonian, integration procedure etc.) in the input file `MCTDHX.inp`.
2. **Analyze the initial state** by choosing the desired quantities of interest in `analysis.inp` and running the analysis program `MCTDHX_analysis_gcc`.
3. **Compute the time-evolution of the initial state** with given Hamiltonian $\hat{H}(t)$. The dynamics of the system is obtained by choosing the numerical task (“propagation mode”, Hamiltonian, integration procedure etc.) in the input file `MCTDHX.inp` and running `MCTDHX_gcc`. Typically, the propagation is calculated by restarting from an initial state determined from a relaxation.
4. **Analyze the computed time-evolving state** by choosing the desired quantities of interest in `analysis.inp` and running the analysis program `MCTDHX_analysis_gcc`.

3 Benchmark against exact solution (ground state)

In this section, we will run our first simulations to obtain the ground-state energy and densities for interacting bosons and fermions for an increasing number of orbitals. We will then see how increasing the number of orbitals leads to progressively more accurate quantitative results. You can run computations for bosons only, for fermions only, or for both. If you have installed the software correctly, you should have already have aliases saved in the `.mctdhxrc` file located in your home directory (`~/`). To activate these aliases, source the file. Open a terminal and type:

```
source ~/.mctdhxrc.
```

Now you will be able to quickly copy the MCTDH-X executables by simply running the command

```
bincp,
```

and to copy sample input files by running

```
inpcp.
```

Another useful alias is

```
cdmx,
```

which will take you directly to the MCDTH-X root directory where the source files, installer etc. are located.

3.1 Harmonic interaction model

We will use the harmonic interaction model (HIM) – an exactly solvable many-body problem – to benchmark the validity of our MCTDH-X calculations. The HIM is a model in which quantum particles interact with each other via a harmonic interparticle interaction [1, 2, 62–64]. The first quantized Hamiltonian can be written in dimensionless units as

$$\hat{H} = \sum_{i=1}^N [\hat{T}(\vec{r}_i) + \hat{V}(\vec{r}_i)] + \sum_{i<j}^N \hat{W}(\vec{r}_i, \vec{r}_j), \quad (10)$$

with

$$\hat{T}(\vec{r}) = -\frac{1}{2} \partial_{\vec{r}}^2, \quad (11)$$

$$\hat{V}(\vec{r}) = \frac{1}{2} \omega^2 \vec{r}^2, \quad (12)$$

$$\hat{W}(\vec{r}_i, \vec{r}_j) = K_0 (\vec{r}_i - \vec{r}_j)^2, \quad (13)$$

respectively the kinetic energy operator, the one-body potential operator, and the two-body interaction operator. Here, ω is the frequency of the harmonic trap, and K_0 is the strength of the two-body interaction.

The exact solution to this Hamiltonian can be obtained if we employ a coordinate transformation

$$\vec{q}_j = \frac{1}{\sqrt{j(j+1)}} \sum_{i=1}^j (\vec{r}_{j+1} - \vec{r}_i), \quad j = 1, \dots, N-1, \quad (14)$$

$$\vec{q}_N = \frac{1}{\sqrt{N}} \sum_{i=1}^N \vec{r}_i, \quad (15)$$

that maps the interacting particles to a collection of non-interacting harmonic oscillators. The transformed Hamiltonian namely reads

$$\hat{H} = \sum_{i=1}^{N-1} \left(-\frac{1}{2} \partial_{\vec{q}_i}^2 + \frac{1}{2} \delta_N^2 \vec{q}_i^2 \right) - \frac{1}{2} \partial_{\vec{q}_N}^2 + \frac{1}{2} \omega^2 \vec{q}_N^2, \quad (16)$$

where $\delta_N = \sqrt{\omega^2 + 2NK_0}$. Note how $\vec{q}_N$ is a center-of-mass operator, i.e. a weighted average over all particle positions, with frequency ω (fourth term), while the other $N-1$ harmonic

oscillators originate from the set of relative coordinates and all have the same frequency δ_N (second term).

The separable form of the HIM problem leads to a solution in terms of a product of N generally different harmonic oscillator wave functions. While this approach is general for multiple dimensions, we will for the purpose of this tutorial limit ourselves to the one-dimensional case. The wavefunction then reads

$$\Psi(x_1, \dots, x_N) = \begin{cases} \left(\frac{\delta_N}{\pi} \right)^{\frac{(N-1)}{4}} \left(\frac{\omega}{\pi} \right)^{\frac{1}{4}} e^{-\frac{\alpha}{2} \sum_{i=1}^N x_i^2 - \beta \sum_{i<j}^N x_i x_j}, & \text{for bosons,} \\ \mathcal{N} \left(\frac{\delta_N}{\pi} \right)^{\frac{(N^2-1)}{4}} \left(\frac{\omega}{\pi} \right)^{\frac{1}{4}} \prod_{1 \leq i < j \leq N} (x_i - x_j) e^{-\frac{\alpha}{2} \sum_{i=1}^N x_i^2 - \beta \sum_{i<j}^N x_i x_j}, & \text{for fermions,} \end{cases} \quad (17)$$

where $\prod_{1 \leq i < j \leq N} (x_i - x_j) = V(x_1, \dots, x_N)$ is the Vandermonde determinant. The relative Jacobi coordinates of fermions give rise to a dimensionless normalization constant, $\mathcal{N}$ in the wavefunction [65, 66]. The coefficients α and β in the wavefunction are written as [66],

$$\alpha = \delta_N \left[1 + \frac{1}{N} \left(\frac{\omega}{\delta_N} - 1 \right) \right], \quad \beta = \alpha - \delta_N.$$

The corresponding total ground-state energy is then simply the sum of the ground-state energy of each oscillator.¹ For bosons, this gives

$$E_{\text{exact, bosons}} = E_{\text{rel}} + E_{\text{c.o.m.}} = \left(\frac{N-1}{2} \delta_N + \frac{\omega}{2} \right). \quad (18)$$

For spin-polarized fermions, the energy is slightly different on account of their different statistics² that leads us to sum $N-1$ harmonic oscillator energies $\epsilon_n = (n+1/2)\delta_N = \frac{2n+1}{2}\delta_N$, yielding

$$E_{\text{exact, fermions}} = \left[\sum_{n=1}^{N-1} \left(\frac{2n+1}{2} \delta_N \right) + \frac{\omega}{2} \right] = \left(\frac{N^2-1}{2} \delta_N + \frac{\omega}{2} \right). \quad (19)$$

3.2 Simulations

We can now use the HIM above to benchmark the validity of our MCTDH-X calculations. The first thing to do when preparing a new computation is to create a separate folder where the program will run. We will treat bosonic and fermionic computations separately, as spin-polarized fermions always require at least $M > N$ orbitals due to the Pauli exclusion principle, whereas for bosons we can perform calculations with $M < N$ since multiple bosons can occupy the same state.

For bosons, we will consider $N = 10$ particles and run 5 different computations with an increasing number of orbitals from 1 to 5. To that end, we need to create 5 different folders. A good structure could be the one shown in Fig. 2, with a parent folder called HIM-bosons and five subfolders

For fermions, we will run several computations with increasing particle number and orbitals:

- Four computations with $N = 2$ particles and $M = 3, 4, 5, 6$ orbitals.
- Three computations with $N = 5$ particles and $M = 6, 7, 8$ orbitals.

¹Recall that the ground-state energy of a quantum harmonic oscillator of frequency ω is $E_0 = \frac{\hbar\omega}{2}$. In this case, since we operate in dimensionless units, we have effectively set $\hbar = 1$.

²Fermions will occupy one by one all the equally-spaced harmonic oscillator levels due to the Pauli principle.

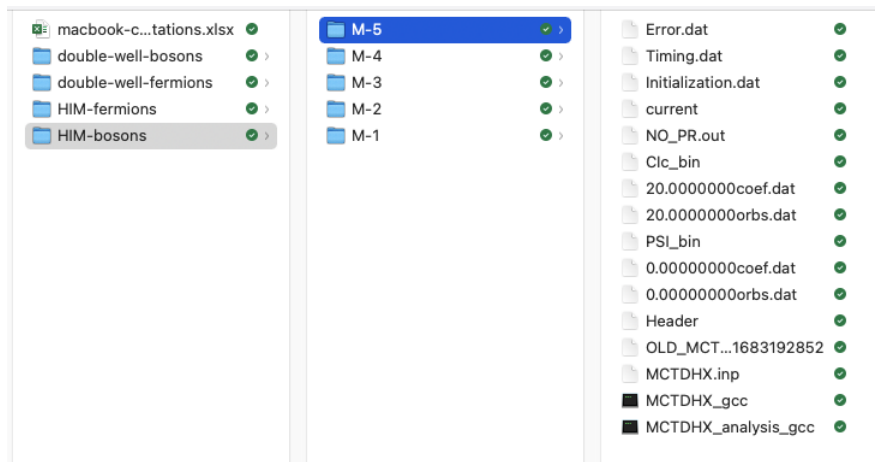


Figure 2: Folder structure for the ground-state bosonic computations.

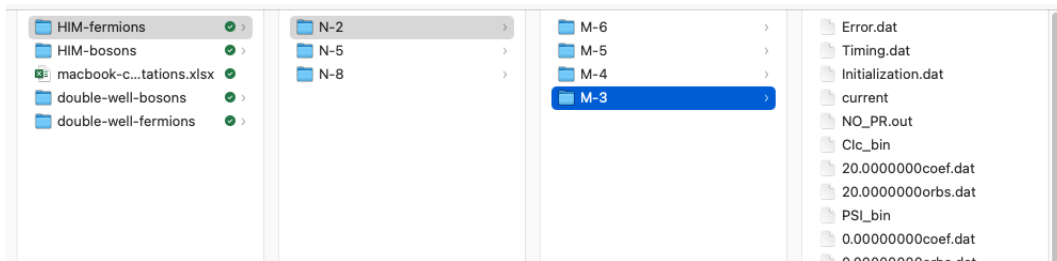


Figure 3: Folder structure for the ground-state fermionic computations.

- Two computations with $N = 8$ particles and $M = 9, 10$ orbitals.

Because we will run simulations of many different cases, it would be best to create separate folder for each case. A good structure could be the one shown in Fig. 3, with a parent folder called HIM-fermions containing folders labelled by N , which in turn contain folders labelled by M .

Next, we need to import the MCTDH-X executables and input files. You already know how to do it, just navigate to each folder and type `bin` and `in` in your console. You should now have the following files: `MCTDHX.inp`, `analysis.inp`, `MCTDHX_analysis_gcc`, `MCTDHX_gcc`. Since we are currently only focusing on performing a relaxation to the ground state to calculate its energy, we can ignore the analysis files for now. To launch our simulation, we first need to modify the input file. Go ahead and use your favorite text editor to open the file `MCTDHX.inp` (e.g. `vim`). The input file should look like the screenshot of Fig. 4.

To set up your computation, you need to change several parameters in the input file. In the following list, we only mention the parameters that need to be changed to set up the current relaxation for harmonic interacting bosons and fermions. As you can see from looking at `MCTDHX.inp` there are many more parameters that can be modified. They are grouped by their function. For instance, there is an entire section of the input file dedicated to parameters used to model multilevel systems (fermions/bosons with internal degrees of freedom), another for Bose-Hubbard lattice Hamiltonians, another for BEC-cavity systems etc. We will not discuss the functionalities of these parameters in this tutorial. Some other parameters are for advanced control of the simulation in terms of how to discretize the coordinate space, which integrator to use, how to handle errors, etc. Unless explicitly stated, you should not modify any other parameter that does not appear on the list below.

- `JOB_TYPE`: this flag tells the program whether it should simulate bosons, fermions, or

use the full configuration interaction method (debugging purposes only). For **bosonic** computations, you should set `JOB_TYPE = 'BOS'`.

For **fermionic** computations, you should set `JOB_TYPE = 'FER'`.

Note that lines that start with an exclamation mark (!) are comment lines and will not be read by the program.

- **Morb**: this parameter controls the number of orbitals used in the simulation. For **bosons**: set it to the number of orbitals for your computation (1 to 5).
For **fermions**: set it to the number of orbitals for your computation (3 to 10, depending on the value of N).
Note that for spin-polarized fermions obeying Pauli exclusion, we require *at least* $M = N$ orbitals. However, this case can be degenerate in MCTDH-X, so make sure to always choose $M \geq N + 1$.
- **Npar**: this parameter controls the number of particles used in the simulation. Since we are benchmarking our results against the ones available in Refs. [1] and [2], we should use the same number of particles.
For **bosons**: set `Npar = 10`.
For **fermions**: set `Npar = 2`, `Npar = 5`, or `Npar = 8`.
- **xlambda_0**: this parameter corresponds to the interparticle interaction strength (K_0 in the notation of the previous section).
For **bosons**: in Ref. [67], $K_0(N - 1) = 0.5$, or $K_0 = 0.05\bar{5}$. Thus set `xlambda_0 = 0.05555555556`.
For **fermions**: In Ref. [2], $K_0 = 0.5$. Thus set `xlambda_0 = 0.5`.
- **mass**: this parameter controls the mass of the particles. In dimensionless units, `mass = 1.0d0` by default.
- **Job_Prefactor**: this is an ordered pair of numbers (equivalent to a complex number) that determines whether the simulation will be conducted in imaginary time (relaxation) or real time (propagation). Since we are interested in doing a relaxation to the ground state now, you should set it to `Job_Prefactor = (-1.0d0, 0.0d0)`.
- **GUESS**: this flag specifies the initial condition for the simulation. `GUESS = 'HAND'` is the default for relaxations and makes the integrator start from a random initial state (or



```

1 System_Parameters
2 !=====
3 !===== System definition
4 !=====
5 JOB_TYPE = 'BOS'           !===== Standard MCTDHB
6 !JOB_TYPE = 'FER'          !===== Standard MCTDHF
7 !JOB_TYPE = 'FCI'          !===== Full CI
8
9 Morb = 1                   !===== Number of Orbitals
10 Npar = 10                  !===== Number of Particles
11 xlambda_0 = 0.05555555556 !===== Strength of the interparticle interaction
12 mass = 1.0d0
13 Job_Prefactor = (-1.0d0, 0.0d0) !===== (0.0d0, -1.0d0) Forward propagation
14 !===== (0.0d0, +1.0d0) Backward propagation
15 !===== (-1.0d0, 0.0d0) "Improved" Relaxation
16 !GUESS = 'BINR'            !===== Restart from binary files
17 !GUESS = 'DATA'            !===== Restart from ASCII files
18 GUESS = 'HAND'             !===== Start from the initial state specified in the Get_Initial_Orbitals and Get_Initial_Coefficients routines.
19
20 NProjections = 2           !===== How often to apply the projection operator
21 Diagonalize_OneBody = .F.  !===== Start from the eigenfunctions of the one-body Hamiltonian h as orbitals.
22 Binary_Start_Time = 0.0d0  !===== If GUESS='BINR' start from this point in time.
23 Restart_State = 1          !===== State from which to restart from a previous block relaxation.
24 Restart_Orbital_FileName = '10.0000000orbs.dat' ! If GUESS='DATA' then the orbitals are read from this ASCII file.
25 Restart_Coefficients_FileName = '10.0000000coef.dat' ! If GUESS='DATA' then the coefficients are read from this ASCII file.
26 Custom_Orbital_Initialization = .F. !===== If GUESS='HAND' Do we use custom initial orbital?
27 Which_Custom_Orbital_Initialization = 'Random' !===== If GUESS='HAND' Which custom initial orbital do we use?
28 Custom_Orbital_Initial_Parameters = 0.d0, 0.d0, 0.d0, 0.d0, 0.d0, 0.d0, 0.d0, 0.d0, 0.d0, 0.d0 !===== Parameters for specifying the initial orbital.
29
30 Fixed_LZ = .F.             !===== In relaxations: Apply a projection to a fixed orbital phase profile?
31 Orblz = 0, 0, 0, 0, 0, 0, 0 !===== How many times 2*pi the phase is going to jump. If any value is -666, the respective orbital is unchanged.
32 Vortex_Seeding = .F.       !===== In propagations: Multiply initial orbitals with phase/density profile?
33 Vortex_Imprint = .F.       !===== In relaxations: Apply a projection operator to a certain orbital density profile?
34 Profile = 'tanh'           !===== If Vortex_Imprint is true, this will select the respective shape of the imprinted profile.
35 NonInteracting = .F.       !===== Omit two-body part of the Hamiltonian?
36 !=====

```

Figure 4: First lines in the input file `MCTDHX.inp`.

a custom initial state if provided). Later on when we perform time evolution, we will use `GUESS = 'BINR'` to restart a computation from binary files belonging to a converged relaxation.

- `DIM_MCTDH`: this parameter determines the dimensionality of the problem. For our benchmark, we will focus on one-dimensional systems and set `DIM_MCTDH=1`.
- `NDVR_X`, `NDVR_Y`, `NDVR_Z`: These three parameters set the number of points in the x, y, and z directions in the Discrete Variable Representation (DVR) of the continuum system.³ Since we are only interested in a 1D problem for now, we can set `NDVR_Y=1` and `NDVR_Z=1`. It is always best to set the number of DVR points to be a power of 2 to avoid numerical rounding errors in binary representation. The number of points should be chosen to be compatible with the *size* of the spatial grid (see next point), i.e. the larger the grid, the more points we require to keep the same accuracy. Typically, `NDVR_X=128` is enough to obtain good results.
- `x_initial`, `x_final`, `y_initial`, `y_final`, `z_initial`, `z_final`: this set of 6 parameters control the spatial extension of the DVR grid, for all three possible directions. For this simulation, you can set `x_initial = -8.0d0` and `x_final = +8.0d0`. Because we are dealing with a 1D problem, the extent of the other spatial dimensions will be ignored.
- `Time_Begin`: This parameter determines the starting time of the computation. Standard is `Time_Begin = 0.0d0`. A different time is only chosen if you want to continue the propagation from a terminated calculation from the last calculated point using the stored orbitals and coefficients.
- `Time_Final`: This parameter determines the final time of the computation, in dimensionless units (i.e. the program will integrate the equations of motion until this time). Heuristically, `Time_Final = 20.0d0` is typically enough to achieve converged results in the energy, i.e. results whose energy does not change in the first 12 decimal digits even when letting the system time evolve further. Note that this does *not* necessarily mean that the numerical values of the calculated energies are exact! This only means that with the current number of orbitals, Krylov space, type of integrator etc. that's the best precision possible. As you will see later, increasing the number of orbitals lead to progressively better (=lower) ground state energies.
- `Output_TimeStep`: this flag tells the program when to write output data in the form of `.orbs` and `.coef` files. If you would like to see these files generated throughout the imaginary time evolution, set something like `Output_TimeStep = 1.0d0`. Otherwise, `Output_TimeStep = 20.0d0` will only produce an initial output (at time 0) and a final output (at time 20).
- `Integration_Stepsize`: this parameter indicates the step size used in the integrator. The standard value for a relaxation is `Integration_Stepsize = 0.1d0`. The standard value for a real time propagation is `Integration_Stepsize = 0.01d0` (because it's more prone to accumulation errors).
- `Write_ASCII`: this flag should be set to true, i.e. `Write_ASCII = .T.` if `.orbs` and `.coef` ASCII files ought to be generated.

³If you want to know more about discretization methods, you can take a look at [these lecture notes](#).

- **Coefficients_Integrator**: MCTDH-X has many different integrators implemented, both for the orbital equation of motion (not listed here) and for the coefficients. While typically you can always use a Runge-Kutta integrator for the orbitals (`Orbital_Integrator = 'RK'`), the coefficient integrator differs depending on whether you are performing a relaxation or a propagation. For a relaxation, set `Coefficients_Integrator = 'DAV'` (Davidson diagonalization). For a propagation, set `Coefficients_Integrator = 'MCS'` (MCTDH short iterative Lanczos routine).
- **whichpot**: this parameter determines the type of one-body potential used in the simulation. There are many potentials listed in the manual and coded in the module `Get_1bodyPotential.F`. In this tutorial, we are interested in a one-dimensional harmonic oscillator, which corresponds to setting `whichpot="H01D"`. The more experienced user will later be able to add customized one-body potentials to the above mentioned list.
- **parameter1 to parameter30**: each one-body potential comes with its own set of parameters that can be modified to control its shape. There can be presently up to 30 parameters to specify the one-body potential. For a simple one-dimensional harmonic oscillator centered around the origin and codified by H01D, there is only one nonzero parameter corresponding to the trapping frequency: `parameter1=1.d0`.
- **Interaction_Type**: this technical flag controls the type of interparticle interaction and how it should be evaluated in the equations of motion. The sample input file provides a brief explanation of all the different types. For time-independent long-ranged interactions, type 4 or type 7 should be used. For harmonic interactions, set `Interaction_Type=4`.
- **which_interaction**: this parameter selects the physical type of interparticle interaction to be simulated (if it is not contact interactions). Each interaction is codified in a 5-6 letter string (see the manual for more information). For harmonic interactions, you should set `which_interaction='HIM'`.

After having set up the input file, you are now ready to launch your first MCTDH-X computation! In the folder of choice (corresponding to $M = 1$, $M = 2$ etc.) where the input file is located, simply run

```
./MCTDHX_gcc.
```

You will see output on the terminal. In particular, you can see the convergence of the energy as a function of the integration time step.

3.3 Discussion of the results

After you have run MCTDH-X relaxations in all the folders with different orbital numbers, we can compare the results and see how the numerical solution converges to the exact one as we increase M . You will see that several different files are generated. In particular:

- **PSI_bin** and **CIc_bin** are the binary representations of orbitals and coefficients, respectively.
- **.orbs** files contain information about the orbitals at every (imaginary) time step that you have chosen to output.

- `.coef` files contain information about the coefficients at every (imaginary) time step that you have chosen to output (if $M > 1$).
- `NO_PR.out` contains the progression of the energy, and the orbital occupations as a function of (imaginary) time.
- `Header` is a header file that contains information about which parameters were used in the computation and is needed to restart computations from a previous time, or to run propagations from relaxations.
- `Initialization.dat` contains log information about the initialization.
- `Error.dat` contains log information about integration errors, matrix inversion errors etc.
- `Timing.dat` contains log information about how long it took for each step in the program execution to run.

Let us explore the physics of the problem by using the files that MCTDH-X produced.

3.3.1 Energy

The energy of a relaxation can easily be read from the standard output while the computation is running. It can also be read from the `NO_PR.out` file. The energy as a function of time is contained in the $(M+2)$ -th column. To get the full time dependence of the energy, you can use:

```
awk '{ print $NF }' NO_PR.out.
```

If you are only interested in energy of the very last time step, you can write:

```
awk '{ print $NF }' NO_PR.out | tail -n1.
```

We now discuss the results for bosons and fermions separately.

Bosons In table 1, you can see a comparison of the ground-state bosonic energies as a function of number of orbitals and the times needed to compute them on a 2 GHz Quad-Core Intel Core i5. You can also see that as we increase the number of orbitals, the numerical solution converges to the exact one exponentially. In Fig. 5 we visualize the relationship between the computation time and the energy convergence displayed in table 1. Locally, we are restricted to $M = 5$ orbitals if we want to keep the computation within a short amount of time. Already for $M = 5$ the computation takes around 25 minutes. This is because the size of the configuration space scales roughly as $\binom{N+M-1}{N} \approx N^M$ when $N \gg M$.⁴ Note, however, that in higher dimensions and on a cluster (actually on any multi-core system), MCTDH-X can use a decomposition of the orbitals in smaller domains that allows for parallelization and faster computation times.

We can also plot the energy visually, for instance using the open-source software `gnuplot`. The syntax for $M = 5$ is for instance

```
plot "NO_PR.out" u 1:7 w l lw 3.
```

Plots for the energy convergence as a function of imaginary time for increasing M are shown in Fig. 6. Try to recreate this plot with `gnuplot` or another visualization software.

⁴This approximation is very crude. In fact, the scaling is superexponential because of the factorials and since we typically use finite/small values for N and M , the Stirling approximation is not very accurate here.

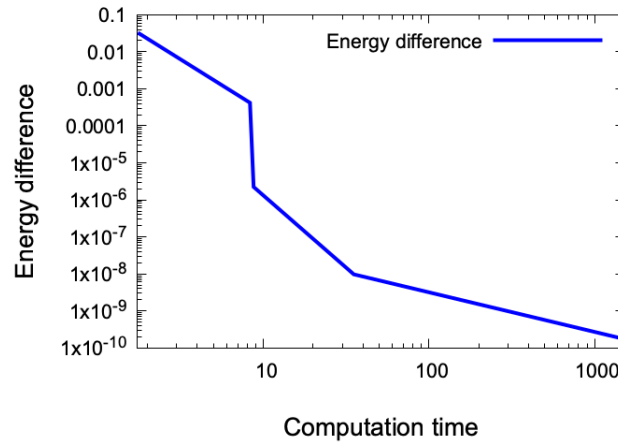


Figure 5: Relationship between the computation time and the energy convergence for $N = 10$ harmonically-interacting bosons and increasing orbital number M , as shown in table 1.

Table 1: Approximate computation times and the corresponding ground-state energies after 20 time steps for $N = 10$ harmonically-interacting bosons and increasing orbital number M . The calculations were performed on a 2 GHz Quad-Core Intel Core i5, 16 GB 3733 MHz LPDDR4X RAM. The bold numbers correspond to the digits that are equal to the exact solution.

Orbital number M	Approximate computation time	Energy at time step 20
1	1.75 seconds	7.07 1067812008208
2	8.31 seconds	7.038 769026440956
3	8.74 seconds	7.0383 50652543779
4	35.19 seconds	7.0383484 25047187
5	25 minutes	7.038348415 486683
exact solution		7.038348415311011

Fermions In table 2, you can see a comparison of the fermionic ground-state energies as a function of number of orbitals and the times needed to compute them on a Quad-Core Intel Core i5. You can also see (at least for $N = 2$ where we have more data points) that as we increase the number of orbitals for a fixed particle number, the numerical solution converges to the exact one exponentially. On a local computer, we are restricted to around $N = 8$ particles and $M = 10$ orbitals if we want to keep the computation within a short amount of time (in the order of minutes). Much like for bosons, the size of the configuration space for fermions scales exponentially, roughly as $\binom{M}{N} \approx \frac{M^N}{N!}$.

Plots for the energy convergence as a function of imaginary time for $N = 2$ and increasing M is shown in Fig. 7. Try to recreate this plot with `gnuplot` or another visualization software. To visualize the energy convergence with `gnuplot`, for instance for $N = 2$, $M = 5$, the syntax is

```
plot "NO_PR.out" u 1:7 w l lw 3.
```

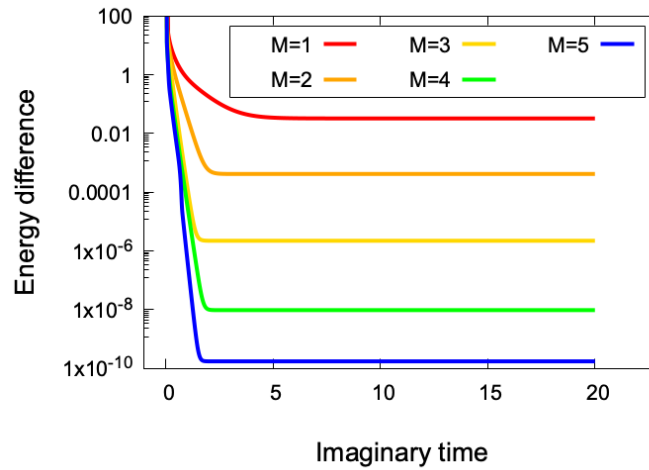


Figure 6: Imaginary-time convergence of the ground-state energy – calculated as $E_M(it = 20) - E_{\text{exact}}$ – for $N = 10$ harmonically interacting bosons in a harmonic potential as a function of increasing orbital number M .

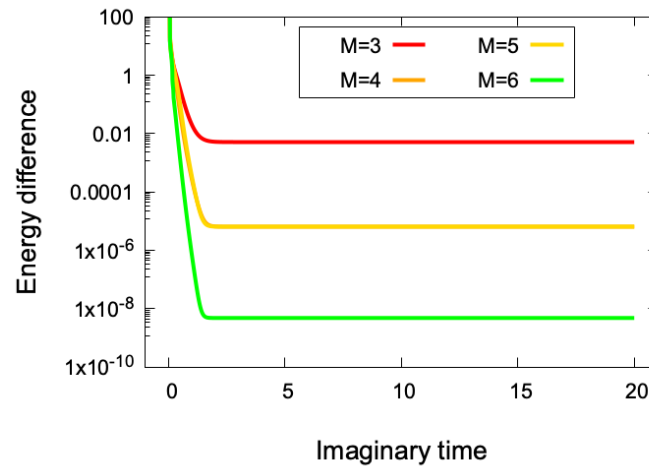


Figure 7: Imaginary-time convergence of the ground-state energy – calculated as $E_M(it = 20) - E_{\text{exact}}$ – for $N = 2$ harmonically interacting fermions in a harmonic potential as a function of increasing orbital number M .

3.3.2 Orbital occupation

We have seen that a higher number of orbitals contributes to a better result for the ground-state energy. It might also be of interest to quantify and visualize this trend in another way. This can be done by plotting the orbital occupations, which are saved in the M columns of the `NO_PR.out` file before the energy column (i.e. column 2 to $M + 1$). This is an important procedure because it tells us whether our results are converging in the chosen number of orbitals (i.e. adding more orbitals does not change the many-body wavefunction by much) or not.

In the case of bosons, this procedure can help us quantify how much correlation we need to include in our calculations to observe the correct physics, think for instance of a superfluid vs. a Mott insulating regime. In the case of fermions, a nonzero occupation in more than N orbitals quantifies how much the many-body wave function deviates from a single Slater determinant and thus how much quantum entanglement is building up in the system [68].

Table 2: Approximate computation times on a 2 GHz Quad-Core Intel Core i5, 16 GB 3733 MHz LPDDR4X RAM and the corresponding ground-state energies after 20 time steps. The bold numbers correspond to the digits that are equal to the exact solution.

Particle number	Orbital number M	Approximate computation time	Energy at time step 20
2	3	7.75 seconds	3 .103244922155683
2	4	14.11 seconds	3.0980 82754434019
2	5	25.32 seconds	3.0980 82754434124
2	6	50.24 seconds	3.0980762 16222958
exact solution			3.0980762113533159
5	6	42.95 seconds	29.933 68010792828
5	7	72.04 seconds	29.898 50111772063
5	8	112.40 seconds	29.894 43423675234
exact solution			29.893876913398137
8	9	166.86 seconds	95.082 44224010051
8	10	247.87 seconds	95.015 31056595735
exact solution			95.000000000000000

Another way to phrase this is that the orbital occupation tells us whether our results can be described by mean-field theories like the Gross-Pitaevskii equation for bosons (equivalent to using a single orbital, i.e. setting $M = 1$) or the Hartree-Fock approximation for fermions (equivalent to using $M = N$), or whether higher orbitals are important. This is also very important for real-time dynamics, because correlated states might appear as a function of time.

Let us plot the orbital occupation for our relaxations, again considering bosonic and fermionic results separately.

Bosons To plot the bosonic orbital occupations with gnuplot for the $M = 5$ case, write

```
plot "NO\_PR.out" u 1:2 w l lw 3 title "fifth orbital",
      "NO\_PR.out" u 1:3 w l lw 3 title "fourth orbital",
      "NO\_PR.out" u 1:4 w l lw 3 title "third orbital",
      "NO\_PR.out" u 1:5 w l lw 3 title "second orbital",
      "NO\_PR.out" u 1:6 w l lw 3 title "first orbital".
```

Fig. 8 shows precisely this. You can see that the convergence in imaginary time to the final orbital configuration is quite fast. Furthermore, the problem is mainly dominated by one orbital, so a mean-field description is enough to describe the qualitative behavior of the system. However, if we want to come close to the *quantitative* value of the ground-state energy, we must include higher orbitals and in fact their population is nonzero. The inset in Fig. 8 shows an enlarged plot around zero, and we can clearly see that the second orbital is contributing to about 0.3%, while the contributions of higher orbitals are even smaller.

The orbital occupations at the end of the imaginary time evolution can be extracted with

```
awk '{ print $2, $3, $4, $5, $6 }' NO_PR.out | tail -n1,
```

and are reported in table 3.

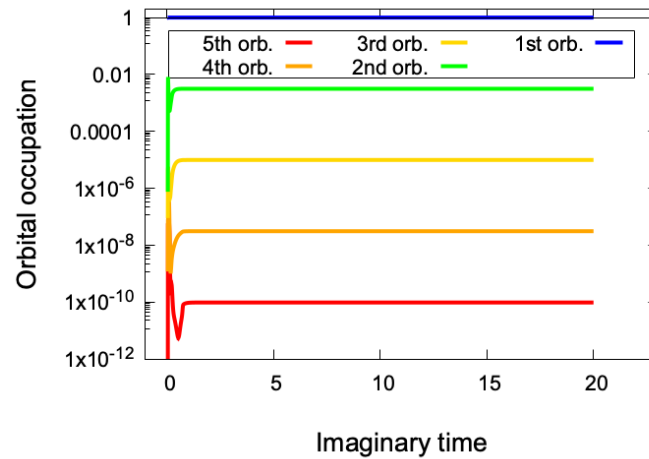


Figure 8: Orbital occupation in the ground state for $N = 10$ harmonically-interacting bosons in a harmonic trap described by $M = 5$ orbitals. Note that in the numerics the orbital occupations are normalized such that they sum to 1 and not N .

Table 3: Orbital occupation in the ground state for $N = 10$ harmonically-interacting bosons in a harmonic trap described by $M = 5$ orbitals. The computations were performed on a 2 GHz Quad-Core Intel Core i5, 16 GB 3733 MHz LPDDR4X RAM.

Orbital	Occupation
1st	0.9968427274690541
2nd	0.3147304166934598E-02
3rd	0.9936893501857101E-05
4th	0.3137224570732360E-07
5th	0.9826348708153463E-10

Fermions The visualization of the orbital occupation for fermions is similar to what we have already done for bosons. To plot the orbital occupations with gnuplot for e.g. the $N = 2$, $M = 5$ case, write

```
plot "NO\_PR.out" u 1:2 w l lw 3 title "fifth orbital",
      "NO\_PR.out" u 1:3 w l lw 3 title "fourth orbital",
      "NO\_PR.out" u 1:4 w l lw 3 title "third orbital",
      "NO\_PR.out" u 1:5 w l lw 3 title "second orbital",
      "NO\_PR.out" u 1:6 w l lw 3 title "first orbital".
```

This is shown in Fig. 9. Once again, the imaginary time convergence to the final orbital configuration is very fast. In this case, the system is very well described by just two orbitals that account for around 50% of the overall population each. In the inset of Fig. 9 we additionally show a zoom of the occupation around zero, where we can distinguish an additional but very small occupation of the third orbital of about 0.04%. These results indicate that the many-body wavefunction is very well described by the usual Slater determinant construction and there is not a lot of correlation between the two fermions.

The orbital occupations at the end of the imaginary time evolution can be extracted with

```
awk '{ print $2, $3, $4, $5, $6 }' NO_PR.out | tail -n1,
```

and are listed in table 4.

Table 4: Orbital occupation in the ground state for $N = 2$ harmonically-interacting fermions in a harmonic trap, described by $M = 5$ orbitals. The computations were performed on a 2 GHz Quad-Core Intel Core i5, 16 GB 3733 MHz LPDDR4X RAM.

Orbital	Occupation
1st	0.4995067585437437
2nd	0.4995067585437435
3rd	0.4932414562564047E-03
4th	0.4932414562563642E-03
5th	0.1493748698862856E-17

3.3.3 Density

Finally, let us take a look at the density of the many-body wavefunction. This is saved in the sixth column of the `.orbs` files for every time step that you chose to output. If we want to check the shape of the density in the ground state, we simply plot this data for the last time step in the relaxation with

```
plot "20.0000000orbs.dat" u 1:6 w l lw 3.
```

Bosons The plot of the density is shown in Fig. 10, together with a comparison with noninteracting bosons in a harmonic trap. You can easily generate the latter results by performing another simulation and choosing $\lambda_0 = 0.0$. As we can see (and not surprisingly), the (attractive) harmonic interaction makes the particles clump together more at the bottom of the trap.

Fermions The plot of the density for $N = 5$ fermions is shown in Fig. 11, together with a comparison with the same number of noninteracting fermions in a harmonic trap. As for the bosons, the attractive harmonic interaction makes the fermions clump together more at the bottom of the trap and reduces the typical ripple-like pattern caused by the Pauli exclusion principle of noninteracting fermions in a harmonic trap. Nevertheless, when compared against

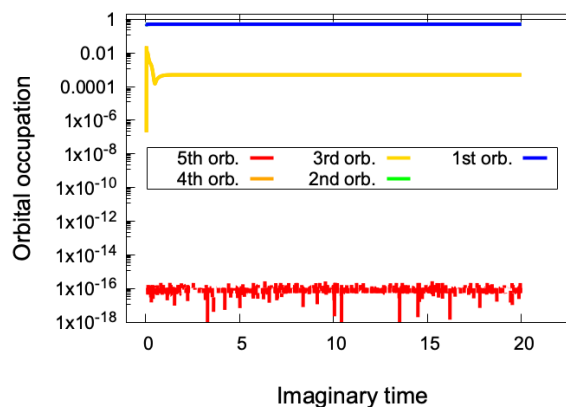


Figure 9: Orbital occupation in the ground state for $N = 2$ harmonically-interacting fermions in a harmonic trap, described by $M = 5$ orbitals. The occupations of the first and second, and of the third and fourth orbital are degenerate. Note that in the numeric the orbital occupations are normalized such that they sum to 1 and not N .

bosons, we still see that fermions occupy a larger space due to the repulsion stemming from the Pauli principle.

3.3.4 Additional exercises

- Try to plot the density for all the computations with different M in the same plot. Can you see a difference? How does this result relate to the orbital occupation results?
- Try to recreate the same results, but for *repulsively* harmonically interacting bosons and fermions (you need to choose a negative K_0). Be aware that if you choose a too large value of $|K_0|$, convergence issues will arise because for harmonic repulsions, the further away the particles are from each other, the stronger they will repel. How do the results look like in terms of energy, occupation, and density? How do they compare to the attractive or noninteracting case?

4 Dynamics

So far we have effectively solved the TISE to obtain information about the many-body ground state. Since MCTDH-X optimizes both orbitals and coefficients through the time-dependent variational principle, though, it is also capable of solving the TDSE to capture the dynamics of a system described by a time-dependent Hamiltonian. The time dependence can be of any sort. It can stem from a periodic drive, it can describe sudden quenches of parameters, or it can mirror a full experimental protocol with any kind of ad-hoc time dependence.

To explore this functionality, here we discuss systems of bosons or fermions in a harmonic trap with a time-dependent barrier. We first use MCTDH-X to relax the system into its ground state. Then, we linearly ramp up a central barrier and study the response of the quantum particles.

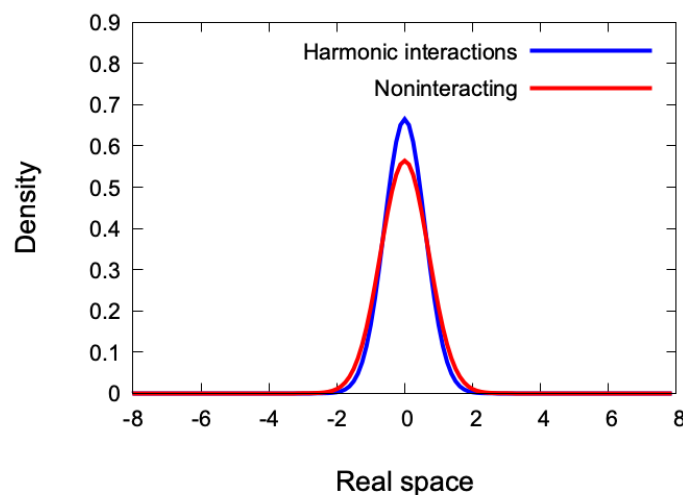


Figure 10: Many-body density for $N = 10$ bosons and $M = 5$ orbitals in a harmonic trap. The blue curve corresponds to harmonically interacting bosons, while the red curve shows noninteracting bosons.

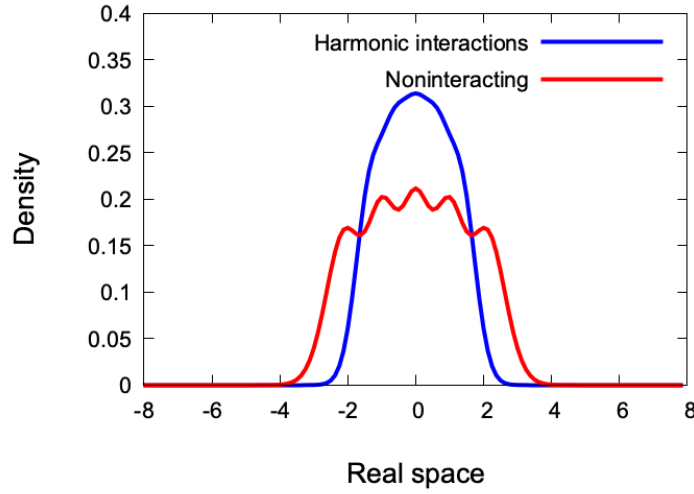


Figure 11: Many-body density for $N = 5$ fermions and $M = 8$ orbitals in a harmonic trap. The blue curve corresponds to harmonically interacting fermions, while the red curve shows noninteracting fermions.

4.1 Relaxation

We will explore the time evolution of a system of quantum particles confined in a harmonic trap with a time-dependent Gaussian barrier, creating an effective double well.

The two-body interaction between the **bosons** is chosen as a contact repulsion of the form

$$\hat{W}(\vec{x}_i, \vec{x}_j) = W_0 \delta(x_i - x_j), \quad (20)$$

where $W_0 = 1$ is the interaction strength and δ is the Dirac delta distribution.

For **fermions**, we will consider interactions that do not have an analytical solution, namely regularized Coulomb repulsion:

$$\hat{W}(\vec{r}_i, \vec{r}_j) = \frac{W_0}{\sqrt{|\vec{r}_i - \vec{r}_j|^2 + \alpha \exp(-\beta |\vec{r}_i - \vec{r}_j|)}}, \quad (21)$$

with $W_0 = 2.0$, $\alpha = 0.01$, $\beta = 100$. This interaction type is labelled as `regC` in the module `source/ini_guess_pot/Get_InterParticle_Potential.F`. You can have a look at its implementation in this module if you like.

To evaluate the dynamics, first we need to prepare the system in a ground state. Hence, we will relax $N = 5$ bosons or fermions by employing MCTDH-X in a 1D harmonic trap (with imaginary time propagation) and then evolve this initial state with a time-dependent Hamiltonian (with real time propagation).

For the ground state simulation, create a new folder (e.g. named `relax`). Then, type `inpcp` to load the input files and `binpcp` to load the executable files. Now perform the relaxation by modifying `MCTDHX.inp` file as in the following:

- `JOB_TYPE='BOS'` for bosons or `JOB_TYPE='FER'` for fermions,
- `Npar=5`,
- `Morb=10`,
- `xlambda_0=1.0d0` (this parameter corresponds to interaction strength, W_0),

- `mass=1.0d0`,
- `Job_Prefactor=(-1.0d0,0.0d0)` (for relaxation),
- `GUESS='HAND'`,
- `DIM_MCTDH=1`,
- `NDVR_X=256`,
- `x_initial=-16.0d0` and `x_final=+16.0d0`,
- `Time_Begin=0.0d0`,
- `Time_Final=20.0d0`,
- `Integration_Stepsize=0.1d0`,
- `Write_ASCII=.T.`,
- `Coefficients_Integrator='DAV'`,
- `whichpot="H01D"`,
- `parameter1=1.d0` (and set all the other potential parameters to zero).

Additionally, for bosons set

- `Interaction_Type=0`,
- `which_interaction='delta'` (this is the contact interaction),
- `Interaction_Parameter1=0.0d0`,
- `Interaction_Parameter2=0.0d0` (and set all the other interaction parameters to zero),

while for fermions set

- `Interaction_Type=4`,
- `which_interaction='regC'` (this is the regularized Coulomb interaction),
- `Interaction_Parameter1=0.01d0` (this parameter corresponds to α),
- `Interaction_Parameter2=100.0d0` (this parameter corresponds to β),
- `Interaction_Parameter3=0.0d0` (set also all the other interaction parameters to zero).

Now, run your imaginary time propagation (relaxation) with `./MCTHDX_gcc`. The computation should last a couple of minutes. Fig. 12 shows the results for density and trapping potential. The ground state energy is around $E_0 = 5.367407139871924$. Fig. 13 shows similar results, but for the fermionic problem (in the figure we additionally compare the fermions with regularized Coulomb repulsions to noninteracting fermions showing how the density spreads out further for the repulsive case - you do not need to do that). The ground state energy for the interacting fermions is around $E_0 = 24.86279037504089$.

4.2 Time evolution

Now we are ready to propagate the simulated initial state using a time-dependent Hamiltonian. The dynamics is explored in a time-dependent confining potential; a harmonic trap with a time-dependent central barrier that is slowly quenched from zero to a significant value and is given as

$$V(x; t) = \frac{1}{2}x^2 + V_0(t)e^{-2x^2}, \quad (22)$$

where the time-dependent barrier height is of the form

$$V_0(t) = \begin{cases} V_{\max}t/\tau, & t < \tau, \\ V_{\max}, & t \geq \tau. \end{cases} \quad (23)$$

The maximum barrier height is kept constant at $V_{\max} = 20$ for bosons and $V_{\max} = 60$ for fermions. We simulate the dynamics for various quenching rates, $\tau = 1, 10$ and 100 , see Fig.14. You can find the implementation of this time-dependent double well in the file `source/ini_guess_pot/Get_1bodyPotential.F` by searching for the string `H01D+td_gauss`.

Now, to simulate the dynamics, create a different folder for each propagation that you want to investigate. Then, copy all the binary files – namely `CIc_bin`, `PSI_bin` and `Header` – and the input file from the previous relaxation folder to the current propagation folder. After that, modify the input file `MCTDHF.inp` for a propagation as in the following inputs (keep the rest of the input file the same):

- `Job_Prefactor=(0.0d0,-1.0d0)`, which triggers forward propagation.
- `GUESS='BINR'`, which will use initial states from the binary files.
- `Binary_Start_Time=20.0d0`, which defines the starting time to be ready from the binary files. Since we let the previous relaxations run up until time step 20, this is the latest available data point (or set it according to your choice of time of relaxation).

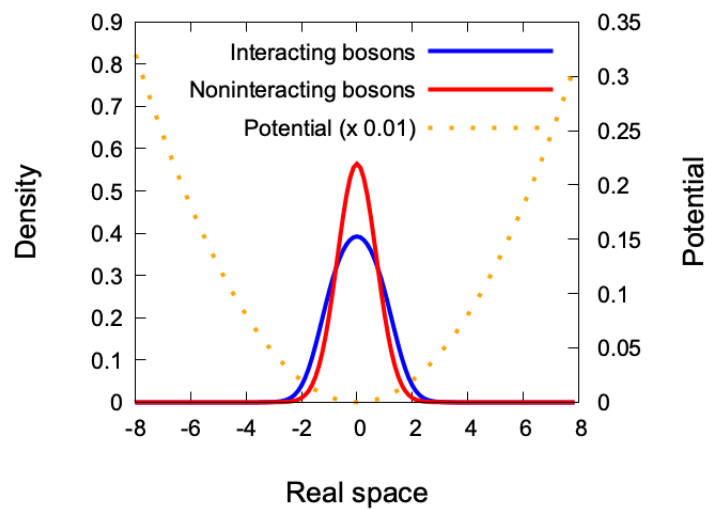


Figure 12: Many-body density for $N = 5$ bosons and $M = 10$ orbitals in a harmonic trap (orange curve, scaled by 0.01). The density for interacting bosons ($W_0 = 1$) is plotted in blue, while the density for noninteracting bosons ($W_0 = 0$) is plotted in red.

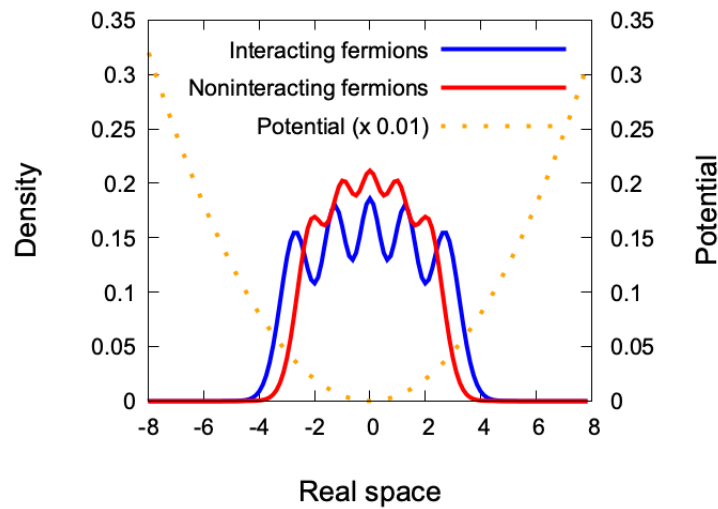


Figure 13: Many-body density for $N = 5$ fermions and $M = 10$ orbitals in a harmonic trap (orange curve, scaled by 0.01). Fermions interacting via a (repulsive) regularized Coulomb interactions (blue) are compared with noninteracting fermions (red).

- `Time_Final=100.0d0` (or you can simulate for longer times depending on the system).
- `Output_TimeStep=0.1d0` (or smaller resolution, depending how often you want to generate data; we want to be able to plot the evolution of the density as time evolves).
- `Integration_Stepsize=0.01d0` (integration of a real-time differential equation is more prone to accumulation errors, so we need to reduce the step size as compared to relaxations).
- `Coefficients_Integrator='MCS'` (we require a different integrator for propagations).

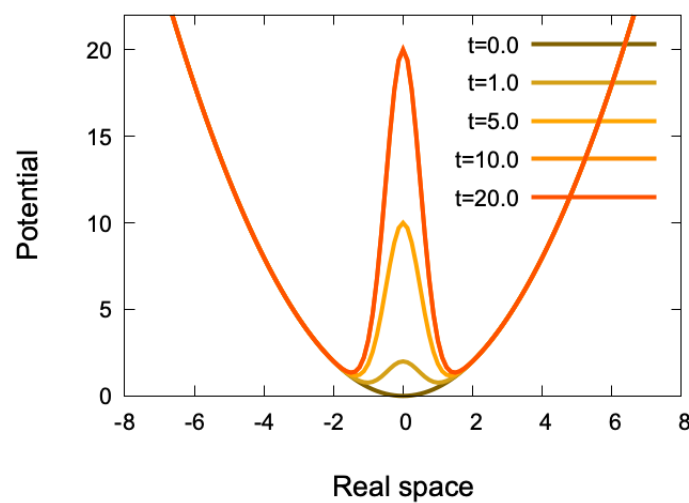


Figure 14: Quenching of the central barrier in the time-dependent potential, see Eq. 23 for quench rate $\tau = 10$. Notice that beyond time $t = 10.0$, the barrier has reached its maximal value and will stay there.

- `whichpot="H01D+td_gauss".`
- `parameter1=1.d0` (harmonic trap depth).
- `parameter2=0.0d0` (harmonic trap displacement).
- `parameter4=1.0d0` or `parameter4=10.0d0` or `parameter4=100.0d0` (quench rate τ).
- `parameter5=0.0d0` (displacement of the Gaussian barrier).
- `parameter7=0.0d0` (and set all the other potential parameters to zero).

Additionally, for bosons set

- `parameter3=20.0d0` (maximal barrier height),
- `parameter6=0.5d0` (standard deviation of the Gaussian barrier),

while for fermions set

- `parameter3=60.0d0` (maximal barrier height),
- `parameter6=1.0d0` (standard deviation of the Gaussian barrier).

We need a higher barrier for fermions because they tend to populate higher energy states due to the Pauli exclusion principle, whereas bosons can coexist in the same energy state even with some moderate repulsion.

Finally, run `./MCTDHX_gcc` to execute your simulations. The computations should take around 30 minutes each. If you have a powerful computing station, you could try to run at least two in parallel, but they will be slower.

4.3 Analysis of propagation

Now, let us analyze the results of the time evolution at different propagation times and compare them across different values of the quench parameter, τ . We will investigate density, natural occupations (a tool to measure the degree of fragmentation) and finally energy as a function of real time. We will also check the convergence of the propagation. We will discuss bosonic and fermionic computations separately.

4.3.1 Bosons

Density To visualize the density, we use the `*orbs.dat` files, as already explained in the previous sections. Figs. 15, 16 and 17 depict the time evolution of the density and one-body confining potential at different time snapshots for the fast quench with $\tau = 1$ (fast quench), $\tau = 10$ (intermediate quench), and $\tau = 100$ (slow quench), respectively.

We begin by describing the dynamics of the fast quench ($\tau = 1$) in Fig. 15. At $t = 0$, the one-body potential is a single harmonic well and the density is centered around the origin in a characteristic Thomas-Fermi shape of an inverted parabola. As the propagation starts (small time $t = 0.1$), a small central barrier is raised, but no visible change in the density can be observed. At $t = 1$, however, the central barrier has reached a significant height, thereby creating an effective 1D double well. The density responds dynamically by splitting into two lobes to the left and right of the barrier. The lobes remain localized in the two wells for larger times $t = 10, 50, 100$. However, the density develops more complicated patterns as the bosons readjust to the new potential landscape. Note that the slight asymmetry displayed

at later times is a consequence of small accumulated errors in the integrator when dealing with such a strong quench, because the potential is not breaking the inversion symmetry with respect to $x = 0$. This can be corrected by employing finer integration step sizes.

The behavior in the intermediate and slow quenches differs strongly from the one in the fast quench. Already for $\tau = 10$ (Fig. 16), we observe a much smoother transition from the Thomas-Fermi profile to the two-peak structure at either sides of the barrier. In the intermediate quench, there are some slight oscillations in the height of the peaks after the barrier has reached its maximal height (cf. $t = 10$, $t = 50$, $t = 100$). This indicates that there is still some internal density reconfiguration happening as a remnant of the quench procedure.

In the slow quench (Fig. 17), instead, the double peak configuration is reached in a very smooth way with minimal disturbance. Here, we are approaching an adiabatic limit and thus the initial ground state should be mapped to the ground state of the Hamiltonian at the final time, in accordance with the adiabatic theorem [69].

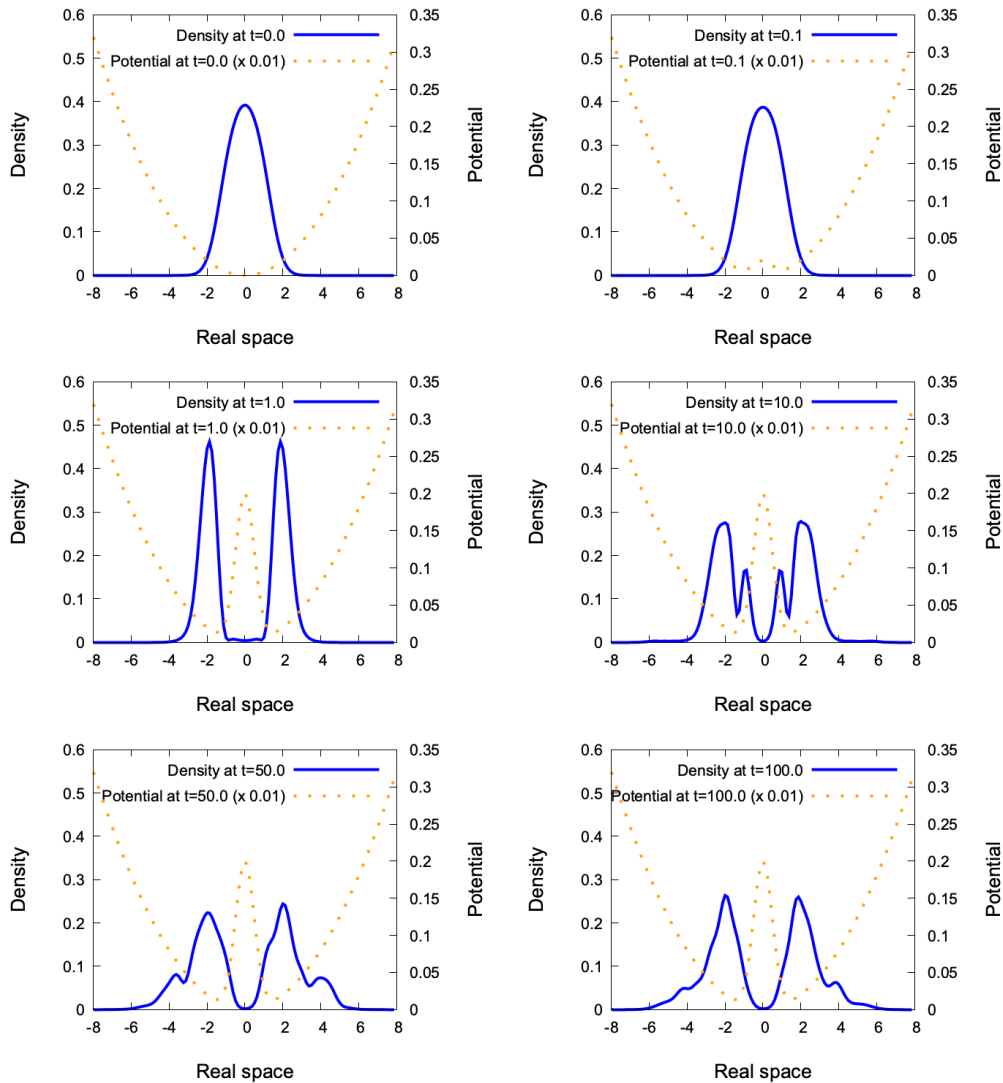


Figure 15: Behavior of the density (solid blue) and one-body potential (dotted orange) as a function of time for 5 bosons in a double well whose central barrier is quenched at a rate $\tau = 1$ (very fast quench).

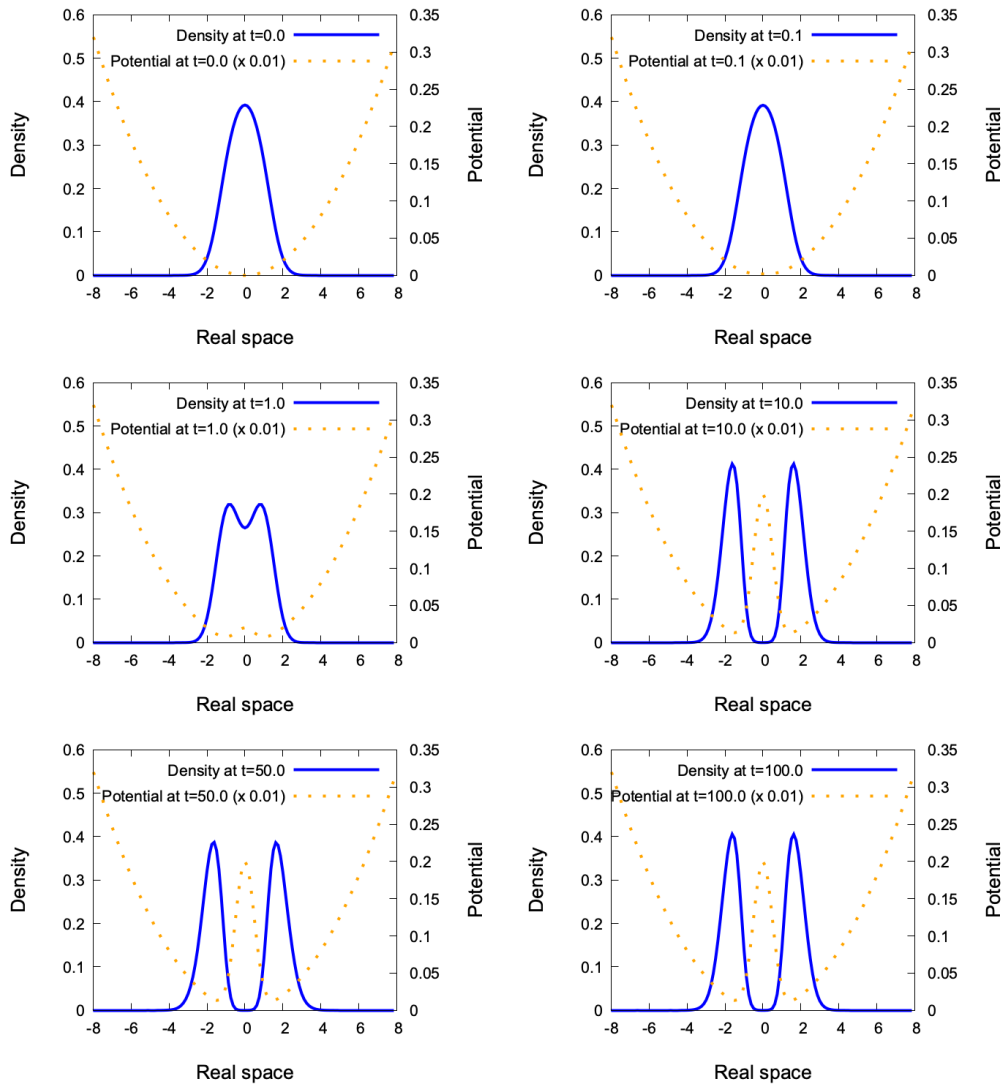


Figure 16: Behavior of the density (solid blue) and one-body potential (dotted orange) as a function of time for 5 bosons in a double well whose central barrier is quenched at a rate $\tau = 10$ (intermediate quench).

Natural occupations The dynamics of the natural occupations $n_i(t)$ are plotted using the file NO_PR.out. Fig. 18 shows the time evolution of these quantities for the three different choices of τ . Recall that, to simulate the dynamics, we employed $M = 10$ self consistent orbitals. In the figure, though, only three natural occupations, n_1/N , n_2/N and n_3/N are shown, since all the other orbitals have much smaller occupations than the third (the occupations are saved from the smallest to the largest in NO_PR.out). In all cases, we can appreciate that the system starts from a superfluid state with a single occupied orbital. The subsequent occupation dynamics depends strongly on the quench rate τ .

For the fast quench with $\tau = 1$, depletion of the initial orbital occurs almost immediately and the condensate evolves into a nearly three-fold fragmented state at large times. The dynamics is not very regular as suggested already by the behavior of the density.

For the intermediate quench with $\tau = 10$, the condensate depletion is visibly reduced. Only the second orbital acquires a sizeable population over time, while the third orbital occupation remains close to zero. Moreover, we observed regular oscillations in the orbital occupations which mirror the oscillations in the density peaks. Nevertheless, the system approaches a

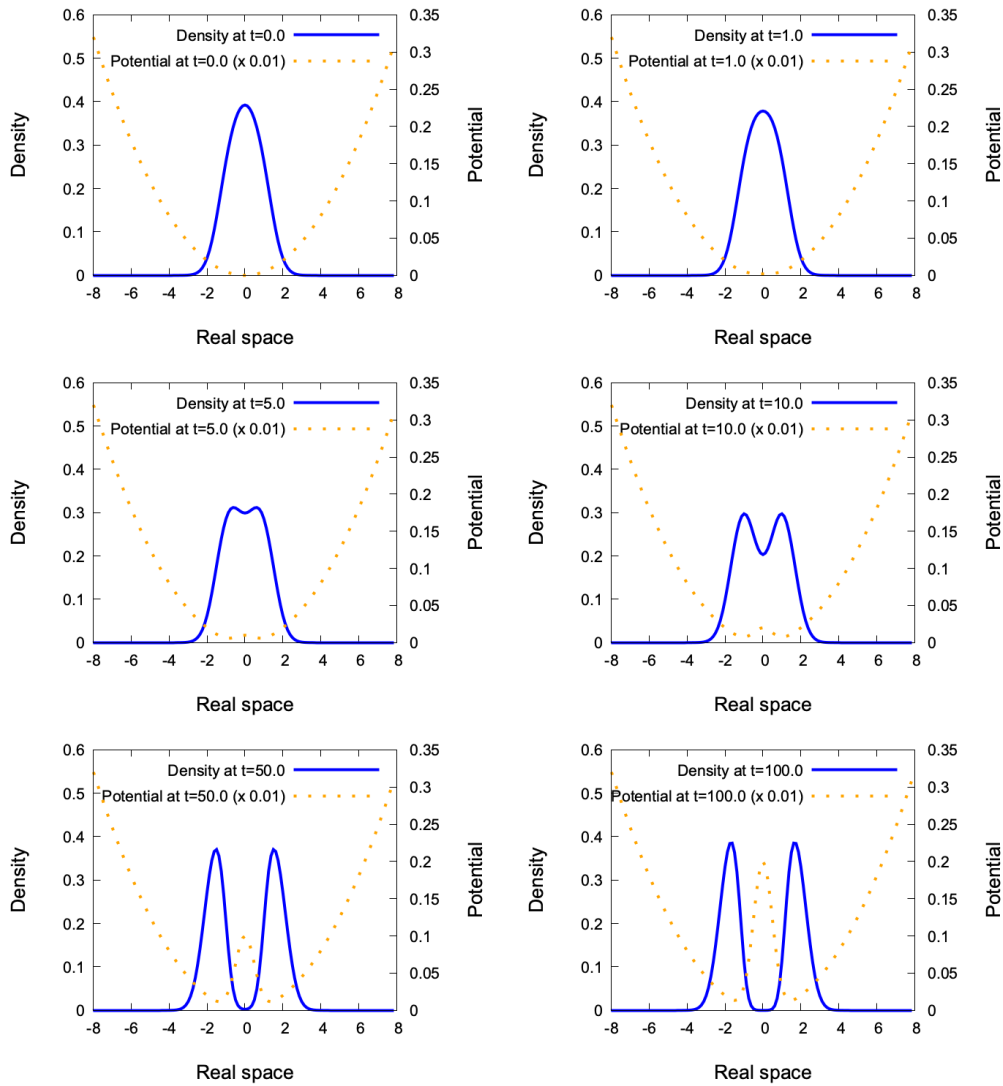


Figure 17: Behavior of the density (solid blue) and one-body potential (dotted orange) as a function of time for 5 bosons in a double well whose central barrier is quenched at a rate $\tau = 100$ (very slow quench).

steady-state with around 80% occupation in the largest orbital and 20% in the second-largest. This oscillation can be understood in an effective two-state model. In the transient time explored here, the many-body state oscillates between two different configurations: one with a larger superfluid component (peaks of first orbital, valleys of the second), and another one with a larger fragmentation (valleys of the first orbital, peaks of the second). If you compare the orbital occupation with the density, you can see that the first configuration (more superfluid) corresponds to the case where the two density peaks are closer to one another, while the second configuration (more fragmented) corresponds to the peaks being further apart. As the many-body state settles into its steady-state configuration, the oscillations progressively dampen and the density becomes distributed in an intermediate “80/20” configuration between the two.

Finally, in the slow, almost adiabatic quench with $\tau = 100$, we observe a much smoother transition to the same 80/20 steady state exhibited in the intermediate quench. The oscillations, though, have a much smaller amplitude in this case.

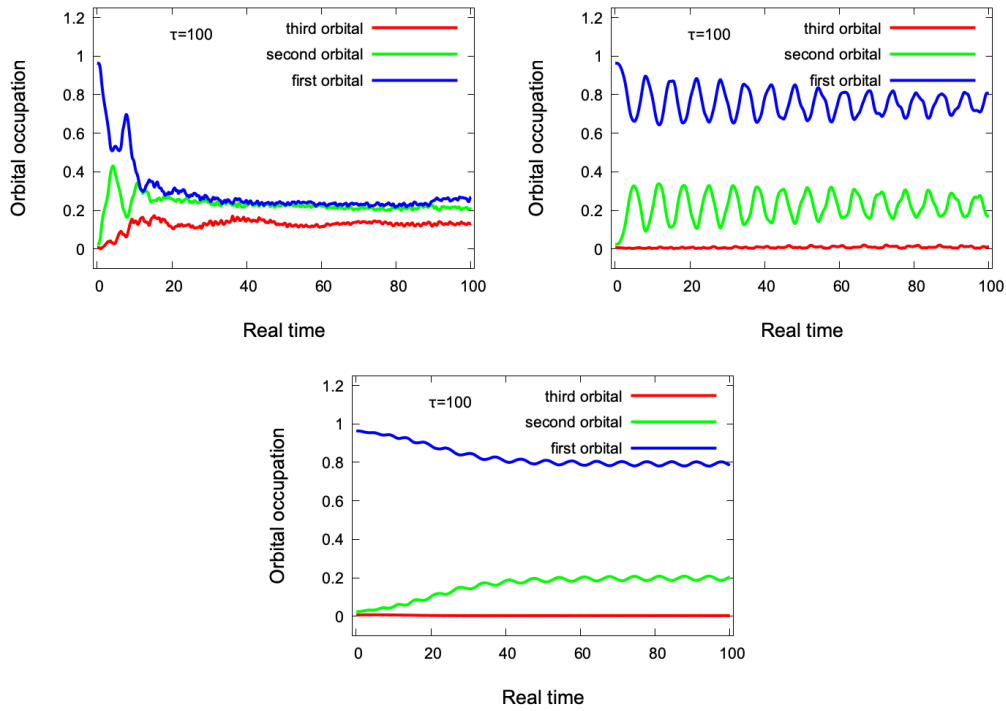


Figure 18: Time evolution of the three leading natural occupations for $N = 5$ bosons in a double well quenched with different rates τ .

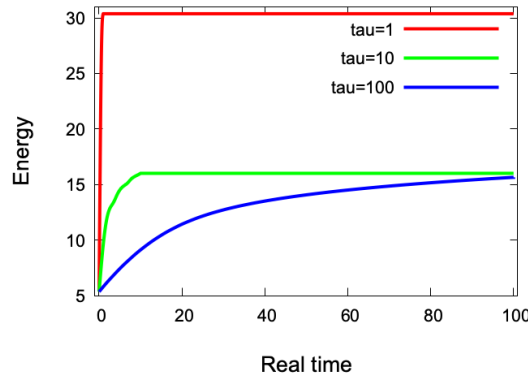


Figure 19: Energy convergence after the quench procedure with $N = 5$ bosons and $M = 10$ orbitals for different values of the quench rate τ .

Energy Since we are changing the parameters of the Hamiltonian by progressively raising the central barrier, we expect the energy to change as a function of time. Intuitively, the energy of the propagated state in the long time limit should be higher than the ground state energy of the initial configuration with no barrier, because the barrier forces the particles to sit at a higher potential energy. We can check our intuition by plotting the energy dynamics from the NO_PR.out file, shown in Fig. 19 for $\tau = 1, 10$ and 100 . For all values of τ , the energy saturates in the steady state. Interestingly, the intermediate and slow quench bring the system to steady states with very similar energy (and as we saw with very similar density). The fast quench ($\tau = 1$), instead, introduces twice as much energy into the system by forcing the particles further away from the center of the potential.

4.3.2 Fermions

We now perform an analysis for similar time-dependent computations involving fermions.

Density In Figs. 20, 21, and 22 we plot some snapshots of the density for the different quenching rates. For this, we again employ the `*orbs.dat` as described in the relaxation section.

As already seen for the bosonic case, when $\tau = 1$, we are performing a fast quench which is known to introduce a lot of energy into the system and drastically reorganize the density in time. In fact, we see a very turbulent dynamics with a lot of oscillations within the two wells once the barrier is raised. Note that, while turbulent, the density remains confined in the double well trap. You can see if you plot it in the full spatial grid, $x = -16$ to $x = +16$. In Fig. 20, we restricted the visualization to the region $x = -8$ to $x = +8$ to better capture local density details.

As we slow down the quench rate ($\tau = 10$), the dynamics becomes smoother and the steady state is more stable. Due to the different quantum statistics, the overall density configuration is quite different than the one exhibited by bosons. Within each peak in both wells, we can observe sub-peaks which are the product of the Pauli exclusion principle. Since the quench is moderate, the density continues to oscillate between different configurations before settling to a steady state. Interestingly, in this case there is no simple two-state picture appearing. Instead, as we will see also for the occupation, there are at least two types of oscillations at play. A first, faster oscillation is similar to the one observed for bosons, where the center of mass of each peak oscillates closer to and further away from the trap center. A second, slower beating pattern appears on top of the faster one, and shows the two density clusters in each well oscillating between a two-peak and a three-peak density profile configuration. This is a manifestation of a complex interplay between long-range Coulomb interactions and the frustration introduced by having an odd number of particles in a two-fold symmetric structure.

Finally, for the slowest quench procedure ($\tau = 100$), the dynamics is quasiadiabatic as already seen for bosons, and the final fragmented state is reached very smoothly.

Orbital occupation We also plot the natural occupations $n_i(t)$ using the file `NO_PR.out` for the quenched fermions. As already seen for bosons, another indication of the very different behavior between fast and slow (adiabatic) quenches is given by the orbital occupation. Due to the different quantum statistics, when dealing with fermions we require at least $M = N + 1$ orbitals as the first N will always be populated. Since in this case $N = 5$, it is thus most instructive to plot and compare the natural orbital occupations of the fifth and sixth highest orbital for the different ramp up times. These are found in the sixth and fifth column of `NO_PR.out`, respectively, and are shown in the left and right panel of Fig. 23.

For $\tau = 1$, i.e. when the barrier is raised very rapidly, the many-body state does not have time to adapt to the quenched configuration and therefore many more orbitals become populated. In particular, the population of the fifth orbital drops rapidly from 20% (indicating one orbital per particle) and stays low throughout the time evolution. Simultaneously, the next orbital (sixth) becomes macroscopically populated.

For the intermediate quench at $\tau = 10$, the fifth orbital maintains at first the initial 20% occupation, but eventually it drops slightly with the same double-oscillation pattern observed in the density. Concomitantly, the sixth orbital acquires an occupation of about 2%, mirroring the same kind of oscillations. This is an indication that the quench is fast enough to perturb the state into a transient (slight) nonequilibrium configuration before the steady state sets in. Note that the simple two-state picture does not apply here. You can check this yourself by plotting the remaining orbitals and verifying that they acquire an occupation in the same order of magnitude (seventh orbital: 1%, eighth orbital: 1%, ninth orbital: 0.5%, tenth orbital: 0.2%).

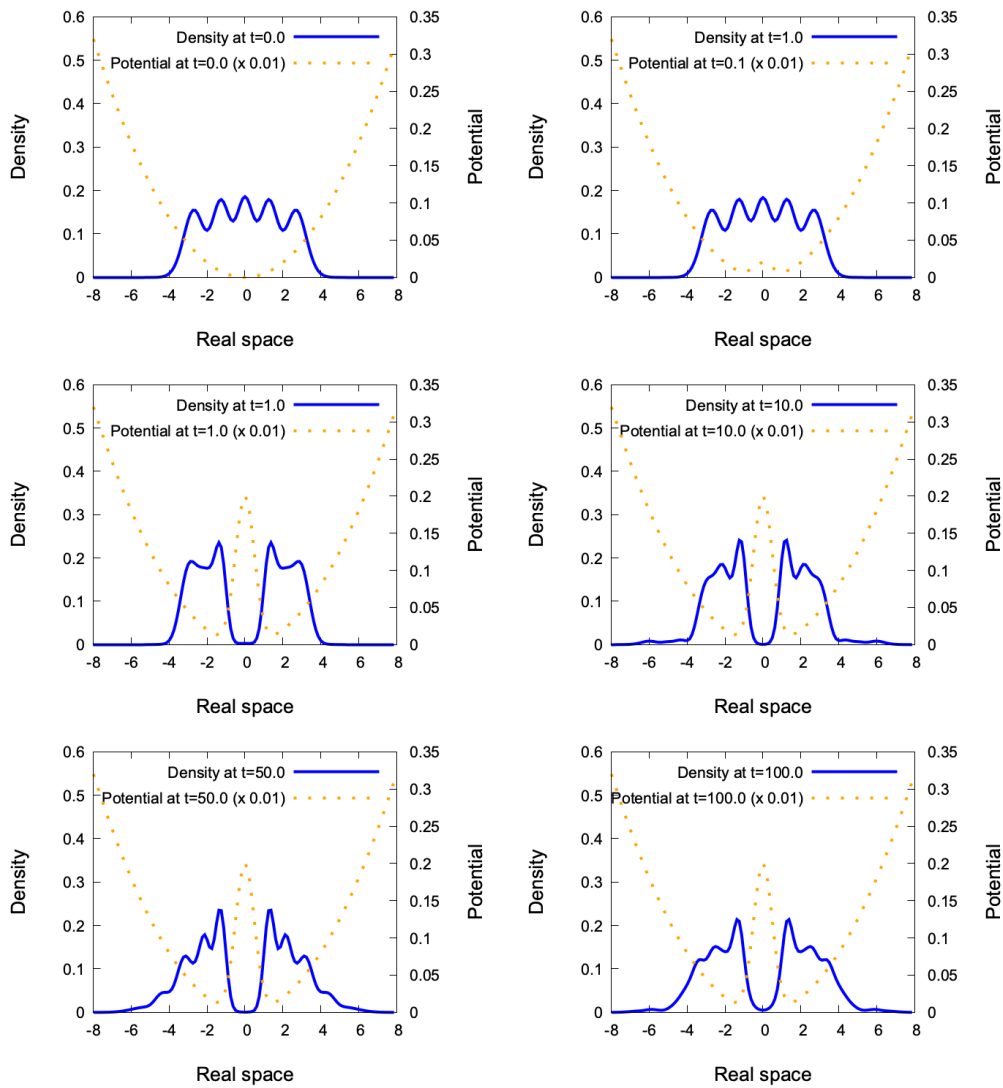


Figure 20: Behavior of the density (solid blue) and one-body potential (dotted orange) as a function of time for 5 fermions in a double well whose central barrier is quenched at a rate $\tau = 1$ (fast quench).

Finally, for $\tau = 100$, we observe a nice adiabatic transition from the initial ground state to the ground state of the final potential, indicated by the practically constant orbital occupation of the fifth orbital at 20% and of the sixth orbital near zero.

Energy The distinction between adiabatic and diabatic quenches can also be seen in the energy in Fig. 24. The energy distinguishes two regimes: the fast quench where the final state is a highly excited state of the final double-well Hamiltonian, and the slow (quasi-adiabatic) quench where we converge to a low-energy state of the final double well (strictly speaking, the ground state is obtained only for an infinitely slow quench $\tau \rightarrow \infty$).

4.4 Additional exercises

What is the true ground state? It is interesting to note that the symmetric low-energy state in the fermionic problem does not actually match the ground state that we would obtain for the double well potential from a relaxation. This is because the system is highly frustrated with

the given odd number of fermions ($N = 5$) for an even number of wells (2). Let us elaborate on what we mean with frustration. The first 4 fermions can sit symmetrically in localized pairs on either side of the wall. The fifth fermion, however, faces a dilemma. To respect the axial symmetry of the potential, it should delocalize across the two wells. However, to minimize the energy contribution from the one-body potential, it would be best to choose one of the two wells to sit in. This, in turn, leads again to an energy penalty due to the Pauli exclusion principle, as we would be cramming three fermions in the same well.

In our initial simulations, it appears that the symmetry-broken configuration is preferred in the relaxation. We can verify this by performing a relaxation in the double-well starting from the ground state of harmonic potential without barrier, see Fig. 25. At intermediate imaginary times, we indeed converge to the symmetric state seen in the adiabatic propagations. At longer imaginary times, however, the algorithm suddenly unlocks a pocket at lower energy with a different and asymmetric density distribution with roughly two particles in one well, and three in the other. In order to plot those energies, follow the instructions from the ground state part of the tutorial.

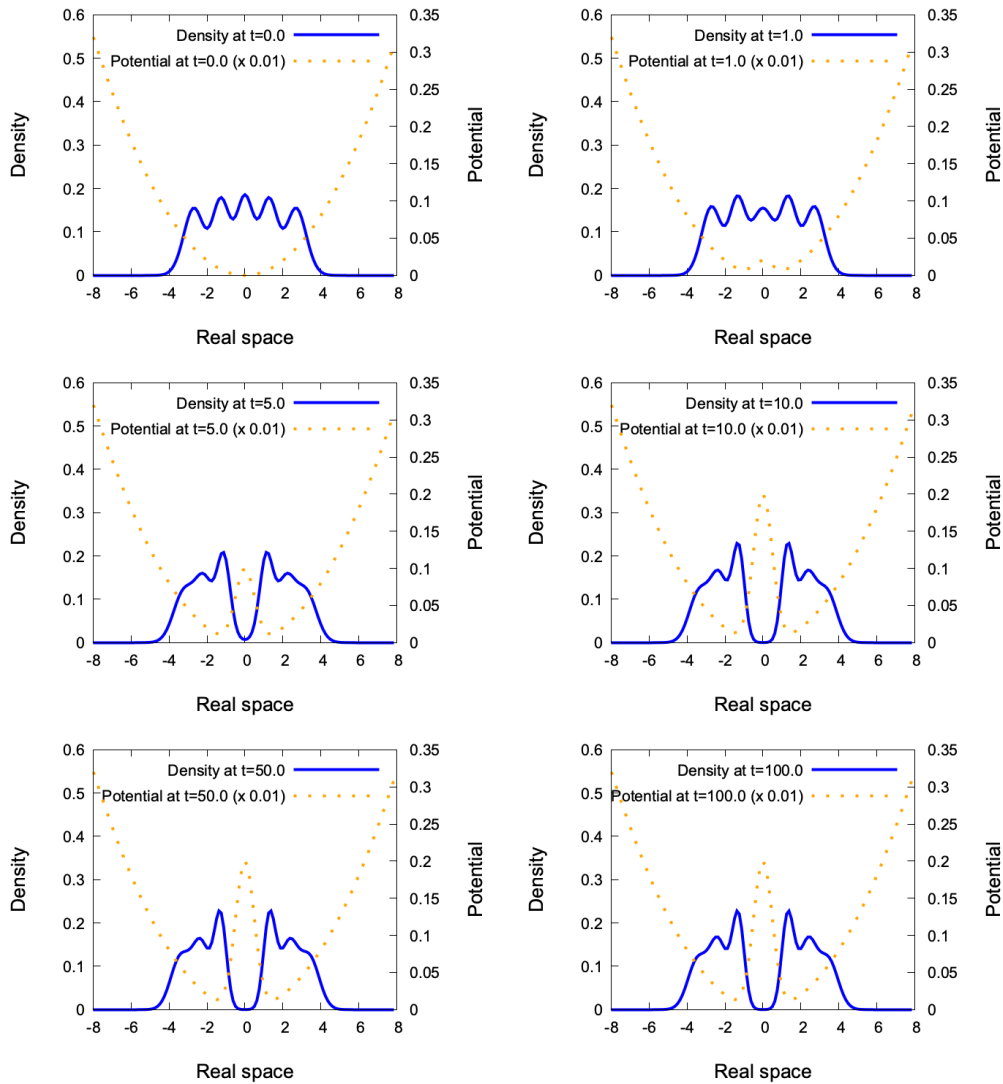


Figure 21: Behavior of the density (solid blue) and one-body potential (dotted orange) as a function of time for 5 fermions in a double well whose central barrier is quenched at a rate $\tau = 10$ (intermediate quench).

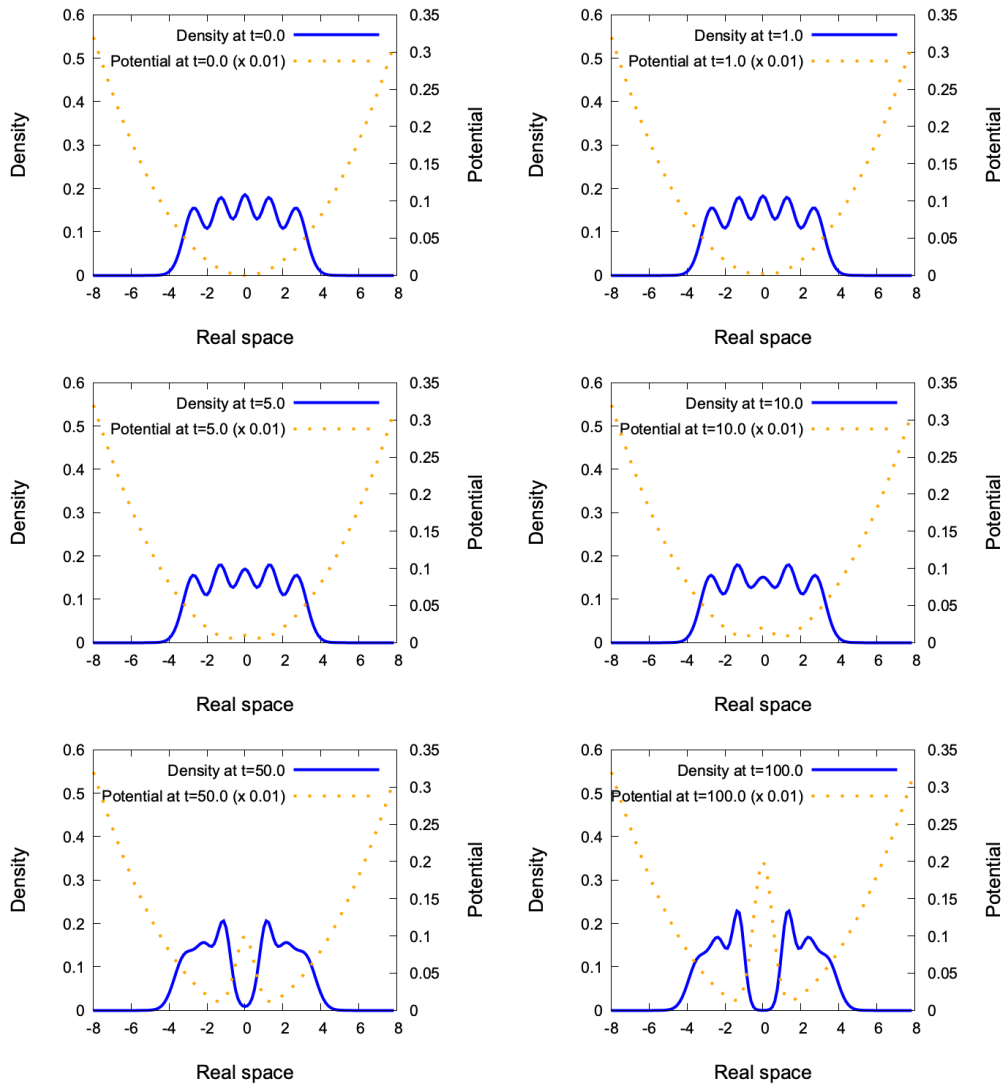


Figure 22: Behavior of the density (solid blue) and one-body potential (dotted orange) as a function of time for 5 fermions in a double well whose central barrier is quenched at a rate $\tau = 100$ (very slow quench).

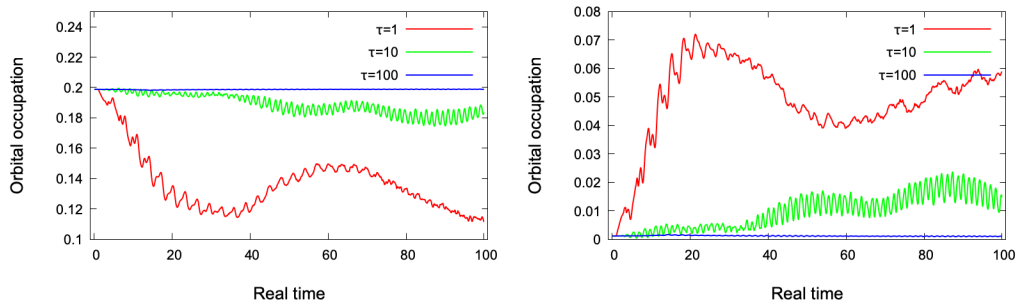


Figure 23: Time evolution of the fifth (left) and sixth (right) leading natural occupations for $N = 5$ fermions with $M = 10$ orbitals in a double well quenched with different rates τ .

Why is the relaxation suddenly breaking the axial symmetry $x_j \rightarrow -x_j$, which is ingrained in the Hamiltonian through the one-body potential and the interparticle interaction? Symmetry-broken solutions emerge when we have non-linear equations of motions and indicate that the many-body solution is particularly interesting, in this case due to frustration. In fact, the linear combination of the symmetry-broken solution and its mirror image will be (very slightly) lower in energy when sandwiched with the (true, linear) many-body Hamiltonian. This problem happens also in attractive bosons in a 1D double well, and already for $M = 1$. The symmetry broken $M = 1$ Gross-Pitaevskii solution (localized in one of the two wells) becomes lower in energy than the $M = 1$ symmetry preserving solution (localized in both wells). This indicates that one needs more orbitals to achieve the true ground state. In the bosonic case, $M = 2$ or $M = 4$ will get the right ground state. This state is a “cat state”, a quantum superposition of two symmetry-broken states. It is called a cat state because it is conceptually similar to Schrödinger’s cat state: a superposition of two macroscopically distinct configurations, such as all particles localized in one well versus all in the other.

The cat state is inherently fragile due to its delicate energy balance and sensitivity to perturbations. In nonlinear systems, numerical algorithms often converge to symmetry-broken states, which are local energy minima, rather than the true ground state represented by the cat state. Limited orbital space in simulations further compounds this issue, as it cannot capture the necessary many-body correlations. Additionally, even in real experiments small perturbations or interactions with the environment can cause decoherence, collapsing the superposition into one of the symmetry-broken states. Achieving the true cat state requires careful control, enhanced orbital resolution, and sophisticated numerical approaches.

How can we fix this? The equations of motion need a large enough number of degrees of freedom (i.e. orbitals) to boil down to the true ground state – see the above example for attractive bosons and $M = 1$. It is simpler to see this process at play for a double well with only $N = 3$ fermions, and for a smaller barrier of height 20 and width 0.5. With lower values of M (e.g. $M = 6$ or $M = 12$), you will get the symmetry broken solution. For $M = 18$, you can manage to restore the symmetry, as shown in Fig. 26. The critical value of M for which the symmetric ground state is restored depends on the interaction strength, the initial shapes of the orbitals, the splitting between the two quasi-degenerate ground and first excited states, and how the numerics is able to handle all of these factors.

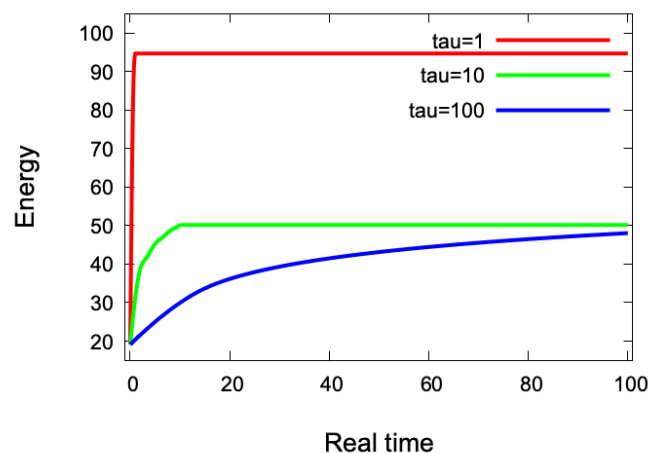


Figure 24: Energy convergence after the quench procedure with $N = 5$ fermions and $M = 10$ orbitals for different values of the quench rate τ .

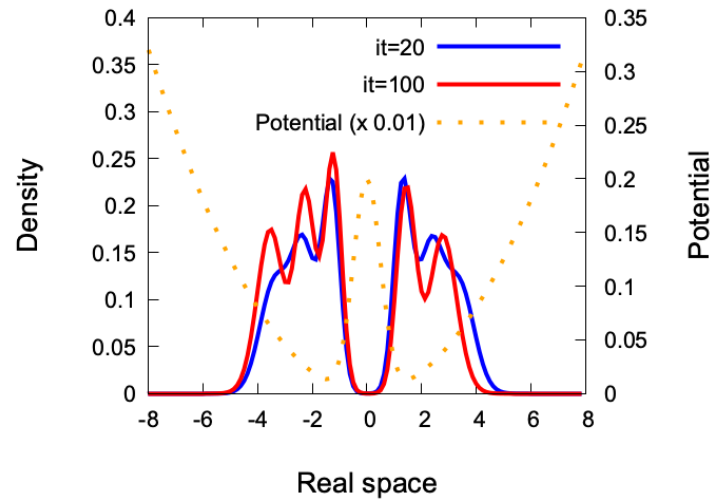


Figure 25: Quasi-degenerate states of $N = 5$ fermions with $M = 10$ orbitals in a double well: ground state (red curve) and excited state (blue curve, similar to the long-time density of an adiabatic quench as in Fig. 22).

Note that the convergence to the ground state is particularly slow for $M = 18$. We reach the symmetric state only around time $t = 160$! One approach to deal with such difficult problems is to start with a smaller grid (e.g. 64 grid points instead of 128) and then interpolate and re-run. MCTDH-X can handle automated grid interpolation on its own: it detects whether the grid has been increased from a previous computation, and performs an interpolation for the higher-resolution grid. Indeed, we can see in Fig. 27 that for 64 grid points the convergence is much faster, and at $t = 40$ we already reach the symmetric state. It is then straightforward to redo a calculation with the larger grid (128 points) using the initial state of the 64-point grid calculation and verify that the symmetry is preserved, as MCTDH-X automatically interpolates initial states defined on a coarser grid.

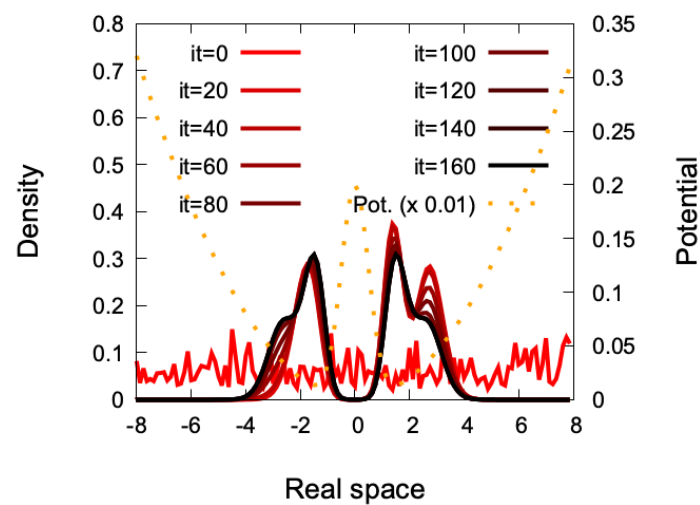


Figure 26: Imaginary time relaxation to the symmetric ground state of $N = 3$ fermions in a double well with $M = 18$ orbitals and 128 grid points.

5 Advanced features

5.1 Analysis

So far we have seen how MCTDH-X can calculate bosonic and fermionic ground state properties such as energy and orbital occupation, and perform real time evolution of the many-body state to generate a time-dependent real-space density. Another important feature is the ability to calculate correlation functions and other observables. This is performed with a separate program execution *after* we have relaxed or propagated the many-body state. The executable in question is `MCTDHX_analysis_gcc`, which is always imported when you run the command `binpcp`. This executable has its own corresponding input file, `analysis.inp`, which is imported with the command `inpcp`. The analysis program takes the binaries and ASCII files calculated during the relaxation or propagation, and extracts observables from the many-body state such as momentum-space densities, Glauber correlation functions, variances, single-shot measurements, and more.

Let us briefly have a look at the variables that can be configured in the analysis input file. We will only focus on the basic ones to generate energies, density distributions, and correlations.

- **Total_Energy:** if set to true (`.T.`), calculates a breakdown of the total energy in kinetic, potential, and interaction energies.
- **Time_From:** this variable tells the program at which time to start performing the analysis. All the time steps from this time until the final time (`Time_To`) will be evaluated.
- **Time_To:** this variable tells the program at which time to end the analysis.
- **Time_Points:** this variable counts the number of time points to perform the analysis at. E.g. if you want all integer times from 0 to 50 included, you need to set `Time_From=0.0d0`, `Time_To=50.0`, and `Time_Points=51`. Note that these times can refer to both a relaxation or a propagation.
- **Density_x:** if set to `.T.`, the program will (re)-calculate the real-space density for all the requested times.

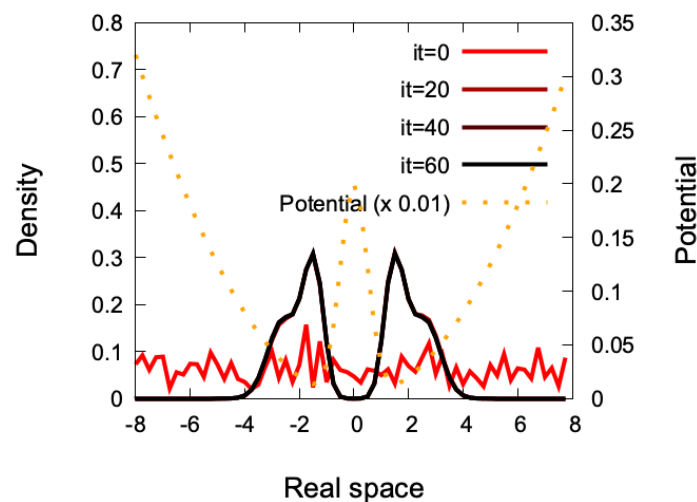


Figure 27: Imaginary time relaxation to the symmetric ground state of $N = 3$ fermions in a double well with $M = 18$ orbitals and 64 grid points.

- **Density_k**: if set to `.T.`, the program will calculate the (diagonal of the one-body) density in k-space for all the requested times.
- **Correlations_X**: if set to `.T.`, the program will calculate the reduced one-body and (the diagonal of) the two-body density matrix in real space:

$$\rho^{(1)}(x, x') = \langle \Psi | \hat{\Psi}^\dagger(x) \hat{\Psi}(x') | \Psi \rangle , \quad (24)$$

$$\rho^{(2)}(x, x') = \langle \Psi | \hat{\Psi}^\dagger(x) \hat{\Psi}^\dagger(x') \hat{\Psi}(x') \hat{\Psi}(x) | \Psi \rangle . \quad (25)$$

These can be used to calculate Glauber one-body and two-body correlation functions as

$$g^{(1)}(x, x') = \frac{\rho^{(1)}(x, x')}{N \sqrt{\rho(x) \rho(x')}} , \quad (26)$$

$$g^{(2)}(x, x') = \frac{\rho^{(2)}(x, x')}{N^2 \rho(x) \rho(x')} . \quad (27)$$

- **Correlations_K**: if set to `.T.`, the program will calculate the reduced one-body and (diagonal of the) two-body densities in k-space.

5.2 Correlations for bosons and fermions

Armed with the knowledge above, we will run our own analysis and calculate one-body and two-body correlation functions for some of the above bosonic and/or fermionic systems.

We will first use the analysis program `MCTDHX_analysis_gcc` to create the files required for plotting the one-body and two-body correlation functions in space.

In the directory of your dynamics calculation, first change the following parameters in the analysis input file `analysis.inp`. If this is not already in your current folder, you can copy it from your relaxation directory.

- **Time_From=0.0d0**: We want to analyze the system from the beginning of the propagation at time $t = 0$.
- **Time_To=100.0d0**: We want to analyze the system until the end of our propagation.
- **Time_Points=101**: We want to evaluate the correlation functions for 101 time steps starting with 0 and ending with 100.
- **xstart = -16.0d0**: This is the beginning of the grid.
- **xend = 16.d0**: This is the end of the grid.
- **Correlations_X=.T.**: Setting this flag to true will calculate the one-body and two-body correlation functions in real space.⁵

Then we run the analysis program from the terminal using

```
./MCTDHX_analysis_gcc.
```

For the case of the above fermionic dynamics calculations, this produces the files `*N4M8x-correlations.dat`. These files contain the values of the one-body and two-body reduced density matrices at different positions x and x' . For example, the real and imaginary

⁵Setting **Correlations_K=.T.** will calculate the one-body and two-body correlation functions in *momentum* space, which is not discussed here.

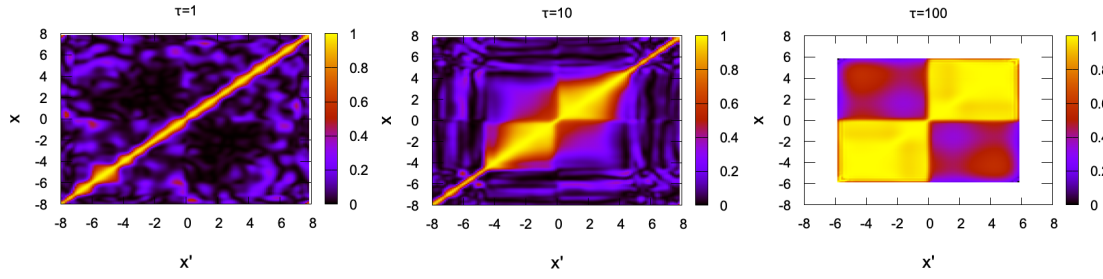


Figure 28: Real-space one-body correlation function $g^{(1)}(x, x')$ at time $t = 99$ for different quench rates τ in the bosonic double-well quench.

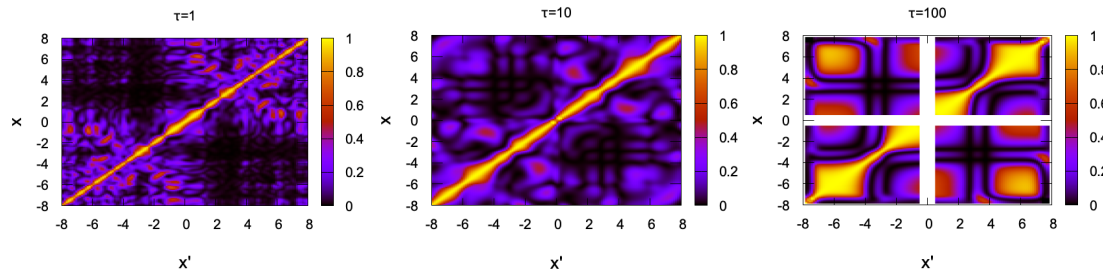


Figure 29: Real-space one-body correlation function $g^{(1)}(x, x')$ at time $t = 99$ for different quench rates τ in the fermionic double-well quench.

part of $\rho^{(1)}(x, x')$ are saved in the 8th and 9th column, while the 7th and 10th column contain $\rho(x)$ and $\rho(x')$, respectively. Please refer to the manual for a full description of the correlation files.

Now that all our necessary files are generated, we will plot the correlation functions in real space. For this, open gnuplot and execute the following lines one by one:

```
set pm3d map,
set cbrange [0:1],
splot "99.0000000N5M10x-correlations.dat" u 1:4:(sqrt($8**2 + $9**2)/sqrt($7*$10)).
```

The lines above will display a plot of the real-space one-body correlation function. For the two-body correlation function, type the following:

```
set pm3d map,
set cbrange [0:1],
splot "99.0000000N5M10x-correlations.dat" u 1:4:($11/($7*$10)).
```

The one-body correlation function $g^{(1)}(x, x')$ at time $t = 99$ and for different ramp up times is illustrated in Fig. 28 for the bosonic setup and in Fig. 29 for the fermionic one. Note that white areas represent artificial numerical singularities due to $\rho(x)$ or $\rho(x')$ being zero.

Different points of $g^{(1)}(x, x')$ can be interpreted as a measure of the coherence. If $g^{(1)}(x, x')$ is large, the quantum states at x and x' are highly coherent and can exhibit strong interference effects. In contrast, if $g^{(1)}(x, x')$ is small or zero for large separations, it indicates that the system lacks long-range coherence, typical of normal fluids or gases. As a special case, wherever the probability is non-zero along the main diagonal, the probability must be one, because every state is perfectly coherent with itself.

Examining the one-body correlation for the bosonic and fermionic problems, we can see that in the fast quench ($\tau = 1$) coherence between the two wells is low, because the particles did not have enough time to adapt to the fast separation of the system into two distinct wells.

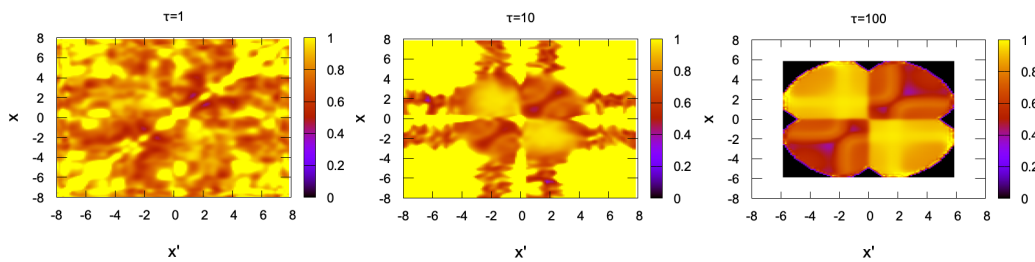


Figure 30: Real-space two-body correlation function $g^{(1)}(x, x')$ at time $t = 99$ for different quench rates τ in the bosonic double-well quench.

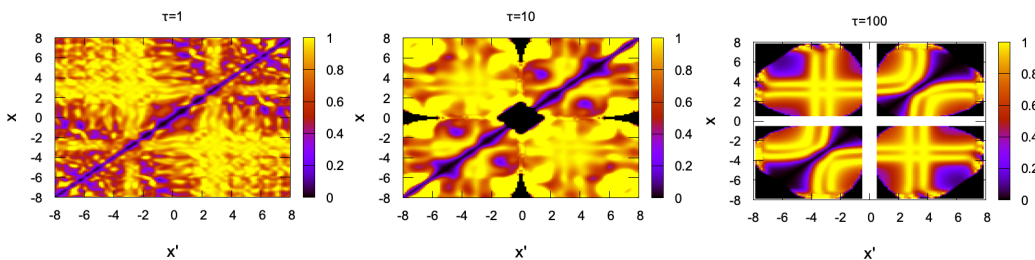


Figure 31: Real-space two-body correlation function $g^{(1)}(x, x')$ at time $t = 99$ for different quench rates τ in the fermionic double-well quench.

As the barrier is raised more slowly, there is more correlation between the two wells as evinced by a larger off-diagonal $g^{(1)}(x, x')$, e.g. between $x = 2$ and $x' = -2$ in the bosonic case.

In the adiabatic limit, we encounter the strongest off-diagonal correlation. The particles are well-localized into two separate peaks, but they retain some correlation across the wells. This is particularly striking for fermions, where we see strong off-diagonal one-body correlation between say $x = 6$ and $x' = -6$. The persistence of correlations across the two wells is evidence of quantum tunneling.

The two-body correlation function $g^{(2)}(x, x')$ at time $t = 99$ and for different ramp up times is illustrated in Fig. 30 for the bosonic setup and in Fig. 31 for the fermionic one. The two-body correlation function measures the joint probability of finding a pair of particles at positions x and x' simultaneously. In bosonic systems, particles tend to bunch together due to Bose-Einstein statistics, leading to $g^{(2)}(x, x')$ being larger than the uncorrelated product at short distances. In fermionic systems, instead, the Pauli exclusion principle leads to anti-bunching, where $g^{(2)}(x, x')$ is smaller than the uncorrelated product at short distances. Therefore, for the (spin-polarized) fermionic two-body correlation function, the Pauli exclusion principle can clearly be seen on the diagonal. Here, the probability is zero, since two fermions cannot coexist in the same state. For electrons, this effect is known as the Fermi hole.

5.3 Videos

To visualize the density as a function of time, MCTDH-X also provides scripts that generate videos automatically, based on the `*orbs.dat` files. For them to work correctly, you should have `mencoder` installed in your system. When you run the MCTDH-X installer, it should have automatically detected `mencoder` and installed the program with the video generation options. If you do not have `mencoder` installed in your system, you can still create your own movies with a different script, e.g. in python.

To create a movie of the density in time, you should run

```
1D-DENSITY_X $1 $2 $3 $4 $5,
```

where \$1 is the starting time, \$2 is the final time, \$3 is the time step, \$4 is the number of orbitals, and \$5 is the number of particles. In the present case of $N = 5$ bosons or fermions and $M = 10$ orbitals with a computation running from 0 to 100 in steps of 0.1, the syntax is

```
1D-DENSITY_X 0 100 0.1 10 5.
```

If you run this script, it should automatically generate a movie called `MCTDHX_Density_X_0_100.mpg` which you can then watch to understand the behavior of the density as the potential is modified.⁶

You can also create time-resolved videos for the one-body and two-body correlation functions using

```
1D-CORR1-X 0 100 1 8 4,
```

and

```
1D-CORR2-X 0 100 1 8 4,
```

respectively. The syntax is the same as for the videos of the time-resolved density. You can also follow the [video tutorial](#) uploaded on YouTube for more information on how to plot quantities obtained from the analysis.

6 Linux/UNIX command cheat sheet

Table 5: Summary of useful Linux/UNIX commands when operating MCTDH-X.

Command	Effect
<code>cp path/to/myfile another/path/</code>	Copies a file to a different location.
<code>ls</code>	Lists all files in the current directory.
<code>ls -a</code>	Lists all files in the current directory, including the hidden ones.
<code>mkdir mydir</code>	Creates a new directory named <code>mydir</code> .
<code>mv path/to/file another/path/</code>	Moves a file to a different location. If the location is the same, but the target filename is different, it renames the file.
<code>pwd</code>	Print the current directory.
<code>rm myfile</code>	Removes (deletes) the file <code>myfile</code> .
<code>rm -r mydir</code>	Removes (deletes) the directory <code>mydir</code> .
<code>source myscript</code>	Executes the content of <code>myscript</code> in the current shell.

⁶If your media player does not have a .mpg decoder, you can convert it to a more common .mp4 format with a free online converter, see e.g. cloudconvert.com.

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Electron transfer and interatomic motion in two-center dielectronic recombination

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(Received 22 November 2024; accepted 24 February 2025; published 12 March 2025)

The recombination of an incoming electron with an atomic cation A^+ , accompanied by energy transfer to a neighboring atom B , which becomes electronically excited and subsequently relaxes radiatively, is investigated. The theory of this process, known as two-center dielectronic recombination (2CDR), is significantly extended to account for the interatomic motion between the two atoms involved. Additionally, the electron transfer mechanism, due to orbital overlap between the atoms, is incorporated into the model. Using the example reaction $e^- + \text{Li}^+\text{He} \rightarrow \text{LiHe}^* \rightarrow \text{LiHe} + \gamma$, we demonstrate that both interatomic motion and electron transfer have a substantial impact on the predicted efficiency of 2CDR. Our findings suggest that 2CDR can dominate over photorecombination across a much broader energy range of the incoming electron than previously estimated. Moreover, 2CDR is particularly efficient when the dimer dissociates during recombination, as this suppresses the energy transfer back to the captured electron, preventing its re-emission.

DOI: [10.1103/PhysRevA.111.032810](https://doi.org/10.1103/PhysRevA.111.032810)

I. INTRODUCTION

The recombination of an incoming free electron with an atomic or molecular cation A^+ is of general interest to a variety of scientific disciplines, such as astrophysics, plasma physics, electrochemistry, and biochemistry [1–3]. In radiative recombination, or photorecombination (PR), the electron is directly captured into a bound state upon the emission of a photon γ , which carries away the excess energy [4,5],

$$e^- + A^+ \rightarrow A + \gamma. \quad (1)$$

If the capturing cation is not isolated in space but in the proximity of an atom or molecule B , then the excess energy can be transferred to electronically excite that neighbor. The

latter can then relax via the emission of a photon,

$$e^- + A^+B \rightarrow AB^* \rightarrow AB + \gamma. \quad (2)$$

This process is referred to as two-center dielectronic recombination (2CDR) [6–9]. Previous works have shown that the 2CDR cross section can dominate over PR by several orders of magnitude, provided the transferred excess energy excites B resonantly. Consequently, 2CDR is highly dependent on the kinetic energy of the incoming electron. However, B^* can also decay through an alternative, competing channel called interatomic Coulombic decay (ICD) [10–14]. In this case, the excitation energy is transferred back to A , which re-emits an electron,

$$e^- + A^+B \rightarrow AB^* \rightarrow A^+B + e^-. \quad (3)$$

This entire process is referred to as two-center resonance scattering (2CRS) [8]. Although it is not directly studied in this work, its potential occurrence must be considered when

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modeling 2CDR, as it implies that not all B^* decay radiatively to complete the recombination process.

Previous studies have investigated 2CDR under the assumption of a fixed distance between the centers [6–8] or during slow atomic collisions [9]. The first objective of this work is to explore the effects of the vibrational and dissociative motion of a weakly bound van der Waals dimer on the 2CDR process.

Second, previous studies assumed that the two centers are sufficiently separated in space such that orbital overlap between them would be negligible. In that case, the Coulomb interaction between the neighbors that mediates the energy transfer simplifies, to leading order, to the interaction between two electric dipoles, thereby neglecting the electron transfer mechanism [15,16]. However, this assumption is not valid if the interatomic distance is comparable to the size of the atoms. It has been shown for related energy-transfer phenomena, such as ICD and interatomic Coulombic electron capture (ICEC) [17–19] that electron transfer can increase the efficiency of the process by several orders of magnitude [11,15,16]. Thus, the second objective of this work is to examine the influence of electron transfer at short interatomic distances on 2CDR. We choose the lithium helium dimer as our test system to apply the newly derived formulas.

This paper is structured as follows: In Sec. II, we introduce the example system, the lithium helium dimer. Section III outlines the pre-existing theory of 2CDR without electron transfer and with a static interatomic distance. We then investigate the effects of interatomic motion (Sec. IV) and electron transfer (Sec. V) separately and then combined (Sec. VI). Finally, we conclude by discussing the overall significance of the results for recombination processes, as well as the limitations of our new models (Sec. VII).

Atomic units (a.u.) are used throughout unless explicitly stated otherwise.

II. THE LITHIUM HELIUM DIMER

The aim of this work is to incorporate interatomic motion and electron transfer into the description of 2CDR and to analyze the respective effects by comparing the obtained cross sections with the already existing theory of 2CDR [6,7]. While the derivations in the following sections should remain as general as possible, it is consistent and favorable to choose a single system and use it throughout this paper to test and compare the different levels of theory. For this purpose, the lithium helium dimers Li^+He , LiHe^* , and LiHe were chosen. They are suitable examples of Van der Waals dimers which are commonly used to study 2CDR and related energy transfer processes [11–13,19–24]. Moreover, considerable attention has been given to the lithium helium dimer particularly in recent years in the contexts of ICD [25–27], resonant two-center photoionization [28,29], or a new process called three-center resonant electron capture [30], which is related to 2CDR. However, in this process B^* does not decay radiatively but via ICD to a third subsystem C . Last, as the goal is to model the interatomic motion of the system during the 2CDR process, the potential energy curves (PECs) of all three states A^+B , AB^* , and AB are required. These data, especially for the AB^* state, are rather scarce in the literature.

TABLE I. Morse potential parameters (in a.u.) of LiHe^+ , LiHe^* (Σ), LiHe^* (Π), and LiHe . D is the potential depth, R_{eq} the equilibrium position, and α scales the width of the potential.

	Li^+He	$\text{LiHe}^* (\Sigma)$	$\text{LiHe}^* (\Pi)$	LiHe
D	2.97×10^{-3}	1.40×10^{-2}	1.13×10^{-2}	5.7×10^{-6}
R_{eq}	3.58	6.46	6.62	11.9
α	1.15	0.44	0.39	0.43

For the lithium helium dimer ($A = \text{Li}$, $B = \text{He}$), with the dipole-allowed excitation $1s^2\ ^1S \rightarrow 1s2p\ ^1P$ in helium, they are reported in Refs. [20,31,32]. This specific excited state of helium is simply referred to as excited helium He^* in the following.

The binding energies of the active electrons in He , He^* , and Li are 24.59, 3.37, and 5.39 eV, respectively [33]. The radiative decay width of He^* is 4.35×10^{-8} a.u. = 1.18×10^{-6} eV [28], and the photorecombination cross section of lithium at the energy corresponding to the resonant excitation of helium is 9.67×10^{-7} a.u. = 27.1 b. This was calculated using the photoionization cross section [34] and the detailed balance equation [18,35]. The vibrational and dissociative motion of the dimers is modeled using the Morse potential [36,37]

$$V_M(R) = D[(1 - e^{-\alpha(R-R_{\text{eq}})})^2 - 1]. \quad (4)$$

It provides a good approximation to the real potential energy curves describing the attraction and repulsion of the atoms. The Morse parameters are obtained by fitting Eq. (4) to PECs reported in the literature. For the initial state Li^+He , the potential from Ref. [32] is taken. For the intermediate state LiHe^* , there are two PECs. The reason is that He^* is not isotropic in space. The binding to the lithium atom therefore depends on whether the p orbital is aligned with the interatomic distance vector, which we choose to lie the z axis (this is called the Σ state) or is perpendicular to it (this is referred to as the Π states) [20]. In this paper, the Σ state is therefore synonymous with $1s2p_z$ excited helium, while the Π states are doubly degenerate and denote the $1s2p_x$ or $1s2p_y$ excited states of helium. The potentials are taken from Ref. [20].

Last, the parameters for the Morse potential of the final state LiHe are taken from Refs. [28,29]. A PEC for this state can be found in Ref. [31]. The Morse parameters are shown in Table I.

Figure 1 shows the Morse potentials employed in this work. The equilibrium distance for LiHe^+ , $\text{LiHe}^* (\Sigma)$, $\text{LiHe}^* (\Pi)$, and LiHe are 1.89, 3.42, 3.50, and 6.30 Å, respectively.

In the 2CDR process, Li^+He is the initial state. For $R \rightarrow \infty$, the intermediate state LiHe^* lies 15.83 eV higher in energy. The incoming electron must thus have roughly this energy, such that 2CDR can proceed resonantly. LiHe^* then decays to LiHe which lies 21.22 eV lower in energy by the emission of a photon. When including the interatomic motion of the dimers, the energies of the vibrational or dissociative states must be taken into account.

The molecular wave functions ρ and eigenenergies E_ρ are obtained by numerically solving the Schrödinger equation in a box on a grid using a discrete variable representation [38]. The size of the grid was chosen to 600 a.u. with a spacing of $1/8$

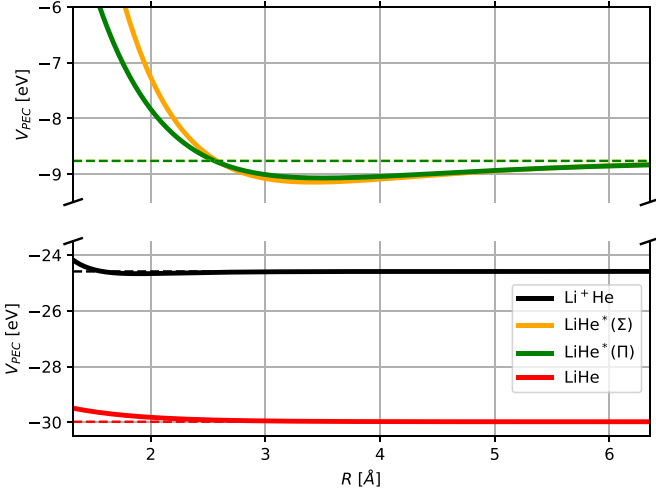


FIG. 1. Morse potential energy curves of Li^+He , $\text{LiHe}^*(\Sigma)$, $\text{LiHe}^*(\Pi)$, and LiHe states. The asymptotic energies are indicated by dashed lines. Here the electronic energy of Li^+He^+ is chosen as the zero of energy.

a.u. ensuring convergence of the cross sections with respect to the grid parameters. In general, the energies can be negative (bound vibrational states) or positive (unbound dissociative states). We find that Li^+He has 5 bound vibrational levels [39], $\text{LiHe}^*(\Sigma)$ has 26 vibrational levels, $\text{LiHe}^*(\Pi)$ has 27 vibrational levels, and LiHe has only 1.

III. 2CDR WITH FIXED INTERATOMIC DISTANCE AND NO ELECTRON TRANSFER

Müller *et al.* developed an asymptotic theory for 2CDR assuming a sufficiently small fixed interatomic distance such that energy transfer between the subsystem is efficient but sufficiently large such that there is negligible orbital overlap and therefore no electron transfer between the two centers [6]. Here we sketch the derivation of that formula for the 2CDR cross section and apply it to the example system LiHe .

The origin of the coordinate system is placed in the center of mass of A^+ . The neighboring atom B is placed at position $\vec{R}$. $R = |\vec{R}|$ is therefore the distance between the two subsystems A and B and shall be a fixed parameter for now. To keep the derivation simple, as in Ref. [6], we treat the two subsystems as two effective one-electron systems. The electron that is captured by A^+ and the electron that transitions into an excited state B^* are *active* while all other electrons are treated implicitly.

Initially, a free electron of asymptotic momentum $\vec{p}$ and energy $\varepsilon_p = p^2/2$ approaches A^+ , described by the state $\phi_{\vec{p}}$. B is in its ground state, described by χ_g and energy ε_g [40]. The total system is thus initially described by $\psi_i = \phi_{\vec{p}} \chi_g$ and energy $E_i = \varepsilon_p + \varepsilon_g$.

The electron then shall get captured into the ground state ϕ_g of A with energy ε_g [41] while the excess energy $\varepsilon_p - \varepsilon_g$ is transferred to subsystem B which is electronically excited to the excited state B^* , denoted χ_e , with energy ε_e . The excitation proceeds resonantly when the transferred energy equals $\varepsilon_e - \varepsilon_g$. The intermediate state of the system is therefore

$\psi_m = \phi_g \chi_e$ with energy $E_m = \varepsilon_g + \varepsilon_e$. B^* is unstable as it can relax either by the emission of a photon or by ICD and the re-emission of an electron. This can be treated elegantly by introducing an imaginary part of the energy $\tilde{E}_m = \varepsilon_g + \varepsilon_e - i\frac{\Gamma_m^B}{2}$ with $\Gamma_m^B = \Gamma_{m,\text{RD}}^B + \Gamma_{m,\text{ICD}}^B$ being the total decay width of B^* in the presence of A and thus the inverse of its lifetime [42,43].

Last, B^* relaxes to its ground state via the emission of a photon while A stays unaltered. The final state of the system is then given by $\psi_f = \phi_g \chi_g \otimes 1_{\vec{k},\lambda}$, where $1_{\vec{k},\lambda}$ describes the emitted photon of asymptotic momentum $\vec{k}$, polarization λ and energy $\omega = ck$. The total energy of the final state is thus $E_f = \varepsilon_g + \varepsilon_g + \omega$.

The Hamiltonian of the whole system is given by

$$\hat{H}(t) = \hat{H}^A + \hat{H}^B + \hat{H}_{\text{RF}} + \underbrace{\hat{V}_{AB} + \hat{V}_{\text{RF}}^A(t) + \hat{V}_{\text{RF}}^B(t)}_{\hat{V}(t)}. \quad (5)$$

Here $\hat{H}^A$ and $\hat{H}^B$ are the unperturbed Hamiltonians that describe the active electron at A and B , respectively. The ϕ and χ states are thus eigenstates of $\hat{H}^A$ and $\hat{H}^B$, respectively. $\hat{H}_{\text{RF}}$ describes the unperturbed radiation field with $1_{\vec{k},\lambda}$ being an eigenstate of that operator. $\hat{V}_{AB} = \frac{1}{\hat{d}_A - (\hat{d}_B + \vec{R})}$ is the Coulomb interaction between the two active electrons that mediates the energy transfer between A and B . Here $\hat{d}_A$ and $\hat{d}_B$ are the position or dipole operators of the electrons with respect to their atomic nuclei. For now we assume that the interatomic distance R is sufficiently large such that there is no orbital overlap between the subsystems. The interatomic interaction then simplifies in leading order to the interaction of two dipoles [6]

$$\hat{V}_{AB}^{dd} = \frac{\hat{d}_A \hat{d}_B - 3(\hat{d}_A \vec{e}_{\vec{R}})(\hat{d}_B \vec{e}_{\vec{R}})}{R^3}. \quad (6)$$

Here $\vec{e}_{\vec{R}} = \vec{R}/R$ is a unit vector pointing from atom A to atom B . Last, $\hat{V}_{\text{RF}}^A(t) = \frac{1}{c} \vec{p}^A \hat{A}(t)$ describes the coupling of the active electron at subsystem A to the radiation field, and analogously for B . Here

$$\hat{A}(t) = \sum_{\vec{k},\lambda} \sqrt{\frac{2\pi c^2}{\omega_k}} (\hat{a}_{\vec{k},\lambda} \vec{e}_{\vec{k},\lambda} e^{i(\vec{k} \cdot \vec{r} - \omega_k t)} + \text{c.c.}) \quad (7)$$

is the quantized vector potential of the radiation field, summing over all momenta and polarizations of the photons, with the corresponding polarization vectors $\vec{e}_{\vec{k},\lambda}$ [44]; c.c. denotes complex conjugate; $\hat{a}_{\vec{k},\lambda}$ ($\hat{a}_{\vec{k},\lambda}^\dagger$) annihilates (creates) a photon with the respective momentum and polarization; and $\hat{V}(t) = \hat{V}_{AB} + \hat{V}_{\text{RF}}^A(t) + \hat{V}_{\text{RF}}^B(t)$ is the total perturbation.

The quantum mechanical transition amplitude for the 2CDR process in second-order time-dependent perturbation theory is then given by

$$b_{2\text{CDR}} = \left(\frac{1}{i}\right)^2 \sum_m \int_{-\infty}^{\infty} dt \langle \psi_f | \hat{V}(t) | \psi_m \rangle e^{-i(\tilde{E}_m - E_f)t} \times \int_{-\infty}^t dt' \langle \psi_m | \hat{V}(t') | \psi_i \rangle e^{-i(E_i - \tilde{E}_m)t'} [45]. \quad (8)$$

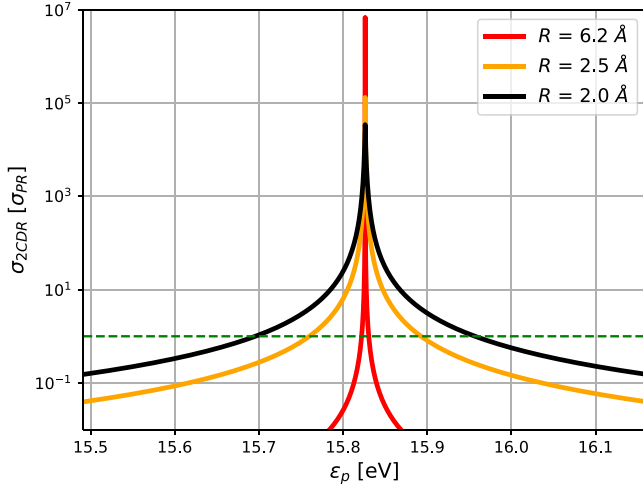


FIG. 2. 2CDR cross section for $e^- + \text{Li}^+\text{He} \rightarrow \text{LiHe}^* (1s2p\ ^1P) \rightarrow \text{LiHe} + \gamma$ in units of the photorecombination cross section of lithium as a function of the energy of the incoming electron ε_p for different interatomic distances. The green dashed line indicates the one-center photorecombination cross section.

The sum runs over all intermediate states. To calculate the 2CDR cross section, we have to take the absolute square of this amplitude and divide by the incoming electron flux which equals the momentum p in the chosen continuum normalization and by the time the interaction acts on the system T . Furthermore, we have to sum over all final states, meaning we integrate over all possible momenta of the emitted photon and sum over its polarization [29,30]. We also average over the solid angle of the incoming electron. For our example system LiHe, the cross section can be written as

$$\sigma_{2\text{CDR}}^{dd, \text{LiHe}}(\varepsilon_p) = \frac{3c^6}{8(\varepsilon_p - \varepsilon_g)^6 R^6} \sigma_{\text{PR}}^{\text{Li}}(\varepsilon_p) (\Gamma_{\text{RD}}^{\text{He}})^2 \times \left[\frac{1}{\Delta^2 + \frac{(\Gamma_{\text{H}}^{\text{He}})^2}{4}} + \frac{2}{\Delta^2 + \frac{(\Gamma_{\text{S}}^{\text{He}})^2}{4}} \right]. \quad (9)$$

The superscript *dd* signifies that only the dipole-dipole term of the Coulomb interaction was used for both the energy transfer from lithium to helium and the possible energy transfer back via ICD. The cross section is proportional to the photorecombination cross section of lithium $\sigma_{\text{PR}}^{\text{Li}}$, measuring the efficiency of the initial electron capture, and the square of the radiative decay width of $\text{He}^* \Gamma_{\text{RD}}^{\text{He}}$, measuring the efficiency of the $\text{He} \rightarrow \text{He}^*$ transition and back. It is also inversely proportional to the sixth power of both the energy transferred between the subsystems $\varepsilon_p - \varepsilon_g$ and the interatomic distance R . Last, there is a Lorentzian profile that peaks at $\Delta = \varepsilon_p - \varepsilon_g - (\epsilon_e - \epsilon_g) = \varepsilon_p - 15.83 \text{ eV} = 0$, thus when the energy transferred from Li to He excites the latter resonantly. The width of that peak is given by the total decay width of He^* , including the radiative and ICD channels. As the efficiency of ICD generally depends on the mutual orientation of the two atoms, the respective widths are different for $1s2p_z$ ($\Gamma_{\text{S}}^{\text{He}}$) and $1s2p_{x/y}$ excited helium ($\Gamma_{\text{H}}^{\text{He}}$) [20].

Figure 2 shows the 2CDR cross section as a function of the kinetic energy of the incoming electron for different

interatomic distances, corresponding to the mean interatomic distance of Li^+He in the vibrational ground state, second excited state, and fourth excited state. These states were only chosen to illustrate the changes in the cross sections as functions of the interatomic distance, while keeping the figure comprehensible. The cross section is given in units of the photorecombination cross section of lithium to show the enhancement factor of 2CDR compared to the competing recombination channel. We see that 2CDR can dominate over photorecombination by multiple orders of magnitude on resonance. However, the cross section decreases quickly off resonance, such that 2CDR is only dominant in a rather small range of the kinetic energy of the incoming electron. In the dipole-dipole approximation the ICD width falls off with the sixth power of the interatomic distance [11]. When increasing R , the Lorentzian peak narrows correspondingly, and 2CDR becomes more dependent on the kinetic energy of the incoming electron. While for $R = 2.0 \text{ \AA}$ the energy interval in which 2CDR dominates over PR is 261 meV wide, it is only 9 meV wide for $R = 6.2 \text{ \AA}$.

IV. INFLUENCE OF INTERATOMIC MOTION

The pre-existing theory presented above assumes the subsystems A and B are at a fixed distance during the 2CDR process [6]. However, real molecular systems composed of two subsystems A and B , like van der Waals dimers, can vibrate around an equilibrium distance or dissociate. To account for these effects, we adapt the approach in Refs. [28,29] for the study of interatomic motion in two-center resonant photoionization [46] which is the inverse process of 2CDR. We choose a Born-Huang ansatz [47] for our wave functions and furthermore employ the Born-Oppenheimer approximation [48] throughout this paper. This means we split up the wave function describing the whole system into four separate wave functions. The first three describe the two active electrons at A and B and the photons in the total system just as in the previous section. However, the new fourth wave function ρ describes the interatomic motion. We can therefore use the same wave functions as in the previous section and multiply them by the new states ρ_i , ρ_m , and ρ_f for the initial, intermediate, and final electronic states, respectively. The calculation of these states was discussed in Sec. II. For 2CDR to occur, the two subsystems need to be relatively close initially such that the energy can get efficiently transferred from A to B . We therefore consider only bound initial states. The system might then be bound or dissociative in the intermediate and final electronic states.

The energies of the states of the total system change compared to the previous section as they gain a contribution from the interatomic motion E_ρ , i.e., the eigenenergies of the ρ states. As in the previous section, the decay of the intermediate state is accounted by adding an imaginary part to its energy [42,43]. As the ICD width strongly depends on the interatomic distance R , the ICD width must also strongly vary between the different molecular states. To eliminate the explicit R dependence of the ICD width, an approximative state-specific width can be defined by averaging Γ_{ICD} over the respective

probability density $|\rho_m|^2$:

$$\Gamma_{\text{ICD},m,\rho_m}^B := \int dR \Gamma_{\text{ICD},m}^B(R) \times |\rho_m(R)|^2 \quad [28,29]. \quad (10)$$

The calculation of the transition amplitude and cross section then proceeds very similarly to the previous section.

$$\sigma_{2\text{CDR}}^{dd,im,\text{LiHe}}(\varepsilon_p) = \frac{3c^6}{8(\epsilon_e - \epsilon_g)^6} (\Gamma_{\text{RD}}^{\text{He}})^2 \sigma_{\text{PR}}^{\text{Li}}(\varepsilon_p) \times \left(\sum_{\text{bound } \rho_{m,\Pi}} \frac{|\langle \rho_{m,\Pi} | \frac{1}{R^3} | \rho_i \rangle|^2}{\Delta_\rho^2 + \frac{(\Gamma_{\rho_{m,\Pi}}^{\text{He}})^2}{4}} + 2 \sum_{\text{bound } \rho_{m,\Sigma}} \frac{|\langle \rho_{m,\Sigma} | \frac{1}{R^3} | \rho_i \rangle|^2}{\Delta_\rho^2 + \frac{(\Gamma_{\rho_{m,\Sigma}}^{\text{He}})^2}{4}} + 2\pi\eta(E_{\rho_m}) \left[\frac{|\langle \rho_{m,\Pi} | \frac{1}{R^3} | \rho_i \rangle|^2}{\Gamma_{\rho_{m,\Pi}}^{\text{He}}} + 2 \frac{|\langle \rho_{m,\Sigma} | \frac{1}{R^3} | \rho_i \rangle|^2}{\Gamma_{\rho_{m,\Sigma}}^{\text{He}}} \right] \right). \quad (11)$$

The superscript *im* signifies that the interatomic motion was included in the model. This expression has strong similarities to the cross section neglecting interatomic motion from Eq. (9) in terms of the prefactors and the proportionality to the photorecombination cross section of lithium and the radiative decay width of He^* . However, there are some important differences. We see in the parentheses two sums corresponding to bound intermediate states and two terms corresponding to unbound intermediate states. Whether the system is bound or unbound in the intermediate electronic state is determined by the kinetic energy of the incoming electron ε_p and the eigenenergy of the initial molecular state E_{ρ_i} . When ε_p is smaller (larger) than $\varepsilon_g + \epsilon_e - \epsilon_g - E_{\rho_i}$, the intermediate molecular state is bound (dissociative).

For the bound states, the two sums run over all bound states of LiHe^* in both the Π and Σ electronic state. As the total energy of the system is not only electronic but also influenced by the energy corresponding to the interatomic motion, there is not only one peak condition $\Delta = 0$, as before, but as many peak conditions $\Delta_\rho = \Delta + E_{\rho_i} - E_{\rho_m} = 0$ as there are bound intermediate states. Furthermore, the simple R^{-6} factor is replaced by squared R^{-3} weighted overlap integrals between the initial and the intermediate vibrational states. These overlaps can be seen as generalized Franck-Condon factors. The higher the overlap between the initial and the intermediate vibrational state, or in a classical picture, the more time the dimer spends at similar interatomic distances in the two states, the higher the efficiency of the transition between the two. The R^{-3} factor leads to overlaps at smaller interatomic distances being weighted more compared to larger distances to account for the higher efficiency of the energy transfer from *A* to *B* at smaller *R*.

When the intermediate state is dissociative, the energy E_{ρ_m} and therefore the intermediate state ρ_m is exactly defined by the condition $\Delta_\rho = 0$. As the unbound states lie in a continuum, there are no Lorentzian profiles but a simple $\Gamma_{\rho_m}^{\text{He}}$ term enters the denominator. Furthermore, there is an additional factor $\eta(E_{\rho_m}) = \sqrt{\frac{2\mu}{E_{\rho_m}}} \frac{R_{\text{max}}}{2\pi}$ which is the density of dissociative states [49], where μ is the reduced mass of the dimer and R_{max} the length of the box in which the molecular states are numerically calculated (see Sec. II).

As we sum over all final states and therefore over all Franck-Condon factors for the intermediate $\rightarrow$ final

We just have to additionally sum over all final molecular states when calculating the cross section. The detailed derivation can be found in the Appendix. The 2CDR cross section for LiHe including the interatomic motion now reads

transition, the cross section is independent of the final vibrational or dissociative state.

Figure 3 shows that the cross section is significantly altered compared to the theory presented in the previous section, which assumed a fixed interatomic distance. The cross section can be divided into two distinct regimes. Below 15.89 eV, we observe a multitude of peaks corresponding to the 26 bound vibrational intermediate states of LiHe^* (Σ) and 27 states of LiHe^* (Π). Above 15.89 eV, we see a continuum corresponding to dissociative intermediate states. In contrast, the previous theory predicted a single peak.

Here only an energy interval corresponding to intermediate dissociation energies of maximally 0.7 eV is shown. The reason is that in our derivations it was assumed that only one electronic energy level is excited in *B*. However, larger dissociation energies correspond to larger kinetic energies of the incoming electron. The energy eventually becomes large enough to involve higher electronic transitions.

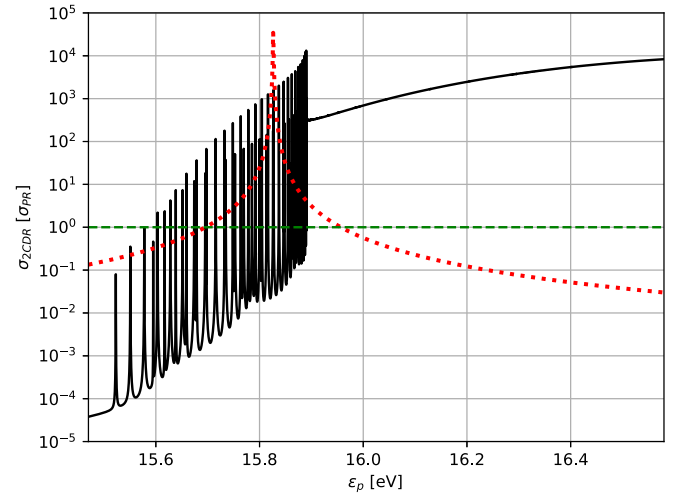


FIG. 3. Cross section for the $e^- + \text{Li}^+\text{He} \rightarrow \text{LiHe}^*(1s2p\ ^1P) \rightarrow \text{LiHe} + \gamma$ two-center dielectronic recombination in units of the photorecombination cross section of lithium using the dipole-dipole approximation as a function of the energy of the incoming electron. Black full line: Including interatomic motion, using Eq. (11). The dimer is initially in its vibrational ground state. Red dotted line: Fixed interatomic distance at the mean distance of the respective initial molecular state, using Eq. (9). The green dashed line indicates the one-center photorecombination cross section of lithium.

A general effect of including interatomic motion is that the 2CDR process can compete with photorecombination over a much larger range of kinetic energies of the incoming electron. Thus, 2CDR may be of significantly greater relevance to recombination processes in nature than previously anticipated.

V. INFLUENCE OF ELECTRON TRANSFER

The dipole-dipole approximation used for the derivations in the previous sections may not be accurate given the small interatomic distances that dimers can have. For example, the ground state and the first three vibrationally excited states of Li^+He have mean interatomic distances between 2 and 3 Å. It has been shown for a variety of systems that lower-order terms of the multipole expansion can dominate the energy transfer between the subsystems at such small R [11,15,16,25,27]. In this section, orbital overlap (i.e., the electron transfer mechanism) is therefore included in the model, initially with a fixed interatomic distance. In the following section, the combination of the effects of electron transfer and interatomic motion are studied. The inspiration for the model presented here is the work of Šenk and coworkers, who included electron transfer in the model of direct ICEC [16].

The two active electrons in the system are indistinguishable particles. Their total spatial electronic wave functions should therefore be antisymmetrized. Furthermore, the dipole-dipole term in the multipole expansion of the Coulomb interaction between the electrons is only the first nontrivial term when there is no orbital overlap between the subsystems, which is not necessarily the case during the vibrational and dissociative motion of the dimer. We therefore also include the monopole-monopole term of the Coulomb interaction. This, along with the antisymmetrization of the ψ wave functions, leads to an additional term proportional to R^{-1} in the transition matrix element from the initial to the intermediate state:

$$\langle \psi_m | \hat{V}_{AB}^{mm} | \psi_i \rangle = -\frac{1}{R} \langle \phi_g | \chi_g \rangle \langle \chi_e | \phi_{\bar{p}} \rangle. \quad (12)$$

This term can be seen as a new channel for electron capture and is schematically depicted in Fig. 4, where it is compared to the dipole-dipole coupling mechanism. The intuitive interpretation of this new channel is that the incoming electron is captured into the excited state B^* , while the initially bound electron at B transitions into the bound state of A . Hence, the term *electron transfer* is used for this channel based on orbital overlap between the neighboring atoms. Note that the same new amplitude was found in Ref. [16] for the direct ICEC process, with the exception that B is not excited but ionized.

The first factor $\langle \phi_g | \chi_g \rangle$ represents the overlap of the two ground-state wave functions centered at atoms A and B , separated by the distance R . In the case of the lithium helium dimers, this would be the overlap of the $1s$ orbital of helium with the $2s$ orbital of lithium. Calculating this overlap as a function of R rigorously would require *ab initio* quantum chemistry tools [50]. However, the aim of this work is to find a relatively simple analytical and intuitive model that describes the overlap, even under a loss of exactness.

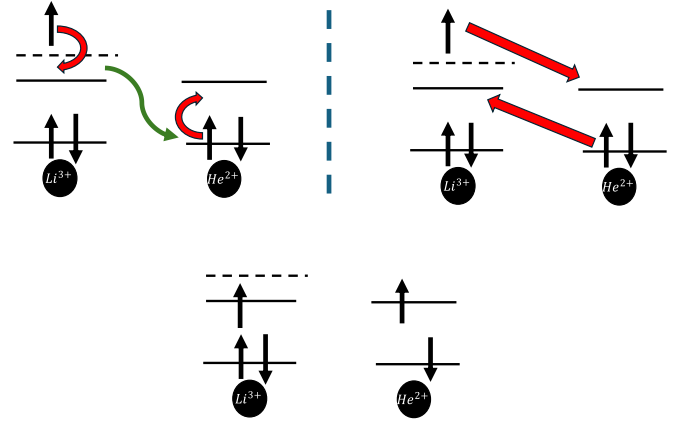


FIG. 4. Schematic depiction of the dipole-dipole (top left) and the new monopole-monopole or electron-transfer channel (top right) for the $e^- + A^+B \rightarrow AB^*$ transition, here shown for $A = \text{Li}$ and $B = \text{He}$. Both channels lead to the same final state (bottom), which forms the intermediate state of the 2CDR process. The black arrows symbolize the electrons. The black solid lines represent atomic electronic energy levels, and the black dashed lines symbolize the onset of the continuum. The red arrows indicate transitions between electronic states. The green arrow indicates the energy transfer via a virtual photon.

Following the work of Šenk and coworkers, we use Gaussian functions to model the orbital overlap [16]. Let us thus write the atomic ground-state wave functions as

$$\phi_g = (\pi a_A^2)^{-\frac{3}{4}} \exp\left(-\frac{r^2}{2a_A^2}\right), \quad (13)$$

$$\chi_g = (\pi a_B^2)^{-\frac{3}{4}} \exp\left(-\frac{(\vec{r} + \vec{R})^2}{2a_B^2}\right). \quad (14)$$

Here a_A and a_B are the widths of the respective Gaussians. Note that this model assumes the ground-state orbitals ϕ_g and χ_g to be isotropic in space around their respective nuclei. This holds true for lithium and helium atoms. The overlap of the two orbitals can now easily be calculated:

$$S_{AB} := \langle \phi_g | \chi_g \rangle = \left(\frac{2a_A a_B}{a_A^2 + a_B^2}\right)^{\frac{3}{2}} \exp\left(-\frac{R^2}{2(a_A^2 + a_B^2)}\right). \quad (15)$$

Intuitively, the overlap decreases with increasing interatomic distance R . In the limit of infinite interatomic distance ($R \rightarrow \infty$), the overlap contribution to the 2DCR process approaches zero.

Now, let us consider the other overlap integral $\langle \chi_e | \phi_{\bar{p}} \rangle$. This is where the model for 2CDR differs from the direct ICEC model presented in Ref. [16]. At first glance, one might expect the states to be orthogonal, resulting in zero overlap since one is a bound state and the other a continuum state. However, electronic states of different energies are only orthogonal if they are eigenstates of the same Hamiltonian. In this case, $|\phi_{\bar{p}}\rangle$ describes an electron with an asymptotic initial momentum $\bar{p}$ approaching A^+B . Close to the neutral atom B , it experiences an effective nuclear charge $Z_i \approx 0$ (where the subscript i denotes *incoming*). Conversely, the state $|\chi_e\rangle$ is a bound state

of B , where the electron perceives an effective charge $Z_b \approx 1$ (the subscript b denotes *bound*).

The overlap $\langle \chi_e | \phi_{\bar{p}} \rangle$ can be explicitly calculated by assuming that the bound excited state is a hydrogen-like atomic orbital and that the incoming electron is represented by a Coulomb wave:

$$\langle \chi_e | \phi_{\bar{p}} \rangle = -4\pi i^{l_b} Y_{l_b}^{-m_b}(\Omega_{\bar{p}}) \int dr r^2 \Lambda_{n_b, l_b, Z_b}(r) \Lambda_{p, l_b, Z_i}(r). \quad (16)$$

Here n_b , l_b , and m_b are the principal, azimuthal, and magnetic quantum numbers of the excited bound state (e.g., 2, 1, 0 for a $2p_z$ excited state). $\Lambda_{n_b, l_b, Z_b}(r)$ describes the radial dependence of the bound state and can be found in most quantum mechanics textbooks [44,45]. $Y_{l_b}^{m_b}(\Omega_{\bar{p}})$ is the spherical harmonic of degree (l_b, m_b) , where $\Omega_{\bar{p}}$ represents the solid angle in momentum space. $\Lambda_{p, l_b, Z_i}(r)$ describes the radial dependence of the Coulomb wave for an asymptotic momentum p , azimuthal quantum number l_b , and charge Z_i , and can be expressed as follows [51]:

$$\Lambda_{p, l_b, Z_i}(r) = (2pr)^{l_b} e^{-\frac{\pi\eta_i}{2}} \frac{|\Gamma(l_b + 1 + i\eta_i)|}{\Gamma(2l_b + 2)} e^{-ipr} \times {}_1F_1(l_i + 1 - i\eta_i, 2l_i + 2, 2ipr). \quad (17)$$

Here Γ is the Gamma function and ${}_1F_1$ is the confluent hypergeometric function of the first kind. The parameter $\eta_i = -\frac{Z_i}{p}$ is the Sommerfeld parameter.

We can then calculate the 2CDR cross section based on this new monopole-monopole term, which is given by:

$$\sigma_{2\text{CDR}}^{mm}(\varepsilon_p) = \frac{4\pi g_A \Gamma_{\text{RD}}^B S_{AB}^2}{p R^2} \left| \int dr r^2 \Lambda_{n_b, l_b, Z_b}(r) \Lambda_{p, l_b, Z_i}(r) \right|^2 \times \sum_{m_b} \frac{1}{\Delta^2 + \frac{\Gamma_{\text{RD}}^B}{4}}. \quad (18)$$

Here g_A is the multiplicity or statistical weight of the atomic state A , representing the number of degenerate electronic states into which the electron can get transferred. The sum runs over all degenerate excited states B^* . This new expression for the 2CDR cross section can be interpreted as follows: The absolute square of the overlap of the two radial wave functions measures the efficiency with which the incoming electron is captured into the excited state B^* . The term S_{AB}^2 measures the overlap between the two atoms, and together with the factor R^{-2} , it quantifies the efficiency of the transition from the ground state χ_g of B to the ground state ϕ_g of A . The term Γ_{RD}^B measures the efficiency of the radiative decay of B^* . The Lorentzian factor, similar to that in the dipole-dipole case, indicates that the closer the energy transferred to B is to the resonance condition ($\Delta = 0$), the more efficiently B is excited, while the possible deexcitation of B via ICD decreases the 2CDR cross section.

In contrast to the dipole-dipole result $\sigma_{2\text{CDR}}^{dd}$, $\sigma_{2\text{CDR}}^{mm}$ is notably not proportional to the photorecombination cross section of atom A , as the incoming electron is captured into the excited state B^* rather than into the ground state of A via a dipole transition.

Before this result can be applied, two additional aspects need to be addressed. First, different channels of a

quantum-mechanical process and their respective transition amplitudes add coherently. Thus, if one wants to combine the new result with the dipole-dipole coupling term, then the transition amplitudes $b_{2\text{CDR}}^{mm}$ and $b_{2\text{CDR}}^{dd}$ must be summed before taking the absolute square to calculate the total cross section. This could potentially lead to interference effects between the new and old channels. However, since the new and old amplitudes scale differently with interatomic distance, they are expected to only be comparable within a small range of R , where interference might be significant. Therefore, the total cross section, including both the monopole-monopole and dipole-dipole channels for 2CDR, is approximatively taken as the incoherent sum of the two:

$$\sigma_{2\text{CDR}} := \sigma_{2\text{CDR}}^{mm} + \sigma_{2\text{CDR}}^{dd}. \quad (19)$$

Second, the monopole-monopole term not only increases the efficiency of energy transfer from A to B but also enhances the possible energy transfer back via ICD. Therefore, it would be inconsistent to use the ICD width calculated solely with the dipole-dipole term [11] in the Lorentzian denominator of the previous equation. We now derive an expression for the ICD width based on the monopole-monopole term, orbital overlap, and electron transfer.

Since ICD is the inverse process of the initial step of 2CDR, the new monopole-monopole ICD transition amplitude, derived from the electron transfer mechanism, is simply the complex conjugate of Eq. (12). The ICD width can be computed by taking the absolute square of this amplitude and integrating over the momentum of the emitted electron [28,29]. We further multiply by the multiplicity of the resulting cation g_{A^+} to account for the different degenerate orbitals from which the electron can be transferred to B .

The monopole-monopole ICD width is then given by

$$\Gamma_{\text{ICD}}^{mm} = 8g_{A^+} \frac{S_{AB}^2}{R^2} \sqrt{2\varepsilon_p} \left| \int dr r^2 \Lambda_{n_b, l_b, Z_b}(r) \Lambda_{q', l_b, Z_i}(r) \right|^2. \quad (20)$$

The total ICD width is again approximatively the sum of the monopole-monopole and dipole-dipole contributions.

Next, let us apply this new formula to the LiHe example. The parameters are $g_{\text{Li}} = 2$, $g_{\text{Li}^+} = 1$, $n_b = 2$, $l_b = 1$, $Z_b = 1$, and $Z_i = 0$. The overlap integral S_{AB} depends on the widths of the Gaussians a_A and a_B . In Ref. [16] for the direct ICEC process, the model results were compared to high-precision *ab initio* R -matrix calculations [52–54]. It was found that $a = 1.63 \times r_c$ provides excellent agreement across various systems. Here r_c represents the covalent radius of the respective atom, a commonly used measure of atomic size in bounded systems. The value 1.63 is a global scaling factor determined by fitting the model results to the *ab initio* calculations. The covalent radii of lithium and helium are 133 and 46 pm, respectively [55].

The radial wave functions in this LiHe example system are expressed as follows:

$$\Lambda_{n_b=2, l_b=1, Z_b=1}(r) = \frac{re^{-\frac{r}{2}}}{\sqrt{24}} [44], \quad (21)$$

$$\Lambda_{p, l_b=1, Z_i=0}(r) = j_1(pr) = \frac{\sin(pr) - pr \cos(pr)}{(pr)^2} [51]. \quad (22)$$

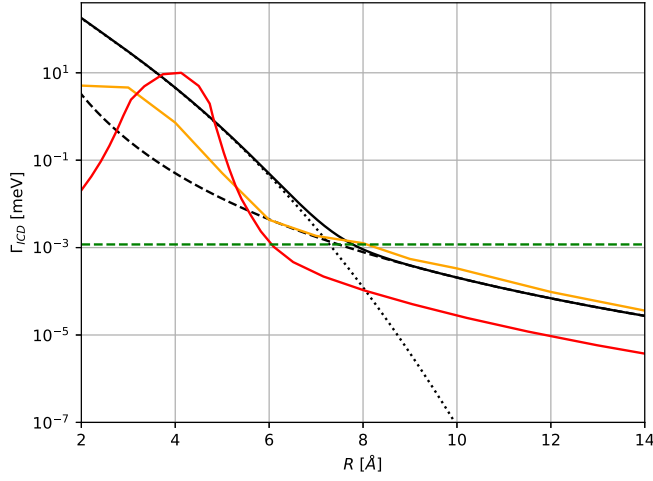


FIG. 5. The ICD width of $\text{He}^* (1s2p\ ^1P)$ Li at interatomic distance R from a lithium atom in the Σ molecular state of LiHe^* . The black dashed line indicates the dipole-dipole term, the black dotted line represents the monopole-monopole term, and the full black line shows the sum of these contributions. The red and orange full lines present *ab initio* calculations from Refs. [20] and [56], respectively. The green dashed line indicates the radiative decay width of He^* for comparison.

Here j_1 denotes the first spherical Bessel function. The radial overlap can be easily calculated. For a general ε_p , the absolute square of the radial overlap can be expressed as:

$$\left| \int dr r^2 \Lambda_{n_b=2, l_b=1, Z_b=1}(r) \Lambda_{p, l_b=1, Z_i=0}(r) \right|^2 = \frac{\varepsilon_p}{48(\varepsilon_p + \frac{1}{8})^6}. \quad (23)$$

At resonance ($\varepsilon_p = 15.83 \text{ eV} = 0.58 \text{ a.u.}$), this overlap equals 0.0974. Figure 5 illustrates the new monopole-monopole ICD width based on electron transfer as a function of the interatomic distance R , comparing it with the ICD width derived from the dipole-dipole interaction and virtual photon transfer. For this analysis, only the Σ state of LiHe^* is shown, as the monopole-monopole width remains consistent while the dipole-dipole width is reduced by a factor of 4 in the Π states.

Notably, $\Gamma_{\text{ICD}}^{mm, \text{He}}$ exceeds $\Gamma_{\text{ICD}}^{dd, \text{He}}$ for interatomic distances smaller than approximately $7.5 \text{ \AA}$. Within the range $R \in [2, 5] \text{ \AA}$, the total ICD width increases by about two orders of magnitude due to the electron transfer, suggesting that at these shorter distances, a greater number of excited helium atoms decay via ICD rather than radiatively. For interatomic distances $R > 8 \text{ \AA}$, the new ICD width declines rapidly due to the exponential dependence on R , making the dipole-dipole term dominant.

The *ab initio* decay widths also show a deviation from the $\propto R^{-6}$ behavior of the dipole-dipole term at smaller interatomic distances. However, this deviation begins at $R \approx 6 \text{ \AA}$, in contrast to $R \approx 7.5 \text{ \AA}$ as indicated by the overlap model presented in this work. Furthermore, the *ab initio* widths decrease again for very small distances, although the reason for this behavior is unclear.

It is crucial to note that the *ab initio* results do not agree very well with one another. While the findings from Ref. [20] show good consistency with our model in the range

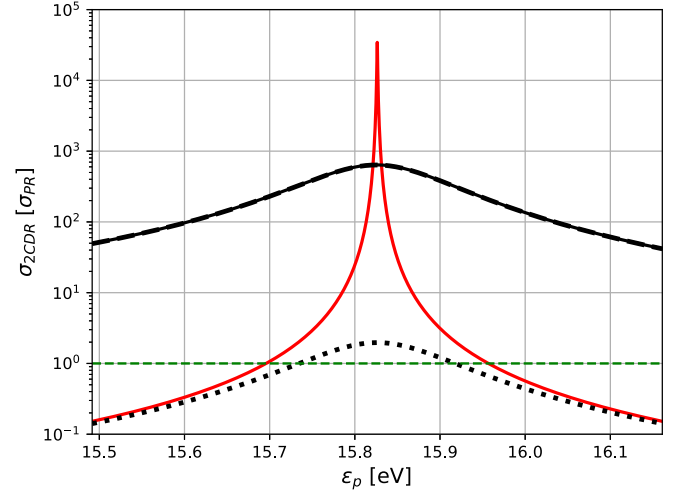


FIG. 6. Cross section for the $e^- + \text{Li}^+\text{He} \rightarrow \text{LiHe}^* (1s2p\ ^1P) \rightarrow \text{LiHe} + \gamma$ 2CDR process in units of the photorecombination cross section of Li as a function of the energy of the incoming electron ε_p . The dashed black line indicates the monopole-monopole term, the dotted black line represents the dipole-dipole term, and the full black line shows the sum of the two. The red line illustrates the case of only dipole-dipole interaction for both the capture process (first step of 2CDR) and the ICD width. The green dashed line indicates the photorecombination cross section. The fixed interatomic distance is set to the average position of the Li^+He dimer in the vibrational ground state ($2 \text{ \AA}$).

$R \in [3, 5] \text{ \AA}$, Ref. [56] suggests that our model overestimates the importance of electron transfer at smaller distances. Conversely, our model agrees perfectly for $R > 8 \text{ \AA}$ with Ref. [56], while Ref. [20] deviates by about one order of magnitude.

Since the same model accounts for the increased efficiency of energy transfer from A to B as well as from B to A, it is consistent to use the ICD widths derived from the new model rather than those reported in the literature for simulating the 2CDR cross section. Henceforth, the total cross section is computed using the black full line (which includes both the dipole-dipole result and the new monopole-monopole/overlap model).

Now, let us calculate the 2CDR cross section, incorporating both the monopole-monopole (electron transfer) and the dipole-dipole terms for energy transfer between the subsystems. The monopole-monopole cross section for LiHe can be expressed as:

$$\sigma_{2\text{CDR}}^{\text{LiHe}, mm}(\varepsilon_p) = \frac{\pi \Gamma_{\text{RD}}^{\text{He}} S_{\text{LiHe}}^2}{12\sqrt{2}} \frac{\sqrt{\varepsilon_p}}{R^2 (\varepsilon_p + \frac{1}{8})^6} \times \left[\frac{2}{\Delta^2 + \frac{(\Gamma_{\Pi}^{\text{He}})^2}{4}} + \frac{1}{\Delta^2 + \frac{(\Gamma_{\Sigma}^{\text{He}})^2}{4}} \right]. \quad (24)$$

Figure 6 displays $\sigma_{2\text{CDR}}^{mm, \text{LiHe}}$, $\sigma_{2\text{CDR}}^{dd, \text{LiHe}}$, and their sum as a function of the energy of the incoming electron, utilizing the total ICD width $\Gamma_{\text{ICD}} = \Gamma_{\text{ICD}}^{mm} + \Gamma_{\text{ICD}}^{dd}$. For comparison, $\sigma_{2\text{CDR}}^{dd, \text{LiHe}}$ using solely Γ_{ICD}^{dd} , corresponding to the theory developed in Sec. III, is also shown. The interatomic distance is chosen

as the average position of the Li^+He dimer in the vibrational ground state ($2 \text{ \AA}$).

The monopole-monopole term dominates the total 2CDR cross section. The inclusion of the monopole-monopole term dramatically alters the cross section. Comparing the black full line with the red line reveals that incorporating the electron transfer decreases the peak heights while increasing the peak width. Although the monopole-monopole term facilitates more efficient energy transfer from A to B , which is favorable for a larger 2CDR cross section, the increased ICD width for the energy transfer back to A overcompensates this by reducing the probability that the helium atom decays radiatively.

While the earlier theory based solely on dipole-dipole interactions predicted that 2CDR efficiency exceeds photorecombination by four to five orders of magnitude at this interatomic distance, this factor is now reduced to two to three orders of magnitude. Moreover, the dipole-dipole approximation underestimates the peak width, as it neglects the ICD width resulting from the monopole-monopole term. A larger peak width is however further supporting our claim that

2CDR may be more significant than previously assumed, as electrons from a broader energy range can recombine through this channel.

VI. INFLUENCE OF BOTH INTERATOMIC MOTION AND ELECTRON TRANSFER

Given that significant portions of the probability densities $|\rho_i|^2$ of the vibrational states of the Li^+He dimer are localized at relatively small interatomic distances $R \lesssim 8 \text{ \AA}$, where the monopole-monopole term can dominate energy transfer (see Fig. 5), it is crucial to investigate the effects of interatomic dynamics and electron transfer comprehensively. In this section, we study the 2CDR cross section, taking into account both the interatomic motion of the dimer and the effects of electron transfer by combining the results from the previous two sections. Thus, the total 2CDR cross section is composed of contributions from both the monopole-monopole and dipole-dipole interactions. The dipole-dipole contribution was derived in Sec. IV and is given in Eq. (11). The monopole-monopole part for LiHe is given by:

$$\sigma_{2\text{CDR}}^{\text{LiHe},im,mm} = \frac{\pi}{6\sqrt{2}} \Gamma_{\text{RD}}^{\text{He}} \frac{\sqrt{\varepsilon_p}}{(\varepsilon_p + \frac{1}{8})^6} \left(2 \sum_{\text{bound } \rho_m, \Pi} \frac{|\langle \rho_m, \Pi | \frac{S_{\text{LiHe}}}{R} | \rho_i \rangle|^2}{\Delta_\rho^2 + \frac{(\Gamma_{\rho_m, \Pi}^{\text{He}})^2}{4}} + \sum_{\text{bound } \rho_m, \Sigma} \frac{|\langle \rho_m, \Sigma | \frac{S_{\text{LiHe}}}{R} | \rho_i \rangle|^2}{\Delta_\rho^2 + \frac{(\Gamma_{\rho_m, \Sigma}^{\text{He}})^2}{4}} + 2\pi\eta(E_{\rho_m}) \left[2 \frac{|\langle \rho_m, \Pi | \frac{S_{\text{LiHe}}}{R} | \rho_i \rangle|^2}{\Gamma_{\rho_m, \Pi}^{\text{He}}} + \frac{|\langle \rho_m, \Sigma | \frac{S_{\text{LiHe}}}{R} | \rho_i \rangle|^2}{\Gamma_{\rho_m, \Sigma}^{\text{He}}} \right] \right). \quad (25)$$

The total decay width $\Gamma_{\rho_m}^{\text{He}}$ is the sum of the radiative decay width and both the monopole-monopole and dipole-dipole ICD widths. These widths are averaged over the respective probability densities $|\rho_m|^2$ [see Eq. (10)]. Figure 7 compares the 2CDR cross section obtained within all levels of theory discussed throughout this paper.

From the previous sections we have seen that the inclusion of both interatomic motion and electron transfer drastically alters the 2CDR cross section. Interatomic motion causes the singular Lorentzian peak to split into multiple peaks corresponding to the number of vibrational intermediate states. Additionally, it renders the cross section relatively constant for dissociative intermediate states (compare the yellow and red dotted lines). Meanwhile, electron transfer generally enhances the energy transfer efficiency between the subsystems, resulting in smaller but wider peaks (compare the blue dotted and red dotted lines).

The combined inclusion of interatomic dynamics and electron transfer leads to another modification of the cross section. The cross section exhibits peaks in the energy region corresponding to bound vibrational intermediate states, but these peaks are significantly broader and lower in height compared to results using only the dipole-dipole term. Without considering electron transfer, the peak widths are much smaller than the distances between consecutive peaks. Consequently, 53 peaks corresponding to 53 bound intermediate states are observable. However, with the inclusion of the monopole-monopole ICD term, the widths increase by roughly two orders of magnitude, making them comparable to the energy

differences between the peaks. As a result, the cross section smooths out in the region of bound intermediate states, leaving only small oscillations of the cross section in response to changes in the incoming electron's kinetic energy.

On the one hand, this indicates that the efficiency of 2CDR on resonance is much lower than predicted in Sec. IV using solely the dipole-dipole interaction. The peak heights are so significantly reduced that 2CDR cannot compete with photorecombination, except near the onset of dissociative intermediate states. The dimer is localized at such small R that the energy transfer back via ICD in the bound intermediate states becomes highly efficient, rendering 2CDR improbable.

On the other hand, the cross section becomes less sensitive to precisely hitting one of the resonance peaks, a potentially challenging task in an experimental setting.

While the peak heights in the bound region decrease due to the inclusion of the monopole-monopole term, the 2CDR cross section increases by approximately one order of magnitude in the dissociative region when the monopole-monopole term and electron transfer is included. This can be understood as follows: The inclusion of electron transfer generally increases the efficiency of energy transfer from subsystem A to B (in this case, from Li to He). Consequently, more electrons are captured by Li^+ , and more helium atoms are excited. As Li and He^* separate in the dissociative intermediate state, the increase in the ICD width is not sufficient to counterbalance the effect of capturing more electrons and exciting more helium atoms. Consequently, the overall efficiency of the total 2CDR process increases.

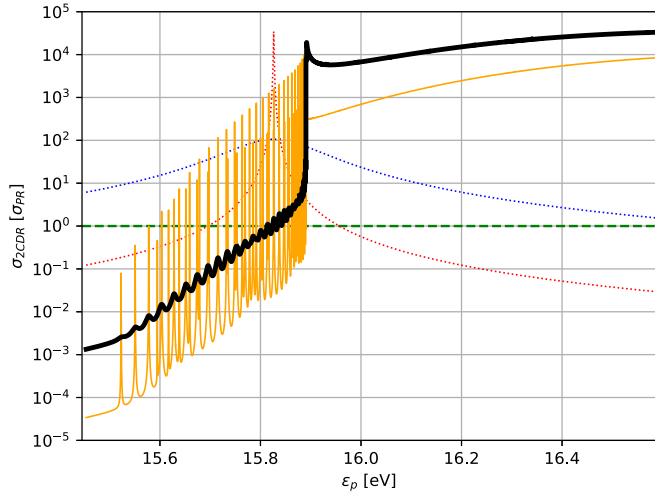


FIG. 7. Cross section for the $e^- + \text{Li}^+\text{He} \rightarrow \text{LiHe}^*(1s2p\ ^1P) \rightarrow \text{LiHe} + \gamma$ 2CDR process in units of the photorecombination cross section of lithium as a function of the incoming electron energy ϵ_p . The Li^+He dimer is initially in its vibrational ground state. The black full line represents the results including interatomic motion and electron transfer, the yellow line shows the results including interatomic motion but using the dipole-dipole approximation, the blue dotted line depicts the cross section for a fixed interatomic distance including electron transfer, and the red dotted line represents the cross section at a fixed interatomic distance using the dipole-dipole approximation. The green dashed line indicates the photorecombination cross section.

This means that the efficiency with which electrons attach to lithium cations in the Li^+He dimer can be effectively controlled by the kinetic energy of the incoming electrons. Higher kinetic energies for which the dimer dissociates favor recombination.

VII. CONCLUSION

In this work, we theoretically investigated the two-center dielectronic recombination (2CDR) process. We studied the effects of relative interatomic motion in van der Waals dimers and electron transfer at small interatomic distances on the relative importance of this process compared to the competing one-center photorecombination. We derived analytical formulas for the 2CDR cross section that incorporate the photorecombination cross section of the capturing cation, the radiative decay width, the lifetime of the neighboring excited atom, the covalent radii of the two species, and generalized Franck-Condon factors that measure the overlap between the changing molecular states during 2CDR.

These formulas were applied to the example $e^- + \text{Li}^+\text{He} \rightarrow \text{LiHe}^*(1s2p\ ^1P) \rightarrow \text{LiHe} + \gamma$.

We found that the interatomic motion of the dimer during the recombination process causes the single Lorentzian peak, predicted by the pre-existing theory, to split into many smaller and narrower peaks and a continuum region where the cross section only weakly depends on the energy of the incoming electron.

Inclusion of electron transfer at smaller interatomic distances can lead to a decrease in the 2CDR cross section. This

occurs because the increased efficiency of electron capture and energy transfer from the capturing atom to the neighbor can be outweighed by the energy transfer back and the re-emission of the captured electron. This is particularly significant when the dimer remains vibrationally bound in the intermediate state, where 2CDR can be dominated by photorecombination even on resonance. This shows that results obtained using the dipole-dipole approximation do not necessarily need to form a lower-limit to the exact results. At least not in a two-step process as 2CDR.

In contrast, for dissociative intermediate and final states of the dimer, 2CDR dominates photorecombination by approximately four orders of magnitude across a broad range of incoming electron energies. This dominance is due to the atoms separating in the dissociative intermediate state reducing the efficiency of energy transfer back, allowing radiative decay to remain relatively likely, thereby completing the 2CDR process. As a result 2CDR may be of high significance for recombination processes in nature as it is relevant on much larger energy ranges of the incoming electron than previously assumed.

The models developed in this work include more physical effects than in previous works, we therefore believe that our results are more accurate. Nevertheless, they should be regarded as a first attempt to generalize the theory of 2CDR. Both the modeling of vibrational and dissociative motion using the Morse potential and the contributions of the new monopole-monopole contribution to the energy transfer between the subsystems were based on various assumptions and approximations that likely affect the precision of the results. Therefore, it is highly desirable to validate the findings of this work through high-precision *ab initio* methods, such as the *R*-matrix method [52–54]. The latter was employed to compare a similar model for the relevance of electron transfer in the related process of direct ICEC [16].

Furthermore, the derived formulas were only tested on the lithium helium dimer. Some results depend on the specific system studied. For example, the smaller equilibrium distance of Li^+He compared to LiHe^* significantly affects the overlap integrals between the initial and intermediate states of 2CDR. Thus, in other systems, the dominance of dissociative over bound intermediate states, as found in this work, may be reduced or even reversed. Systems where electron attachment processes are crucial, such as plasmas, or biochemical environments involving alkali and alkaline earth metals surrounded by water molecules, could be particularly interesting for further investigation.

Treating 2CDR and photorecombination as two channels of the same overall process necessitates accounting for their interference, which can result in Fano profiles in the total recombination cross section [6]. These effects were not studied in this work.

ACKNOWLEDGMENTS

We thank the ANR-DFG for financial support of the QD4ICEC project. We acknowledge DFG Grant No. FA 1989/1-1 and ANR Grants No. ANR-22-CE92-0071-01 and No. ANR-22-CE92-0071-02. J.P.D. acknowledges financial support from the COST Action CA18212–Molecular

Dynamics in the GAS phase (MD-GAS), supported by COST (European Cooperation in Science and Technology). Financial support for the work of A.M. has been gratefully received from the Research Foundation—Flanders (FWO) within the Junior Postdoctoral Fellowship Mandate 1232922N. E.F. gratefully acknowledges financial support from the research and service facility LISA⁺ of the University of Tübingen. F.M.P. gratefully acknowledges partial financial support of CONICET (PIP-KE311220210100787CO), SECYT-UNC (Res. 233/2020), and ANPCYT-FONCyT, PICT-2018 No. 3431. N.S. thanks the Indo-French Centre for the Promotion of Advanced Research—CEFIPRA (Project 6704-2).

APPENDIX

Given the discussion in Sec. IV, the initial state of 2CDR including the interatomic motion can be written as

$$\Psi_i = \psi_i \rho_i = \phi_{\bar{p}} \chi_g \rho_i. \quad (\text{A1})$$

Here ρ_i describes the interatomic motion of the dimer in the initial electronic state. This might in principle be a bound state with vibrational quantum number v_i or an unbound dissociative state. For the 2CDR process it is, however, favorable to have a bound initial state, such that the atoms are initially not too far apart. The initial energy is given by

$$E_i = \varepsilon_p + \epsilon_g + E_{\rho_i}, \quad (\text{A2})$$

where E_{ρ_i} is the eigenenergy of ρ_i and is negative for bound states and positive for dissociative states.

In the intermediate state the electron is captured into the ground state ϕ_g , whereas subsystem B is excited into state χ_e ,

$$\Psi_m = \psi_m \rho_m = \phi_g \chi_e \rho_m. \quad (\text{A3})$$

Note that the intermediate interatomic state ρ_m is an eigenstate to a different Hamiltonian than ρ_i as the electronic structure ($A^+B \rightarrow AB^*$) and therefore the PEC has changed. The state might be bound or dissociative. The intermediate energy is given by

$$E_m = \varepsilon_g + \epsilon_e + E_{\rho_m}. \quad (\text{A4})$$

The decay of the intermediate state is, as in the previous section, described by a complex energy,

$$\tilde{E}_m = \varepsilon_g + \epsilon_e + E_{\rho_m} - i \frac{\Gamma_{m,\rho_m}^B}{2}. \quad (\text{A5})$$

Here Γ_{m,ρ_m}^B is the total decay width of B^* in the electronically excited state m and vibrational state ρ_m . To lose the explicit R dependence of the ICD width a state-specific width can be defined by averaging Γ_{ICD} over the respective probability density $|\rho_m|^2$:

$$\Gamma_{\text{ICD},m,\rho_m}^B := \int dR \Gamma_{\text{ICD},m}^B(R) \times |\rho_m(R)|^2 \quad [28,29]. \quad (\text{A6})$$

$\Gamma_{\text{ICD},m,\rho_m}^B$ thus depends on the electronic state m and interatomic state ρ_m .

Finally, subsystem B relaxes back to its ground state and emits a photon of momentum $\vec{k}$, polarization λ and energy $\omega = ck$,

$$\Psi_f = \psi_f \rho_f = \phi_g \chi_g \rho_f \otimes 1_{\vec{k},\lambda}. \quad (\text{A7})$$

Also ρ_f is an eigenstate to a different PEC as the electronic state of the system has changed to AB . The final energy is given by

$$E_f = \varepsilon_g + \epsilon_g + E_{\rho_f} + \omega. \quad (\text{A8})$$

The goal is to derive the cross section of 2CDR but now including the molecular dynamics of the system. The respective transition amplitude in second-order time-dependent perturbation theory is given by

$$b_{2\text{CDR}}^{dd,im} = \left(\frac{1}{i}\right)^2 \sum_{m,\rho_m} \int_{-\infty}^{\infty} dt \langle \Psi_f | \hat{V}_{\text{RF}}(t) | \Psi_m \rangle e^{-i(\tilde{E}_m - E_f)t} \\ \times \int_{-\infty}^t dt' \langle \Psi_m | \hat{V}_{AB}^{dd} | \Psi_i \rangle e^{-i(E_i - \tilde{E}_m)t'}. \quad (\text{A9})$$

This expression looks very similar to the corresponding one in Eq. (8) for a fixed interatomic distance. The difference is that the ψ were replaced by Ψ that include the interatomic wave functions ρ and the sum does not only run over the intermediate electronic states but also over all intermediate interatomic states. Note again that the molecular states themselves depend on the electronic excitation. The summation over ρ_m is therefore not independent on the summation over m . To denote these differences to Eq. (8) a superscript im was added referring to the interatomic motion.

Most steps in the derivation of the cross section $\sigma_{2\text{CDR}}^{dd,im}$ are very similar to the one for fixed nuclei. The time integral over dt' is easily solvable

$$\int_{-\infty}^t dt' e^{-i(E_i - \tilde{E}_m)t'} = i \frac{e^{-i(E_i - \tilde{E}_m)t}}{E_i - E_m + i \frac{\Gamma_{m,\rho_m}^B}{2}}. \quad (\text{A10})$$

The time integral over dt then gives again a δ distribution that guarantees total energy conservation $E_i = E_f$. One finds

$$b_{2\text{CDR}}^{dd,im} = -2\pi i \sum_{m,\rho_m} \frac{\delta(E_i - E_f)}{E_i - E_m + i \frac{\Gamma_{m,\rho_m}^B}{2}} \\ \times \langle \Psi_f | \hat{V}_{\text{RF}}(0) | \Psi_m \rangle \langle \Psi_m | \hat{V}_{AB}^{dd} | \Psi_i \rangle \\ = -2\pi i \sum_{m,\rho_m} \frac{\delta(E_i - E_f)}{\Delta_\rho + i \frac{\Gamma_{m,\rho_m}^B}{2}} \langle \chi_g | \hat{V}_{\text{RF}}(0) | \chi_e \rangle \langle \rho_f | \rho_m \rangle \\ \times \int dR \langle \psi_m | \hat{V}_{AB}^{dd} | \psi_i \rangle(R) \times \rho_m^* \times \rho_i. \quad (\text{A11})$$

Here the subscript ρ in $\Delta_\rho = E_i - E_m$ points to the resonance position now not only depending on the involved electronic energies but also on the energies corresponding to the interatomic motion. Furthermore, using that $\hat{V}_{AB}^{dd}$ ($\hat{V}_{\text{RF}}$) does (does not) depend on R the following simplifications can be used,

$$\langle \Psi_m | \hat{V}_{AB}^{dd} | \Psi_i \rangle = \int dR \langle \psi_m | \hat{V}_{AB}^{dd} | \psi_i \rangle \times \rho_m^* \times \rho_i, \quad (\text{A12})$$

$$\langle \Psi_f | \hat{V}_{\text{RF}}(0) | \Psi_m \rangle = \underbrace{\langle \psi_f | \hat{V}_{\text{RF}}(0) | \psi_m \rangle}_{=1} \underbrace{\int dR \rho_f^* \times \rho_m}_{=\langle \rho_f | \rho_m \rangle} \\ = \underbrace{\langle \phi_g | \phi_g \rangle}_{=1} \underbrace{\langle \chi_g | \hat{V}_{\text{RF}}(0) | \chi_e \rangle}_{=\langle \rho_f | \rho_m \rangle} \quad (\text{A13})$$

To obtain the cross section, one has to take the absolute square of the transition amplitude, average over the direction of the

incoming electron $\Omega_{\vec{p}}$, integrate over all momenta of the emitted photon $\vec{k}$ and sum over its polarization λ , and divide by the incoming velocity $j = p$ and time of perturbation [29,30]. Additionally, the summation over the final states now also includes a summation over the final interatomic states,

$$\begin{aligned}\sigma_{2\text{CDR}}^{dd,im} &= \frac{1}{Tp} \sum_{\rho_f} \sum_{\lambda} \int \frac{d^3k}{(2\pi)^3} \int \frac{d\Omega_{\vec{p}}}{4\pi} |b_{2\text{CDR}}^{dd,im}|^2 \\ &= \frac{1}{p} \sum_{\rho_f} \sum_{\lambda} \int \frac{d^3k}{(2\pi)^2} \delta(E_i - E_f) |\langle \chi_g | \hat{V}_{\text{RF}}(0) | \chi_e \rangle|^2 \\ &\quad \times \int \frac{d\Omega_{\vec{p}}}{4\pi} \left| \sum_{m,\rho_m} \frac{1}{\Delta_{\rho} + i\frac{\Gamma_{\rho_m,m}^B}{2}} \langle \rho_f | \rho_m \rangle \right. \\ &\quad \times \left. \int dR \langle \psi_m | \hat{V}_{AB} | \psi_i \rangle \times \rho_m^* \times \rho_i \right|^2.\end{aligned}\quad (\text{A14})$$

Here it was assumed, like in the fixed interatomic distance case, that due to the resonant character of 2CDR effectively only one (degenerate) electronic intermediate state is excited. $|\langle \chi_g | \hat{V}_{\text{RF}}(0) | \chi_e \rangle|^2$ could therefore be pulled out of the summation over the intermediate electronic states as it must be the same for every of these degenerate states. It can be related to the dipole moment $\vec{d}_B^{e \rightarrow g}$ describing the electron transition from the excited to the ground state of atom B . The integration over the photon momentum and the summation over the polarization is completely equivalent to the derivation with a fixed interatomic distance. Furthermore, one can separate the transition dipole moments from the interatomic wave functions

$$\begin{aligned}\int dR \langle \psi_m | \hat{V}_{AB} | \psi_i \rangle \times \rho_m^* \times \rho_i \\ = [\vec{d}_A^{\vec{p} \rightarrow g} \vec{d}_B^{g \rightarrow e} - 3(\vec{d}_A^{\vec{p} \rightarrow g} \vec{e}_{\vec{R}})(\vec{d}_B^{g \rightarrow e} \vec{e}_{\vec{R}})] \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle.\end{aligned}\quad (\text{A15})$$

Here $\vec{d}_A^{\vec{p} \rightarrow g}$ is the transition dipole moment describing the electron capture at atom A . $\vec{d}_B^{g \rightarrow e}$ is the transition dipole moment describing the excitation of atom B .

Now, to significantly simplify the calculation, let us assume that the electronic ground state of A has S symmetry as it is the case for Li. The angular integral over $d\Omega_{\vec{p}}$ can then be written as (with $\vec{e}_{\vec{R}} = \vec{e}_z$)

$$\begin{aligned}\int \frac{d\Omega_{\vec{p}}}{4\pi} \left| \sum_{m,\rho_m} \frac{1}{\Delta_{\rho} + i\frac{\Gamma_{\rho_m,m}^B}{2}} \langle \rho_f | \rho_m \rangle \right. \\ \times \left. \int dR \langle \psi_m | \hat{V}_{AB} | \psi_i \rangle \times \rho_m^* \times \rho_i \right|^2 \\ = \frac{g_A}{3} |\vec{d}_A^{\vec{p} \rightarrow g}|^2 |\vec{d}_B^{g \rightarrow e}|^2 \\ \times \left[\sum_{\rho_m,m} \frac{\vec{d}_B^{g \rightarrow e}}{|\vec{d}_B^{g \rightarrow e}|} \vec{e}_x \frac{\langle \rho_f | \rho_m \rangle \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle}{\Delta_{\rho} + i\frac{\Gamma_{\rho_m,m}^B}{2}} \right]^2\end{aligned}$$

$$\begin{aligned}+ \left[\sum_{\rho_m,m} \frac{\vec{d}_B^{g \rightarrow e}}{|\vec{d}_B^{g \rightarrow e}|} \vec{e}_y \frac{\langle \rho_f | \rho_m \rangle \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle}{\Delta_{\rho} + i\frac{\Gamma_{\rho_m,m}^B}{2}} \right]^2 \\ + 4 \left[\sum_{\rho_m,m} \frac{\vec{d}_B^{g \rightarrow e}}{|\vec{d}_B^{g \rightarrow e}|} \vec{e}_z \frac{\langle \rho_f | \rho_m \rangle \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle}{\Delta_{\rho} + i\frac{\Gamma_{\rho_m,m}^B}{2}} \right]^2.\end{aligned}\quad (\text{A16})$$

The cross section thus reads

$$\begin{aligned}\sigma_{2\text{CDR}}^{dd,im} &= \sum_{\rho_f} \frac{4g_A}{9c^3 p} (E_i - E_f') (\epsilon_e - \epsilon_g)^2 \\ &\quad \times |\vec{d}_A^{\vec{p} \rightarrow g}|^2 |\vec{d}_B^{g \rightarrow e}|^2 |\vec{d}_B^{e \rightarrow g}|^2 \\ &\quad \times \left[\sum_{\rho_m,m} \frac{\vec{d}_B^{g \rightarrow e}}{|\vec{d}_B^{g \rightarrow e}|} \vec{e}_x \frac{\langle \rho_f | \rho_m \rangle \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle}{\Delta_{\rho} + i\frac{\Gamma_{\rho_m,m}^B}{2}} \right]^2 \\ &\quad + \left[\sum_{\rho_m,m} \frac{\vec{d}_B^{g \rightarrow e}}{|\vec{d}_B^{g \rightarrow e}|} \vec{e}_y \frac{\langle \rho_f | \rho_m \rangle \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle}{\Delta_{\rho} + i\frac{\Gamma_{\rho_m,m}^B}{2}} \right]^2 \\ &\quad + 4 \left[\sum_{\rho_m,m} \frac{\vec{d}_B^{g \rightarrow e}}{|\vec{d}_B^{g \rightarrow e}|} \vec{e}_z \frac{\langle \rho_f | \rho_m \rangle \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle}{\Delta_{\rho} + i\frac{\Gamma_{\rho_m,m}^B}{2}} \right]^2.\end{aligned}\quad (\text{A17})$$

As a last step, using the detailed balance equation [18,35] one can relate the absolute squares of the dipole matrix elements to the photorecombination cross section of A σ_{PR}^A [45,57] and the radiate decay width of the excited states of B Γ_{RD}^B [44] to obtain the 2CDR cross section including interatomic dynamics while using the dipole-dipole approximation,

$$\begin{aligned}\sigma_{2\text{CDR}}^{dd,im}(\epsilon_p) &= \sum_{\rho_f} \frac{3c^6 (E_i - E_f') (\Gamma_{\text{RD}}^B)^2}{16(\epsilon_e - \epsilon_g)^4 (\epsilon_p - \epsilon_g)^3} \sigma_{\text{PR}}^A(\epsilon_p) \\ &\quad \times \left[\sum_{\rho_m,m} \frac{\vec{d}_B^{g \rightarrow e}}{|\vec{d}_B^{g \rightarrow e}|} \vec{e}_x \frac{\langle \rho_f | \rho_m \rangle \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle}{\Delta_{\rho} + i\frac{\Gamma_{\rho_m,m}^B}{2}} \right]^2 \\ &\quad + \left[\sum_{\rho_m,m} \frac{\vec{d}_B^{g \rightarrow e}}{|\vec{d}_B^{g \rightarrow e}|} \vec{e}_y \frac{\langle \rho_f | \rho_m \rangle \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle}{\Delta_{\rho} + i\frac{\Gamma_{\rho_m,m}^B}{2}} \right]^2 \\ &\quad + 4 \left[\sum_{\rho_m,m} \frac{\vec{d}_B^{g \rightarrow e}}{|\vec{d}_B^{g \rightarrow e}|} \vec{e}_z \frac{\langle \rho_f | \rho_m \rangle \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle}{\Delta_{\rho} + i\frac{\Gamma_{\rho_m,m}^B}{2}} \right]^2.\end{aligned}\quad (\text{A18})$$

The formula obtained in Eq. (A18) holds for general excitations of the B atom but is very lengthy and complicated to use in practice due to the coherent summation over the intermediate interatomic states and the incoherent sum over the final molecular states. It is thus favorable to simplify the expression, if it comes with negligible errors. This also helps its interpretation and therefore the understanding of the effects of interatomic motion on the 2CDR process. First, note that in the case of a $^1S \rightarrow ^1P$ intermediate excitation of B^* , as in the example of LiHe^* , the coherent sum over the electronic excitations disappears, which comes very handy for further

simplifications,

$$\begin{aligned} \sigma_{2\text{CDR}}^{dd,im,1S \rightarrow 1P}(\varepsilon_p) &= \sum_{\rho_f} \frac{3c^6(E_i - E'_f)(\Gamma_{\text{RD}}^B)^2}{8(\epsilon_e - \epsilon_g)^4(\varepsilon_p - \varepsilon_g)^3} \sigma_{\text{PR},A}(\varepsilon_p) \\ &\times \left[\sum_{\rho_{m,\Pi}} \frac{1}{\Delta_\rho + i\frac{\Gamma_{\rho_{m,\Pi}}^B}{2}} \langle \rho_f | \rho_{m,\Pi} \rangle \langle \rho_{m,\Pi} | \frac{1}{R^3} | \rho_i \rangle \right]^2 \\ &+ 2 \left[\sum_{\rho_{m,\Sigma}} \frac{1}{\Delta_\rho + i\frac{\Gamma_{\rho_{m,\Sigma}}^B}{2}} \langle \rho_f | \rho_{m,\Sigma} \rangle \langle \rho_{m,\Sigma} | \frac{1}{R^3} | \rho_i \rangle \right]^2. \end{aligned} \quad (\text{A19})$$

The summation now runs over the molecular states corresponding to the Π and Σ electronic intermediate states. Further note that the resonance condition for a given electronic excitation and a fixed initial interatomic state,

$$\Delta_\rho = E_i - E_m = \varepsilon_p + \epsilon_g + E_{\rho_i} - \varepsilon_g - \epsilon_e - E_{\rho_m} \stackrel{!}{=} 0, \quad (\text{A20})$$

naturally splits up the kinetic energy range of the incoming electron into one corresponding to bound intermediate states

$$(E_{\rho_m} < 0),$$

$$\varepsilon_p < \varepsilon_g + \epsilon_e - \epsilon_g - E_{\rho_i}, \quad (\text{A21})$$

and one to unbound dissociative intermediate states ($E_{\rho_m} > 0$),

$$\varepsilon_p > \varepsilon_g + \epsilon_e - \epsilon_g - E_{\rho_i}. \quad (\text{A22})$$

These two cases can be treated separately.

For bound intermediate states the following approximations can be made. Molecular binding energies, in for example LiHe^* , are of the order of hundreds of meV. The binding energies of Li^+He and LiHe are even one and four orders of magnitude smaller, respectively (see Table I). One can thus use in Eq. (A19) $E_i - E'_f = \varepsilon_p + \epsilon_g + E_{\rho_i} - \varepsilon_g - \epsilon_e - E_{\rho_f} \approx \varepsilon_p - \varepsilon_g$. Furthermore, as only kinetic energies of the incoming electron close to the electronic resonance are relevant, one can further approximate $\varepsilon_p - \varepsilon_g \approx \epsilon_e - \epsilon_g$. The error introduced through this simplification is much smaller than those of other used approximations like the neglect of orbital overlap between the atoms. The cross section for bound intermediate states can thus be written as

$$\begin{aligned} \sigma_{2\text{CDR}}^{dd,im,1S \rightarrow 1P,b}(\varepsilon_p) &= \frac{3c^6}{8(\epsilon_e - \epsilon_g)^6} (\Gamma_{\text{RD}}^B)^2 \sigma_{\text{PR},A}(\varepsilon_p) \sum_{\rho_f} \left[\sum_{\rho_{m,\Pi}} \frac{1}{\Delta_\rho + i\frac{\Gamma_{\rho_{m,\Pi}}^B}{2}} \langle \rho_f | \rho_{m,\Pi} \rangle \langle \rho_{m,\Pi} | \frac{1}{R^3} | \rho_i \rangle \right]^2 \\ &+ 2 \left[\sum_{\rho_{m,\Sigma}} \frac{1}{\Delta_\rho + i\frac{\Gamma_{\rho_{m,\Sigma}}^B}{2}} \langle \rho_f | \rho_{m,\Sigma} \rangle \langle \rho_{m,\Sigma} | \frac{1}{R^3} | \rho_i \rangle \right]^2. \end{aligned} \quad (\text{A23})$$

The coherent summation over the bound vibrational states can be turned into an incoherent one. To proof this, note that the interatomic states corresponding to any electronic state form a complete basis

$$\sum_{\rho} |\rho\rangle \langle \rho| = 1. \quad (\text{A24})$$

One can then calculate

$$\begin{aligned} \sum_{\rho_f} \left| \sum_{\rho_m} \frac{1}{\Delta_\rho + i\frac{\Gamma_{\rho_m}^B}{2}} \langle \rho_f | \rho_m \rangle \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle \right|^2 &= \sum_{\rho_f} \sum_{\rho_m} \sum_{\rho'_m} \frac{1}{\Delta_\rho + i\frac{\Gamma_{\rho_m}^B}{2}} \frac{1}{\Delta_\rho - i\frac{\Gamma_{\rho'_m}^B}{2}} \langle \rho_f | \rho_m \rangle \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle \langle \rho'_m | \rho_f \rangle \langle \rho_i | \frac{1}{R^3} | \rho'_m \rangle \\ &= \sum_{\rho_m} \sum_{\rho'_m} \frac{1}{\Delta_\rho + i\frac{\Gamma_{\rho_m}^B}{2}} \frac{1}{\Delta_\rho - i\frac{\Gamma_{\rho'_m}^B}{2}} \langle \rho'_m | \underbrace{\sum_{\rho_f} \langle \rho_f | \rho_m \rangle \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle \langle \rho_i | \frac{1}{R^3} | \rho'_m \rangle}_{=1} \\ &= \sum_{\rho_m} \sum_{\rho'_m} \frac{1}{\Delta_\rho + i\frac{\Gamma_{\rho_m}^B}{2}} \frac{1}{\Delta_\rho - i\frac{\Gamma_{\rho'_m}^B}{2}} \underbrace{\langle \rho'_m | \rho_m \rangle}_{=\delta_{\rho_m, \rho'_m}} \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle \langle \rho_i | \frac{1}{R^3} | \rho'_m \rangle \\ &= \sum_{\rho_m} \frac{1}{\Delta_\rho^2 + \frac{(\Gamma_{\rho_m}^B)^2}{4}} \left| \langle \rho_m | \frac{1}{R^3} | \rho_i \rangle \right|^2. \end{aligned} \quad (\text{A25})$$

The cross section thus simplifies to the following expression:

$$\sigma_{2\text{CDR}}^{dd,im,1S \rightarrow 1P,b}(\varepsilon_p) = \frac{3c^6(\Gamma_{\text{RD}}^B)^2}{8(\epsilon_e - \epsilon_g)^6} \sigma_{\text{PR}}^A(\varepsilon_p) \left[\sum_{\text{bound } \rho_{m,\Pi}} \frac{1}{\Delta_\rho^2 + \frac{(\Gamma_{\rho_{m,\Pi}}^B)^2}{4}} \left| \langle \rho_{m,\Pi} | \frac{1}{R^3} | \rho_i \rangle \right|^2 + \sum_{\text{bound } \rho_{m,\Sigma}} \frac{2}{\Delta_\rho^2 + \frac{(\Gamma_{\rho_{m,\Sigma}}^B)^2}{4}} \left| \langle \rho_{m,\Sigma} | \frac{1}{R^3} | \rho_i \rangle \right|^2 \right] \quad (\text{A26})$$

The superscript signifies that this expression only holds in this form for a $^1S \rightarrow ^1P$ transition in atom B and only for the energy range corresponding to bound intermediate states.

Turning now to the energy range corresponding to dissociative intermediate molecular states one starts again from Eq. (A19). While there is a finite number of discrete bound vibrational states, there is a continuum of unbound dissociative states. However, in practice we performed the calculation with an artificially discrete spectrum for the dissociative states. This can be achieved by confining the wave functions to a finite region in space (i.e., within a box). The boundary conditions then lead to a countably infinite number of states of positive energy. By letting the size of the box to go to infinity, or in practice to make the box large enough compared to length scale of the potential under consideration, the error introduced goes to zero [45]. In this work, all molecular states are calculated on a finite grid that gives rise to a finite number of dissociative states. There is thus an upper limit for the latter energy. The size of the grid was chosen sufficiently large, such that states of large-enough dissociative energy for the examples of interest are included. The step size between the grid points was chosen sufficiently small to have a sufficiently small energy spacing between two consecutive dissociative states, such that one can speak of a quasicontinuum of unbound molecular states.

The dissociative states thus have the same normalization condition as the bound states $\langle \rho_m | \rho_{m'} \rangle = \delta_{\rho_m, \rho_{m'}}$. The handling of Kronecker deltas is much easier in practice than that of Dirac deltas.

For energies of the incoming electron corresponding to unbound dissociative intermediate states one can use that while $\Gamma_{\rho_m, m}^B$, Δ_ρ and $\langle \rho_m | \frac{1}{R^3} | \rho_i \rangle$ vary relatively slowly in E_{ρ_m} , $\langle \rho_f | \rho_m \rangle$ is very heavily peaked at the condition $E_{\rho_m} = E_{\rho_f}$. The explanation for this is that the interatomic potentials are rather weak. The interatomic states behave thus, except for a small region of small R , like free particles in a box. They are thus eigenfunctions to very similar Hamiltonians (kinetic energy with a very weak potential) and are therefore almost orthogonal. It also means that the transition from the intermediate to the final electronic state does not influence the molecular state of the dimer. If the intermediate state is dissociative and the atoms fly apart with dissociation energy E_{ρ_m} , then the radiative decay of B^* does not influence the dissociation. One can thus use $\langle \rho_f | \rho_m \rangle \approx \delta_{E_{\rho_f}, E_{\rho_m}}$ to collapse the summation over the intermediate interatomic states,

$$\begin{aligned} \sigma_{2\text{CDR}}^{dd, im, ^1S \rightarrow ^1P, ub}(\varepsilon_p) &= \sum_{\rho_f} \frac{3c^6(E_i - E'_f)(\Gamma_{\text{RD}}^B)^2}{8(\epsilon_e - \epsilon_g)^4(\varepsilon_p - \varepsilon_g)^3} \sigma_{\text{PR}}^A(\varepsilon_p) \\ &\times \left[\frac{1}{\Delta_\rho^2 + \frac{(\Gamma_{\rho_m, \Pi}^B)^2}{4}} \left| \langle \rho_m, \Pi | \frac{1}{R^3} | \rho_i \rangle \right|^2 \right. \\ &\left. + \frac{2}{\Delta_\rho^2 + \frac{(\Gamma_{\rho_m, \Sigma}^B)^2}{4}} \left| \langle \rho_m, \Sigma | \frac{1}{R^3} | \rho_i \rangle \right|^2 \right], \\ &\text{evaluated at } E_{\rho_m} = E_{\rho_f}. \end{aligned} \quad (\text{A27})$$

Despite the artificial discretization of the continuum energies, the summation over the final interatomic states can be turned

into an integration over the final interatomic energy E_{ρ_f} . Let ξ_f be the quantum number that numbers all unbound final interatomic states of positive energy from low to high energy. One can then write

$$\sum_{\rho_f} = \sum_{v_f} + \sum_{\xi_f} \underbrace{[E_{\rho_f}(\xi_f + 1) - E_{\rho_f}(\xi_f)]}_{\Delta E_{\rho_f}} \frac{(\xi_f + 1) - (\xi_f)}{\Delta E_{\rho_f}}. \quad (\text{A28})$$

Here v_f is the vibrational quantum number of the bound final states. For a very fine discrete energy spacing between two consecutive dissociative states one thus finds

$$\sum_{\rho_f} \approx \sum_{v_f} + \int dE_{\rho_f} \eta(E_{\rho_f}), \quad (\text{A29})$$

where the error goes to zero in the limit of an infinitely fine energy spacing [58]. However, since $E_{\rho_f} \approx E_{\rho_m} > 0$ holds in the unbound intermediate energy range, the summation over bound final states is obsolete. Here η is the density of states that counts the number of states per energy interval. As mentioned before, the interatomic potentials are relatively weak and the dissociative final states behave almost exactly like free particles in a box. The density of states of the unbound final states is thus, in a very good approximation, given by the expression for a free particle of energy E_{ρ_f} in a one-dimensional box $\eta(E_{\rho_f}) = \sqrt{\frac{2\mu}{E_{\rho_f}}} \frac{R_{\text{max}}}{2\pi}$, where μ is the reduced mass of the dimer and R_{max} the length of the box [49,59]. The cross section can thus be written in the dissociative region as

$$\begin{aligned} \sigma_{2\text{CDR}}^{dd, im, ^1S \rightarrow ^1P, ub} &= \int dE_{\rho_f} \eta(E_{\rho_f}) \frac{3c^6(E_i - E'_f)(\Gamma_{\text{RD}}^B)^2}{8(\epsilon_e - \epsilon_g)^4(\varepsilon_p - \varepsilon_g)^3} \sigma_{\text{PR}}^A \\ &\times \left[\frac{1}{\Delta_\rho^2 + \frac{(\Gamma_{\rho_m, \Pi}^B)^2}{4}} \left| \langle \rho_m, \Pi | \frac{1}{R^3} | \rho_i \rangle \right|^2 \right. \\ &\left. + \frac{2}{\Delta_\rho^2 + \frac{(\Gamma_{\rho_m, \Sigma}^B)^2}{4}} \left| \langle \rho_m, \Sigma | \frac{1}{R^3} | \rho_i \rangle \right|^2 \right], \\ &\text{evaluated at } E_{\rho_m} = E_{\rho_f}. \end{aligned} \quad (\text{A30})$$

The integration over the energy of the final state can be performed using that the Lorentzian profile converges to a δ distribution for decreasing width Γ [45],

$$\frac{1}{\Delta_\rho^2 + \frac{(\Gamma_{\rho_m}^B)^2}{4}} \approx \frac{2\pi}{\Gamma_{\rho_m}^B} \delta(\Delta_\rho). \quad (\text{A31})$$

We also approximate again $E_i - E'_f \approx \varepsilon_p - \varepsilon_g \approx \epsilon_e - \epsilon_g$ for simplicity, as we assume that we only consider dissociative energies much smaller than the electronic energy differences.

The 2CDR cross section for dissociative intermediate states using the dipole-dipole approximation and in the special case of a $^1S \rightarrow ^1P$ excitation at B , can thus finally be written as

$$\sigma_{2\text{CDR}}^{dd,im,^1S \rightarrow ^1P,ub}(\varepsilon_p) = \eta(E_{\rho_m}) \times \frac{3\pi c^6 (\Gamma_{\text{RD}}^B)^2 \sigma_{\text{PR}}^A(\varepsilon_p)}{4(\epsilon_e - \epsilon_g)^6} \times \left[\frac{|\langle \rho_{m,\Pi} | \frac{1}{R^3} | \rho_i \rangle|^2}{\Gamma_{\rho_m,\Pi}^B} + 2 \frac{|\langle \rho_{m,\Sigma} | \frac{1}{R^3} | \rho_i \rangle|^2}{\Gamma_{\rho_m,\Sigma}^B} \right]. \quad (\text{A32})$$

Equations (A26) and (A32) are much easier to implement in a computer code than the more general expression (A18). It should be noted that in practice, the discrete energy spectra of the dissociative states is of course not infinitely fine. However, since the $\langle \rho_m | \frac{1}{R^3} | \rho_i \rangle$ overlaps and $\Gamma_{\rho_m}^B$ change relatively slowly with E_{ρ_m} it is sufficient to evaluate them at the discrete intermediate dissociation energy E_{ρ_m} that is closest to the energy condition in Eq. (A20).

Finally, by adding up Eq. (A26) for bound intermediate states and Eq. (A32) for dissociative intermediate states we successfully derived Eq. (11).

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Electronic-decay-process spectra including nuclear degrees of freedom

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(Received 14 May 2024; accepted 2 January 2025; published 22 January 2025)

In the field of chemistry, where nuclear motion has traditionally been a focal point, we now explore the ultrarapid electronic motion spanning attoseconds to femtoseconds, demonstrating that it is equally integral and relevant to the discipline. The advent of ultrashort attosecond pulse technology has revolutionized our ability to directly observe electronic rearrangements in atoms and molecules, offering a time-resolved insight into these swift processes. Prominent examples include Auger-Meitner decay and interparticle Coulombic decay. However, the real challenge lies in interpreting these observations, where theoretical models are indispensable. Building upon the analytical framework introduced by Fasshauer and Madsen [*Phys. Rev. A* **101**, 043414 (2020)], which analyzed the spectra of electrons emitted during electronic decay processes from a purely electronic perspective, we extend this theoretical base to include nuclear dynamics, utilizing the Born-Oppenheimer approximation to deepen our understanding of the intricate interaction between electronic and nuclear motion in these processes. We illustrate the impact of incorporating nuclear degrees of freedom in several theoretical cases characterized by different numbers of vibrational bound states in both the electronic resonance and the electronic final state. This approach not only clarifies complex spectral features and unusual peak shapes but also demonstrates a method for extracting the energy differences between multiple vibrational resonance states through their distinctive interference patterns.

DOI: [10.1103/PhysRevA.111.013112](https://doi.org/10.1103/PhysRevA.111.013112)

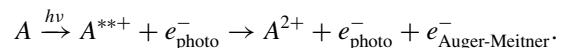
I. INTRODUCTION

Since the advent of ultrashort laser pulses in the attosecond and femtosecond range [1], it has in principle become possible to study the time evolution of chemical reactions in detail. However, the duration of a laser pulse is inversely proportional to its energetic width, and this width, for the current state of the art, needs to include at least one half cycle of the mean photon energy. Hence, ultrashort laser pulses typically have mean photon energies in the extreme ultraviolet (XUV) or even x-ray range. We therefore aim to understand the processes initiated by these ultrashort laser pulses and what information we can extract from their respective time-resolved spectra.

The interaction of ultrashort laser pulses with matter prompts ionizations and excitations from the inner shells of atoms and molecules. The resulting excited states can then decay under electronic rearrangement and emission of an electron, which carries the excess energy. Such electronic decay processes have been known for many years. The Auger-

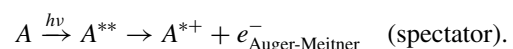
Meitner process was discovered about 100 years ago [2,3] and also the first theoretical prediction of the interparticle Coulombic decay (ICD) is more than two decades old [4].

The different electronic decay processes can be distinguished by the number of involved entities (atoms, molecules, or weakly bound conglomerates) and the kind of electronic rearrangement during the process. In the Auger-Meitner process, only one entity A is involved. After primary ionization from an inner shell, the vacancy is filled by an electron from an outer shell and another electron is emitted:



Here, we indicate an inner-shell vacancy by two stars $**$.

After an inner-shell excitation, the excited electron can either fill the vacancy itself and cause the emission of another electron (participator resonant Auger-Meitner process) or it can stay excited while another electron fills the vacancy and a third electron is emitted (spectator resonant Auger-Meitner process):



After the spectator Auger-Meitner process, the system is necessarily still excited and will decay further, whereas for the participator Auger-Meitner process with only one decay channel, this is not the case. However, when more channels are

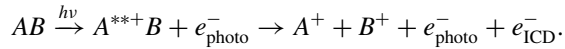
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accessible, it is also possible to create an excited state, which will decay further.

The Auger-Meitner process is found in a variety of different systems like atoms, molecules, and solids. As a consequence and because it is element specific, Auger-Meitner electron spectroscopy is used for surface analysis in metallurgy, quality analysis of microelectronics, as well as basic studies of chemical reaction mechanisms [5]. It has also been a test process for time-resolved measurements in general [6–8] and is often observed as a side product of modern x-ray spectroscopies [9].

In the ICD process, the energy released during the vacancy filling is transferred through space to a different entity, which consequently emits the ICD electron:



After the process, the two involved entities are both positively charged and therefore repel each other. The ICD process also has its resonant variants (RICD), in analogy to the Auger-Meitner process.

ICD and ICD-like processes occur in many different systems with weakly interacting units such as noble-gas clusters [10–13], proteins [14], solvents [11,12,15–20], as well as semiconductors [21–23] and are discussed as a key mechanism of radiative DNA damage [24–28].

In this paper, we will focus on the resonant electronic decay processes, which are initiated by inner-shell excitation rather than by ionization.

For time-resolved spectroscopy of electronic decay processes, most of the developed theory considers atomic systems [29,30], for the description of which the purely electronic Schrödinger equation suffices. However, for Auger-Meitner processes of molecules, molecules bound to a surface, like in heterogeneous catalysis, or an ICD process, the nuclear degrees of freedom will affect the spectra of the emitted electrons. Since numerical solutions of both the electronic and the nuclear dynamics are expensive to solve numerically, we aim for an analytical description following the basic formulation of Ref. [31], from which we can draw conclusions about basic properties. Moreover, by careful observation of the assumptions we make in our derivations, it will be possible to assign further properties observed in experiment to those parts which we neglect.

The analytical description of time-independent spectra of electronic decay processes dates back to the work by Fano [32]. His basic theory focuses on purely electronic wave functions. It is though not without limitations. They encompass the interaction of several resonance states via one continuum [32], the interaction of several resonance states via several continuum states, also called overlapping resonance states [30,33], incoherences that translate to complex values of the Fano parameter q [29], and the usually well-justified assumption that the background, q and the decay width Γ are practically constant in the proximity of the resonance [34–36]. It has been generalized to quantum defect theory for molecules as well [37–41]. The latter has been investigated in a time-dependent approach for rotationally autoionizing states of the hydrogen molecule [42]. Despite the Fano theory’s limitations, which we may address in future work, we will provide a similar

ansatz for the wave function of a decaying state including both electronic and nuclear eigenstates of the system for noninteracting resonance states within the Born-Oppenheimer approximation, show general properties of the time-resolved spectra for selected cases, and discuss the limits of our approach based on the approximations we introduce.

The paper is structured as follows: In Sec. II, we choose an ansatz for the Fano wave function including nuclear degrees of freedom for one electronic resonance and one electronic final state and derive the corresponding coefficients. We then derive the working expressions for the simulation and analysis of the time-resolved kinetic-energy spectra of the emitted electron. In Sec. III, we have collected all the general parameters which we use to simulate the spectra for different showcases presented in Sec. IV. We discuss the limitations and consequences of our introduced approximations in Sec. V and summarize in Sec. VI.

II. THEORY

The electronic decay processes we intend to describe fully time dependently are schematically illustrated in Fig. 1 for the specific case of two nuclear bound states in the resonance state and one nuclear bound state in the electronic final state. The aim is to find a description for any combination of nuclear bound states in the electronic resonance and final states.

Starting from the ground state $|G\rangle$, we excite the system with an XUV pulse with a mean photon energy Ω and thereby create a coherent superposition of the two nuclear states $|\chi_\lambda\rangle$ of the electronic resonance state $|r\rangle$. The minimum of the potential-energy curve is E_r and the energies of the nuclear states E_λ are determined relative to E_r . These resonance states can then, under emission of an electron, decay to a continuum state characterized by an electronic final state $|E\rangle$ and a nuclear final state $|\chi_\mu\rangle$ with a lifetime τ_λ . The continuum states related to spectator resonant electronic decay processes can couple to other continuum states under emission of a photon. These processes are usually several orders of magnitude slower than the electronic decay process and are therefore neglected in this paper. Alternatively to arriving in the continuum via a decaying resonance state, a simultaneous direct excitation and ionization (spectator) or a direct ionization (participator) channel is also possible, which is denoted “dir” in the figure.

From the derivations of Ref. [31], we know that the time-independent Fano wave function is essential to the description of the time-resolved spectra. We therefore first discuss the derivation of approximative Fano wave functions including nuclear degrees of freedom and afterwards derive the expression for the time- and energy-differential ionization probability.

A. Derivation of the Fano coefficients including nuclear wave functions

Fano’s purely electronic and time-independent wave function for one resonance and one final state is [32]

$$|\Psi_E\rangle = a(E)|r\rangle + \int dE' b_{E'}(E)|E'\rangle. \quad (1)$$

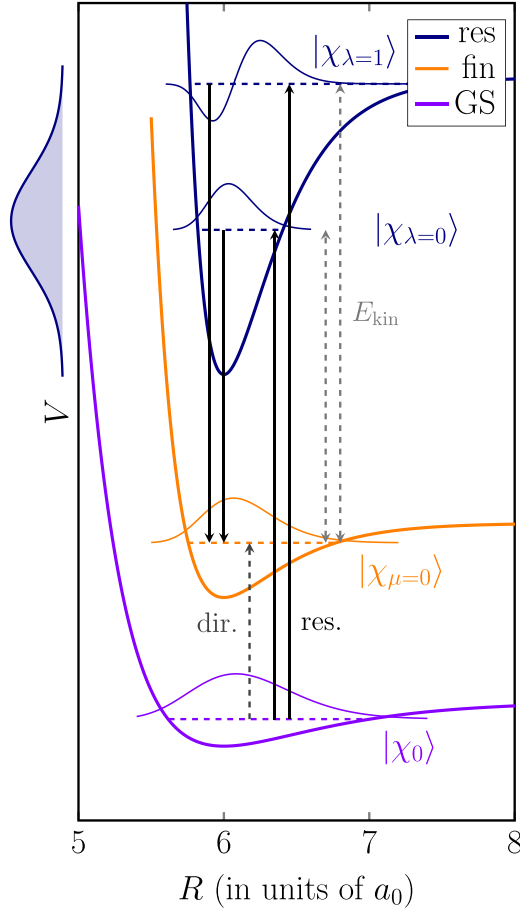


FIG. 1. Illustration [43] of the energy levels in the model systems used in this paper. The three potential curves belong to the electronic ground state (lower curve in violet), final state (middle curve in orange), and resonance state (upper curve in dark blue). For each potential, the position of the bound vibrational eigenstates is indicated by dashed lines (here one in both the electronic ground state and the final state, and two in the resonance state, which corresponds to case 4 in Sec. IV D) together with the corresponding vibrational eigenfunction and our chosen symbolic designation. The one-headed arrows depict possible pathways for the transition from the electronic ground state to the final state, either directly (dashed arrow) or via one of the vibrational eigenstates of the electronic resonance state (solid arrows). The double-headed arrow labeled “ E_{kin} ” corresponds to the kinetic energy of the RICD electron emitted following the transition from the resonance state to the final state, in this case between the vibrational ground states. The Gaussian function on the left represents the initiating ultrashort laser pulse, which is energetically centered around the energy of the vibrational ground state of the electronic resonance state, relative to the electronic ground state.

Here, $|r\rangle$ is the electronic wave function of the bound resonance state and $|E'\rangle$ is the electronic continuum wave function including both the bound final state and the emitted free electron. Both are considered to be eigenstates of the Hamilton operator $\hat{H}_0$ of the nondecaying system, while $|\Psi_E\rangle$ is an eigenstate of Fano’s Hamiltonian $\hat{H}_F$ which also includes what he termed the configuration-interaction operator. The latter is mediating the electron-electron interaction which is causing

the decay. a and b are coefficients, which are determined for the different cases.

We extend this ansatz to include nuclear degrees of freedom in the Born-Huang expansion [44] by adding a summation over the different nuclear eigenstates of the two respective potential-energy curves. Hereby, we assume the electronic wave functions to be adiabatic wave functions:

$$|\Psi_E\rangle = \sum_{\lambda} a_{\lambda}(E) |r\rangle |\chi_{\lambda}\rangle + \sum_{\mu'} \int dE' b_{E',\mu'}(E) |E'\rangle |\chi_{\mu'}\rangle. \quad (2)$$

In order to determine the coefficients, we follow the same strategy as for the pure electronic Fano ansatz in Ref. [32] and solve the following set of equations assuming the Born-Oppenheimer approximation [45,46]:

$$\begin{aligned} \langle r | \hat{H} | \Psi_E \rangle &= \sum_{\lambda} \langle r | \hat{H} a_{\lambda}(E) | r \rangle |\chi_{\lambda}\rangle \\ &+ \sum_{\mu'} \int dE' \langle r | \hat{H} b_{E',\mu'}(E) | E' \rangle |\chi_{\mu'}\rangle \\ &= E \langle r | \Psi_E \rangle, \end{aligned} \quad (3)$$

$$\begin{aligned} \langle E'' | \hat{H} | \Psi_E \rangle &= \sum_{\lambda} \langle E'' | \hat{H} a_{\lambda}(E) | r \rangle |\chi_{\lambda}\rangle \\ &+ \sum_{\mu'} \int dE' \langle E'' | \hat{H} b_{E',\mu'}(E) | E' \rangle |\chi_{\mu'}\rangle \\ &= E \langle E'' | \Psi_E \rangle. \end{aligned} \quad (4)$$

Here, the Hamilton operator of which $|\Psi_E\rangle$ is an eigenstate, as in Fano’s ansatz, consists of the Hamiltonian $\hat{H}_0$ of the nondecaying system, which involves both electronic and nuclear operators and is diagonal in the chosen electronic basis, and the purely electronic so-called configuration-interaction operator $\hat{V}$ coupling the electronic resonance and continuum eigenstates with each other:

$$\hat{H} = \hat{H}_F = \hat{H}_0 + \hat{V}. \quad (5)$$

The vibronic eigenfunctions $\{|r\rangle |\chi_{\lambda}\rangle\}$ and $\{|E\rangle |\chi_{\mu}\rangle\}$ of $\hat{H}_0$ are characterized by their respective energies, which we choose to give as the sum of the minimum energy of the electronic potential-energy curve plus the energy of the different vibrational levels ($E_{r,\min} + E_{\lambda}$ and $E_{\text{fin},\min} + E_{\mu}$). For a shorter notation, we will from here on denote the minima of the electronic potential curves as E_r and E_{fin} . The matrix elements for the Fano-type Hamiltonian and its constituents are compiled in Appendix A. We assume that the coefficients are not explicitly dependent on either the electronic or the nuclear coordinates to obtain

$$\begin{aligned} \langle r | \hat{H}_F | \Psi_E \rangle &= \sum_{\lambda} a_{\lambda}(E) (E_r + E_{\lambda}) |\chi_{\lambda}\rangle \\ &+ \sum_{\mu'} \int dE' b_{E',\mu'}(E) V_{rE'} |\chi_{\mu'}\rangle. \end{aligned} \quad (6)$$

We project out the contribution of a single nuclear eigenfunction $\langle \chi_{\lambda'} |$ and in doing so assume that the electronic configuration-interaction term $V_{E'} = \langle r | \hat{V} | E' \rangle = V_{E'}^*$ does not directly depend on the nuclear coordinates. We have then

renamed $\lambda' \rightarrow \lambda$:

$$\begin{aligned} \langle \chi_\lambda | \langle r | \hat{H}_F | \Psi_E \rangle &= a_\lambda(\underline{E})(E_r + E_\lambda) \\ &+ \sum_{\mu'} \int dE' b_{E',\mu'}(\underline{E}) V_{rE'} \langle \chi_\lambda | \chi_{\mu'} \rangle \\ &= \underline{E} a_\lambda(\underline{E}). \end{aligned} \quad (7)$$

Analogously, we obtain

$$\begin{aligned} \langle \chi_{\mu'} | \langle E' | \hat{H}_F | \Psi_E \rangle &= \sum_\lambda a_\lambda(\underline{E}) V_{E'r} \langle \chi_{\mu'} | \chi_\lambda \rangle \\ &+ b_{E',\mu'}(\underline{E})(E' + E_{\mu'}) \\ &= \underline{E} b_{E',\mu'}(\underline{E}). \end{aligned} \quad (8)$$

By solving Eq. (8) for $b_{E',\mu'}(\underline{E})$ we arrive at

$$\begin{aligned} b_{E',\mu'}(\underline{E}) &= \sum_\lambda \frac{a_\lambda(\underline{E}) V_{E'r} \langle \chi_{\mu'} | \chi_\lambda \rangle}{\underline{E} - E' - E_{\mu'}} \\ &+ \sum_\lambda a_\lambda(\underline{E}) V_{E'r} \langle \chi_{\mu'} | \chi_\lambda \rangle z(\underline{E}) \delta(\underline{E} - E' - E_{\mu'}). \end{aligned} \quad (9)$$

Here, we implicitly assume that the first part of the sum becomes the principal part upon integration ($\mathcal{P} \int$) over one of the energies. For only one resonance and one final state, we would insert this expression into Eq. (7) and solve for $z(\underline{E})$. However, when including nuclear wave functions, we arrive at

$$\begin{aligned} (\underline{E} - E_r - E_\lambda) a_\lambda(\underline{E}) &= \sum_{\mu',\lambda'} \mathcal{P} \int dE' \frac{a_{\lambda'}(\underline{E}) |V_{E'r}|^2 \langle \chi_\lambda | \chi_{\mu'} \rangle \langle \chi_{\mu'} | \chi_{\lambda'} \rangle}{\underline{E} - E' - E_{\mu'}} \\ &+ \sum_{\mu',\lambda'} a_{\lambda'}(\underline{E}) |V_{(\underline{E}-E_{\mu'})r}|^2 z(\underline{E}) \langle \chi_\lambda | \chi_{\mu'} \rangle \langle \chi_{\mu'} | \chi_{\lambda'} \rangle. \end{aligned} \quad (10)$$

An analytical closed-form solution of this equation is not possible because only the decay of several resonance states to the same final state or the decay of one resonance state into several final states can be properly normalized in the way discussed by Fano [32]. In our case, the sum over μ' or λ' prevents this normalization. We therefore make the assumption that the nuclear wave functions of the resonance state are not coupled via the continuum and hence introduce $\delta_{\lambda,\lambda'}$, which corresponds to Mies's nonoverlapping resonances [33]. This approximation is valid when, for a given μ' , the Franck-Condon factor for λ is significantly larger than for all other values of λ' . Then, all contributions other than the one for $\lambda' = \lambda$ are small and a large part of the sum is covered by the main contribution. This situation might be realized in case of parallel potential surfaces of the electronic states, although this case is rather unlikely because these electronic states belong to different charge states. Another scenario would see the potential surfaces shifted such that only one for the bound nuclear wave functions, namely the uppermost, has significant overlap with the nuclear wave functions of the other electronic state. We note that, in this case, dissociative states, which have not been considered in this paper but are the subject of ongoing investigations, will gain in relevance.

With this in mind, we deduce

$$z(\underline{E}) = \frac{\underline{E} - E_r - E_\lambda - \sum_{\mu'} F_{\mu'}(\underline{E})}{W_\lambda}. \quad (11)$$

Here, W_λ is the weighted sum of absolute squares of the configuration-interaction terms of the different nuclear final states for a single nuclear resonance state

$$W_\lambda = \sum_{\mu'} |V_{(\underline{E}-E_{\mu'})r}|^2 |\langle \chi_\lambda | \chi_{\mu'} \rangle|^2 \quad (12)$$

$$\text{and } F_{\mu'}(\underline{E}) = \mathcal{P} \int dE' \frac{|V_{E'r}|^2 |\langle \chi_\lambda | \chi_{\mu'} \rangle|^2}{\underline{E} - E' - E_{\mu'}}.$$

Here, we have assumed that the electronic coupling matrix elements $V_{(\underline{E}-E_{\mu'})r}$ are independent of the interparticle distance R . In reality, they exhibit a structure dependence, e.g., an exponential behavior for Auger-Meitner processes or an R^{-3} dependence for ICD processes within the asymptotic approximation [47–50]. This effect will be discussed separately in a follow-up paper.

Let us put this expression in Eq. (11) into perspective by comparing it to its purely electronic counterpart for the decay of one electronic resonance state to several electronic final states:

$$z_{\text{el}}(\underline{E}) = \frac{\underline{E} - E_r - \sum_f F_f(\underline{E})}{\sum_f |V_{rf}|^2}. \quad (13)$$

The similarities between them are obvious. The only difference is weighting the different decay widths by the Franck-Condon factors $|\langle \chi_\lambda | \chi_{\mu'} \rangle|^2$.

By again using $\delta_{\lambda,\lambda'}$ consistently in the normalization of the wave function by calculating $\langle \Psi_E | \Psi_E \rangle$ while, analogously to Fano, using

$$\begin{aligned} &\frac{1}{(\underline{E} - E' - E_{\mu'})(\underline{E} - E' - E_{\mu'})} \\ &= \frac{1}{\underline{E} - E} \left(\frac{1}{\underline{E} - E' - E_{\mu'}} - \frac{1}{\underline{E} - E' - E_{\mu'}} \right) \\ &+ \pi^2 \delta(\underline{E} - E) \delta[E' - (\underline{E} - E_{\mu'})], \end{aligned} \quad (14)$$

$$\begin{aligned} &\delta(\underline{E} - E' - E_{\mu'}) \delta(\underline{E} - E' - E_{\mu'}) \\ &= \delta(\underline{E} - E) \delta\left(E' - \frac{1}{2}(\underline{E} + E - 2E_{\mu'})\right), \end{aligned} \quad (15)$$

and by assuming that $F(\underline{E})$ is real, we obtain

$$\sum_\lambda |a_\lambda(\underline{E})|^2 W_\lambda [\pi^2 + |z(\underline{E})|^2] \delta(\underline{E} - \underline{E}) = \delta(\underline{E} - \underline{E}). \quad (16)$$

To solve this equation for the coefficient of only one vibrational eigenstate of the resonance state λ , we assume that the contributions of the different vibrational eigenstates are equally distributed among all N_λ vibrational bound states of the resonance state to give

$$|a_\lambda(\underline{E})|^2 W_\lambda [\pi^2 + |z(\underline{E})|^2] = 1/N_\lambda. \quad (17)$$

We finally determine the coefficients within the applied approximations to be

$$a_\lambda(\underline{E}) = -\frac{\sqrt{W_\lambda}}{\sqrt{N_\lambda} \sqrt{[E - E_r - E_\lambda - \sum_{\mu''} F_{\mu''}(\underline{E})]^2 + \pi^2 W_\lambda^2}}, \quad (18)$$

$$b_{E',\mu'}(\underline{E}) = \sum_{\lambda'} \frac{V_{E'r} a_{\lambda'}(\underline{E}) \langle \chi_{\mu'} | \chi_{\lambda'} \rangle}{E - E' - E_{\mu'}} + \sum_{\lambda'} \frac{[E - E_r - E_{\lambda'} - \sum_{\mu''} F_{\mu''}(\underline{E})] V_{E'r} a_{\lambda'}}{W_{\lambda'}} \times \delta(E - E' - E_{\mu'}) \langle \chi_{\mu'} | \chi_{\lambda'} \rangle. \quad (19)$$

Because the $F_{\mu'}(\underline{E})$ are small shifts in the energy position of the resonance state $|r\rangle |\chi_\lambda\rangle$ caused by the interaction with the continuum, which are further damped by Franck-Condon factors, we neglect them in the following.

We therefore have a formulation equivalent to the one provided by Fano, which now includes nuclear degrees of freedom.

B. Derivation of the time-dependent formulation for the description of time-resolved electronic decay spectra including nuclear degrees of freedom

The relevant property for the description of the time evolution of ICD processes is the time- and energy-differential ionization probability obtained from the time-dependent wave function $|\Psi(t)\rangle$ by

$$P(E_{\text{kin}}, t) = \sum_i |\langle E_i | \Psi(t) \rangle|^2. \quad (20)$$

Here $|E_i\rangle$ denotes a continuum state with energy E_i , which entails both the kinetic energy E_{kin} of the emitted electron and the energy of the final cationic state i . The electronic continuum states are orthogonal to all electronic bound states of the system and the nuclear eigenstates of each electronic state are orthogonal among each other. Atomic units are used throughout unless stated otherwise.

We obtain the wave function of the system by solving the time-dependent Schrödinger equation

$$i \frac{\partial}{\partial t} |\Psi(t)\rangle = H(t) |\Psi(t)\rangle \quad (21)$$

for the Hamiltonian

$$H(t) = H_F + H_X(t). \quad (22)$$

Here, H_F is the Hamiltonian of the unperturbed system as defined in Eq. (5) and H_X describes the electromagnetic field of the exciting laser pulse.

We are going to use the formalism of time-evolution operators $U(t, t_0)$, which adhere to a specific Hamiltonian and describe the propagation of a system from time t_0 to time t :

$$|\Psi(t)\rangle = U(t, t_0) |\Psi(t_0)\rangle. \quad (23)$$

As a starting point for using time-dependent perturbation theory, we split off the explicitly time-dependent part of the

Hamiltonian from the rest:

$$U(t, t_0) = U_F(t, t_0) - i \int_{t_0}^t dt' U_F(t, t') H_X(t') U(t', t_0), \quad (24)$$

where $U_F(t, t_0)$ is the time-evolution operator of the system described by the zeroth-order Hamiltonian H_F and $H_X(t')$ will be treated as a small perturbation.

Since the time-evolution operator $U(t, t_0)$ appears on both sides of this integral equation, it can be solved iteratively by repeated insertion of Eq. (24) into itself:

$$U(t, t_0) = U_F(t, t_0) - i \int_{t_0}^t dt' U_F(t, t') H_X(t') U_F(t', t_0) + O[(H_X)^2]. \quad (25)$$

The term up to first order is then given by

$$|\Psi(t)\rangle = U_F(t, t_0) |\Psi(t_0)\rangle - i \int_{t_0}^t dt' U_F(t, t') H_X(t') U_F(t', t_0) |\Psi(t_0)\rangle. \quad (26)$$

We assume that the intensity of the exciting laser is so low that its interaction with the system can be described within the dipole approximation. Therefore, we can describe our system within first order of perturbation theory in $H_X(t')$. Starting from the ground state $|G(t_0)\rangle$, our wave function is given by

$$|\Psi(t)\rangle = U_F(t, t_0) |G(t_0)\rangle - i \int_{t_0}^t dt' U_F(t, t') H_X(t') U_F(t', t_0) |G(t_0)\rangle. \quad (27)$$

We are free to choose an energy reference and therefore select $E_G = 0$. This conveniently removes the time dependence from the ground state, since $|G(t_0)\rangle = \exp\{-iE_G t_0\} |G\rangle = |G\rangle$.

We rewrite the time-evolution operator $U_F(t, t')$ analogously to Eq. (24):

$$U_F(t, t') = U_0(t, t') - i \int_{t'}^t dt'' U_0(t, t'') V U_F(t'', t'). \quad (28)$$

Here $U_0(t, t')$ is the free-particle time-evolution operator. The second part therefore describes the consecutive interaction of the laser pulse with the system and the decay.

By inserting Eq. (28) into Eq. (27) we arrive at

$$|\Psi(t)\rangle = U_F(t, t_0) |G\rangle - i \int_{t_0}^t dt' U_0(t, t') H_X(t') |G\rangle - \int_{t_0}^t dt' \int_{t'}^t dt'' U_0(t, t'') V U_F(t'', t') H_X(t') |G\rangle. \quad (29)$$

The time-evolution operator $U_F(t'', t')$ in the last integral again describes the contribution of the Hamiltonian $H_0 + V$ of Eq. (5). This is analogous to the Hamilton operator used in Fano's description [32] of a decaying resonance state, which is why we chose the subscript F also for the time-evolution operator.

We now introduce the separation of electronic and nuclear wave functions. For the ground state, we assume the following product ansatz of the electronic wave function $|g\rangle$ and the vibrational-ground-state wave function $|\chi_0\rangle$:

$$|G\rangle = |g\rangle |\chi_0\rangle. \quad (30)$$

In order to determine the probability amplitude for one specific final state, we project on one electronic continuum state $|E\rangle$ and one vibrational state $|\chi_\mu\rangle$ of this final state, characterized by their respective energies of the ionized system and the kinetic energy of the emitted electron. Inserting the resolution of the identity behind the time-evolution operator U_0 in both the second and the third term on the right-hand side yields

$$\begin{aligned} \langle \chi_\mu | \langle E | \Psi(t) \rangle &= \langle \chi_\mu | \langle E | U_F(t, t_0) | g \rangle | \chi_0 \rangle - i \int_{t_0}^t dt' \langle \chi_\mu | \langle E | U_0(t, t') H_X(t') | g \rangle | \chi_0 \rangle \\ &\quad - \int_{t_0}^t dt' \int_{t'}^t dt'' \langle \chi_\mu | \langle E | U_0(t, t'') V U_F(t'', t') H_X(t') | g \rangle | \chi_0 \rangle \\ &= \langle \chi_\mu | \langle E | U_F(t, t_0) | g \rangle | \chi_0 \rangle - i \int_{t_0}^t dt' \sum_{\mu'} \int dE' \langle \chi_\mu | \langle E | U_0(t, t') | E' \rangle | \chi_{\mu'} \rangle \langle \chi_{\mu'} | \langle E' | H_X(t') | g \rangle | \chi_0 \rangle \\ &\quad - \int_{t_0}^t dt' \int_{t'}^t dt'' \sum_{\mu'} \int dE' \langle \chi_\mu | \langle E | U_0(t, t'') | E' \rangle | \chi_{\mu'} \rangle \langle \chi_{\mu'} | \langle E' | V U_F(t'', t') H_X(t') | g \rangle | \chi_0 \rangle. \end{aligned} \quad (31)$$

The time-evolution operator $U_0(t, t')$ solves the time-dependent Schrödinger equation for the Hamiltonian $\hat{p}^2/2 + E_{\text{fin}} + E_\mu$. The corresponding wave functions with wave vector $\vec{k}$ are $|\Psi_{\vec{k}}^0(t)\rangle = |\vec{k}\rangle \exp[-i \int_{-\infty}^t dt'' (\frac{1}{2}\vec{k}^2 + E_{\text{fin}} + E_\mu)]$. Its projection formulation propagating a system from time t' to time t is given by

$$\begin{aligned} U_0(t, t') &= \int d\vec{k} |\Psi_{\vec{k}}^0(t)\rangle \langle \Psi_{\vec{k}}^0(t')| \\ &= \sum_{\vec{\mu}} \int d\tilde{E} |\tilde{E}(t)\rangle |\chi_{\vec{\mu}}(t)\rangle \langle \chi_{\vec{\mu}}(t')| \langle \tilde{E}(t')| \\ &= \sum_{\vec{\mu}} \int d\tilde{E} \exp\left[-i \int_{t'}^t dt''' (\tilde{E} + E_{\vec{\mu}})\right] |\tilde{E}\rangle |\chi_{\vec{\mu}}\rangle \langle \chi_{\vec{\mu}}| \langle \tilde{E}|. \end{aligned} \quad (32)$$

At this point we only consider the kinetic energy of the emitted electron and can therefore write the projection of a general continuum state $\langle E|$ on the free-particle time-evolution operator in the following way:

$$\langle \chi_\mu | \langle E | U_0(t, t') | E' \rangle | \chi_{\mu'} \rangle = \int d\tilde{E} \sum_{\vec{\mu}} \langle \chi_\mu | \langle E | \exp[i\Phi_0(E, t, t')] | \tilde{E} \rangle | \chi_{\vec{\mu}} \rangle \langle \chi_{\vec{\mu}} | \langle \tilde{E} | E' \rangle | \chi_{\mu'} \rangle \quad (33)$$

$$\begin{aligned} &= \int d\tilde{E} \sum_{\vec{\mu}} \langle \chi_\mu | \langle E | \tilde{E} \rangle | \chi_{\vec{\mu}} \rangle \exp\left[-i \int_{t'}^t dt''' (\tilde{E} + E_{\vec{\mu}})\right] \langle \chi_{\vec{\mu}} | \langle \tilde{E} | E' \rangle | \chi_{\mu'} \rangle \\ &= \exp\left[-i \int_{t'}^t dt''' (E_{\text{kin}} + E_{\text{fin}} + E_\mu)\right] \delta(E - E') \delta_{\mu, \mu'}, \end{aligned} \quad (34)$$

where E_{kin} is the kinetic energy relative to the final cationic state $E_{\text{fin}} + E_\mu$ and $\Phi_0(E, t, t')$ is the time-dependent phase.

The first term of the right-hand side of Eq. (31) vanishes because of the orthogonality between electronic bound and continuum eigenstates. The nonzero terms of Eq. (31) are given by

$$\begin{aligned} \langle \chi_\mu | \langle E | \Psi(t) \rangle &= -i \int_{t_0}^t dt' \exp\left[-i(t-t')(E_{\text{kin}} + E_{\text{fin}} + E_\mu)\right] \langle \chi_\mu | \langle E | H_X(t') | g \rangle | \chi_0 \rangle \\ &\quad - \int_{t_0}^t dt' \int_{t'}^t dt'' \exp\left[-i(t-t'')(E_{\text{kin}} + E_{\text{fin}} + E_\mu)\right] \langle \chi_\mu | \langle E | V U_F(t'', t') H_X(t') | g \rangle | \chi_0 \rangle. \end{aligned} \quad (35)$$

The second term can be solved by substituting the configuration-interaction operator

$$\hat{V} = \sum_{\mu'} \sum_{\lambda} \int dE' |E'\rangle |\chi_{\mu'}\rangle \langle \chi_{\mu'} | \chi_{\lambda} \rangle V_{E'r} \langle \chi_{\lambda} | \langle r | + \sum_{\mu'} \sum_{\lambda} \int dE' |r\rangle |\chi_{\lambda}\rangle \langle \chi_{\lambda} | \chi_{\mu'} \rangle V_{rE'} \langle \chi_{\mu'} | \langle E' | \quad (36)$$

and inserting the resolution of the identity

$$\mathbb{1} = \sum_{\lambda'} |r\rangle |\chi_{\lambda'}\rangle \langle \chi_{\lambda'}| \langle r| + \sum_{\mu''} \int dE'' |E''\rangle |\chi_{\mu''}\rangle \langle \chi_{\mu''}| \langle E''| \quad (37)$$

between the Fano propagator and the operator of the exciting field to yield

$$\begin{aligned} \langle \chi_{\mu} | \langle E | \Psi(t) \rangle &= -i \int_{t_0}^t dt' \exp[-i(t-t')(E_{\text{kin}} + E_{\text{fin}} + E_{\mu})] \langle \chi_{\mu} | \langle E | H_X(t') | g \rangle | \chi_0 \rangle \\ &\quad - \sum_{\lambda, \lambda'} \int_{t_0}^t dt' \int_{t'}^t dt'' \exp[-i(t-t'')(E_{\text{kin}} + E_{\text{fin}} + E_{\mu})] V_{Er} \langle \chi_{\mu} | \chi_{\lambda} \rangle \langle \chi_{\lambda} | \langle r | U_F(t'', t') | r \rangle | \chi_{\lambda'} \rangle \\ &\quad \times \langle \chi_{\lambda'} | \langle r | H_X(t') | g \rangle | \chi_0 \rangle \\ &\quad - \sum_{\lambda, \mu''} \int dE'' \int_{t_0}^t dt' \int_{t'}^t dt'' \exp[-i(t-t'')(E_{\text{kin}} + E_{\text{fin}} + E_{\mu})] V_{Er} \langle \chi_{\mu} | \chi_{\lambda} \rangle \langle \chi_{\lambda} | \langle r | U_F(t'', t') | E'' \rangle | \chi_{\mu''} \rangle \\ &\quad \times \langle \chi_{\mu''} | \langle E'' | H_X(t') | g \rangle | \chi_0 \rangle. \end{aligned} \quad (38)$$

Since we describe the interaction between the system and the exciting XUV field in the dipole approximation, the corresponding Hamilton operator in the length gauge is given by $H_X(t') = -\mu \mathcal{E}_X(t') = \mu \frac{d}{dt'} A_X(t') f_X(t')$, where $\mathcal{E}_X(t')$ denotes the time-dependent field strength of the XUV laser, while μ denotes the dipole operator, $A_X(t') = A_{0X} \cos(\Omega t')$ is the vector potential of the laser field in the direction of the linear polarization, and $f_X(t')$ is the Gaussian pulse envelope. We assume the transition dipole matrix element from the ground state to the continuum to be independent of the energy of the continuum state,

$$\langle E_i | \mu | g \rangle = \langle c | \mu | g \rangle, \quad (39)$$

over the energy range of interest:

$$\begin{aligned} \langle \chi_{\mu} | \langle E | \Psi(t) \rangle &= +i \langle c | \mu | g \rangle \int_{t_0}^t dt' \exp[-i(t-t')(E_{\text{kin}} + E_{\text{fin}} + E_{\mu})] \langle \chi_{\mu} | \chi_0 \rangle \mathcal{E}_X(t') \\ &\quad + \langle r | \mu | g \rangle \sum_{\lambda, \lambda'} \int_{t_0}^t dt' \int_{t'}^t dt'' \exp[-i(t-t'')(E_{\text{kin}} + E_{\text{fin}} + E_{\mu})] V_{Er} \langle \chi_{\mu} | \chi_{\lambda} \rangle \langle \chi_{\lambda} | \langle r | U_F(t'', t') | r \rangle | \chi_{\lambda'} \rangle \\ &\quad \times \langle \chi_{\lambda'} | \chi_0 \rangle \mathcal{E}_X(t') \\ &\quad + \langle c | \mu | g \rangle \sum_{\lambda, \mu''} \int dE'' \int_{t_0}^t dt' \int_{t'}^t dt'' \exp[-i(t-t'')(E_{\text{kin}} + E_{\text{fin}} + E_{\mu})] V_{Er} \langle \chi_{\mu} | \chi_{\lambda} \rangle \langle \chi_{\lambda} | \langle r | U_F(t'', t') | E'' \rangle | \chi_{\mu''} \rangle \\ &\quad \times \langle \chi_{\mu''} | \chi_0 \rangle \mathcal{E}_X(t'). \end{aligned} \quad (40)$$

The Fano matrix elements including nuclear dynamics require a thorough inspection. We assume a Born-Oppenheimer ansatz of the wave function, in which the electronic solutions are parametrically dependent on the nuclear coordinates and the coefficients do not directly depend on either the electronic or nuclear coordinates. It is therefore possible to use the following projection formulation:

$$\begin{aligned} U_F(t'', t') &= \int d\mathbf{E} |\Psi_{\mathbf{E}}(t'')\rangle \langle \Psi_{\mathbf{E}}(t')| \\ &= \int d\mathbf{E} |\Psi_{\mathbf{E}}\rangle \langle \Psi_{\mathbf{E}}| \exp[-i\mathbf{E}(t'' - t')] \\ &= \int d\mathbf{E} \exp[-i\mathbf{E}(t'' - t')] \left[\sum_{\lambda'', \lambda'''} a_{\lambda''}(\mathbf{E}) a_{\lambda'''}^*(\mathbf{E}) |r\rangle |\chi_{\lambda''}\rangle \langle \chi_{\lambda'''}| \langle r| + \sum_{\lambda'', \tilde{\mu}} \int d\tilde{\mathbf{E}} \tilde{a}_{\lambda''}(\mathbf{E}) \tilde{b}_{\tilde{\mathbf{E}}, \tilde{\mu}}^*(\mathbf{E}) |r\rangle |\chi_{\lambda''}\rangle \langle \chi_{\tilde{\mu}}| \langle \tilde{\mathbf{E}}| + \dots \right] \\ &= \int d\mathbf{E} \exp[-i\mathbf{E}(t'' - t')] \left[\sum_{\lambda''} a_{\lambda''}(\mathbf{E}) a_{\lambda''}^*(\mathbf{E}) |r\rangle |\chi_{\lambda''}\rangle \langle \chi_{\lambda''}| \langle r| + \sum_{\lambda'', \tilde{\mu}} \int d\tilde{\mathbf{E}} \tilde{a}_{\lambda''}(\mathbf{E}) \tilde{b}_{\tilde{\mathbf{E}}, \tilde{\mu}}^*(\mathbf{E}) |r\rangle |\chi_{\lambda''}\rangle \langle \chi_{\tilde{\mu}}| \langle \tilde{\mathbf{E}}| + \dots \right]. \end{aligned} \quad (41)$$

Because we assume that there is no coupling between nuclear eigenstates of the same electronic eigenstate via the continuum, λ'' needs to be equal to λ''' .

As already mentioned, the derivation of the coefficients of Eqs. (18) and (19) relies on several, in part crude, approximations. For a quantitative comparison to experiment, these should be checked carefully. However, they are feasible for this qualitative description of the influence of nuclear dynamics on time-resolved spectroscopy on electronic decay processes. The Fano integrals

can then be solved by contour integration in the negative complex half plane as shown in Appendix B. Inserting them into Eq. (40) yields our working equation:

$$\begin{aligned}
\langle \chi_\mu | \langle E | \Psi(t) \rangle = & + i \langle c | \mu | g \rangle \int_{t_0}^t dt' \exp[-i(t-t')(E_{\text{kin}} + E_{\text{fin}} + E_\mu)] \langle \chi_\mu | \chi_0 \rangle \mathcal{E}_X(t') \\
& + \frac{\langle r | \mu | g \rangle}{N_\lambda} \sum_\lambda \int_{t_0}^t dt' \int_{t'}^t dt'' \exp[-i(t-t'')(E_{\text{kin}} + E_{\text{fin}} + E_\mu)] \\
& \times V_r \langle \chi_\mu | \chi_\lambda \rangle \langle \chi_\lambda | \chi_0 \rangle \exp[-i(t''-t')(E_r + E_\lambda - i\pi W_\lambda)] \mathcal{E}_X(t') \\
& - \frac{i\pi \langle c | \mu | g \rangle}{N_\lambda} \sum_{\lambda, \mu''} \int_{t_0}^t dt' \int_{t'}^t dt'' \exp[-i(t-t'')(E_{\text{kin}} + E_{\text{fin}} + E_\mu)] \\
& \times |V_r|^2 \langle \chi_\mu | \chi_\lambda \rangle \langle \chi_\lambda | \chi_{\mu''} \rangle \langle \chi_{\mu''} | \chi_0 \rangle \exp[-i(t''-t')(E_r + E_\lambda - i\pi W_\lambda)] \mathcal{E}_X(t'). \tag{42}
\end{aligned}$$

The first part describes the direct ionization into the continuum final state, while the second part of Eq. (42) describes the excitation from the ground state to the resonance state followed by a decay to the continuum final state. The third part describes the excitation to a continuum state, which then couples to the resonance state, which then again decays into either the same or a different continuum final state.

The first integral thus corresponds to the direct ionization process. The second (double) integral is identical for the resonance and the indirect terms. They have, though, different prefactors and are weighted differently for the nuclear states. For the case of a slowly varying envelope function ($\frac{d}{dt'} f_X(t') \approx 0$) and only considering the absorption of an XUV photon (neglecting the emission), these two integrals are solved analytically for times after the exciting pulse. The direct term for a specific value of μ is given by

$$\begin{aligned}
& - \frac{A_{0X} \Omega \langle c | \mu | g \rangle}{2} \langle \chi_\mu | \chi_0 \rangle \exp[-it(E_{\text{kin}} + E_{\text{fin}} + E_\mu)] \exp\left[-\frac{\sigma^2}{2}(E_{\text{kin}} + E_{\text{fin}} + E_\mu - \Omega)^2\right] \\
& \times \text{Re}\left\{\text{erf}\left[\frac{1}{\sqrt{2}\sigma}\left(\frac{T_X}{2} + i\sigma^2(E_{\text{kin}} + E_{\text{fin}} + E_\mu - \Omega)\right)\right]\right\}, \tag{43}
\end{aligned}$$

where Re denotes the real part and erf denotes the error function. The resonance and indirect ionization terms without their respective prefactors and weights are given by

$$\begin{aligned}
& - \frac{A_{0X} \Omega}{4(E_r + E_\lambda - i\pi W_\lambda - E_{\text{kin}} - E_{\text{fin}} - E_\mu)} \exp[-it(E_r + E_\lambda - i\pi W_\lambda)] \\
& \times \exp\left[-\frac{\sigma^2}{2}(E_r + E_\lambda - i\pi W_\lambda - \Omega)^2\right] [\text{erf}(\tau_{1,\text{max}}) - \text{erf}(\tau_{1,\text{min}})] \\
& + \frac{A_{0X} \Omega}{4(E_r + E_\lambda - i\pi W_\lambda - E_{\text{kin}} - E_{\text{fin}} - E_\mu)} \exp[-it(E_{\text{kin}} + E_{\text{fin}} + E_\mu)] \\
& \times \exp\left[-\frac{\sigma^2}{2}(E_{\text{kin}} + E_{\text{fin}} + E_\mu - \Omega)^2\right] [\text{erf}(\tau_{2,\text{max}}) - \text{erf}(\tau_{2,\text{min}})] \tag{44}
\end{aligned}$$

with $\tau_{1,\text{max}} = \frac{1}{\sqrt{2}\sigma}(\frac{T_X}{2} - i\sigma^2(E_r + E_\lambda - i\pi W_\lambda - \Omega))$, $\tau_{1,\text{min}} = -\frac{1}{\sqrt{2}\sigma}(\frac{T_X}{2} + i\sigma^2(E_r + E_\lambda - i\pi W_\lambda - \Omega))$, $\tau_{2,\text{max}} = \frac{1}{\sqrt{2}\sigma}(\frac{T_X}{2} - i\sigma^2(E_{\text{kin}} + E_{\text{fin}} + E_\mu - \Omega))$, and $\tau_{2,\text{min}} = -\frac{1}{\sqrt{2}\sigma}(\frac{T_X}{2} + i\sigma^2(E_{\text{kin}} + E_{\text{fin}} + E_\mu - \Omega))$. Here, σ is the standard deviation of the Gauss distribution in time and T_X is the duration of the exciting XUV pulse. The different τ 's are the upper and lower limits of the integral after the coordinate transformation that allows us to formally solve the outer integral of the resonance and the indirect terms in Eq. (42).

The absolute square of the sum of all these terms gives the ionization probability for one specific nuclear final state. In order to determine the total spectrum, the contributions of all final states need to be added up according to Eq. (20).

III. COMPUTATIONAL DETAILS

In the following, we will show the results for different cases with different numbers of nuclear bound states of either the resonance state or the final state, which were all obtained by the script NUCLEAR_DYN within a locally modified version of ELDEST [51,52].

We use Morse potentials in the simulations:

$$V_{\text{Morse}} = D\{1 - \exp[-\alpha(R - R_0)]\}^2. \tag{45}$$

These are beneficial for our description because the vibrational wave functions are known analytically [53–55] and the evaluation of the Franck-Condon integrals is therefore possible without prior numerical solution of the nuclear Schrödinger equation. In our implementation, we use the recursive definition given in Eq. (49) of Ref. [56]. In order to

TABLE I. Parameters of the Morse potentials defined in Eq. (45) and used for the simulations.

No.	α_{res} (a.u.)	D_{res} (eV)	α_{fin} (a.u.)	D_{fin} (eV)
1	4.9512	0.01	21.6296	0.11
2	21.6296	0.11	17.0028	0.51
3	4.9512	0.01	4.9121	0.81
4	15.3994	0.50	21.7512	0.10
5	4.4414	0.04	23.9911	0.12
6	10.8894	0.50	5.1507	0.10
7	5.1507	0.10	10.8894	0.50

compensate for the integration over R instead of αR used in Ref. [56], we included an additional factor of $\sqrt{\alpha}$ in the normalization constant.

However, the general findings, which we will discuss later, will also hold for other types of interatomic potentials.

Unless stated otherwise, the parameters of the Morse potentials were optimized for a given number of bound states, of which as many as possible have significant Franck-Condon overlaps between (a) the ground and resonance state and (b) the resonance and final state for equal equilibrium distances. Moreover, the energy differences between the vibrational ground state and first excited state are of the size usually found in existing chemical systems, especially diatomic molecules. We used $\alpha_{\text{max}} = 30.0$ and $D_{\text{max}} = 6.0$ eV and a purely electronic Fano q parameter of 1 [see Eq. (46)]. The electronic ground state is chosen such that it only contains one nuclear bound state and its parameters are kept constant. All parameters can be found in Table I.

We choose all configuration-interaction terms V_r to be real and to correspond to a lifetime of $\tau = \frac{1}{2\pi|V_r|^2} = 20$ fs to allow for an easier comparison between the different cases.

The electronic energies of the resonance states are chosen such that the energy difference between the vibrational ground state of the electronic ground state and the vibrational ground state of the resonance state has an energy of 50 eV. This allows us to use the same parameters for the initiating pulse, which is chosen to have a mean photon energy of 50 eV and $n_X = 10$ cycles within the full width at half maximum (FWHM) of the Gaussian pulse. This results in an FWHM of 1.2 fs. The pulse is modeled for a total of 5σ . Moreover, the electronic final state is chosen such that the secondary electron emitted during a transition from the vibrational ground states of the resonance state to the vibrational ground state of the final state is 10 eV.

In order to extract oscillation frequencies from the calculated time-resolved spectra, we employed a fast Fourier transform (FFT). To this end, we evaluated the signal for one specific kinetic energy, discarded the first eight data points to exclude the buildup phase from the signal, and performed the FFT on the remaining data points. The central frequency of a peak was chosen as the center of its FWHM.

IV. RESULTS

The basic findings for the purely electronic case have already been reported elsewhere [31]. We summarize them here,

to allow a better comparison of the following showcases to the hitherto known case.

The shape of the signal after long times is a Fano profile convoluted with a Gaussian. The former's shape is described by the ratio between the contribution of the resonance part to the direct part of the wave function, which are included in the Fano parameter

$$q = \frac{\langle r|\mu|g \rangle}{\langle c|\mu|g \rangle \pi V_{Er}^*}, \quad (46)$$

so that the Fano profile may be described as

$$\frac{|\langle \Psi_E|\mu|g \rangle|^2}{|\langle E|\mu|g \rangle|^2} = \frac{(q + \epsilon)^2}{1 + \epsilon^2}, \quad (47)$$

where $\epsilon = \frac{E_{\text{kin}} + E_{\text{fin}} - E_r}{\pi |V_{Er}|^2}$ [ignoring $F(E)$, as we do throughout this paper] denotes a reduced energy variable [32].

The maxima and minima of the purely electronic Fano line shape are given by

$$E_{\text{kin,max}} = E_r + E_\lambda - E_{\text{fin}} - E_\mu + \frac{\pi |V_{Er}|^2}{q}, \quad (48)$$

$$E_{\text{kin,min}} = E_r + E_\lambda - E_{\text{fin}} - E_\mu - q\pi |V_{Er}|^2. \quad (49)$$

During the buildup of the Fano profile, oscillations in both energy and time are observed [31] originating from interference effects of the different pathways.

Moreover, the total lifetime of the resonance state can not be extracted from experimental data by a simple exponential fit, which assumes a sudden population of the resonance state. Instead, one needs to take the population of the resonance state over the entire pulse duration into account.

A. Case 1: One vibrational bound state in the electronic resonance state and one vibrational bound state in the electronic final state

This case, for which we used parameters 1 of Table I for the simulation, is the most fundamental one. Since only one nuclear resonance state and one nuclear final state are considered, the derived and used expressions are exact within the limits of the Born-Oppenheimer approximation, the independence of the electronic bound-continuum coupling matrix element V_{Er} of the nuclear coordinates, and the purely electronic Fano theory [31].

As to be expected from the purely electronic case, the spectrum (shown in Fig. 2) contains a time-resolved buildup of a Fano profile convoluted by the Gaussian caused by the shape of the initiating laser pulse.

Including the nuclear degrees of freedom changes the details of the spectrum even in this most simple of cases. In our description, there are two main reasons for that.

First, the effective decay width W_λ of this decay being 21.71 fs is slightly different from the purely electronic one of 20 fs. This deviation from the input lifetime is mainly artificial, though: According to Eq. (12), the decay width is weighted with $|\langle \chi_{\lambda=0}|\chi_{\mu=0} \rangle|^2$, the Franck-Condon factor between the vibrational resonance state and the vibrational final state. In this case, its value is 0.921. But analytical sum rules for Franck-Condon factors imply that for a given vibrational resonance state $|\chi_\lambda\rangle$, the sum of its Franck-Condon factors

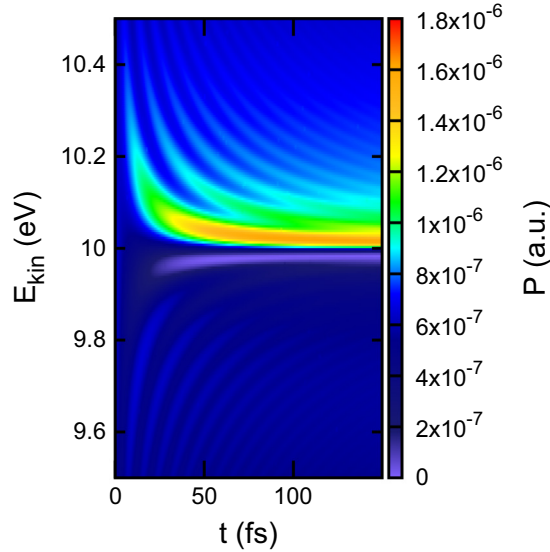


FIG. 2. Time-resolved kinetic-energy spectrum of the RICD electron for one vibrational state in the electronic resonance state and one vibrational state in the electronic final state.

over all vibrational bound final states plus the integral of its Franck-Condon density over all vibrational continuum final states must be equal to unity. Given that only one bound final state exists in the example system examined in this case, the above figure of 0.921 already represents the bound-states term in the sum rule. On the other hand, vibrational continuum states are not considered in this paper. This explains the missing 7.9% of Franck-Condon contributions. It should be noted, though, that even if vibrational continuum states of the final state were to be included, such states with an energy above the energy of the given vibrational resonance state would not contribute to the decay of the latter because the energy criterion for the RICD process would be violated for these channels. Thus in each instance, the lifetime of the resonance state will still be increased with respect to the purely electronic value, albeit to a much smaller extent than the one yielded by our present simulation.

Second, the shape of the signal is altered compared to the purely electronic one because the relative contributions of the different pathways are changed by the Franck-Condon overlaps.

Both effects, the Franck-Condon weighting leading to different relative contributions of the pathways and to an effective decay width W_λ (the latter being underestimated to some extent by neglecting continuum vibrational states), affect the line shape of the kinetic-energy distribution of the emitted electron. The shape still resembles a Fano profile, though, and we will discuss changes in peak shapes like the positions of minima and maxima based on an effective q parameter to make it comparable to literature in the field. It has to be noted, however, that this effective q parameter is not rigorously defined.

For a more narrow ground-state potential and shifted potential-energy curves of the resonance and final states, the different classes of Franck-Condon overlaps (ground state–resonance state, ground state–final state, and resonance

state–final state) will in most cases be affected differently by alterations of the potentials in both width and shifts along the internuclear axis. As a result, the direct, resonance and indirect pathways are weighted differently, which leads to a change in shape and amplitude of the peak. We will not discuss shifting of the potential-energy surfaces along the internuclear axis in detail in the following, but we keep in mind that it can impact the individual peaks. In extreme cases, decay channels can become insignificant by shifting the potentials with respect to each other.

B. Case 2: One vibrational bound state in the resonance state and two vibrational bound states in the final state

In this case, parameters 2 of Table I were used for the simulation. Since only the final state has several vibrational bound states, the derived and used expressions are again exact within the limits of the Born-Oppenheimer approximation, the independence of the electronic bound-continuum coupling matrix element V_{Er} of the nuclear coordinates, and the purely electronic Fano theory.

The total decay width is determined as the sum over the partial decay widths as given by Eq. (12). In this case, the effective decay width of 21.45 fs again deviates from the purely electronic one of 20 fs mainly due to incompleteness of the basis set of vibrational eigenfunctions. The sum of the Franck-Condon factors for the vibrational resonance state over both vibrational bound final states equals 0.941. The distance to unity is therefore smaller than in the previous case, which means that by ignoring the vibrational continuum states of the final state, a lesser error in the effective decay width is introduced in the present case. It should not be forgotten, though, that part of the lifetime prolongation is in fact physical due to some channels being closed for energetic reasons, as discussed in the previous subsection.

The corresponding time-resolved spectrum shown in Fig. 3 has two Fano peaks with maxima at 10.015 and 9.785 eV corresponding to the transitions $\mu = 0 \leftarrow \lambda = 0$ and $\mu = 1 \leftarrow \lambda = 0$, respectively.

We notice that the intensities of the two peaks differ and the overall spectrum is more complex than in case 1.

The corresponding Franck-Condon overlaps then determine the boost of the different decay peaks. In this particular case, they are $\langle \chi_{\mu=0} | \chi_0 \rangle = 0.38$ and $\langle \chi_{\mu=1} | \chi_0 \rangle = 0.82$. Consequently, the direct contribution for the final state with $|\chi_{\mu=1}\rangle$ is higher than that for the vibrational ground state.

The direct parts of the transition amplitudes also affect both the relative peak intensity and the peak shape of the corresponding decay peaks by changing the relative contributions of the direct, the resonance, and the indirect terms. The other contributions are affected by the Frank-Condon overlaps involving the resonance state. In this example, they are $\langle \chi_\lambda | \chi_0 \rangle = 0.87$, $\langle \chi_{\mu=0} | \chi_\lambda \rangle = 0.55$, and $\langle \chi_{\mu=1} | \chi_\lambda \rangle = 0.80$. Since $\langle \chi_{\mu=1} | \chi_\lambda \rangle$ is larger than $\langle \chi_{\mu=0} | \chi_\lambda \rangle$, the transition from the resonance state to the vibrational excited final state is favored.

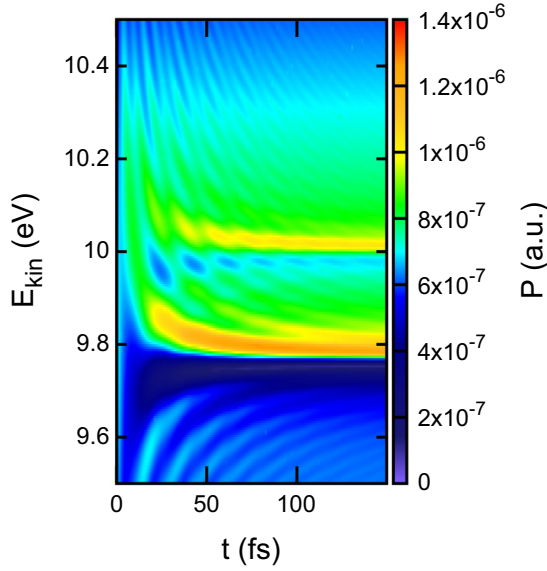


FIG. 3. Time-resolved RICD spectrum for one vibrational state in the electronic resonance state and two different vibrational states in the electronic final state. Two peaks are visible, one for each vibrational state in the final state. The peak at 10 eV corresponds to the vibrational $0 \leftarrow 0$ transition, while the one at 9.8 eV corresponds to the $1 \leftarrow 0$ transition. Both peaks exhibit the characteristic Fano profile. For a detailed discussion, see the main text.

In order to determine the relative contributions of the different pathways to the respective signal, we need to compare $\langle \chi_\mu | \chi_0 \rangle$ to the product $\langle \chi_\mu | \chi_\lambda \rangle \langle \chi_\lambda | \chi_0 \rangle$ according to Eq. (42). These products are 0.48 ($\mu = 0$) and 0.69 ($\mu = 1$). Hence, for the vibrational ground state of the electronic final state with $\mu = 0$, the relative contribution of the resonance pathway is increased, while it is decreased for the vibrational excited state with $\mu = 1$. Qualitatively, this leads to the same effect as increasing an effective Fano parameter for the vibrational ground state of the final state and decreasing such an effective Fano parameter for the vibrational excited state. The minima and maxima of the peaks are shifted in energy with respect to a purely electronic q parameter. The maximum and minimum of the peak corresponding to the decay into the vibrational ground state of the electronic final state are shifted towards lower kinetic energies with respect to the energies expected for the purely electronic q parameter, while they are shifted towards higher energies for the peak corresponding to the decay to the vibrational excited state of the electronic final state.

During buildup of the signals, the interference-induced oscillations in time and energy of the two peaks overlap to yield a complex pattern. Despite the resulting additional oscillation pattern in time, this is not due to an additional interference effect, because the different final-state contributions are, according to Eq. (20), simply added up to yield the total spectrum.

A Fourier analysis of the oscillations in time for an exemplary kinetic energy of 9.6 eV shows two peaks with periods of 25 and 10 fs. They correspond to the interference between the resonance and the two direct pathways as already expected from the study of the purely electronic case [31].

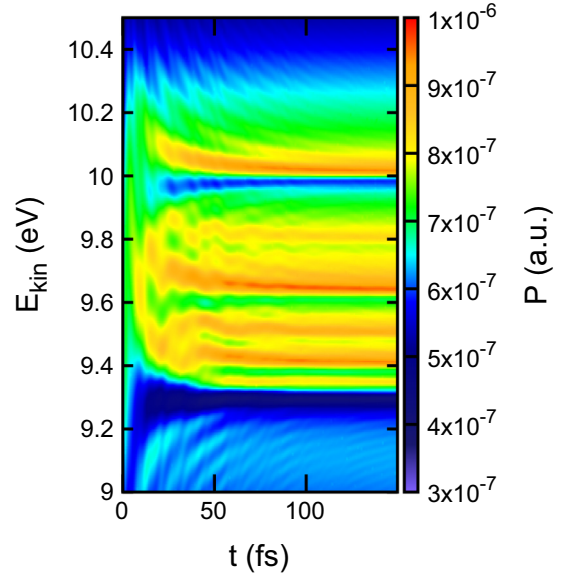


FIG. 4. Time-resolved RICD spectrum for one vibrational state in the electronic resonance state and seven vibrational states in the electronic final state.

C. Case 3: One vibrational bound state in the resonance state and several vibrational bound states in the final state

In this case, parameters 3 of Table I were used for the simulation of the time-resolved RICD spectrum shown in Fig. 4. The final state has seven vibrational bound states with energies between 0.1158 and 0.8090 eV with respect to the electronic minimum energy. As for case 2, only the final state has several vibrational bound states, and therefore, the exactness is only limited by the same assumptions as in cases 1 and 2.

Analogous to case 2, the overall spectrum is broadened towards lower kinetic energies by the possibility of ending in multiple vibrational final states. Moreover, the individual peak intensities and shapes are affected by the different Franck-Condon overlaps in the same way as in case 2. This is also reflected in the effective decay width of this case following Eq. (12), which corresponds to 20.28 fs, although the deviation with respect to the purely electronic case is, again, overestimated due to the neglected contributions of vibrational continuum states and only in part physical. Consequently, the manifold of signals yields a spectrum in which the oscillations in energy of the individual peaks become smeared out throughout the spectrum.

Despite having seven unique vibrational states in the electronic final state, only six clearly separated positive signals are visible. The two highest vibrational excited states are too close to be resolved and are instead combined into one peak as shown in the orange curve of Fig. 5 at around 9.3 eV.

D. Case 4: Two vibrational bound states in the resonance state and one vibrational bound state in the final state

This case provides the opportunity to discuss several features, among them the coherence between the two vibrational states in the resonance state. In order to give a thorough

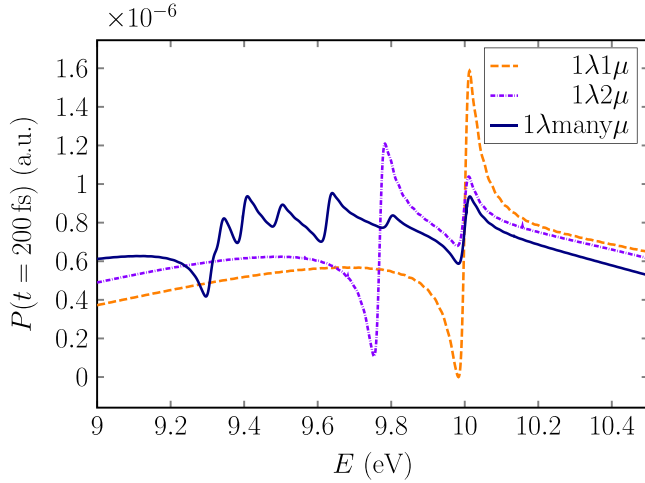


FIG. 5. RICD spectra at time $t = 200$ fs for cases 1 (dashed curve in orange), 2 (dash-dotted curve in violet), and 3 (solid curve in dark blue).

analysis, we have therefore chosen to display different sets of parameters.

1. Large energy splitting between the vibrational resonance states, $q = 1$

In this case, parameters 4 of Table I were used for the simulation. Here, the potential-energy curve of the resonance state supports two vibrational bound states, which are split by 0.241 eV. The effective lifetimes of these two states are 111.93 and 37.67 fs for the vibrational ground and excited state, respectively. These are significantly larger than the input values for the purely electronic lifetime of 20 fs each. This may indicate a serious incompleteness of the vibrational eigenfunctions basis set, especially in the case of the vibrational ground state of the resonance state. However, as of yet, we did not quantify to which degree this prolongation of lifetimes is actually physical due to decay channels through high-lying states being energetically inaccessible.

The simulation with these parameters yields the spectrum shown in Fig. 6. It is characterized by two peaks, corresponding to the vibrational states of the electronic resonance state. Contrary to cases 2 and 3, the signal corresponding to the vibrational excited state of the resonance state has a higher kinetic energy than the one corresponding to its vibrational ground state. Furthermore, the spectrum is not broadened by the possibility of exciting into several vibrational final states in the indirect pathway and, hence, the peak of the vibrational excited state of the electronic resonance state is slightly disfavored by the energy profile of the laser pulse.

Again, the Franck-Condon parameters influence the peak intensity and shape, and since $\langle \chi_\mu | \chi_0 \rangle = 0.91$ is significantly larger than both the products of $\langle \chi_{\lambda=0} | \chi_0 \rangle = 0.38$ with $\langle \chi_\mu | \chi_{\lambda=0} \rangle = 0.42$ and $\langle \chi_{\lambda=1} | \chi_0 \rangle = 0.63$ with $\langle \chi_\mu | \chi_{\lambda=1} \rangle = 0.73$, the effective values of the Fano parameter are decreased. This favors the direct pathway relative to the pathway via the resonance state. Among the resonance pathways, the signal corresponding to the route via the vibrational excited state of

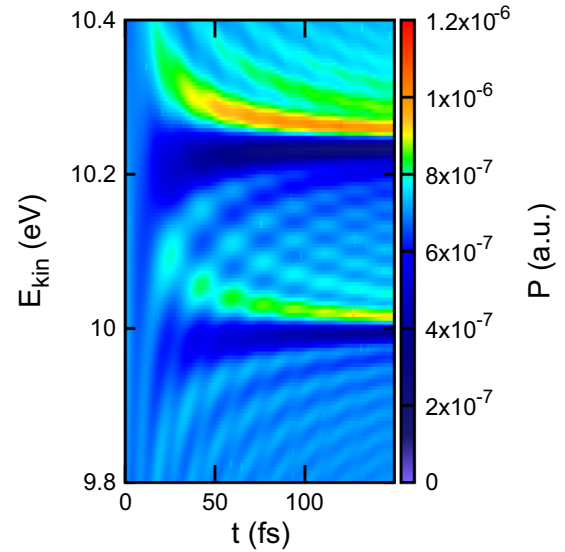


FIG. 6. Time-resolved RICD spectrum for two vibrational states in the electronic resonance state and a single vibrational state in the electronic final state. The peak at 10 eV corresponds to the vibrational $0 \leftarrow 0$ transition, while the one at 10.2 eV corresponds to the $0 \leftarrow 1$ transition. Both peaks again exhibit the characteristic Fano profile, plus an additional interference pattern created by the additional pathway via the vibrational excited state in the resonance state. For a detailed discussion, see the main text.

the resonance state is significantly favored over the one via its vibrational ground state.

The overall spectrum has a complex pattern created by the interference of both the direct and resonance pathways. Moreover, in this case, it should also be possible to observe the interference between the pathways via the two different vibrational resonance states through an oscillation in time as per

$$P \propto \cos[(E_{\lambda=1} - E_{\lambda=0})t]. \quad (50)$$

Figure 7 allows for a more detailed analysis of the interference pattern. It shows the oscillations in time at energies 10.12 eV [Fig. 7(a)], which is chosen to include the minima and maxima of the observed interference pattern of the spectrum, and 10.25 eV [Fig. 7(b)], which is close to the maximum of the peak corresponding to the pathway via the vibrational excited state of the electronic resonance state.

From earlier studies of time-resolved Fano profiles [29,31,57,58], we know that for one resonance state, the peak first builds up and then decreases exponentially according to the electronic decay. In Ref. [31], we showed that the interference between the direct pathway and the resonance pathway additionally leads to an oscillation in time, the frequency of which is determined by the energy difference between the investigated energy of the cut through the spectrum and the theoretical resonance position.

For the case of two resonance states, irrespective of whether it is an electronic or a vibrational state, the interference between the contributions of the two resonance pathways to the wave function leads to another oscillation, the period of which is determined by the energy difference between the

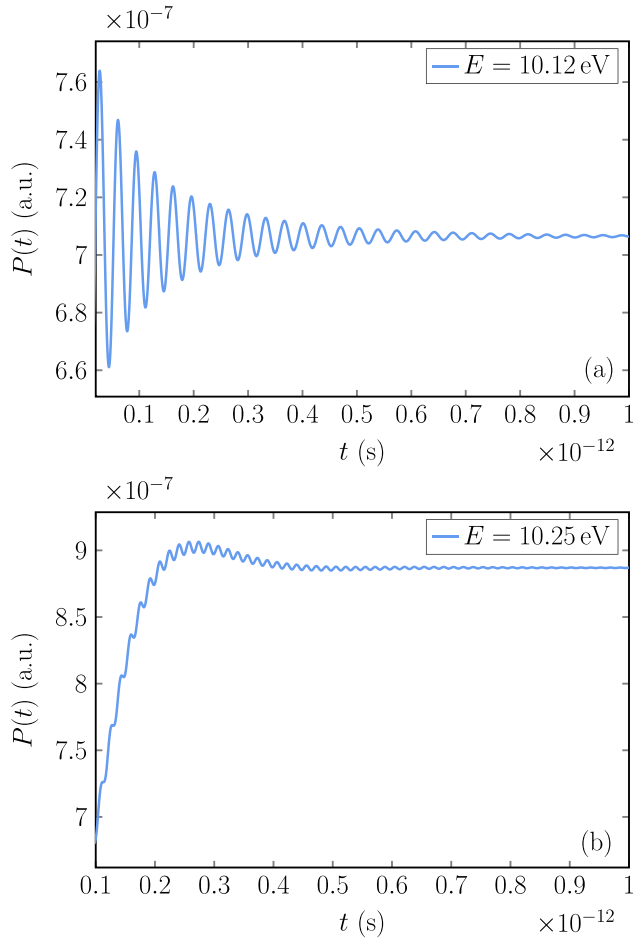


FIG. 7. Profiles in time for two vibrational states within the resonance state and one vibrational state within the final state (Fig. 6). They have been evaluated at kinetic energies of (a) 10.12 eV and (b) 10.25 eV. A few data points which were affected by numerical noise have been discarded.

two resonance states. Equation (50) is an instance for such an oscillation. For the energy difference of this example, one would expect one cycle to last for 17 fs.

In Fig. 7(a), the cut between the peaks shows a clear oscillation in time with decreasing intensity. Its full period is 33.6 fs and hence twice the period one would expect for the resonance-resonance interference pattern. In Fig. 7(b) with the cut close to the resonance, buildup occurs according to earlier studies. Overlaying this feature, an oscillation is visible which after ≈ 200 fs has a stable period of 16.3 fs, close to the above theoretical value of 17 fs.

In neither case is the oscillation caused by the resonance-resonance interference but rather it is caused by the interference of the direct with the respective resonance pathways. For the case of Fig. 7(a), considering the kinetic energy of 10.12 eV, the energy difference to the kinetic energy corresponding to the decay from the vibrational ground state of the resonance state is given by 0.12 eV corresponding to an oscillation period of 34.5 fs. This is in good agreement with the observed 33.6 fs. The relationship with the period of the resonance-resonance interference is only coincidental.

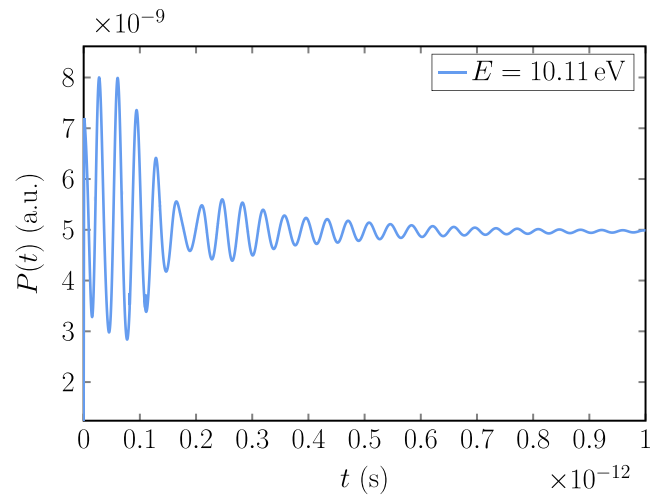


FIG. 8. Profile in time for two vibrational states within the resonance state and one vibrational state within the final state (similar to Fig. 6) for $q = 10$, evaluated at a kinetic energy of 10.11 eV. A few data points which were affected by numerical noise have been discarded.

For the case of Fig. 7(b) with a kinetic energy of 10.25 eV, the observed period almost equals the expected resonance-resonance interference period. However, at this kinetic energy, the period of the oscillation caused by the interference between the direct and the resonance parts of the neighboring peak is the same as the period of the resonance-resonance interference. It is therefore not possible to distinguish between the two close to a resonance energy.

2. Large energy splitting between the vibrational resonance states, $q = 10$

In Sec. IV D 1, the contributions of the resonance pathways were comparably small. Whether the resonance-resonance interference is strong enough to have an impact on the overall signal depends on both the intrinsic property of the q parameter—the larger q , the larger the resonance contribution—and the energetic width of the resonance part, which is inversely proportional to the temporal width and therefore also the number of cycles of the exciting pulse. It can hence be manipulated: the shorter the pulse, the larger the resonance signal at kinetic energies different from the peak maximum. This can directly be seen by inspection of the second part of Eq. (44). In order to highlight the resonance-resonance interference and its properties, we increase the purely electronic Fano parameter q from 1 to 10.

The resulting time-resolved spectrum is very similar to that for $q = 1$ in Fig. 6. The Fourier analysis of the oscillation pattern evaluated at a kinetic energy of 10.11 eV and shown in Fig. 8 is, however, significantly different. It shows three different oscillations with periods 36.9, 31.9, and 17.7 fs. The first two periods correspond to the two interferences of the two different vibrational resonance pathways with the direct pathway. The one with a period of 17.7 fs however corresponds to the resonance-resonance interference, which from the energy difference is expected to have a period of 17.2 fs.

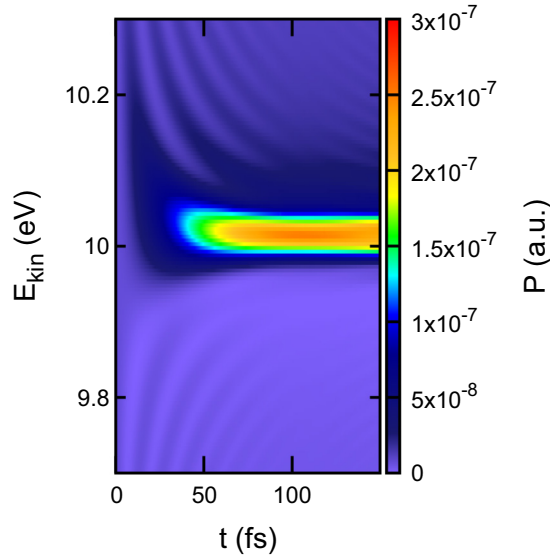


FIG. 9. Time-resolved RICD spectrum for two energetically close vibrational states in the electronic resonance state and a single vibrational state in the electronic final state for $q = 10$.

3. Small energy splitting between the vibrational resonance states, $q = 10$

Until now, we have seen scenarios in which the vibrational resonance states were well separated in energy. However, this is not necessarily the case, and even most likely not. Using parameters 5 given in Table I yields an energy difference for the vibrational resonance states of 0.0191 eV. As in Sec. IV D 2 we have chosen a larger Fano parameter of $q = 10$ in order to both narrow the individual peaks and increase the contribution of the resonance pathways. Nevertheless, the corresponding peaks in the spectrum cannot be resolved, as shown in Fig. 9.

However, if the contributions of the resonance parts of the wave function are substantial, the resonance-resonance interference can in principle be observed at energies that are different from the kinetic energy corresponding to the resonance and hence be distinguished from direct-resonance interferences. Furthermore, from the oscillation period of the signal, the energy difference between the two resonance states can be determined.

In Fig. 10, we give an example for such an oscillatory variation in signal intensity for the parameter set 5 at a kinetic energy of 9.8 eV. It shows two oscillations. On the one hand, the oscillation with a period of 21 fs is caused by the interference of the direct term with either of the resonance ones. Since they are energetically so similar, the difference in the oscillation periods is not visible. It is only in the Fourier-transformed signal that a double peak can be seen, corresponding to oscillation periods of 18.7 and 20.9 fs, respectively. On the other hand, the oscillation with the longer period of ≈ 220 fs is caused by the resonance-resonance interference.

We note that it may be experimentally difficult to resolve these variations in signal intensities in low intensity areas.

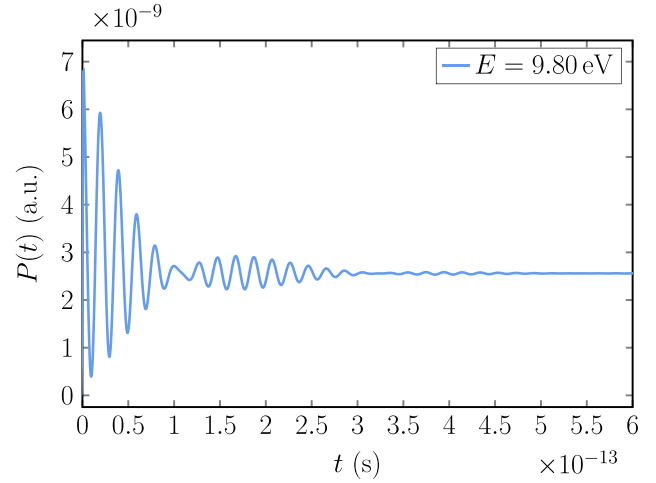


FIG. 10. Profile in time for two energetically close vibrational states within the resonance state and one vibrational state within the final state for $q = 10$ (Fig. 9), evaluated at a kinetic energy of 9.80 eV. A few data points which were affected by numerical noise have been discarded.

E. Case 5: Two vibrational bound states in the resonance state and two vibrational bound states in the final state

1. Large energy splitting between the vibrational resonance states

In this case, parameters 6 of Table I were used for the simulation. Both the resonance and the final state support two vibrational bound states. This is the smallest possible case in which all hitherto discussed properties are combined. The energy differences of the vibrational states are 0.2434 eV for the resonance state and 0.0493 eV for the final state.

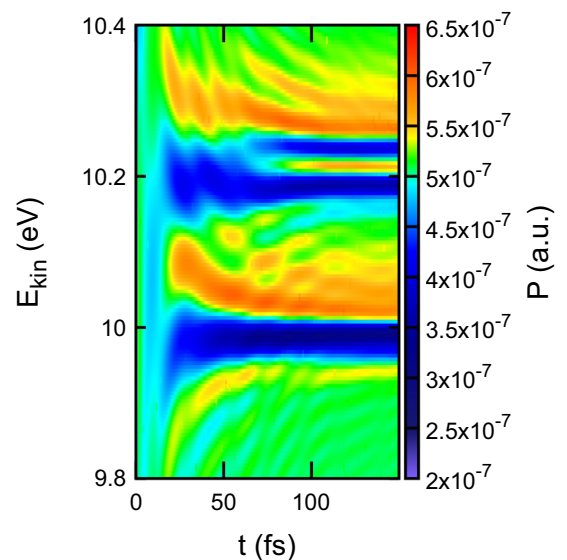


FIG. 11. Time-resolved RICD spectrum for two vibrational states in both the electronic resonance and final state with a large energy difference between the vibrational resonance states and a small energy difference between the vibrational final states.

These parameters lead to the spectrum shown in Fig. 11. It is characterized by two large peaks, which are split into the two peaks for the different vibrational final states.

Since the energy difference between the two vibrational final states is very small, the width of the overall peak is hardly affected by their presence.

The Franck-Condon overlaps for the transition between the ground and the final state relevant for the direct pathway are $\langle\chi_{\mu=0}|\chi_0\rangle = 0.60$ and $\langle\chi_{\mu=1}|\chi_0\rangle = 0.49$, which indicates that the direct pathways contribute with similar weights. The Franck-Condon overlaps relevant for the decay from the resonance states are more interesting. They are $\langle\chi_{\lambda=0}|\chi_0\rangle = 0.40$, $\langle\chi_{\lambda=1}|\chi_0\rangle = 0.33$, $\langle\chi_{\mu=0}|\chi_{\lambda=0}\rangle = 0.87$, $\langle\chi_{\mu=1}|\chi_{\lambda=0}\rangle = -0.27$, $\langle\chi_{\mu=0}|\chi_{\lambda=1}\rangle = 0.37$, and $\langle\chi_{\mu=1}|\chi_{\lambda=1}\rangle = 0.57$. Hence, the peak intensities and shapes are affected, in accordance with decreased effective Fano q parameters. Moreover, $\langle\chi_{\mu=1}|\chi_{\lambda=0}\rangle$, the Franck-Condon overlap between the vibrational ground state of the resonance state and the vibrational excited state of the final state, is negative and so is the corresponding effective Fano parameter. Under sign change of the effective q parameter, the peak shape becomes its own mirror image, which therefore explains the unexpected behavior for the peak at 9.95 eV. In this particular example, its minimum coincides with the minimum of the neighboring peak and the typical Fano line shape becomes more difficult to identify.

At a kinetic energy of 10.02 eV, an interference pattern is present that includes an oscillation with an apparent period of ≈ 21 fs. Fourier analysis reveals this to be in fact two oscillations with periods of 19 and 24 fs, respectively, which are too close for the two oscillations to be distinguishable in the time-resolved signal. The energy difference between the vibrational resonance states relates to an oscillation with a 17-fs period, which fits nicely. However, the signals corresponding to direct-resonance interference that involves the vibrational excited state of the resonance state indicate oscillations with periods of 19 and 24 fs for $\mu = 0, 1$, respectively. An unambiguous attribution of the observed oscillations to the underlying pathways that give rise to them is therefore impeded: The interference pattern is obviously more complicated than in case 4 due to the manifold of different contributions for any chosen kinetic energy.

2. Small energy splitting between the vibrational resonance states

When the parameters of the resonance- and the final-state potentials are interchanged (parameters 7 of Table I), the energy difference between the two resonance states becomes very small and the two larger signals are clearly separated from one another as illustrated in Fig. 12. This may allow for an easier interpretation of the interference spectrum.

Compared to the spectrum in Fig. 11, the different direct pathways boost only those parts of the spectrum where the peaks are. Due to the Franck-Condon overlaps of this example, one part of the double peak around 9.8 eV is hardly visible, and we will therefore focus on the other double peak. As in the first example of this case, the negative sign of $\langle\chi_{\mu=0}|\chi_{\lambda=1}\rangle$, the Franck-Condon overlap between the vibrational excited state of the resonance state and the vibrational ground state of the final state, leads to an unusual line shape for the peak around 10.04 eV. However, there is also a clear contrast to the previous example, in that the small energy

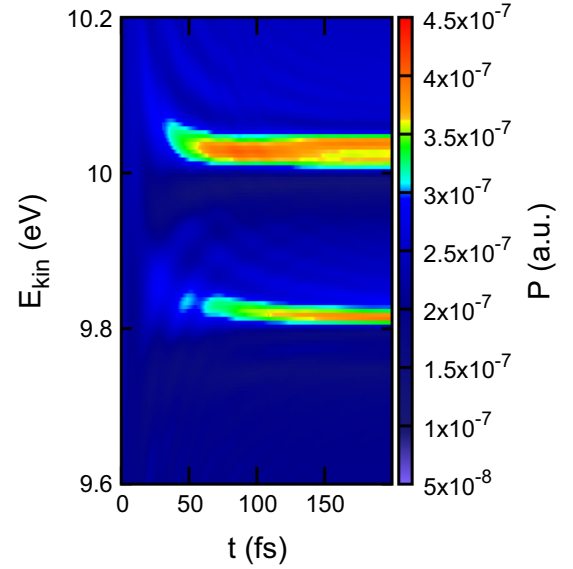


FIG. 12. Time-resolved RICD spectrum for two vibrational states in both the electronic resonance and final state with a small energy difference between the vibrational resonance states and a large energy difference between the vibrational final states.

difference between the two vibrational states of the resonance state and their approximately even contributions to the spectrum in the double peak around 10 eV should, according to Eqs. (42) and (50), lead to a clear oscillation pattern in time caused by the resonance-resonance interference with comparatively long periods.

Due to this long oscillation period, the resonance-resonance interference should already close to the peak maxima be distinguishable from the interference with the direct pathway. This allows an evaluation with more significant peak intensity. We therefore focus on the time-resolved pattern for a kinetic energy of 10.01 eV close to the $0 \leftarrow 0$ peak, which is shown in Fig. 13 after the first 145 fs. Upon first

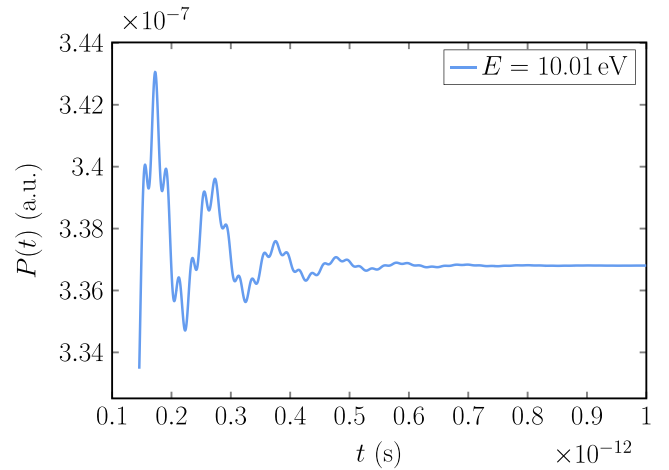


FIG. 13. Profile in time for two energetically close vibrational states within the resonance state and two energetically more distant vibrational states in the final state (Fig. 12), evaluated at a kinetic energy of 10.01 eV. A few data points which were affected by numerical noise have been discarded.

TABLE II. Oscillation periods for the different interference combinations.

No.	Characteristics	T (fs)
1	$\mu = 0, \lambda = 0$	414
2	$\mu = 1, \lambda = 0$	16
3	$\mu = 0, \lambda = 1$	105
4	$\mu = 1, \lambda = 1$	20
5	$\lambda = 0, \lambda = 1$	84

inspection, the signal can be described by two overlapping oscillations with very different frequencies, the amplitude of which is decreased exponentially. A Fourier analysis of the signal shows that the dominant and the perturbing oscillation have periods of 100 fs and only 20 fs, respectively.

According to the absolute square of Eq. (42), five different kinds of oscillations could in principle be observable involving all possible combinations of vibrational states in the electronic resonance $\lambda = 0, 1$ and final state $\mu = 0, 1$ as well as the resonance-resonance contribution from the two different vibrational states $\lambda = 0, 1$.

The corresponding theoretical periods are given in Table II.

The observed low-frequency oscillation is most likely inflicted by the interference between contributions from the vibrational excited resonance state and the vibrational ground state (parameters 3 of Table II), which also has a non-negligible contribution at 10.01 eV. The observed high-frequency oscillation can predominantly be attributed to the interference between the contributions from the two vibrational excited states (parameters 4 of Table II), because the contributions from the pathway involving the vibrational ground state of the resonance state are disfavored by the Franck-Condon overlaps. The oscillation caused by the interference of the two resonance states decaying to the vibrational ground state is not visible, because the other contributions cover them.

V. DISCUSSION

In this paper, we have derived expressions for the time-resolved description of electronic decay processes including nuclear degrees of freedom. In the following, we would like to discuss the approximations and assumptions introduced in these derivations presented in Sec. II.

(1) We use the Born-Oppenheimer approximation throughout the paper. Therefore, the derived expressions will not be applicable when strong nonadiabatic couplings exist which involve the resonance or the final states.

(2) We assume that the transition dipole moment matrix elements $\langle E|\mu|g\rangle$ are independent of the energy of the final state.

(3) Such independence of the energy of the final state is also assumed for the coupling matrix elements V_{Er} . Consequently, the effective decay width W_λ , Eq. (12), is considered to be independent of energy.

(4) In this paper, we only consider bound vibrational eigenstates. Therefore, the introduced nuclear bases are not necessarily complete. This assumption manifests itself in the

reduced overall decay widths [Eq. (12)] and therefore the observed increased lifetimes with respect to the purely electronic case. Moreover, these contributions are also missing in the simulated spectra. Their inclusion will be subject to future work.

(5) In the above simulations, we discussed time-resolved spectra involving multiple resonance states in combination with several final states. In a rigorous treatment, it is only possible to include either several resonance or several final states, but not several states of both kinds. In order to still treat their combination, we have introduced a few approximations, the impact of which we would like to discuss in more detail.

(a) In the derivation of the coefficients of the Fano wave function, we assume that different resonance states do not couple via the continuum. In this case, the only meaningful contribution in Eq. (10) is the one for $\lambda' = \lambda$. Phenomenologically, this means that no lifetime sharing between the different vibrational states of the resonance state is possible. (See Sec. II A for a discussion of possible realizations.) For the molecular Auger-Meitner process with large decay widths, this is in many cases a crude approximation. However, for the RICD process with longer lifetimes, this approximation becomes feasible, as can, e.g., be estimated from the ICD process of the neon dimer [59].

(b) We neglect the impact of $F_{\mu'}(E)$. Neglecting $F(E)$ in the purely electronic solution for one resonance and one final state results in neglecting a small shift in the resonance energy, while the overall shape of the corresponding peak remains the same. This effect is more pronounced when several resonance states are involved. By neglecting $F_{\mu'}(E)$, we neglect shifts of all resonance energies, which can change the energy differences between them. Additionally, we also neglect changes in the respective decay widths and hence lifetimes. Strong couplings via the continuum will therefore lead to qualitatively different spectra than those shown in this paper. In extreme cases for two resonance states, one resonance state can combine the entire decay capability of the system into itself, while the other state is stabilized. It would be beneficial to go beyond the current limitations in future work.

(c) The approximation of negligible couplings of different resonance states via the continuum leads to an underdetermined expression in Eq. (16). We therefore assume equal contributions of $|a_\lambda(E)|^2 W_\lambda [\pi^2 + |z(E)|^2]$ for all vibrational resonance states. This approximation is very likely incorrect. If the contributions for different λ are not equal, it will change the relative size of the different contributions and introduce additional prefactors for each resonance or indirect contribution. The overall shape of the equations would not change though.

(6) In the Fano wave function, the coefficients b of the continuum states are expressed as sums of contributions of the resonance states, Eq. (19). In a fashion related to the above assumption, we neglect the contributions of all vibrational states $|\chi_{\lambda'}\rangle$ of the resonance state in this description except the one where $\lambda' = \lambda$. This greatly reduces the complexity of the expressions and facilitates the integration necessary when evaluating the Fano matrix elements; see Appendix B. The solution of these integrals including the contributions of other states $|\chi_{\lambda'}\rangle$ with $\lambda' \neq \lambda$ will be discussed in a future study.

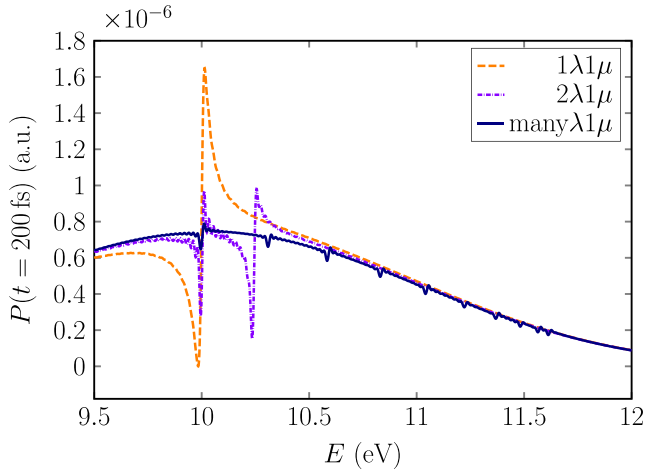


FIG. 14. Spectra at time $t = 200$ fs for cases 1 (dashed curve in orange) and 4.1 (dash-dotted curve in violet) as well as a case with ten vibrational resonance states (solid curve in dark blue).

VI. SUMMARY

In this section, we want to summarize the general results presented in Sec. IV within the approximations discussed in Sec. V.

As we have previously shown in Ref. [31], the signal shape for a single decay is given by the convolution of the corresponding Fano line shape and the Fourier transform of the envelope of the exciting laser pulse. If the mean photon energy of the laser diverges from the resonance energy, the decay peak is damped, compared to the same peak on resonance (see Fig. 4 of Ref. [31]).

The Fano parameter q [see Eq. (46)] determines the relative contributions of the different pathways to the final signal, and hence, the larger q (the larger the relative contribution of the resonance pathway), the more the maximum is moved towards the kinetic energy corresponding to the resonance and the minimum of the characteristic Fano line shape is moved to $-\infty$ [see Eqs. (48) and (49)]. Hence, the line shape becomes a Lorentzian convoluted with a Gaussian, a so-called Voigt profile. Furthermore, the smaller the decay width (the longer the lifetime), the less pronounced the Fano line shape is, according to Eq. (46).

Specific to several possible final states in general, and vibrational final states in particular, are several direct pathways and, correspondingly, several peaks at kinetic energies lower than the decay between the vibrational ground states. This can clearly be seen in Fig. 5, where the spectrum after 200 fs is compared between cases 1, 2, and 3.

Analogously, we compare the spectra 200 fs after the center of the pulse for several vibrational resonance states in Fig. 14. In this case, the kinetic energy increases with the vibrational quantum number of the decaying state.

When several vibrational resonance states exist, all but one are automatically excited off resonance, and hence, their resonance parts are weighted differently by the corresponding direct pathway, which can clearly be seen in Fig. 14.

The Fano line shape is created by the interference between the contributions of the different pathways to the total wave function. As we have seen in all cases, this line shape is affected by the inclusion of the nuclear degrees of freedom. The Franck-Condon overlaps alter the relative contributions of the different pathways and hence lead to different effective Fano parameters.

We have earlier shown in Ref. [31] that the interference between the different pathways is also responsible for the predicted oscillations in time and energy even for only one resonance and one final state. Inspection of Eq. (42) as well as Eqs. (43) and (44) infers that each vibrational resonance state contributes separately to the wave function. These contributions can therefore also interfere and cause additional time-dependent variations of the signals, which follow Eq. (50). The corresponding interference pattern can then be used to gather information about the wave packet of the system and therefore the electronic and nuclear motion.

The resonance-resonance interference signal is only part of the overall signal. In order to observe it, one needs a system with a large q and to focus on energy regions with sufficient intensity but not at the kinetic energies corresponding to the resonance energies themselves. As discussed in case 4, a short initiating pulse can help creating the necessary peak intensity away from the kinetic energies of the electron corresponding to a resonant excitation.

The complexity of a spectrum as well as its time dependency is increased by the number of involved decaying and final states and so is the interference spectrum. In addition to the different interferences, overlapping signals can also lead to patterns which merely look similar to interference patterns. A Fourier analysis, though, can help to distinguish between overlapping signals and interference patterns, as we have discussed in detail in Secs. IV B and IV D.

ACKNOWLEDGMENTS

E.F. and A.V.R. gratefully acknowledge funding through the Core Facility LISA⁺ of the University of Tübingen. E.F. acknowledges COST Action Grant No. CA18222 (Attosecond Chemistry). We would further like to thank Nicolas Sisourat for a helpful comment on the completeness of our basis of vibrational states.

APPENDIX A: TIME-INDEPENDENT HAMILTONIAN MATRIX ELEMENTS IN THE VIBRONIC BASIS

The time-independent Hamilton operator $\hat{H}_F = \hat{H}_0 + \hat{V}$ defined in Eq. (5) in analogy to the one used by Fano [32] is expressed via the elements of its matrix representation. The basis of the vibronic Hilbert space $\mathcal{H} = \mathcal{H}_{\text{el}} \otimes \mathcal{H}_{\text{nuc}}$ used throughout this paper is composed of the adiabatic product states $\{|r\rangle |\chi_\lambda\rangle\}$ and $\{|E\rangle |\chi_\mu\rangle\}$. The electronic and the nuclear states are taken to be orthonormalized as $\langle r|r\rangle = 1$, $\langle E'|E''\rangle = \delta(E' - E'')$ and $\langle r|E'\rangle = 0$ as well as $\langle \chi_\lambda|\chi_{\lambda'}\rangle = \delta_{\lambda,\lambda'}$ and $\langle \chi_{\mu'}|\chi_{\mu''}\rangle = \delta_{\mu',\mu''}$.

As discussed in Sec. II A, the first part of the Hamiltonian, $\hat{H}_0$, acts on both the electronic and the nuclear states. The

vibronic basis states are assumed to be eigenstates of $\hat{H}_0$, which therefore takes a diagonal form:

$$\langle \chi_\lambda | \langle r | \hat{H}_0 | r \rangle | \chi_{\lambda'} \rangle = (E_r + E_\lambda) \delta_{\lambda, \lambda'}, \quad (\text{A1})$$

$$\langle \chi_{\mu'} | \langle E' | \hat{H}_0 | E'' \rangle | \chi_{\mu''} \rangle = (E' + E_{\mu'}) \delta(E' - E'') \delta_{\mu', \mu''}, \quad (\text{A2})$$

$$\langle \chi_\lambda | \langle r | \hat{H}_0 | E' \rangle | \chi_{\mu'} \rangle = 0. \quad (\text{A3})$$

The second part of the Hamiltonian, $\hat{V}$, couples the electronic resonance state to the electronic continuum states. It does not act on the nuclear states and hence is the identity function in their subspace, $\hat{V} = \hat{V}_{\text{el}} \otimes \mathbb{1}_{\text{nuc}}$. Abbreviating the electronic matrix elements, this leads to

$$\langle \chi_\lambda | \langle r | \hat{V} | E' \rangle | \chi_{\mu'} \rangle = V_{rE'} \langle \chi_\lambda | \chi_{\mu'} \rangle, \quad (\text{A4})$$

$$\langle \chi_\lambda | \langle r | \hat{V} | r \rangle | \chi_{\lambda'} \rangle = \langle \chi_{\mu'} | \langle E' | \hat{V} | E'' \rangle | \chi_{\mu''} \rangle = 0, \quad (\text{A5})$$

and $V_{E'r} = V_{rE'}^*$.

In total, the Fano-type Hamiltonian $\hat{H}_F = \hat{H}_0 + \hat{V}$ in the chosen vibronic basis reads

$$\langle \chi_\lambda | \langle r | \hat{H}_F | r \rangle | \chi_{\lambda'} \rangle = (E_r + E_\lambda) \delta_{\lambda, \lambda'}, \quad (\text{A6})$$

$$\langle \chi_{\mu'} | \langle E' | \hat{H}_F | E'' \rangle | \chi_{\mu''} \rangle = (E' + E_{\mu'}) \delta(E' - E'') \delta_{\mu', \mu''}, \quad (\text{A7})$$

$$\langle \chi_\lambda | \langle r | \hat{H}_F | E' \rangle | \chi_{\mu'} \rangle = V_{rE'} \langle \chi_\lambda | \chi_{\mu'} \rangle, \quad (\text{A8})$$

$$\langle \chi_{\mu'} | \langle E' | \hat{H}_F | r \rangle | \chi_\lambda \rangle = V_{E'r} \langle \chi_{\mu'} | \chi_\lambda \rangle. \quad (\text{A9})$$

This, together with the Fano-type wave function $|\Psi_E\rangle$ given in Eq. (2) representing an eigenstate of the Fano-type Hamiltonian discussed above, $\hat{H}_F |\Psi_E\rangle = E |\Psi_E\rangle$, yields the equations in Sec. II A.

APPENDIX B: EVALUATION OF THE FANO MATRIX ELEMENTS

The Fano integrals can now be solved by contour integration in the negative complex half plane, where we employ Eq. (41), use $\langle r | r \rangle = 1$, $\langle E | E' \rangle = \delta(E - E')$, and $\langle E | r \rangle = 0$ as well as $\langle \chi_\lambda | \chi_{\lambda'} \rangle = \delta_{\lambda, \lambda'}$ and $\langle \chi_\mu | \chi_{\mu'} \rangle = \delta_{\mu, \mu'}$, and furthermore ignore the effects of $F_{\mu'}(E)$:

$$\langle \chi_\lambda | \langle r | U_F(t'', t') | r \rangle | \chi_{\lambda'} \rangle = \sum_{\lambda''} \int d\underline{E} \langle \chi_\lambda | \langle r | a_{\lambda''}(\underline{E}) | r \rangle | \chi_{\lambda''} \rangle \langle \chi_{\lambda''} | \langle r | a_{\lambda'}^*(\underline{E}) | r \rangle | \chi_{\lambda'} \rangle \exp[-i\underline{E}(t'' - t')] \quad (\text{B1})$$

$$= \sum_{\lambda''} \int d\underline{E} \delta_{\lambda, \lambda''} \delta_{\lambda'', \lambda'} a_{\lambda''}(\underline{E}) a_{\lambda'}^*(\underline{E}) \exp[-i\underline{E}(t'' - t')] \quad (\text{B2})$$

$$= \int d\underline{E} \exp[-i\underline{E}(t'' - t')] |a_\lambda(\underline{E})|^2 \delta_{\lambda, \lambda'} \quad (\text{B3})$$

$$= \int d\underline{E} \frac{\exp[-i\underline{E}(t'' - t')] W_\lambda}{N_\lambda [(\underline{E} - E_r - E_\lambda)^2 + \pi^2 W_\lambda^2]} \delta_{\lambda, \lambda'}. \quad (\text{B4})$$

Note that the effective decay width W_λ is, according to Eq. (12), in principle dependent on the energy of the final state, $W_\lambda = \sum_{\mu'} |V_{(\underline{E}-E_{\mu'})r}|^2 |\langle \chi_\lambda | \chi_{\mu'} \rangle|^2 = W_\lambda(E)$. We now assume the electronic coupling matrix element V_{Er} to be independent of the continuous kinetic energy of the emitted electron and to be sufficiently described by the discretized energy difference between the resonance and the final state and therefore denote it V_r . We incorporate the discretized final states by summing over them in the expression for the effective decay width, which now has become independent of the energy: $W_\lambda(\underline{E}) = |V_r|^2 \sum_{\mu'} |\langle \chi_\lambda | \chi_{\mu'} \rangle|^2 = W_\lambda$. Treating it as a constant inside the integral and evaluating the latter yields the Fano matrix element:

$$\frac{1}{N_\lambda} \delta_{\lambda, \lambda'} \exp[-i(E_r + E_\lambda - i\pi W_\lambda)(t'' - t')]. \quad (\text{B5})$$

Analogously,

$$\begin{aligned} & \int dE'' \langle \chi_\lambda | \langle r | U_F(t'', t') | E'' \rangle | \chi_{\mu''} \rangle \\ &= \sum_{\lambda'', \tilde{\mu}} \int dE'' \int d\underline{E} \int d\tilde{E} \exp[-i\underline{E}(t'' - t')] \langle \chi_\lambda | \langle r | a_{\lambda''}(\underline{E}) | r \rangle | \chi_{\lambda''} \rangle \langle \chi_{\tilde{\mu}} | \langle \tilde{E} | b_{E, \tilde{\mu}}^*(\underline{E}) | E'' \rangle | \chi_{\mu''} \rangle \end{aligned} \quad (\text{B6})$$

$$= \int dE'' \int d\underline{E} \exp[-i\underline{E}(t'' - t')] a_\lambda(\underline{E}) b_{E'', \mu''}^*(\underline{E}) \quad (\text{B7})$$

$$\begin{aligned} &= \int dE'' \int d\underline{E} \exp[-i\underline{E}(t'' - t')] a_\lambda(\underline{E}) \sum_{\lambda'} \left(\frac{V_{rE''} a_{\lambda'}^*(\underline{E}) \langle \chi_{\lambda'} | \chi_{\mu''} \rangle}{\underline{E} - E'' - E_{\mu''}} \right. \\ &\quad \left. + \frac{\underline{E} - E_r - E_{\lambda'}}{W_{\lambda'}} V_{rE''} a_{\lambda'}^*(\underline{E}) \delta(\underline{E} - E'' - E_{\mu''}) \langle \chi_{\lambda'} | \chi_{\mu''} \rangle \right) \end{aligned} \quad (\text{B8})$$

$$\begin{aligned}
&= \int d\underline{E} \exp[-i\underline{E}(t'' - t')] a_{\lambda}(\underline{E}) \sum_{\lambda'} \left(a_{\lambda'}^*(\underline{E}) \langle \chi_{\lambda'} | \chi_{\mu''} \rangle \mathcal{P} \int dE'' \frac{V_{rE''}}{\underline{E} - E'' - E_{\mu''}} \right. \\
&\quad \left. + \frac{\underline{E} - E_r - E_{\lambda'}}{W_{\lambda'}} V_{r(\underline{E} - E_{\mu''})} a_{\lambda'}^*(\underline{E}) \langle \chi_{\lambda'} | \chi_{\mu''} \rangle \right). \quad (\text{B9})
\end{aligned}$$

We again assume the coupling matrix element V_{Er} to be independent of the final state, $V_{Er} = V_r$ and $V_{rE} = V_r^*$. Then the principal value of the integral in the first summand is zero. Furthermore, the effective decay width again becomes independent of the energy, $W_{\lambda}(\underline{E}) = W_{\lambda}$. The Fano matrix element then reads as

$$\int d\underline{E} \exp[-i\underline{E}(t'' - t')] V_r^* a_{\lambda}(\underline{E}) \sum_{\lambda'} \frac{\underline{E} - E_r - E_{\lambda'}}{W_{\lambda'}} a_{\lambda'}^*(\underline{E}) \langle \chi_{\lambda'} | \chi_{\mu''} \rangle. \quad (\text{B10})$$

Due to the sum over λ' , several terms contribute to the Fano matrix element. This renders further equations quite involved. Therefore, we make the assumption that the only vibrational eigenstate $|\chi_{\lambda'}\rangle$ of the electronic resonance state $|r\rangle$ that contributes to the description of the chosen final state $|E''\rangle |\chi_{\mu''}\rangle$ is the chosen vibrational eigenstate $|\chi_{\lambda}\rangle$. This means that in Eq. (19) for the Fano coefficient of the final state, $\delta_{\lambda,\lambda'}$ is introduced so that all λ' are replaced by λ and the sum over all λ' drops out. Since the present expression for the Fano matrix element has been derived by inserting Eq. (19) into Eq. (B7), the same is true here:

$$\int d\underline{E} \exp[-i\underline{E}(t'' - t')] V_r^* |a_{\lambda}(\underline{E})|^2 \frac{\underline{E} - E_r - E_{\lambda}}{W_{\lambda}} \langle \chi_{\lambda} | \chi_{\mu''} \rangle \quad (\text{B11})$$

$$= \frac{1}{N_{\lambda}} V_r^* \langle \chi_{\lambda} | \chi_{\mu''} \rangle \int d\underline{E} \frac{(\underline{E} - E_r - E_{\lambda}) \exp[-i\underline{E}(t'' - t')]}{(\underline{E} - E_r - E_{\lambda})^2 + \pi^2 W_{\lambda}^2} \quad (\text{B12})$$

$$= -\frac{i\pi}{N_{\lambda}} V_r^* \langle \chi_{\lambda} | \chi_{\mu''} \rangle \exp[-i(E_r + E_{\lambda} - i\pi W_{\lambda})(t'' - t')]. \quad (\text{B13})$$

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Impact of the nuclear motion on the interparticle Coulombic electron capture

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(Received 31 January 2024; accepted 13 September 2024; published 7 October 2024)

Interparticle Coulombic electron capture (ICEC) is an environment-enabled electron capture process by means of which a free electron can be efficiently attached to a system (i.e., ion, atom, molecule, or quantum dot). The excess electron attachment energy is simultaneously transferred to a neighboring system (the environment) which undergoes ionization. ICEC has been theoretically predicted in van der Waals and hydrogen bonded systems as well as in quantum dot arrays. The theoretical approaches employed in these works range from analytical models to *ab initio* electronic structure and dynamical calculations. A common assumption in these approaches is that nuclei remain fixed during ICEC. In this paper, we use full explicit electron-nuclear dynamics simulations to show that the relative nuclear motion between the two species involved in ICEC enables the electron attachment at kinetic energies of the incoming electron far below the vertical energy threshold (i.e., at the equilibrium geometry of the system). ICEC is therefore more efficient than expected.

DOI: [10.1103/PhysRevA.110.042804](https://doi.org/10.1103/PhysRevA.110.042804)

I. INTRODUCTION

Interparticle Coulombic electron capture (ICEC) is an environment-assisted process in which a free electron can efficiently attach to an acceptor *A* (i.e., atom, molecule, quantum dot). The excess attachment energy is transferred to a neighboring electron-donor system *B* which is thus ionized under emission of the so-called ICEC electron. The energy transfer is driven by the electronic correlation.

ICEC has been theoretically investigated in several systems, from van der Waals and hydrogen bonded dimers to quantum dot arrays [1–4]. Analytical models, *ab initio* electronic structure, and dynamical calculations were used to study ICEC (see Ref. [5] and references therein). A common assumption in these approaches is that nuclei remain fixed during ICEC. However, based on observations on the related

interparticle Coulombic decay (ICD) [6], nuclear dynamics should play an important role in modulating the efficiency of the process and/or influencing the final state of the system.

Describing the coupled electron-nuclear dynamics is a challenging task and represents an active field of research [7–11]. In the case of ICEC, the theoretical description of the coupled electron-nuclear dynamics is even more difficult since free electrons are involved and the underlying basis has to be able to account for continuum states [12,13]. In this paper, we investigate the full explicit electronic and nuclear dynamics of ICEC in a system consisting of two electrons confined in a one-dimensional potential and a single nuclear degree of freedom (DOF). Reducing the dimensionality of the electronic configuration space allows us to achieve a numerically exact description of the coupled electron-nuclear dynamics in ICEC. This simple model also captures the inter-

play between inelastic vibrational excitation and ICEC. Our work represents a step towards an accurate description of electron attachment processes for species that are surrounded by an environment. Our results show that the relative nuclear motion between the two species involved in ICEC plays a major role, since it allows the electron attachment to take place far below the vertical energy threshold given by the potential energies at equilibrium nuclear geometry. ICEC is therefore more efficient than expected [4].

II. MODEL FOR ELECTRON-DIMER COLLISION DYNAMICS

We propose a simple model to investigate the impact of the nuclear dynamics on the ICEC process. It consists of a dimer of two atoms A and B with two active electrons subject to a one-dimensional potential. The full Hamiltonian is given by

$$H = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{1}{2} \frac{\partial^2}{\partial x_1^2} - \frac{1}{2} \frac{\partial^2}{\partial x_2^2} + V_{e,e}(x_1, x_2) + V_{N,N}(R) + \sum_{i=1}^2 V_{N,e}(x_i, R), \quad (1)$$

where x_1 and x_2 are the electron coordinates and R the distance between the atoms. The reduced mass of the A and B species is $\mu = \frac{m_A m_B}{m_A + m_B}$. We use atomic units throughout the paper hence the Bohr radius is $a_0 = 1$, $\hbar = 1$, and $m_e = 1$, nevertheless we include the energy equivalence in eV in the text for it is common use and ease in comparison.

In (1), we employ screened Coulomb potentials of the form

$$V_{e,e}(x_1, x_2) = \frac{e^{-\alpha_{ee}|x_1 - x_2|^2}}{\sqrt{|x_1 - x_2|^2 + \beta_{ee}}}, \quad (2)$$

$$V_{N,N}(R) = \frac{e^{-\alpha_R R^2}}{\sqrt{R^2 + \beta_R}}, \quad (3)$$

$$V_{N,e}(x_i, R) = -\frac{e^{-\alpha_{Ae}|x_i + \frac{\mu}{m_A}R|^2}}{\sqrt{|x_i + \frac{\mu}{m_A}R|^2 + \beta_{Ae}}} - \frac{e^{-\alpha_{Be}|x_i - \frac{\mu}{m_B}R|^2}}{\sqrt{|x_i - \frac{\mu}{m_B}R|^2 + \beta_{Be}}}, \quad (4)$$

where the β parameters are used for cutoff and the α parameters set a range for the interactions.

The choice of the model parameters (see the Appendix) is aimed at recreating the energies and equilibrium distance of a typical rare gas dimer. Specifically, in this paper we consider a model for $(\text{NeHe})^+$. It has been previously investigated, with an R -matrix approach, in its full electronic dimensionality but within the fixed-nuclei approximation [4]. The initial and final states for ICEC have only one electron attached to the atoms, while the other electron is in the continuum. The potential energy curves (PECs), obtained by diagonalizing the one-electron part of the Hamiltonian in Eq. (1), are shown in Fig. 1. The masses and the one-electron Hamiltonian itself are given in the Appendix.

The ground state PEC shows an equilibrium distance around $R_{\text{eq}} = 2.08$ a.u. ≈ 1.04 Å, which is close to the experimental value of NeHe^+ [14], and the ionization energy is $E(R_{\text{eq}}) = -1.02$ a.u. ≈ -27.211 eV. The vertical energy difference between the lowest excited and the ground states

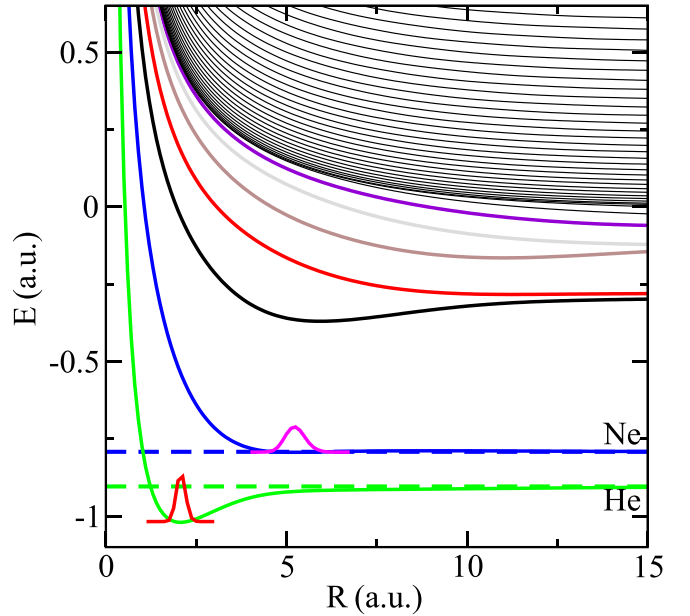


FIG. 1. PECs of the one-electron NeHe^+ model. The ground (green) and first excited states (blue) are the ones involved in the ICEC process. Other excited state PECs are shown in black, red, brown, gray, and purple. The first ionization energies for the He and Ne atom are displayed as dashed green and blue lines, respectively. Also, a bundle of black PECs is shown at higher energies which corresponds to the quasicontinuum states. Superimposed to the ground and first excited PECs are the R -reduced densities NeHe^+ (thick solid red and magenta lines, respectively).

at R_{eq} is 0.474 a.u. ≈ 12.989 eV. The separated atom energies ($R \rightarrow \infty$) for the ground and first excited states are those of the experimental ionization energies for each of the atoms ($E_{\text{He},I} = 0.904$ a.u. $= 24.587$ eV and $E_{\text{Ne},I} = 0.792$ a.u. $= 21.565$ eV) [15,16].

The PECs shown in Fig. 1 have qualitatively different behavior depending on the distance R . Furthermore, in the context of ICEC, we are only interested in the two lowest states. While the ground state exhibits a clear minimum and corresponds to a state where the bound electron is located around the helium center (i.e., the initial ICEC state), the first excited state is mostly repulsive (antibonding) and exhibits only a shallow minimum around $R_{\text{eq}} = 5$ a.u. ≈ 2.5 Å. Note that in the latter state, the bound electron is localized mostly on the neon atom (i.e., the final ICEC state—see the Appendix).

III. NUMERICAL METHODS FOR THE COLLISION DYNAMICS

The electron-nuclear dynamics is investigated with the multiconfiguration time-dependent Hartree (MCTDH) software package (version 86.5) [17–22]. Within the fixed nuclei approximation, the algorithm was successfully applied to compute ICEC reaction probabilities in paired quantum dots in several configurations [3,12,23], and also for ICD electron dynamics in quantum dots including two- and three-electron processes and external fields [13,24–26]. Details on the

MCTDH approach and computational details in the context of ICEC are given in these works and in the Appendix.

The initial state of the simulations is the ground state of NeHe^+ multiplied by a Gaussian wave packet representing the incoming electron (WP_i), and then symmetrized with respect to electron exchange (i.e., we consider spin singlet states). The Gaussian wave packet $f_{\text{WP}_i}(x)$ has a spatial width Δx_{WP_i} . $\Delta \varepsilon_{\text{WP}_i}(E_T)$ is the energy distribution of the incoming WP_i peaked around $\varepsilon_{\text{WP}_i}$. The initial ground state for NeHe^+ , $\phi_i(x, R)$, is constructed using the ground electronic state $\phi_0(x; R)$ times the solution for the nuclear wave function $\chi_0(R)$ in the ground PEC $E_0(R)$ (green curve in Fig. 1). We computed the full and fixed-nuclei dynamics for three different incoming Gaussian wave packets with mean energies at $\varepsilon_{\text{WP}_i} = 0.6, 0.5, 0.3$ a.u. $\approx 16.33, 13.6, 8.16$ eV and energy dispersion $\Delta \varepsilon_{\text{WP}_i} = 0.06$ a.u. ≈ 1.63 eV. The energies for the incoming electron cover therefore excitation energies: (i) well above, (ii) barely above, and (iii) below the vertical excited state energy (blue curve) as shown in Fig. 1.

The MCTDH wave function has been represented in a sine discrete variational representation basis (sine-DVR) [27]. The numbers of functions and states have been carefully chosen to obtain converged bound and continuum states (black curves in Fig. 1) involved in the collision and dissociation process, leading to the electronic x_i grid $[-300$ a.u., 300 a.u.] with 1500 points and the nuclear R grid $[0$ a.u., 17 a.u.] with 500 points. After the incoming electron impinges on NeHe^+ , the capture and emission process leads to the dissociation of NeHe^+ . There are at least three timescales to consider, the one of the nuclear DOF and those of the incoming and the outgoing electron. Specifically, the outgoing electron has different momenta when it comes from elastic scattering or from ICEC. The ICEC electron is expected to be comparably slow. However, with the selected incoming electron energies, the elastic electron is fast and is far away from the dissociating Ne-He^+ pair before the dissociation is noticeable. Hence, we numerically remove the elastic electron from the grid edges to allow for the observation of the slow dissociation by placing a complex absorbing potential (CAP) to the last points of the x_i DVRs [18]. For the R DVR, also CAPs are used, since after dissociation the density will eventually reach the grid end.

The CAPs used are defined as

$$W_{\pm}^{(q)} = -i\eta(q \mp q_{\text{CAP}})^3 \Theta(q \mp q_{\text{CAP}}), \quad (5)$$

where q is one of x_1 , x_2 , or R . The intensity η is set up to reduce the transmission and reflection from the CAP [28]. For the electronic coordinates we locate the CAP at $x_{\text{CAP}} = \pm 254$ a.u. setting the intensity to $\eta = 6.52 \times 10^{-6}$ a.u., while for the nuclear coordinate we used $R_{\text{CAP}} = \pm 7$ a.u. and $\eta = 4.87 \times 10^{-4}$ a.u.

IV. ICEC QUANTIFICATION FROM REACTION PROBABILITIES

The absorption described at the end of Sec. III leads to a reduction of the density, which can be measured and distinguished from the ICEC electron density. This enables us to quantify the amount of ICEC and elastic probabilities. The

reaction probability is defined as [12,18]

$$\text{RP}_f(E_T) = |S_{\phi_f, \phi_i}(E_T)|^2 = 2 \frac{\text{Re} \int_0^\infty g_f(\tau) e^{iE_T \tau / \hbar} d\tau}{\pi |\Delta \varepsilon_{\text{WP}_i}(E_T)|^2}, \quad (6)$$

with

$$g_f(\tau) = \int_0^\infty \langle \Psi(t) | P_{\phi_f}^{(q_2, q_3)} W_+^{(q_1)} P_{\phi_f}^{(q_2, q_3)} | \Psi(t + \tau) \rangle dt \quad (7)$$

and

$$\Delta \varepsilon_{\text{WP}_i}(E_T) = \sqrt{\frac{m^*}{2\pi p_i}} \int_{-\infty}^\infty f_{\text{WP}_i}(x) e^{ip_i x} dx, \quad (8)$$

where Eq. (8) is the appropriate Fourier transform which uses the incoming momentum p_i [29]. Since the reaction probability is the flux normalized by the WP energy distribution, it gives WP-independent results valid for energies around the peak energy of the WP. The projector $P_{\phi_f}^{(q_2, q_3)}$ allows to compute the absorbed flux energy distribution of the process with the initial state, $\phi_i(x_1, x_2, R)$, and two final states at the moment of absorption: The elastic channel for any vibrational level $\phi_{f, \text{el}}(x_2) = \phi_0(x_2; R) \otimes \text{I}$, and the elastic channel for the ground vibrational level $\phi_{f, \text{el}, 0}(x_2, R) = \phi_0(x_2; R) \otimes \chi_0(R)$. From these two fluxes we can compute the contribution to the ICEC inelastic channel $\text{RP}_{\text{ICEC}} = \text{I} - \text{RP}_{f, \text{el}}$ and to the inelastic vibrationally excited channels $\text{RP}_{\text{vib.exc.}} = \text{RP}_{f, \text{el}} - \text{RP}_{f, \text{el}, 0}$.

In the case where $q_1 = x_1$, $\phi_f(x_2, R)$ is a projector onto a state of the product Hilbert space of x_2 and R . $P_{\phi_f}^{(q_2, q_3)}$ may also be omitted, giving the total absorbed flux, or can be used to project only onto an electronic state $\phi_f(x_2)$, leaving an identity for the R coordinate part of the Hilbert space.

V. RESULTS FOR THE ICEC-INDUCED DISSOCIATION DYNAMICS

In Fig. 2, we report the time-dependent electronic densities along x_1 for the full electron-nuclear coupled dynamics (top panels) and for the fixed-nuclei approximation (bottom) [12]. In each panel, the electronic density at lowest times (following a diagonal green dashed line as a guide to the eye) corresponds to the incoming ($x_1 < 0$) and elastically scattered electron ($x_1 > 0$). The elastic channel energies are $\varepsilon_i = 0.6, 0.5, 0.3$ a.u. $\approx 16.33, 13.6, 8.16$ eV (from left to right). Inelastic processes, which can be ICEC or vibrational excitation (the latter is only possible in the full electron-nuclear coupled dynamics simulations), are seen as higher-density areas above the main elastic line with different slopes than those of the elastic ones (i.e., slower outgoing electron). The superimposed lines represent inelastic channel $\varepsilon_i + E_0(R_{\text{eq}}) - E_1(R_{\text{eq}})$ (yellow dashed-dotted) and elastic channel (green dashed) energies.

At the highest incoming electron energy, the time-dependent electronic density of the full electron-nuclear coupled dynamics is similar to that obtained under the fixed-nuclei approximation (left panels). At lower electron energies, differences between the two densities appear. The difference is particularly significant at the lowest incoming energy (i.e., $\varepsilon_i = 0.3$ a.u.) for which ICEC is forbidden within the fixed-nuclei approximation (right panels). The

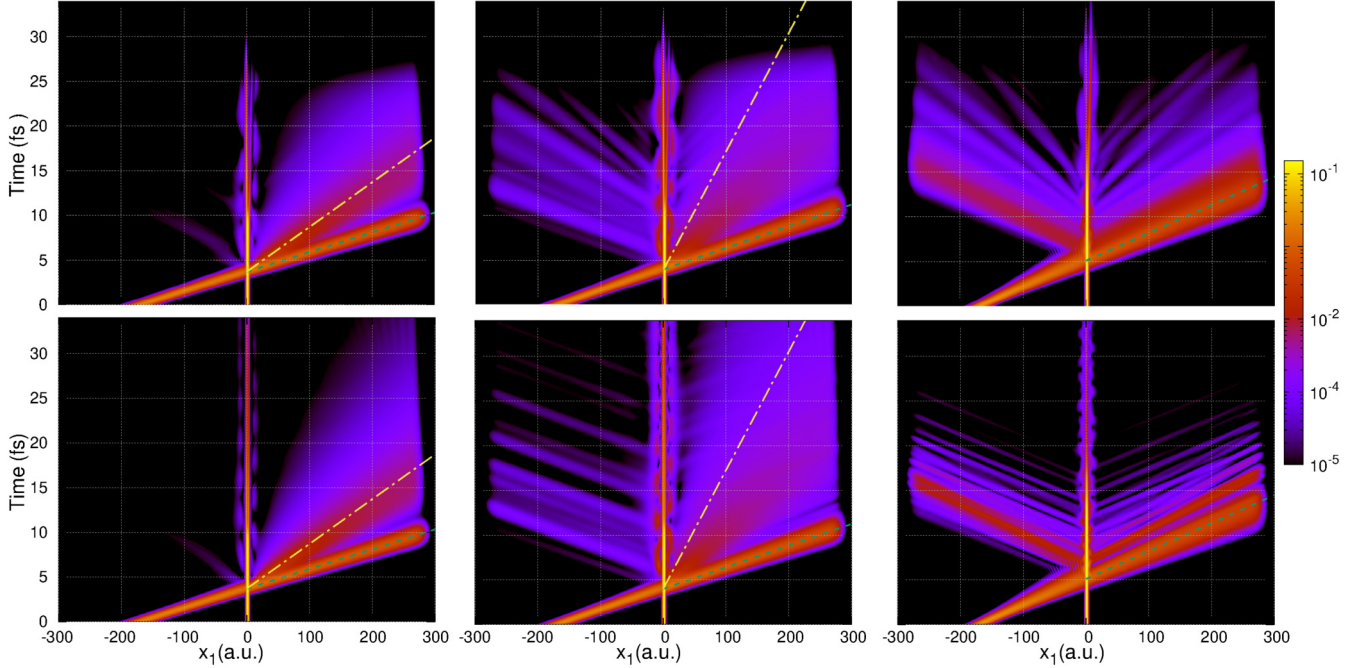


FIG. 2. Time and spatial evolution of the electron density (total density integrated in x_2 and R) in a.u.^{-1} units according to the color bar (log scale) for the full electron-nuclear coupled (upper panels) and fixed-nuclei dynamics (lower panels) for three different incoming electron energies ($\varepsilon_i = 0.6, 0.5, 0.3$ a.u. $\approx 16.33, 13.6, 8.16$ eV from left to right).

time-dependent electronic density within the latter exhibits the main elastic line and several “delayed” lines parallel to the main one. These lines correspond to the incoming electron being trapped by the atoms for some time before being reemitted with the same energy as the incoming one. In contrast, the time-dependent electronic density of the full electron-nuclear dynamics displays lines that are not parallel to the main elastic one, which demonstrates that inelastic processes are more likely if the vibrational DOF is taken into account.

To gain further insight we evaluated the ICEC probabilities for both frameworks. They are reported in Table I. These results show that the ICEC probability is significant (around 6%) below the vertical threshold (i.e., at $\varepsilon_i = 0.3$ a.u.) for which ICEC is energetically forbidden within the fixed-nuclei approach. This is the main result of this work. Conversely, for incoming electron energies above the vertical threshold the ICEC probabilities are slightly smaller in the case of full electron-nuclear dynamics. However, the sums of the full dynamics ICEC probability and vibrational excitation reproduce the ICEC probabilities of the fixed-nuclei simulations above

the vertical threshold. The behavior of ICEC probability is not monotonous, which derives from the intricate dependence of it on the electronic state’s shapes, the incoming electron energies, and coupling interactions. This comparison illustrates the strong interplay between the ICEC and the vibrational inelastic processes, which can only be considered in the case of full electron-nuclear dynamics.

Our coupled electron-nuclear simulations also provide the time-dependent densities along the R coordinate. These densities are reported in Fig. 3. It is shown that at the time $t \approx 5$ fs, when the incoming electron approaches the dimer, the dimer stretches and finally dissociates within 5–10 fs. This is the ultrafast stretching dynamics that allows ICEC below the vertical threshold.

VI. CONCLUSIONS

In conclusion, the electronic and nuclear dynamics of the interparticle Coulombic electron capture process was investigated. We have performed numerically exact time-dependent quantum simulations for a system consisting of two electrons confined in a one-dimensional potential and one nuclear degree of freedom. Our results demonstrate that the relative nuclear motion between the two species (A - B) involved in ICEC enables electron attachment far below the vertical energy threshold as dictated by the potential energy curves. ICEC can therefore take place for a much broader range of incoming electron energies owing to the vibrational degree of freedom. The strong interplay between vibrational excitation and ICEC was also discussed. Our work illustrates the major role played by the nuclear degree of freedom and opens the way to a more accurate description of electron attachment processes in the presence of an environment.

TABLE I. Inelastic probabilities (ICEC and vibrational excitation) computed within the full electron-nuclear dynamics simulations (first two rows) and within the fixed-nuclei dynamics (only ICEC in this case; lowest row). Equations for each quantity are described by (6) and in the text.

ε_i in a.u.	0.3	0.4	0.5	0.6
ICEC (Full dyn.)	6%	10%	15%	10%
Vib. exc. (Full dyn.)	21%	6%	3%	8%
ICEC (Fixed nuclei)	0%	0%	18%	18%

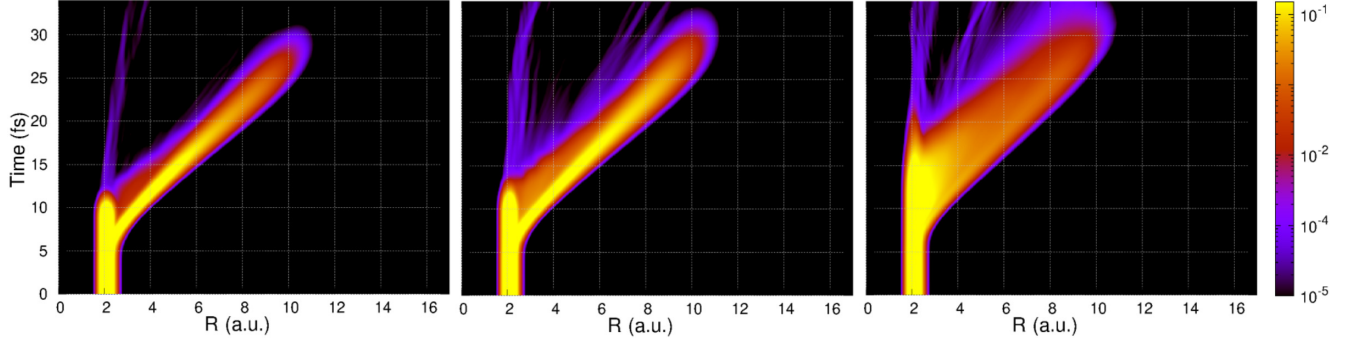


FIG. 3. Time-dependent nuclear densities (total density integrated in x_1 and x_2) in a.u.^{-1} units according to the color bar (log scale) for three different incoming electron energies ($\varepsilon_i = 0.6, 0.5, 0.3 \text{ a.u.} \approx 16.33, 13.6, 8.16 \text{ eV}$, from left to right).

ACKNOWLEDGMENTS

We thank the ANR-DFG for financial support of the QD4ICEC project. The respective DFG grants are BA 3770/5-1 and FA 1989/1-1; the ANR grants are ANR-22-CE92-0071-01 and ANR-22-CE92-0071-02. E.F. gratefully acknowledges financial support from the research and service facility LISA⁺ of the University of Tübingen. F.M.P. gratefully acknowledges partial financial support of CONICET(PIP-KE311220210100787CO), SECYT-UNC (Res. 233/2020) and ANPCYT-FONCyT, PICT-2018 N° 3431. Financial support for the work of A.M. has been gratefully received from the Research Foundation – Flanders (FWO) within the junior postdoctoral fellowship mandate 1232922N, and from the Fulbright Schuman-Program Award issued by The Commission for Educational Exchange between the United States, Belgium, and Luxembourg.

This recognition does not imply that the Government of the United States or any agency representing it has endorsed the conclusions or approved the contents of this publication.

APPENDIX: FITTING OF THE PARAMETERS USED IN THE CALCULATIONS

1. Description

In the following, we use atomic units where the Bohr radius is $a_0 = 1$, $\hbar = 1$, and $m_e = 1$. The energies of a one electron atom with charge Z and mass m_A are $E_n = -\frac{Z^2}{2n^2} \mu_A$ with $\mu_A = \frac{m_A}{m_A + 1}$ in these units. The three potentials employed in this work can be described by the same potential function form,

$$V(x, y, \alpha, \beta, c_m) = \frac{e^{-\alpha|x-c_my|^2}}{\sqrt{|x-c_my|^2 + \beta}}, \quad (\text{A1})$$

TABLE II. List of mass constants.

Parameter	Value	Units
m_{Ne}	36443.98900696	a.u. (m_e)
m_{He}	7294.29954142	a.u. (m_e)
m_T	43738.28854838	a.u. (m_e)
μ	6077.81834003	a.u. (m_e)
μ_{Ne}	0.99997256	a.u. (m_e)
μ_{He}	0.99986292	a.u. (m_e)
m_{Ne}	19.99244017	u (atomic mass units)

$$V_{e,e}(x_1, x_2) = V(x_1, x_2, \alpha_{ee}, \beta_{ee}, 1), \quad (\text{A2})$$

$$V_{N,N}(R) = V(R, 0, \alpha_R, \beta_R, 0), \quad (\text{A3})$$

$$V_{N,e}(x_i, R) = -V\left(x_i, R, \alpha_{Ne,e}, \beta_{Ne,e}, -\frac{\mu}{m_{Ne}}\right) - V\left(x_i, R, \alpha_{He,e}, \beta_{He,e}, \frac{\mu}{m_{He}}\right). \quad (\text{A4})$$

They are explicitly shown in Eqs. (2)–(4) in the main text. We chose the parameter values such that we reproduce the properties of the NeHe^+ dimer (cf. Tables II and III). The particular linear setup is such that Ne is at the “left” (negative x_i values) and He is at the “right” (positive x_i values). The nuclei center of mass is at $x_i \equiv 0$.

2. Atomic parameters for Ne and He

A model Hamiltonian for the atoms can be constructed with the Hamiltonian

$$H = -\frac{1}{2\mu_A} \frac{\partial^2}{\partial x_1^2} + V(x_1, 0, \alpha_{A,e}, \beta_{A,e}, 0), \quad (\text{A5})$$

where A can be He or Ne.

We used different procedures to estimate the parameters in the atomic potentials. First, we match the first ionization energy E_{ioniz} of each atom to the ground state of the atomic potential $E_A(\alpha, \beta)$,

$$E_A(\alpha, \beta) = E_{\text{ioniz}}. \quad (\text{A6})$$

This implicit equation has a numerical solution $\beta_{A,e}(\alpha)$, which is shown in Fig. 4. The values used for the

TABLE III. List of parameters for the potentials.

Parameter	Value	Units
$\alpha_{\text{Ne},e}$	0.0102	a.u.
$\beta_{\text{Ne},e}$	0.655	a.u.
$\alpha_{\text{He},e}$	0.0139	a.u.
$\beta_{\text{He},e}$	0.473	a.u.
α_R	0.01205	a.u.
β_R	0.01	a.u.
$\alpha_{e,e}$	0.02	a.u.

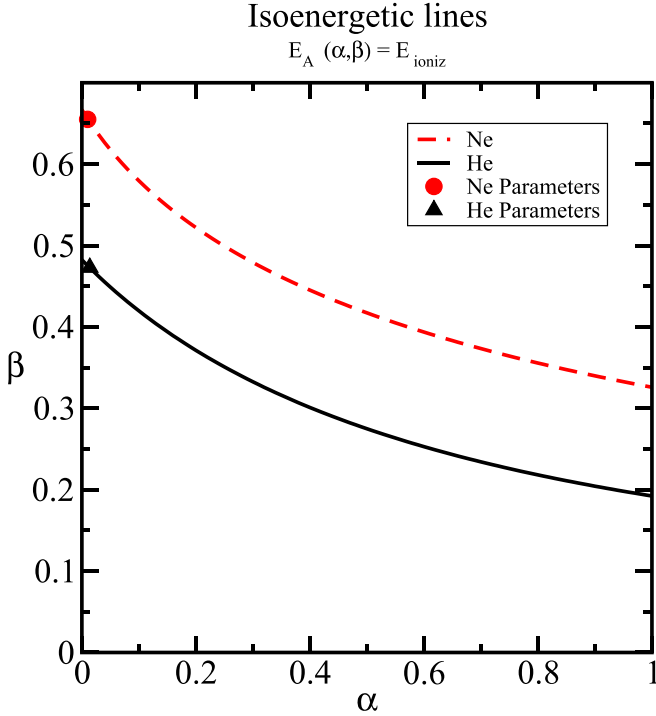
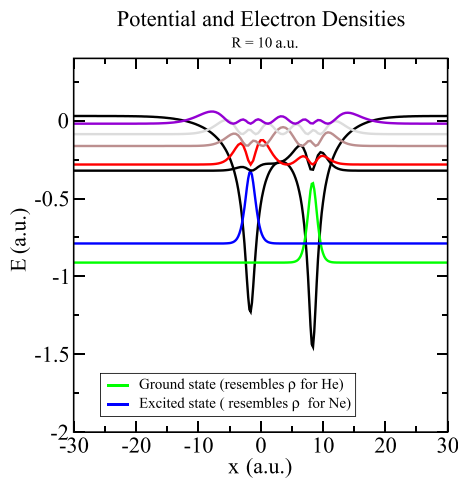


FIG. 4. Isoenergetic lines obtained from (A6). The red dot and black triangle are the ones used in the dynamical calculations for neon and helium, respectively.

ionization energies are $E_{\text{He},I} = 24.587 \text{ eV} = 0.904 \text{ a.u.}$ for He and $E_{\text{Ne},I} = 21.565 \text{ eV} = 0.792 \text{ a.u.}$ for Ne [15].

To select an α value from the curve we chose approximate sizes for the electron cloud of Ne and He needed to reproduce the bonding distance between He and Ne in the NeHe molecule. Hence, recalling that He-Ne bonding is around 2–3 Å, we find the ground states that give standard deviations, $r_{\text{size},A} = \Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$, close to $r_{\text{size},\text{He}} = 3 \text{ Å} \approx 6 \text{ a.u.}$ and $r_{\text{size},\text{Ne}} = 3.5 \text{ Å} \approx 7 \text{ a.u.}$ The $\alpha_{A,e}$ values obtained with this procedure are listed in Table III.



The value of β is determined by Eq. (A6) which reproduces the first ionization energy of each atom. The selected values are listed also in Table III and pinpointed in Fig. 4.

3. Potential energy curves for the one electron model for NeHe⁺

Here, we describe how we computed the potential energy curves (PECs) of Fig. 1 of the main text. The one-electron model in the field of the two nuclei is described by the Hamiltonian

$$H = -\frac{1}{2\mu_{e2N}} \frac{\partial^2}{\partial x_1^2} + V_{N,e}(x_1, R) + V_{N,N}(R), \quad (\text{A7})$$

where μ_{e2N} is the reduced mass of one electron against the two nuclei, $\mu_{e2N} = \frac{m_A + m_B}{m_A + m_B + 1}$. We used a sine-DVR representation to compute the one-electron energies, $E_i(R)$, and states, $\varphi_i(x; R)$, as a function of the parameter R .

There are parameters which need to be selected in this model α_R, β_R . The screening α_R is chosen as $(\alpha_{\text{Ne},e} + \alpha_{\text{He},e})/2$, so the screening is similar to that of the atoms, and no long-range effects dominate the limit $R \rightarrow \infty$. The value $\beta_R = 0.01 \text{ a.u.}$ was chosen more or less arbitrarily, since it is a cutoff parameter.

It is also interesting to analyze the shape of the one electronic states at different values of the R parameter. Figure 5 shows those states at $R = R_{\text{eq}} = 2.1 \text{ a.u.}$ and $R = 10 \text{ a.u.}$

4. Potential energy curves for the two-electron BO model $2e^- + (\text{NeHe})^{2+} \approx \text{NeHe}$

The equilibrium distance between nuclei for the complete model for HeNe, represented by Eq. (1) of the main text, can be estimated using a model with two electrons and fixed nuclei. The distance R is treated as a parameter and the PECs can be computed. The Hamiltonian is

$$H = -\frac{1}{2} \frac{\partial^2}{\partial x_1^2} - \frac{1}{2} \frac{\partial^2}{\partial x_2^2} + V_{e,e}(x_1, x_2) + V_{N,N}(R) + \sum_{i=1}^2 V_{N,e}(x_i, R). \quad (\text{A8})$$

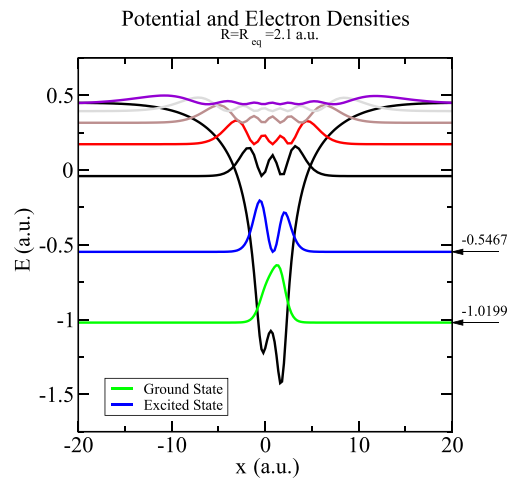


FIG. 5. The electron densities for the ground (green) and first excited states (blue) and second to sixth excited states (black, red, brown, gray, and purple, respectively) of Hamiltonian (A7) (same color code as in Fig. 1). Two R values are shown: $R = R_{\text{eq}} = 2.1 \text{ a.u.}$ (right panel), which is the equilibrium distance for the ground PEC, and $R = 10 \text{ a.u.}$ (left panel) depicting why the first excited state PEC (blue) is asymptotically named with Ne.

Here, the $e - e$ interaction parameter $\alpha_{e,e}$ must be selected. The PECs obtained for different values of $\alpha_{e,e}$ show that the minimum location and energy depend on $\alpha_{e,e}$ which must then be selected accordingly. We have se-

lected a value of $\alpha_{e,e} = 0.02$ a.u. for the simulations, which gave an equilibrium distance for NeHe of $R_{\text{eq}} = 6.6$ a.u. ≈ 3.3 Å, a value close to the *ab initio* equilibrium distance ≈ 3 Å [6].

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TOPICAL REVIEW

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To cite this article: Annika Bande *et al* 2023 *J. Phys. B: At. Mol. Opt. Phys.* **56** 232001

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Topical Review

Interatomic Coulombic electron capture: the story so far

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Received 26 June 2023, revised 2 October 2023

Accepted for publication 26 October 2023

Published 13 November 2023



Abstract

Inter-particle Coulombic electron capture (ICEC) is an environment-enabled electron capture process by means of which a free electron can be efficiently attached to a system (e.g. ion, atom, molecule, or quantum dot (QD)). The excess electron attachment energy is simultaneously transferred to a neighbouring system which concomitantly undergoes ionization (or excitation). ICEC has been theoretically predicted in van-der-Waals and in hydrogen-bonded systems as well as in QD arrays. The theoretical approaches employed in these works range from analytical models to electronic structure and (quantum) dynamical calculations. In this article, we provide a comprehensive review of the main theoretical approaches that have been developed and employed to investigate ICEC and summarize the main conclusions learned from these works. Since knowledge on ICEC is still in its early stage, we conclude this review with our own views and proposals on the future perspectives for the research in ICEC.

Keywords: electron attachment, interparticle Coulombic electron capture, clusters

(Some figures may appear in colour only in the online journal)

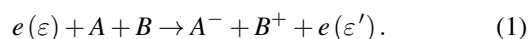
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1. Introduction

Electron attachment is a fundamental process of great importance in many areas of basic and applied science. It plays a central role in astrophysics [1, 2], plasma physics [3], and accelerator physics [4]. Furthermore, it underlies the reduction and oxidation properties of matter and thus it is also of relevance to electrochemistry [5, 6], photochemistry [7], high-energy chemistry [8], biology [9] as well as to novel applications of solid state devices [10, 11].

Electron attachment to atoms, molecules and clusters has been investigated for decades (see e.g. the Reviews [12, 13] and papers of this special issue). Gas-phase electron capture processes are well understood from diverse experiments as well as from theoretical investigations (see [14] and references therein). However, in clusters and even more so in condensed phase, the nature of these reactions is still an open field of research. We address in this review one of the possible electron capture processes, namely the inter-particle Coulombic electron capture (ICEC), which takes place only in systems embedded in an environment.

ICEC is a process in which a free electron can efficiently attach to an acceptor A (i.e. ion, atom, molecule, quantum dot (QD), etc). The excess attachment energy is transferred to a neighbouring system B which gets ionized (or excited),



The ICEC process exists in several variants. If the excess energy is used to ionize the neighbour, which emits the so-called ICEC electron, then the process is called direct ICEC (see figure 1). This naming is independent of whether the electron is captured into the lowest possible orbital (figure 1(a)) or into an energetically higher-lying orbital (figure 1(b)). In the latter case, the system subsequently relaxes via photon emission or via another environmentally assisted pathway.

It is also possible that the transferred excess energy is used to create a resonance state, i.e. a bound state in the continuum. This process is therefore called resonant ICEC. The resonance state can subsequently relax under emission of a photon, which is alternatively also discussed in the research literature as *two-centre dielectronic recombination* [16–19]. Hence the process is considered as an inverse process to a resonant inter-particle Coulombic decay (ICD) [20], see figure 2(a). We note, that the latter process has also been considered for positron attachment [21]. Another possibility is that the resonance state relaxes by transferring the excess energy to a third site, which is ionized [22]. Alternatively, it can undergo a participator resonant ICD upon emission of an electron, if the electron was initially captured into an electronically excited state (figure 2(b)).

In contrast to the delocalized nature of the resonance state in the resonant ICEC process, it is also possible to create a resonance state localized on A , if the initial kinetic energy of the captured electron matches an internal energy difference of this unit (see figure 3). This resonance state can then decay via several pathways, e.g. a participator resonant ICD illustrated in figure 3(a) or a spectator resonant ICD shown in figure 3(b). Due to its initiation by a two-electron process on unit A this

process is called dielectronic ICEC. The analogue process in photorecombination [23] at a single site was observed in the case of dielectronic recombination of isolated cations induced by capture into a Rydberg state [24]. For every single process in the above manifold, energy conservation is required.

ICEC was discovered through analytical scattering theory [19, 20, 25]. Indeed, it was shown that the ICEC process led to a strong enhancement of the electron attachment (or capture) cross sections compared to isolated A . This was demonstrated in several systems such as Ne^+ surrounded with Xe atoms or benzene (Bz) molecules, He^+ in the presence of Ar and Bz, or the $\text{Mg}^+ - \text{Br}^-$ system [20, 25].

As such, ICEC constitutes an efficient process for reducing a species while oxidizing one of its neighbours. It should be noted that the two species involved in ICEC may have different ionization potentials thus enabling the modulation of the energy of the ICEC electron. Such electrons, typically of a few electron-Volts of kinetic energy, are known to be highly genotoxic, because they can undergo dissociative electron attachment (DEA) of biomolecules [26–28]. Note that the cross section for DEA strongly depends on the kinetic energy of the free electron. ICEC might thus be a general process underlying the damage of living cells under ionizing radiation as well as a major actor in the electron-mediated chemistry which leads to the formation of pre-biotic species in interstellar environments.

It is fair to say that the research field of ICEC is just at its infancy. Indeed, including the initial works in which scattering theory was applied to describe the most fundamental ICEC processes, all of the ICEC mechanisms described so far have been discovered from a purely theoretical perspective. As a result of this, various theoretical methods and approximations have been developed to account for the very different nature of the systems prone to exhibit any (or several) of the ICEC pathways. The first aim of this review is to present a global overview of the different ICEC processes together with an introduction to the different classes of materials and systems for which ICEC was found to be relevant. This is followed by a detailed summary of the main conclusions learned from these works. We conclude this review with our own point of view on the perspectives for the largely unexplored research field of ICEC.

2. ICEC between two distant partners

In order to be observable, the environment-assisted electron capture needs to fulfil energy conservation and to be at least as efficient as the normal photo-recombination. This efficiency is characterized by the cross section of the process, which gives the probability of an incoming electron with wavevector k being captured and an electron with wavevector k' being emitted. For a general inelastic scattering event involving several channels, the cross section reads [29]:

$$\sigma_{\text{ICEC}}(k) = \frac{1}{g_{\text{in}}} \sum_{\text{in, out}} \int \frac{d\Omega_{\mathbf{k}}}{4\pi} \int d\Omega_{\mathbf{k}'} \frac{m_e^2}{(2\pi\hbar^2)^2} \frac{k'}{k} |T(\text{out} \leftarrow \text{in})|^2. \quad (2)$$

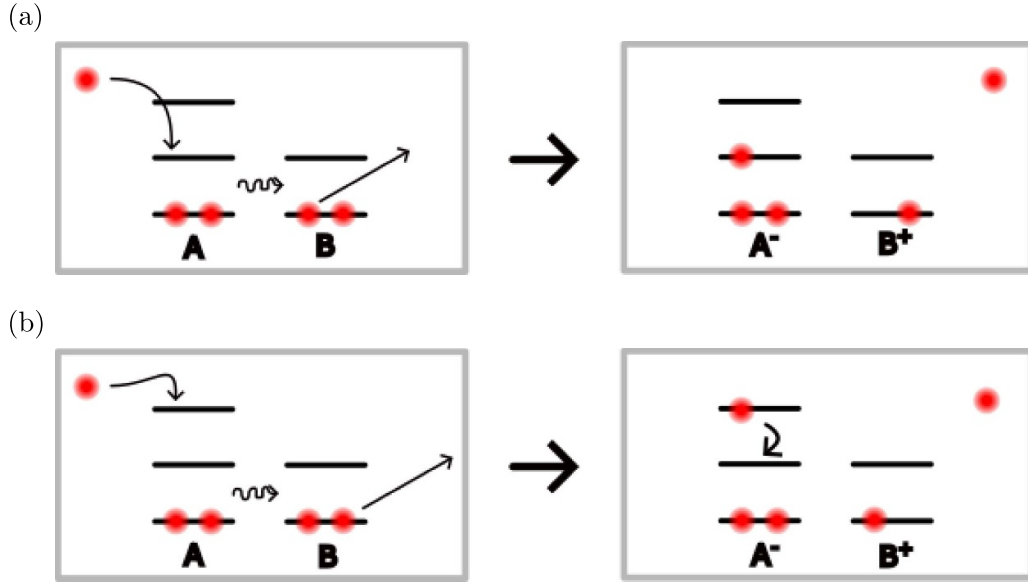


Figure 1. Direct ICEC processes. Reproduced from [15]. CC BY 4.0.

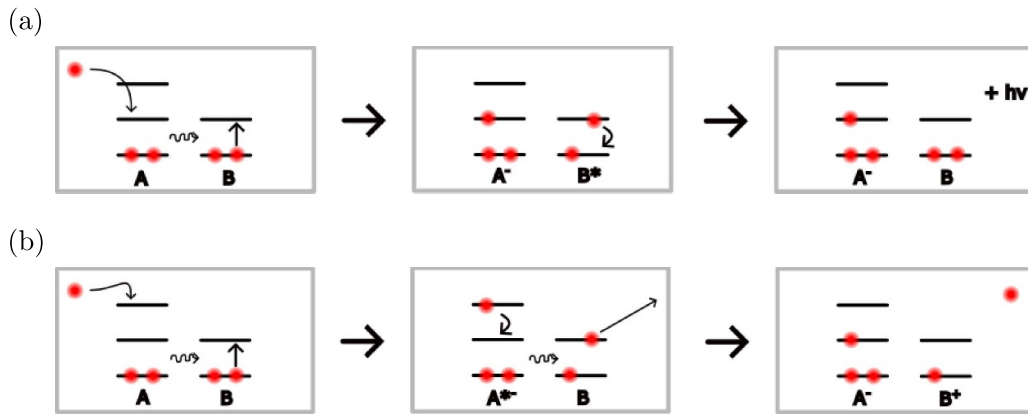


Figure 2. Resonant ICEC processes. Reproduced from [15]. CC BY 4.0.

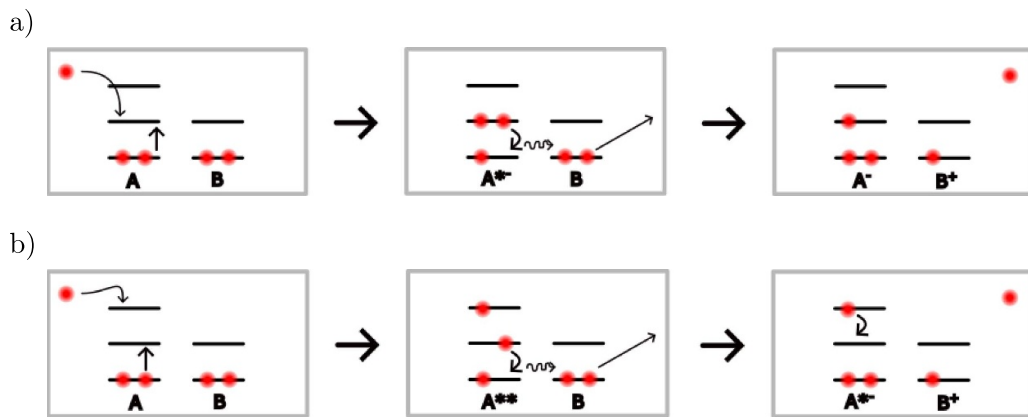


Figure 3. Dielectronic resonance-enhanced ICEC processes. Reproduced from [15]. CC BY 4.0.

Here, the scattering T -matrix describes the interaction between the two (appropriately normalized) continuum states, the total cross section includes contributions from all incoming and outgoing channels, the integration over the solid angles

of the incoming and outgoing electrons $\Omega_{\mathbf{k}}$ and $\Omega_{\mathbf{k}'}$, respectively, ensures that all possible spatial directions are taken into account and the multiplicity of the initial state g_{in} averages over all possible initial states and thereby normalizes

the cross section to the interaction with a single incoming electron.

This expression of the cross section can be simplified for systems with weakly interacting units. In such cases, it is possible to estimate the cross section directly from the intrinsic properties of the units as well as their geometry [25]. Furthermore, the long-range Coulomb interaction between electrons on the different sites moderates the energy transfer through space, which according to quantum field theory is the transfer of a virtual photon [30].

These estimates allow us to understand, how the cross section is influenced by the different system parameters and can guide the choice of systems for both numerical simulations and experiments. From a historical perspective, the asymptotic estimates were the first evidence for the existence of ICEC.

In the following, we summarize the energy balance condition, the derivation of the cross section estimate, i.e. the asymptotic approximation, what we can learn from it and how it impacts the ICEC efficiency in different systems.

2.1. Asymptotic approximation

Our aim here is to describe the ICEC process for two separate and weakly interacting units (A and B). In this context, we speak of the *asymptotic regime* and the *asymptotic approximation* when sites A and B are sufficiently separated such that their interaction causes an only marginal disturbance of the units' wavefunctions and their individuality can be asserted. In this case and based on the energies long before the incoming electron interacts with our system AB and long after the emitted electron has left it, the energy balance involves the kinetic energy of the captured and emitted electrons at infinite distance ε and ε' as well as the electron affinity $EA^{(A)}$ of A and the ionization potential $IP^{(B)}$ of B as [20, 25]:

$$EA^{(A)} + \varepsilon = IP^{(B)} + \varepsilon' = h\nu. \quad (3)$$

Here, $h\nu$ represents the transferred energy.

When considering ICEC in this spirit, as a virtual photon mechanism, the entire process can be rationalized in terms of cross sections for the intermediate steps, as it is the case for the ICD asymptotic equation [31–33]. Due to the weak interaction between the units, it is possible to use first order perturbation theory in equation (2). In this way, the wavefunction can be expressed as the product of the wavefunction for the incident electron adhering to incoming boundary conditions (+) plus unit A and the wavefunction of unit B, including the electron emitted during the process adhering to outgoing boundary conditions (−) for the initial and final state:

$$|\mathbf{k}; \Phi_{AB}+\rangle = |\mathbf{k}; \Phi_A+\rangle |\Phi_B\rangle \quad (4)$$

$$|\mathbf{k}'; \Phi_{A-B}+\rangle = |\Phi_A-\rangle |\mathbf{k}'; \Phi_B+\rangle. \quad (5)$$

Consequently, the smaller the overlap of the partners' wavefunctions are, i.e. the further the partners are apart, the better this approximation becomes. It is therefore called the asymptotic approximation. The overlap is strictly depending on and characteristic of the different systems.

Using this product wavefunction, the Coulomb interaction between charges located on A with charges on B functions as a perturbation operator. Performing a multipole expansion on this Coulomb interaction, truncation after the dominant term, and application of the principle of detailed balance [34] yields

$$\sigma_{ICEC,i}(\varepsilon) = \frac{3(\hbar c)^4}{4\pi} \frac{\sigma_{PI}^{(B)}(\varepsilon')}{R^6 (h\nu_i)^4} \sigma_{PR}^{(A)}(\varepsilon), \quad (6)$$

as cross section for a single direct ICEC channel i of a single AB pair. This expression can be attributed to the interaction between dipoles located at the two involved partners. Here, $\sigma_{PR}^{(A)}(\varepsilon)$ is the photo-recombination cross section of A, $\sigma_{PI}^{(B)}(\varepsilon')$ is the photoionization cross section of B, and R is the distance between A and B.

As can directly be seen from equation (6), ICEC dominates over photo-recombination for a specific channel, whenever the prefactor to the photo-recombination cross section exceeds unity. In decreasing priority, this is the case when:

1. the **partners are in proximity**. Hence, a small interparticle distance R increases the probability for an ICEC process. However, for a system-dependent small interparticle distance, the asymptotic cross section in equation (6) becomes a lower bound and more accurate methods become necessary for an accurate description of ICEC.
2. the **transferred energy $h\nu$ is low**. Both a slow incoming electron and a weak potential capturing the electron related to the electron affinity are favourable for the observation of ICEC.
3. the **ionization cross section of B is high**.

Since cross sections are additive, the total ICEC cross section is then given by the sum over all individual ICEC channel contributions $\sigma_{ICEC} = \sum_i \sigma_{ICEC,i}$. Not only does the energetic accessibility of several ICEC channels increase the total ICEC cross section, but it also increases the probability to have one channel with a particularly high ICEC cross section where only a comparatively small amount of energy is transferred between the partners as illustrated in figure 1(b).

An ICEC channel is characterized by the capturing and emitting states as well as by the electron emitting partner. Hence, within the asymptotic approximation and under the assumption of distinguishable partners, the total ICEC cross section scales linearly with the number of equivalent and equidistant partners N .

In the case of the dielectronic resonance-enhanced ICEC processes depicted in figure 3 with the localized electron capture process, an asymptotic expression can straightforwardly be deduced [20]:

$$\sigma_{dICEC} = \frac{\pi}{k^2} \frac{g_d}{g_{in}} \frac{\Gamma_{PR} \Gamma_{ICD}}{(\varepsilon - \varepsilon_R)^2 + \Gamma^2/4}. \quad (7)$$

Here, g_d and g_{in} are the weights of the decaying and the initial state, respectively, $\mathbf{k}$ is the absolute wave vector of the incident electron, and ε_R is the energy of the decaying state.

The successive electron capture and electronic decay via resonant ICD (RICD) processes of a single ICEC pathway

imprints the characteristic Lorentzian line shape of an electronic decay process on equation (7). Its width is hereby given by the total decay width Γ , which constitutes the sum over the decay width of all possible decay mechanisms including ICD, photo-recombination and autoionization [35]. The signal is scaled by the RICD decay width Γ_{ICD} as well as the photo-recombination decay width Γ_{PR} . Most notably, the ICD width is usually several orders of magnitude larger than the photo-recombination width. If no other pathways are energetically accessible, the total width can be approximated to the ICD width ($\Gamma \approx \Gamma_{\text{ICD}}$). In this scenario and when the kinetic energy of the incident electron ε matches the resonance energy ε_R , the cross section is significantly enhanced by this dielectronic pathway, as can be seen from equation (7).

If an autoionization process is energetically allowed, its decay width is usually of the same order of magnitude than an ICD width. Since it enters equation (7) via the total decay width in the denominator, the larger the autoionization width, the smaller is the ICEC cross section.

Furthermore, a dielectronic resonance-enhanced ICEC process is most probable, when the multiplicity of the capturing state (g_d) is higher than the one of the initial state (g_{in}), and when the incident electron energy fits well with a resonance of unit A. Moreover, deduced from the asymptotic approximation of the ICD decay width, the ICEC cross section is high, when both the transition dipole moment on unit A as well as the ionization cross section of unit B are high. Additionally, and as for the direct ICEC case, a ν^{-4} -dependence benefits small virtual photon energies whereas the R^{-6} dependence favours close partners.

In order to assess nano-sized components performing ICEC, the so-called ICEC radius R_{ICEC} was recently defined as the distance at which ICEC and photo-recombination are equally efficient [36]. Its working expressions were deduced from the asymptotic ICEC cross section in equation (6) utilizing the fact that the cross section in this approximation does not carry any information about the system size. For a single pair and channel i , this distance is given by [36]

$$R_{\text{ICEC},i} = \left(\frac{3(\hbar c)^4}{4\pi} \frac{\sigma_{\text{PI}}^{(\text{B})}(\varepsilon'_i)}{(h\nu_i)^4} \right)^{\frac{1}{6}}. \quad (8)$$

$R_{\text{ICEC},i}$ is a quantity more easily comparable across experiments and theoretical systems by taking the free variable parameter of intermolecular distance R out of the equation as

$$\sigma_{\text{ICEC},i} R_i^6 = \sigma_{\text{PR}}^{(\text{A})} R_{\text{ICEC},i}^6, \quad (9)$$

which has successfully been applied to different systems and degrees of theory since (cf discussion in section 3.3) [37]. With its definition, the ICEC radius is on equal footing to the closely related field of Förster resonance energy transfer (FRET). Its respective parameter, the Förster radius, provides an evaluation of the reach of the long-range energy transfer for a specific system and incident energy.

Analogue to the FRET quantum yield, which indicates the probability of FRET to occur after excitation by one photon, the ICEC efficiency can be defined as [36]

$$\eta_{\text{ICEC}} = \frac{R_{\text{ICEC}}^6}{R^6 + R_{\text{ICEC}}^6}. \quad (10)$$

Considering the possibility of multiple ICEC and photo-recombination channels, the individual contributions should be combined in a weighted sum to yield the total ICEC radius [36]

$$R_{\text{ICEC}}(\varepsilon) = \frac{3(\hbar c)^4}{4\pi} \sum_i w_{i,\varepsilon} \frac{\sigma_{\text{PI}}^{(\text{B})}(\varepsilon'_i)}{(h\nu_{i,\varepsilon})^4}. \quad (11)$$

Here, multiple channels, each of which becomes energetically available at different incident electron energies, have been included.

The ICEC radius is expected to be of significance to evaluate theoretical and experimental systems since it directly relates to the product of the amplification factor ($\sigma_{\text{ICEC}}/\sigma_{\text{PR}}$), and the respective interatomic distance R to the sixth power which can be shown—for each individual capture channel, i , at the same time as for the collective sum of contributions from all available capture channels to the overall ICEC—to be:

1. limited in magnitude from above by quantity R_{max} for all incident energies as

$$\frac{\sigma_{\text{ICEC}}}{\sigma_{\text{PR}}} R^6 = R_{\text{ICEC},i}^6 \leq R_{\text{max}}^6 = \frac{3(\hbar c)^4}{4\pi} \max_{\varepsilon} \left[\frac{\sigma_{\text{PI}}^{(\text{B})}(\varepsilon)}{\varepsilon^4} \right], \quad (12)$$

which can be estimated exclusively from the accessible photoionization cross section of the assisting partner; and

2. predictable in its large-energy behaviour (where $\varepsilon \gg \text{EA}^{(\text{A})}$ in equation (3)) converging to the captor-independent distance R_{∞} as function of incident energy ε :

$$\frac{\sigma_{\text{ICEC}}}{\sigma_{\text{PR}}} R^6 = R_{\text{ICEC},i}^6 \xrightarrow{\varepsilon \rightarrow h\nu} R_{\infty}^6(\varepsilon) = \frac{3(\hbar c)^4}{4\pi} \frac{\sigma_{\text{PI}}^{(\text{B})}(\varepsilon)}{\varepsilon^4}, \quad (13)$$

which is thereby independent of the particular species capturing the free electron species and even the capturing channel i .

The overall characteristic distance of the ICEC process exhibits a maximum, defining an optimal starting energy for the experimental observation of ICEC in any system. Moreover, it has been shown to be bound by the same quantities R_{max} in magnitude and $R_{\infty}(\varepsilon)$ in its large-energy convergent behaviour as each individual channel i described in equations (12) and (13). These quantities are solely dependent on the assisting partner molecule and provide an easily accessible first estimate for feasibility of ICEC in any potential future experimental setup. Hence, the ICEC radius depends on the intrinsic properties of the individual units and provides a new and intuitive design tool.

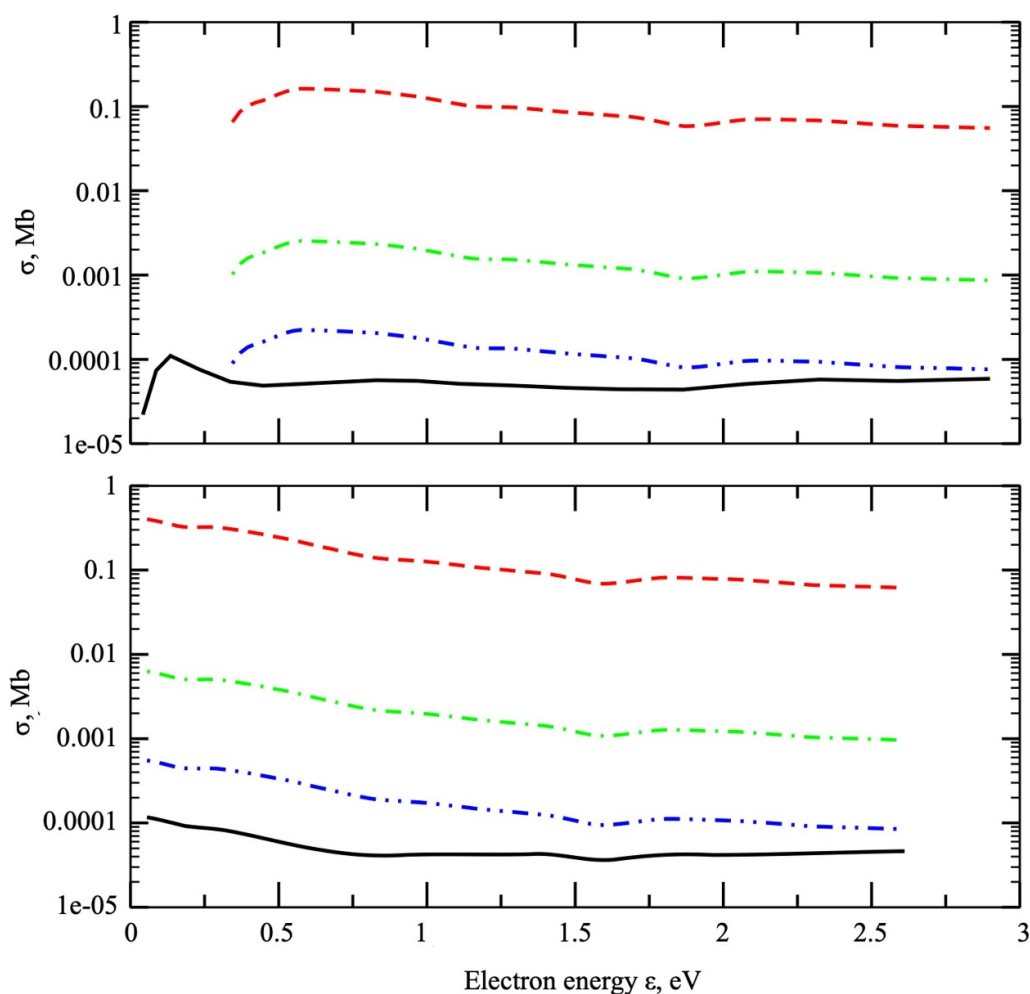


Figure 4. ICEC cross sections for a capture into the ground states for upper panel: $\text{Br} + \text{Cl}^-$ and lower panel: $\text{Cl} + \text{Br}^-$ at different interatomic distances. The solid black line shows the photo-recombination cross section of the electron capturing unit, while the coloured lines account for different internuclear distance, where blue corresponds to 3 nm, green to 2 nm and red to 1 nm, respectively. Reproduced from [25]. © IOP Publishing Ltd. All rights reserved.

2.2. Systems

Real systems exhibit at least a subset of the above-mentioned processes. Hence, the cross sections can never be accounted for by a single effect. In the following, we introduce the systems investigated within the asymptotic approximation and highlight the effects of channel openings, distance dependence, energy of the incident electron, and ionization cross sections of unit B.

2.2.1. $\text{Br} + \text{Cl}^-$ and $\text{Cl} + \text{Br}^-$. One of the first ICEC processes to be investigated was the electron capture on a halogen atom accompanied by the electron emission from a different halide [20, 25]. When considering the net reaction only, that is ignoring the electron on both sides of the chemical equation,



one may assume that an electron is transferred from the halide to the halogen atom. While this charge exchange process can

occur at very small interatomic distances, where the components' wavefunction significantly overlap, at larger distances an ICEC process is a much more plausible explanation. As a consequence, the electron can here be seen as a catalyst for the net electron transfer reaction.

In this halogen-halide example the importance of channel openings based on the energy balance can be illustrated in a disentangled way. For reasonably slow incident electrons, only a capture to the ion's ground state is energetically accessible. While the ICEC process is available for any electron energy in the $\text{Cl} + \text{Br}^- \rightarrow \text{Cl}^- + \text{Br}$ case (see lower panel in figure 4), the reverse process requires a minimum kinetic energy of the incident electron of at least 0.288 eV [25]. This becomes noticeable by a later onset of the ICEC cross section in the upper panel of figure 4.

In addition to this, figure 4 shows that the ICEC process (coloured lines) is more efficient than the corresponding photo-recombination process (solid black line) for as much as 3 nm. This can be attributed to both the low transferred energy between the units as well as the high photo-ionization cross section of the bromide and chloride anions.

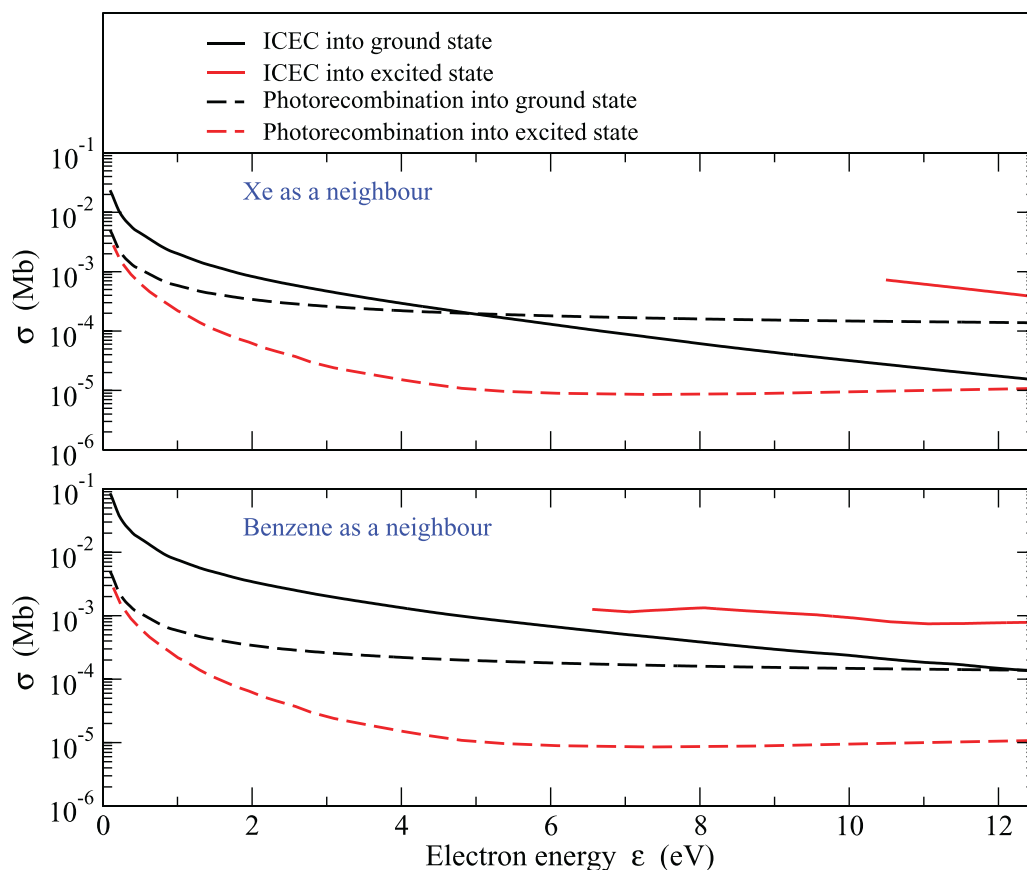


Figure 5. ICEC cross sections for an electron capture of different kinetic energies ϵ by a neon-cation with either a xenon atom or a benzene molecule as partner. The ICEC cross sections are given as solid lines with an ICEC process for an electron capture into the ground state is shown in black and an ICEC process initiated by an electron capture into an excited state is shown in red. The respective photo-recombination cross sections are given as dashed lines as comparison. The simulations were carried out for an interparticle distance of 1 nm. Reprinted figure with permission from [20], Copyright (2010) by the American Physical Society.

2.2.2. Ne^+ with Xe or benzene. When the electron is captured by the neon cation and ICEC proceeds with either a xenon atom or a benzene molecule in the vicinity a plethora of different processes is possible. Consequently, this constitutes an ideal showcase scenario despite the low absolute ICEC cross sections caused by the rather high energy transferred between the two units, particularly in the case of a capture into the ground state.

With a ground state electron affinity of 21.565 eV and ionization potentials of $\text{SIP}(\text{Xe}) = 12.13$ eV and $\text{SIP}(\text{Bz}) = 9.45$ eV, the direct ICEC channel is open for all kinetic energies of the incident electron. This can be seen in figure 5 as solid black line. The ICEC cross section decreases for higher incident electron energies, because the transferred energy increases and lowers the cross section according to equation (6). The detailed behaviour of the ICEC cross sections is caused by the energy dependence of the neighbours photo-ionization cross section.

Alternatively, the neon cation can also capture the electron into the excited $3p$ -Rydberg state with an electron affinity of 2.943 eV. The direct ICEC channel for a capture into an excited state is therefore closed for slow incident electrons. However, it opens at higher kinetic energies of the incident electron and is shown as solid red lines in figure 5. Because the

single ionization potential of benzene is lower than of xenon, the ICEC channel for a capture into the excited state opens at lower incident electron energies.

The corresponding photo-recombination cross sections of the neon cation are also displayed in figure 5 as dashed lines. Please note that the photo-recombination cross sections significantly decrease upon capture of the incident electron into an excited state. Therefore, the corresponding cross sections are usually neglected. For the ICEC process, on the other hand, an electron capture into an excited state reduces the energy being transferred between the two units. Therefore, according to equations (6) and (7), the corresponding cross section for an electron capture into an excited state is larger than for an electron capture into the ground state.

As already mentioned, the neon cation in combination with a xenon atom or a benzene molecule can undergo different types of ICEC. As shown in [20], a dielectronic resonance-enhanced ICEC process is initiated by an electron capture into one of the Rydberg p -orbitals under excitation of another electron from the $2s$ orbital to the $2p$ -orbital. Here, the ICEC cross section was shown to be governed by the efficiency of the RICD process following the electron capture into the resonance state.

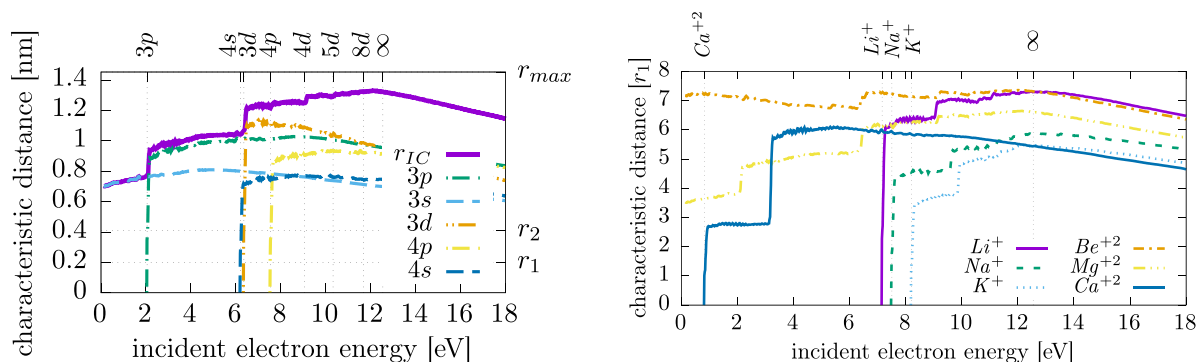


Figure 6. The ICEC radius for water-assisted capture as function of energy, (left) across different capture channels for the established theory test case of $[e^- + \text{Mg}^{2+}]$ near H_2O , and (right) across different biorelevant alkaline and alkaline-earth cations in water assistance in terms of the characteristic length of their respective hydration shell radii r_1 . Reprinted from [36], with the permission of AIP Publishing.

2.2.3. Alkali or alkaline earth metal ion with a water molecule.

A yet rare example of a testbench system for different levels of theoretical approaches toward ICEC is the bio-relevant magnesium dication Mg^{2+} in proximity of an assisting water molecule which has been originally proposed for ICEC [25] and discussed for its potential cascades of related intermolecular energy transfer processes [38, 39], before it has been reinterpreted and expanded across the other alkaline and alkaline-earth cations in terms of their respective ICEC radius [36]. It is thus an interesting system to test alternative numerical approaches beyond the asymptotic approximation (cf section 3.3 for a discussion on R -matrix investigations of a microhydrated proton as technical precursor system, and section 5.3 for a discussion on its perspectives towards microhydrated alkaline and alkaline-earth metal cations) [36].

Within the original communication of ICEC, assisted electron capture into the ground state $3s$ orbital was suggested for Mg^{2+} in proximity of a water molecule at selected fixed distances [25, 40]. Despite ignoring any capture channels beyond the ground state, it demonstrates that ICEC is efficient and dominant over environment-independent photorecombination of Mg^{2+} for fixed examples of intermolecular distance between Mg^{2+} and assisting water molecule [25, 40]. This provided the initial postulate for ICEC as an efficient capture process in general, however it was not yet addressed at that time how to compare different systems and different interatomic distances consistently, nor how to relate Mg^{2+} with water to typical distances like first or second hydration shell radius (r_1 , r_2), or how to evaluate the intermolecular reach of ICEC, as well as the role of excited orbitals as capture channels.

Motivated by its biological relevance as hydrated mineral, and by the question on secondary slow-electron processes in biological systems in consequence of initial radiation damage [28], Mg^{2+} with water has been reinvestigated since then on its potential for non-local energy transfer cascades through ICD and electron transfer mediated decay (ETMD) [38, 41]. It remained unclear then what the net effect of multistate capture would contribute through ICEC: the capturing state for electron capture cannot be controlled externally; instead all electronic states that meet the energy threshold arising from

equation (3) are contributing to the overall ICEC cross section which provides a stark contrast to the conceptual investigation of a selected distinct two-site excited state decaying through ICD and related decay processes [36].

With the very recent interpretation of an intermolecular-distance-independent scaled amplification factor in form of the ICEC radius (cf equation (9)) [36], it was thus possible to investigate the contribution of all open capture channels to the dominant range of ICEC in water assistance with respect to the environment-independent photorecombination of Mg^{2+} with a free electron. Figure 6 (left panel) shows the respective contributions of leading individual capture channels to the overall ICEC radius as function of incident electron energy. It has thereby been shown that the primary contribution to ICEC can not intuitively be attributed to a ground state capture.

Moreover, the representation of ICEC in terms of its ICEC radius provided a clear indication for consistent step over from ICEC to ETMD at the energetic conceptual limit of 0 eV as incident free energy threshold. ICEC is exothermic for Mg^{2+} near H_2O , that means the ICEC pathway is already open at the 0 eV free energy edge. Conceptually this extends down to 2.32 eV below the electronic continuum threshold [36, 42, 43]. The ICEC radius and the energetic difference according to equation (3) therefore indicate that Mg^{2+} would be able to steal an energetically highly bound electron by assistance of the water molecule as conceptual extension of ICEC from low energetic free electrons to bound Rydberg electrons through ETMD. On the other hand, it was found that the large energy behaviour of each capture channel's contribution to the ICEC radius becomes independent of the particular channel. Instead, it shows a clear signature of the assisting water molecule and can be therefore easily predictable theoretically and recognisable by potential future experiments.

In the picture of the ICEC radius, it was thus possible to compare the interatomic range of ICEC to a typical distance for the system of Mg^{2+} with an assisting water molecule: the first hydration shell radius, r_1 , that indicates a natural equilibrium distance between the cation and the next neighbour water molecule in a solution. It was found here that even with the restriction of a pure dimer interaction, still neglecting the multiple available contributing partner molecules in a condensed

matter environment, ICEC dominates over photorecombination to up to 6.5 multiples of r_1 [36].

Furthermore, the biological importance of Mg^{2+} in interaction with water imposes the question on ICEC efficiency with respect of other alkaline and alkaline-earth cations that act as essential nutrient minerals and often show a complex antagonistic relationship with respect to biological absorption in the presence of each other in solution [44]. In this context, it appears more relevant to accommodate for the differences in typical equilibrium distances of the respective mineral in water. It was thus compared across the board for alkaline monocations and alkaline-earth dications from Li^+ to K^+ , and from Be^{2+} to Ca^{2+} in terms of their respective hydration shell radius r_1 , as presented in figure 6 (right panel). It has thereby been shown that ICEC is endothermic for the alkaline monocations and for the calcium dication but has a significant dominance over photorecombination at typical intermolecular distances from its energetic threshold onward. At its respective optimal incident energy every individual investigated cation reaches dominance over photorecombination, as indicated by its respective ICEC radius, for intermolecular distances between 5.5 multiples of its respective typical r_1 (in case of K^+) and 7.35 multiples of r_1 (in the case of Be^{2+}) [36]. Moreover, it has been made apparent that across the board, the higher energy behaviour of the ICEC radius is consistently independent on the particular electron captor species, and instead purely determined by the assisting water molecule according to equation (13).

3. ICEC in atomic and molecular dimers

So far, for large donor-acceptor distances within the virtual photon approximation, we have neglected the orbital overlap between the donor and acceptor species. However, in nature, it is likely that the two subsystems approach one another enough so that the absence of orbital overlap is not a valid approximation anymore. Hence, to go beyond the asymptotic limit, one has to employ a method that explicitly includes the possibility of orbital overlap.

3.1. The R -matrix approach

The R -matrix technique allows to go beyond the asymptotic derivation very efficiently. In particular, in this approach the electron correlation, which is the driving force of ICEC, can be properly accounted for. The R -matrix method has been widely and successfully employed to describe scattering between molecules, atoms and electrons as well as reactions in nuclear, atomic, and molecular physics. It has been only recently that its usefulness in the context of ICEC has been established [37, 45, 46].

The R -matrix theory divides a physical problem into an inner and an outer region separated by a sphere of radius a centred at the centre of mass of the system. The inner region contains the multi-particle description of the full system composed of $N + 1$ electrons. In the outer one only a free particle (here the incoming or the outgoing ICEC electron) is treated

and its interaction with the N remaining particles (electrons) is described in terms of a multipole expansion of the N -electronic density.

The wave function ansatz of the inner-region wavefunction is in terms of a configuration interaction (CI) expansion:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_{N+1}) = A \sum_{ij} \alpha_{ijk} \phi_i(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) u_{ij}(\mathbf{x}_{N+1}) + \sum_i \beta_{ik} \chi_i(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_{N+1}) \quad (15)$$

ϕ_i is the many-particle CI wavefunction of the so-called target state i , u_{ij} are orbitals introduced to represent the scattered electrons, both the incoming and the ICEC electron. The operator A ensures the antisymmetry of the wavefunction. In the second term, χ_i are the so-called L^2 configurations that allow correlation and polarization effects. The R -matrix at the boundary a between the inner and outer regions can be obtained from the solutions of the time-independent Schrödinger equation using the above ansatz (i.e. from the diagonalization of the Hamiltonian CI-matrix). The R -matrix is then numerically propagated from $r = a$ to ∞ , where the scattering amplitudes ($f_{0j}(\Omega)$) are extracted, from which cross sections and resonance widths can then be obtained. A detailed description of the R -matrix method can be found in these reviews [47, 48].

The R -matrix method has been employed to study ICEC in the mixed rare-gas clusters $\text{Ne}^+ @ \text{He}_n$ as well as to investigate the ICEC electron attachment to a proton in the neighbourhood of a water molecule [37, 45, 46]. We summarize in what follows the main findings.

3.2. ICEC in mixed rare-gas clusters

The first application of the R -matrix approach in ICEC was published in 2018 and dealt with the $\text{Ne}^+ \text{-He}$ dimers as well as larger clusters, i.e. $\text{Ne}^+ @ \text{He}_{20}$. The aim of this work was threefold: (1) to investigate the effect of the orbital overlaps on the ICEC cross sections, (2) to determine the validity of the virtual photon approximation and (3) to study ICEC in large-sized clusters that can be probed experimentally.

The main findings are that when the donor and the acceptor species are close enough, the ICEC process can be up to two orders of magnitude larger than predicted by the virtual photon approximation formula and up to four to five orders of magnitude larger than radiative recombination cross sections. To illustrate this, in figure 7 we display the ICEC cross sections for two incoming electron energies as a function of the NeHe^+ distance. It is clearly shown that the virtual photon approximation underestimates the cross sections for distances below 3.5 Å whereas for larger distances it becomes valid. In [45], it was also shown that an additive pairwise approximation (i.e. the ICEC cross sections in the presence of several acceptor neighbours are the sum of the cross sections for each donor-acceptor pair) is valid in these mixed rare-gas clusters. To demonstrate the validity of this additive pairwise approximation the authors compared, for the same Ne-He distances the ICEC cross sections, computed with the R -matrix

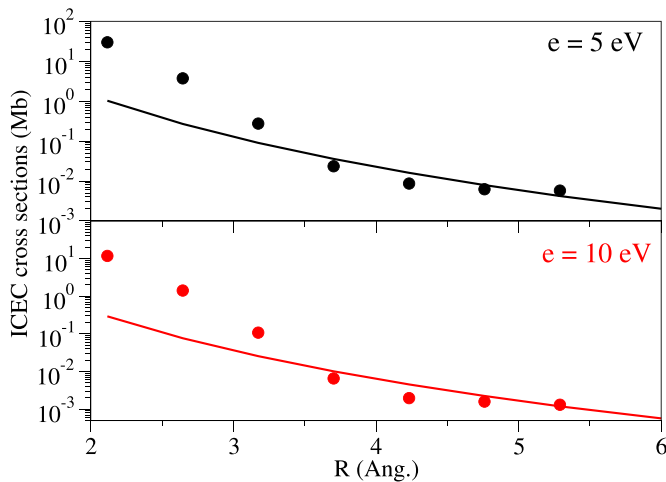


Figure 7. ICEC cross sections as a function of the NeHe distance for two incoming electron energies: 5 eV (top panel) and 10 eV (bottom panel). The lines report the cross sections from the virtual photon approximation. The dots show the ICEC cross sections obtained from the *R*-matrix calculations (see [45] for details). Reprinted figure with permission from [45], Copyright (2018) by the American Physical Society.

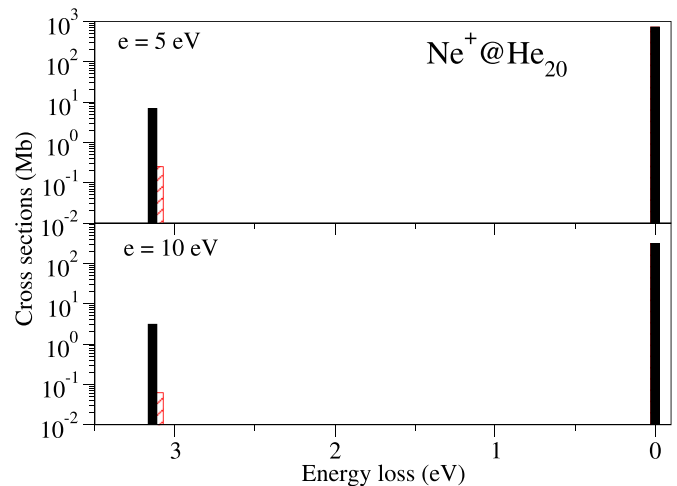


Figure 8. Energy loss (or ICEC) spectra (in Mb) for Ne^+ embedded in He_{20} clusters for two incoming electron energies: 5 eV (top panel) and 10 eV (bottom panel). Full black bars report the *ab initio* *R*-matrix calculations. Red dashed bars show results obtained employing the asymptotic formula (see [45] for details). Reprinted figure with permission from [45], Copyright (2018) by the American Physical Society.

method, for Ne^+ -He with that of Ne^+ - He_2 where the ion is centred between the two helium atoms. They found that the ratio between the corresponding cross sections ($\sigma_{\text{He}_2}/\sigma_{\text{He}}$) is approximately two.

Using the additive pairwise approximation, the ICEC cross sections in larger systems can easily be calculated. The energy loss (or ICEC) spectra for Ne^+ embedded in He_{20} clusters for two incoming electron energies are shown in figure 8. It should be highlighted that the wavefunction for $\text{Ne}^+@ \text{He}_{20}$ employed to model ICEC was taken from a variational quantum Monte Carlo calculation (see [45] for more details). Energy loss spectra are generally employed in electron-molecule collision experiments. The energy loss peak corresponding to ICEC is sufficiently high to be measured: they are equal to about 7 and 3 Mb for $e = 5$ and 10 eV, respectively. In both cases, they are higher by nearly two orders of magnitude than predicted by the asymptotic formula, and four to five orders of magnitude higher than the radiative recombination cross sections. It should also be noted that the ICEC cross sections are only two orders of magnitude smaller than the elastic ones, illustrating quantitatively the ICEC efficiency. These results should pave the way to the first experimental observations of ICEC (see section 5).

3.3. ICEC in the proton-water dimer

The second study on ICEC using the *R*-matrix approach focused on the electron recombination with a proton in the presence of a water molecule. This represents a simple model for microhydrated cations which are relevant in radiation biological damage [37, 46]. The authors focused on proton-water distances between 3 and 8 Å. These values correspond to the second and third hydration shells in condensed phases, respectively. While this range is relevant to biological and

biochemical systems, it should be noted that as protons are extremely reactive they would also strongly interact with the first shell of water molecules. This, of course, may influence the ICEC process between the proton and a second water molecule in a higher shell. The *R*-matrix results reported in [37, 46] are therefore only a very first step in modelling and understanding ICEC in biological and biochemical systems.

Unexpectedly, the *ab initio* ICEC cross sections for a proton-water systems exhibit some structures. These features were shown to be Fano profiles coming from interference between two pathways leading to the same final states, the direct ICEC pathway and the one via a series of metastable electronic states where the incoming electron is temporarily bound to the donor-acceptor system. Several of those metastable states, contributing to the Fano interferences, were identified: $\text{H}(1s)\text{-H}_2\text{O}(^3A_1, 1b_2 \rightarrow 2b_2)$, $\text{H}(1s)\text{-H}_2\text{O}(^1A_1, 1b_2 \rightarrow \text{Rydberg})$ but also $\text{H}^+ \text{-H}_2\text{O}^-$ and $\text{H}^{*-} \text{-H}_2\text{O}^+$.

Figure 9 shows the ICEC cross sections (for $e + \text{H}^+ \text{-H}_2\text{O}(\tilde{X}) \rightarrow \text{H}(1s)\text{-H}_2\text{O}^{+(*)} + e'$) as a function of the energy of the incoming electron, the cross sections were multiplied by R^6 in order to compare the different distances on the same scale. The *R*-matrix ICEC cross sections exhibit these Fano profiles that are superimposed to the smooth cross sections computed within the virtual photon approximation (see [37, 46] for further details). Due to these Fano interferences, the ICEC cross sections can be substantially enhanced or suppressed. This opens the way to control of electron recombination processes.

To gain further insights into the interferences between the quantum paths, the authors analysed the Fano profiles by fitting them with the following equation (see [49])

$$\sigma \propto \frac{(\tilde{E} + q)^2}{1 + \tilde{E}^2}. \quad (16)$$

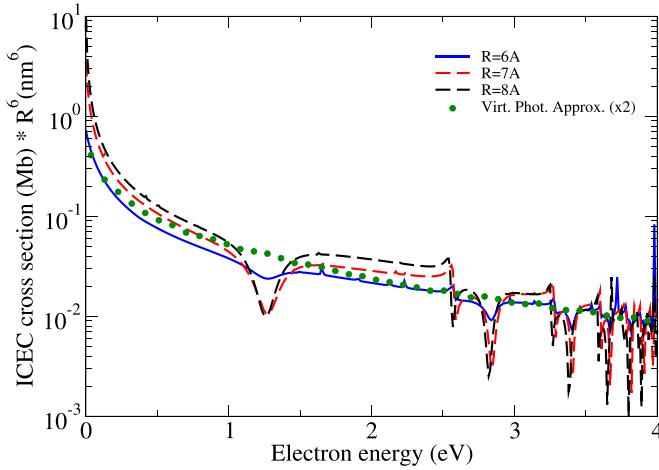


Figure 9. Total ICEC cross sections multiplied by R^6 (for $e + \text{H}^+ - \text{H}_2\text{O}(\tilde{X}) \rightarrow \text{H}(1s) - \text{H}_2\text{O}^{+(*)} + e'$) as a function of the energy of the incoming electron. The results computed with the R -matrix approach for different distances between the proton and the oxygen atom of the water molecule are represented by lines. These results are compared with those of the virtual photon approximation (green dots). The cross sections obtained from the virtual photon approximation were multiplied by 2 for visualization (see [37, 46] for details). Reprinted figure with permission from [37], Copyright (2021) by the American Physical Society. Reprinted figure with permission from [46], Copyright (2021) by the American Physical Society.

In the above equation, q is the asymmetry parameter and $\tilde{E}$ is called the reduced energy

$$\tilde{E} = 2(\epsilon - E_i) / \Gamma_i \quad (17)$$

where E_i and Γ_i are the position and width of the resonance state, respectively. In Fano theory, the asymmetry parameter q is defined as a ratio of the transition probabilities to the resonance state and to the continuum. When $|q|$ is of the order of 1, the transitions through the continuum and resonance state are of the same strength, resulting in the asymmetric Fano profile. In the limit where $|q|$ is very large, the transition to the continuum is very weak and the transition through the resonance state largely dominates. Conversely, in the case where $q = 0$ the cross section is described by a symmetrical dip around the position of the resonance state. In [37, 46], the authors found $q = 0.03$ for the lowest profile and between 0.6 and 1.0 for the higher ones, showing that around the incoming electron energy of 1.3 eV the ICEC process is mostly a direct process. It should be noted, however, that although there is nearly no transition through the resonance state, the presence of the latter leads to a substantial decrease of the ICEC cross sections in the respective electron energy range. At higher electron energies the paths through the resonance states play an equally important role as the direct one.

In [46], which is a follow-up paper of [37], the authors investigated the partial ICEC cross sections in the proton-water system. This study showed that the Fano interferences favour ionization of the water molecule in the $(3a_1^{-1}, {}^2A_1)$ state compared to direct photoionization. Ionization of water is an important process for radiation damage studies. The

results reported in [46] demonstrated that the environment around water can significantly change the ionization of these molecules and should therefore be taken into account in future investigations.

The works summarized above have demonstrated that the R -matrix method is a powerful tool to investigate ICEC in atomic and molecular clusters. It is also clear that much more has to be learned in ICEC. These works represent therefore only the very first step in the *ab initio* study of ICEC.

4. ICEC in quantum dots

As seen, the concept of ICEC is rather simple. It requires nothing beyond two spatially separated subsystems with one (or few) bound electronic levels fulfilling the ICEC energy condition. Therefore, building on the existing examples of atoms and molecules, the next logical step is to use ‘artificial atoms’ or QDs. These are nanostructures that share optical and/or other properties with naturally occurring atoms [50, 51]. A similar generalization as we show here for ICEC was possible for the related ICD process [52, 53].

In this section we explain the standard models used to compute electronic properties in few-electron QDs (section 4.1). Given the small number of active electrons, the QD models allow an execution of explicit electron-dynamics calculations of ICEC. This has in the past been done with the multiconfiguration time-dependent Hartree method (MCTDH, cf section 4.2). Investigations so far targeted ICEC involving only two electrons, one in each QD, where direct ICEC has been observed (section 4.3). Moreover, a novel resonance-enhanced pathway has been discovered and analyzed in connection with the ICD (sections 4.4 and 4.5).

4.1. Modelling paired semiconductor quantum dots

QDs are semiconducting, solid-state materials shrunk to nanometer size that were first experimentally obtained by Chang *et al* [54] and by Reed *et al* [55]. Numerous nanoscale materials have been developed since then [10, 56]. The very common GaAs semiconductors (doped with Al or In) are our focus here. Other common III–V semiconductor QDs are made of InP [57, 58]. Significant examples of II–VI semiconductors are CdS [11], ZnO, or ZnS [58] and even silicon-based materials [59] have been designed and created relying on the advanced silicon manufacturing technology. Finally, it should be highlighted that carbon-based structures are promising candidates that aim to provide ecologically responsible and sustainable technological applications [60, 61].

The electronic structure is determined by the material. Given its effective mass m^* and the dielectric constant ϵ_r of a typical semiconductor ($\epsilon_r \approx 10\epsilon_0$ and $m^* \approx 0.05m_e$), the effective Bohr radius $a^* \approx a_0 \frac{\epsilon_r m_e}{\epsilon_0 m^*}$ of an artificial hydrogen atom, i.e. a single-electron spherical QD, is about 10 nm (see chapter 5 of [62] for an introduction to effective-mass theory).

Effectively, QDs are structures whose conduction band states are occupied only by a few active electrons. Occupation with conduction band electrons results from optical excitation,

charging via electromagnetic fields [57, 63], or doping [64]. The QDs can thus be described by a simple model potential that confines electrons in a potential (e.g. square well, Gaussian, etc).

The simplicity of these systems readily enables QD design via geometry and size. Another means of control and design these nanostructures is by employing more than one QD [57, 65–67]. In this case, the simplest system of interacting QDs is a pair, which can be categorized in two groups as a function of interaction strength. Coupled, or double, QDs (DQD) are molecule-like constructions, where the orbitals resemble molecular orbitals. Conversely, paired QDs (PQDs) are more distant and, as a consequence, they exhibit atom-like, separate orbitals in each QD; electron exchange can be excluded here. Since ICEC is clearly identified for well-separated sites, this section focuses on PQDs.

In figure 10(a) the ICEC process in general Gaussian binding potentials is visualized as it applies to PQDs. An electron impinging from the left is captured by the left potential into its L_0 level while the right potential, originally binding an electron on the R_0 level, is ionized. The energy conservation

$$E_T = E_{R_0} + \varepsilon = E_{L_0} + \varepsilon', \quad (18)$$

applies [20] (see also equation (3)).

In equation (18) the energies of the incoming (i) and the outgoing (f) electrons are defined through their associated momenta $p_{i,f}$ according to $\varepsilon = p_i^2/2$ and $\varepsilon' = p_f^2/2$ with the mass being unity in our effective atomic units. $\Delta E = E_{R_0} - E_{L_0}$ is here the transferred excess energy. Depending on the relative energy of the two levels involved, L_0 and R_0 , the emitted electron can have a higher ($\Delta E > 0$) or lower ($\Delta E < 0$) momentum than the initial one, $\varepsilon' = \varepsilon + \Delta E$.

Many experimental devices used in transport studies embed the QD in a nanowire, a nanostructure with quasi-dimensional geometry [57, 68–71]. Hence we propose to study the two-electron effective-mass model for a PQD in a nanowire. The Hamiltonian is explicitly given by

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2) = \hat{h}(\mathbf{r}_1) + \hat{h}(\mathbf{r}_2) + \frac{1}{\varepsilon_r |\mathbf{r}_1 - \mathbf{r}_2|}, \quad (19)$$

where ε_r in the Coulomb interaction term is the relative dielectric permittivity and

$$\hat{h}(\mathbf{r}_i) = -\frac{1}{2m^*} \nabla_i^2 + V_c(x_i, y_i) + V_l(z_i), \quad (20)$$

is a one-electron Hamiltonian in which

$$V_c(x_i, y_i) = \frac{1}{2} m^* \omega^2 (x_i + y_i)^2 \quad \text{and} \quad (21)$$

$$V_l(z_i) = -V_L e^{-b_L(z_i + R/2)^2} - V_R e^{-b_R(z_i - R/2)^2}, \quad (22)$$

are the transversal confined and the longitudinal open potentials, respectively. R is the distance between the centres of the QDs, $b_{L,R}$ are parameters quantifying the sizes of the left (L) and right (R) QDs, and $V_{L,R}$ represent their energetic depths.

Since our main goal is to provide a simple model in which ICEC is clearly spotted, we proposed to solve the above general nanowire model in the strong lateral confinement regime. This allows to derive a set of effective one-dimensional working equations. In fact, if V_L and V_R are both much smaller than $\hbar\omega$, one can prove that the wave function ansatz,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(z_1, z_2) \phi_0(x_1, y_1) \phi_0(x_2, y_2), \quad (23)$$

reproduces very well the 3D model results [72], provided that ϕ_0 is the 2D harmonic oscillator ground state. Using (23), a two-particle one-dimensional Hamiltonian can be found for $\psi(z_1, z_2)$ (an example of what is called envelope function [73]), where the Coulomb term is replaced by the effective interaction,

$$V_{\text{eff}}(z_{12}) = \sqrt{\frac{\pi}{2}} \frac{1}{l} e^{\zeta^2} (1 - \text{erf}(\zeta)), \quad (24)$$

which depends on $\zeta = |z_1 - z_2|/\sqrt{2}l$ and the electron–electron distance scaled by the confinement size $l = \sqrt{\langle \phi_0 | x^2 | \phi_0 \rangle}$. This term has no divergence at $\zeta = 0$ (for finite l) and scales as $\frac{1}{|z_1 - z_2|}$ for long electron distances.

4.2. MCTDH for electron dynamics

The numerical demonstration of the inter-QD Coulombic electron capture could, in principle, be done by means of electronic-structure theory through consideration of the initial and final states only, which can be many if continuum is concerned. However, an explicit electron dynamics description, achieved through the explicit solution of the time-dependent Schrödinger equation, can be numerically advantageous regarding the description of the electronic continuum, despite the potentially higher computational cost arising from the time propagation. Furthermore, they provide complementary physical insight into the process.

Several explicit electron dynamics methods exist [74], but, whatever the choice to describe ICEC, the method has to be flexible to properly describe different kinds of electronic states. Indeed, the ICEC process involves free electrons (captured and emitted) as well as bound electrons in the initially and finally occupied QD orbitals. In our case, MCTDH is the method of choice owing to its versatility in describing such quickly changing character of the electrons; for more details we refer the reader to the first works on the method and the book [75–77]. One of the main reasons behind this is the use of a time-dependent basis (with an underlying time-independent discrete-variable representation) in combination with compact (low-rank) sum-of-products *ansätze* for the representation of all quantities involved in the MCTDH dynamics such as operators or, in particular, the wavefunction. It should be highlighted that the latter can be readily antisymmetrized.

In the specific example of a QD in a wire with quasi one-dimensional confinement, the initially scattering electron is defined as a one-dimensional Gaussian wavepacket,

$$f_{WP_i}(z) = \frac{1}{\sqrt{\Delta z} (2\pi)^{1/4}} e^{-1/4(z-z_0/\Delta z)^2} e^{ip_i(z-z_0)}, \quad (25)$$

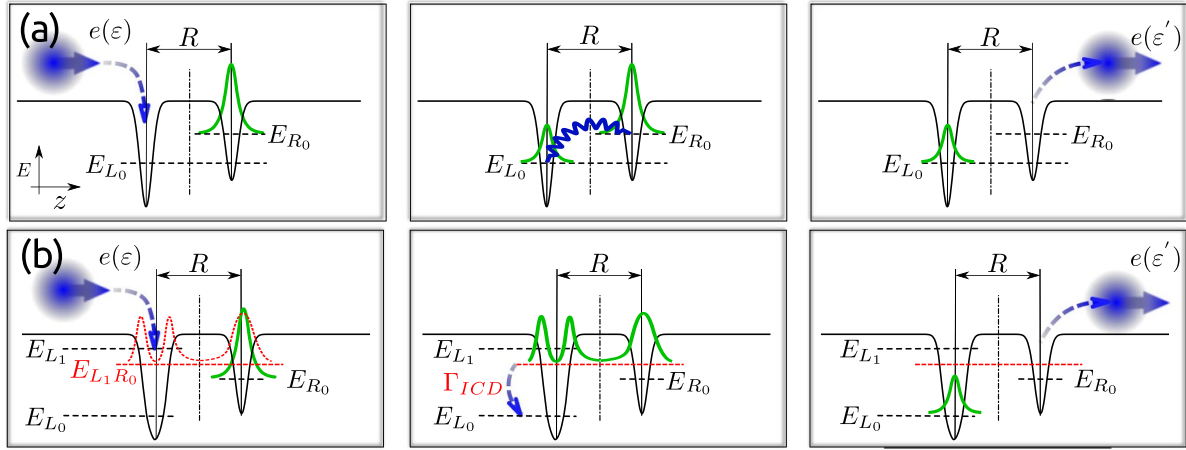


Figure 10. Schematic representation of two-electron ICEC processes in QDs. (a) In direct ICEC, the left QD captures a free electron (blue left) with kinetic energy ε into the level L_0 . Simultaneously, the excess energy is transmitted and the electron from the R_0 level of the neighbouring QD is emitted with energy ε' . (b) In the resonance-enhanced ICEC process the capture of the electron $e(\varepsilon)$ from the left occurs into the resonance state L_1R_0 , which is delocalized over both QDs and decays via ICD, releasing likewise an electron of energy ε' .

with an initial spatial width Δz approaching on the z axis from z_0 with the initial momentum p_i . Note that the Gaussian is spatially broad when compared to the bound R_0 function. So in order to avoid the overlap of both single-electron initial functions, the Gaussian has to be placed relatively far from the QD pair, i.e. the absolute value of z_0 needs to be large, leading likewise to a significantly larger grid as known from the previous ICD MCTDH investigations [52]. It should be emphasized that such large one-dimensional grids lead to computational and numerical issues when dealing with high-dimensional calculations. Hence, the utilization of tensor decomposition methods is imperative [78], whether in a grid-based [79] or grid-free [80] form.

With respect to the electronic wavefunction, the two single-electron wavefunctions, the Gaussian and the R_0 eigenfunction, combine antisymmetrically into the triplet state

$$\Psi(z, z', t=0) = 1/\sqrt{2} (f_{WP_i}(z) \phi_{R_0}(z') - \phi_{R_0}(z) f_{WP_i}(z')). \quad (26)$$

The propagation can most illustratively be followed through the visualization of the time evolution of the electronic density $\rho(z, t) = \int |\Psi(z, z', t)|^2 dz'$, from which momenta of the initial and final wavepackets can be qualitatively deduced. Furthermore, this quantity directly provides the relative importance of the different channels as well as the relative timings.

A quantitative analysis is available through the measurement of the electron flux into complex absorbing potentials (CAPs) [81]. The CAPs themselves, $\hat{W}_{\mp} = -i\eta(z \pm z_{\text{cap}})^n \Theta(z \pm z_{\text{cap}})$, prevent electrons from artificial reflection at both ends of the grid. $\Theta(z)$ is the Heaviside function and the intensive strength parameter η is chosen as to minimize both reflection and transmission through the CAP, as this maximizes the absorption of density. To measure the ICEC electron only (not any non-reactive incoming electron), we use the projected flux [82],

$$g_{L_0}(\tau) = 2 \int_0^\infty \langle \Psi(t) | P_{L_0}^{(1)} \hat{W}_+^{(2)} P_{L_0}^{(1)} | \Psi(t+\tau) \rangle dt. \quad (27)$$

This quantity records only the absorption of one electron in positive z direction (W_+), while the other is bound to the L_0 state. One can normalize the projected flux in relation to the energy spread, $|\Delta E_{WP_i}(E_T)|^2$, of the initial wavepacket giving with that a reaction probability (RP) of [82],

$$RP = 100 \times \frac{2\text{Re} \int_0^\infty g_{L_0}(\tau) e^{-iE_T\tau} d\tau}{\pi |\Delta E_{WP_i}(E_T)|^2}. \quad (28)$$

It should be highlighted that this quantity is wavepacket independent.

4.3. Direct ICEC

The first case in which ICEC was observed with MCTDH was the scenario shown in figure 10(a) [72, 83]. As an illustrative example, we consider two GaAs QDs of size ≈ 10 nm separated by a distance of $R \approx 100$ nm and with $\Delta E = 1.55$ meV. The size of impinging wavepacket is $\Delta z_{WP_i} \approx 100$ nm and it has an energy of $\varepsilon_{WP_i} = 1.542$ meV (see [84] for more details).

The visualization of the electron density as function of z and time (see figure 11) clearly shows how the incoming wavepacket approaches the R_0 -bound electron represented by a thin density around $z = R/2$, the latter remains qualitatively unchanged over time. The scattering electron impinges from beyond $z = -980$ nm with a much broader spatial width distribution. Within 15–18 ps in time the ever widening wavepacket reaches the bound electron and Coulomb repulsion causes it to be scattered back to a large extent. However, a small fraction of the electron density leaves the PQD system to the right with a momentum of $p_f = 0.0485$ meV·ps nm⁻¹, at the instant of the interaction. This change in momentum perfectly matches the expectation for ICEC in a case where $\Delta E > 0$; note that under different energy settings a decelerating ICEC process is likewise possible [85]. This constitutes the first manifestation of ICEC in an electron dynamics calculation [72, 83].

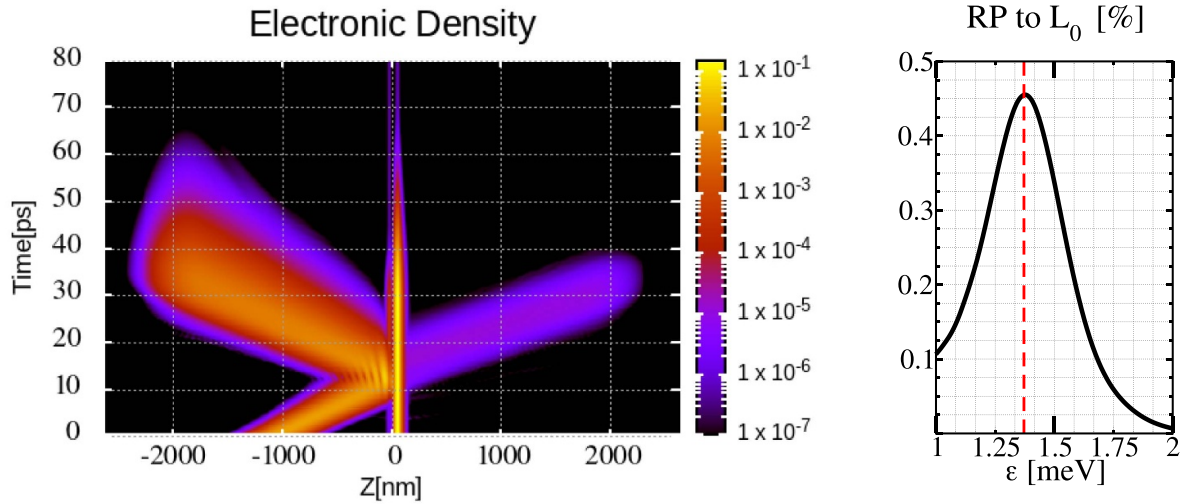


Figure 11. Time-dependent electronic density for an ICEC process in a PQD and its corresponding reaction probability. Note that the incoming electronic density from the left has a different slope than the emitted ICEC electron to the right, indicating the inelastic momentum transfer derived from equation (18). The reaction probability shows a Gaussian shaped energy dependence with a peak value of $\approx 0.5\%$. Reproduced from [72]. © IOP Publishing Ltd. All rights reserved.

As a second analysis, the RP for ICEC was calculated according to equation (28). It is a function of the energy of the incoming electron with a near-Gaussian shape that peaks at one certain $\varepsilon_i^{(\text{peak})}$. With a 0.5% value, the maximal RP is very low but nonetheless proof that an intricate process such as ICEC in QDs is possible. The RP distribution as a function of ε implies two things. First, incoming electrons of different velocities can undergo ICEC, each at its own probability. Second, there is an energy selectivity for ICEC. A comparison of system parameters reveals that $\varepsilon_i^{(\text{peak})}$ locates at $\varepsilon_i^{(\text{peak})} \approx E_{L_0} - 2E_{R_0} = 1.37$ meV which in turn maps back to the total energy during ICEC, $E_T^{(\text{peak})} = -\Delta E$.

Another analysis to confirm the inelastic scattering quality of the direct ICEC process is via the Gaussian shape of the energy-resolved projected flux representation [86]. Figure 12(a) shows predominantly the setting (b_L parameter different from the default introduced above) of a direct ICEC process. Here the expected Gaussian peak ‘G’ appears at the total energy, i.e. at $E_T = -2.2$ meV.

4.4. Resonance-enhanced ICEC in quantum dots

With the notion of ICEC enhancement in mind (cf section 2) [20, 25], which is presumably caused by additional resonance channels, we also sought such resonance-enhanced pathways in QDs with the tool of reaction probability as well as the projected energy-resolved flux.

From previous research, we know that an L_1R_0 state can decay via ICD into a final state with an electron in the L_0 level and the other in the ionization continuum, as depicted in panel (b) of figure 10 [52]. L_1 is the upper of two states in the left QD, for which the explicit energies $E_{L_0} = -5.22$ meV and $E_{L_1} = -0.57$ meV were used. They locate below and above, respectively, the sole level R_0 of the right QD. They satisfy

both the ICD energy condition $E_{L_1} - E_{L_0} \geq |E_{R_0}| = 2.92$ meV and the ICEC energy condition $E_T = E_{R_0} + \varepsilon = E_{L_0} + \varepsilon'$ with $\Delta E > 0$. To keep the investigation simple, a direct capture into the L_1 level is energetically forbidden by design.

By simple inspection of the density evolution in figure 13 we can observe how the impinging electron approaches the PQD and is progressively captured into the final L_0 level. This process includes the instantaneous backscattering along a persistent slope as well as direct ICEC with a reduced slope according to the velocity of the ICEC electron. In addition, over a time interval about 2.5 times as long as the completed backscattering, electron density is leaving the paired QD system predominantly to the left side. It fades exponentially and is a clear indication that the ICD resonance has temporarily been populated. A second indication for this is that at the position $-R/2$ where the left dot is located, a double-peaked density, signature of the excited L_1 level, appears at the moment of scattering.

The reaction probability energy distribution in this example is much more narrow and peaks at a lower $\varepsilon_i^{(\text{peak})} = 0.59$ meV, to which it is difficult to assign a shape. This means that the energy selectivity is significantly enhanced for ICEC. But in that case it happens at a significantly higher probability of 22%. Comparison with the energy parameters of the system shows that such strong enhancement is obtained when $E_T \approx E_{L_1R_0} = 0.61$ meV + E_{R_0} (solid green line in figure 13). Again the time-energy uncertainty allows one to obtain a resonance decay time of $\tau_{\text{ICEC}}^{\text{GaAs}} = 14.26$ ps, which is ten times slower than direct ICEC. Hence, the resonance enhanced ICEC process is highly probable and more selective in energy than direct ICEC. However, it is slower than direct ICEC.

The RP alone and likewise the energy-dependent projected flux of the given case are not fully clear on the interplay among the direct and the resonance-enhanced ICEC channel. Comparison among different settings (here different b_L)

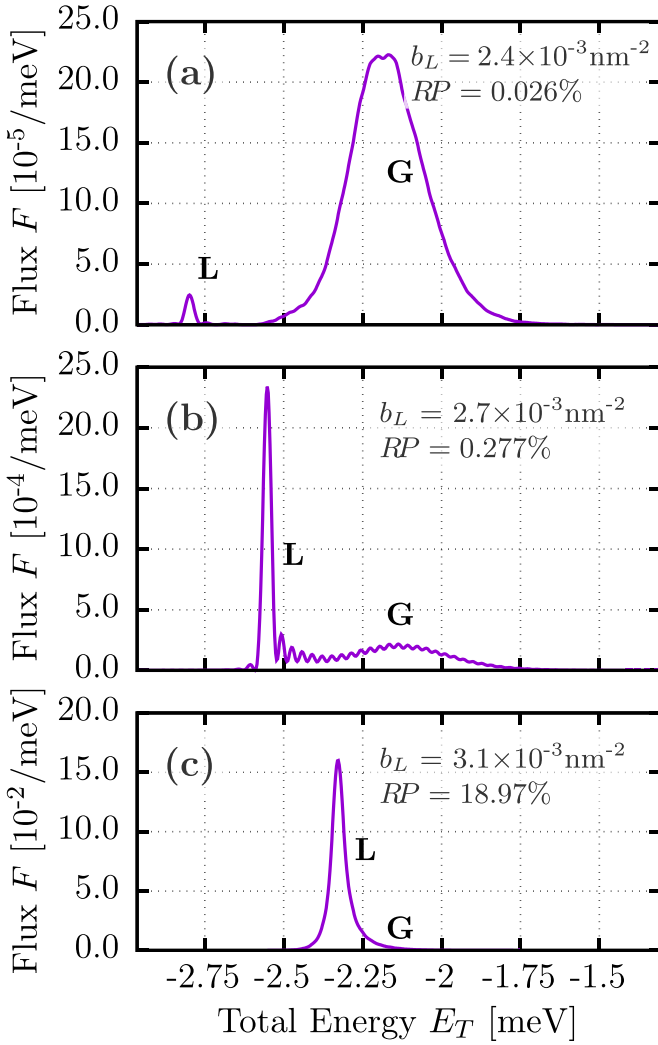


Figure 12. All panels show the flux as function of the total energy E_T for different b_L giving different RP's. 'G' and 'L' denote a Gaussian and Lorentzian flux and refer to the direct ICEC and the resonance-enhanced ICEC process, respectively.

returns figures of still rather low RP, with two distinct peaks (figures 12(a) and (b)). One is the Gaussian peak of direct ICEC at constant energy position, the second one indicated with 'L'. From panels (a) to (c) the energy $|E_{L_1}|$ decreases and the 'L' peak energy follows this change from $E_T = -2.798$ meV over -2.549 meV to -2.324 meV while the peak intensity more and more dominates over that of the Gaussian and enhances at the same time the overall flux. The peak is rationalized to be a Lorentzian, the standard distribution after the decay of a resonance state [87]. Including the ICD rate Γ_{ICD} it reads

$$F_{L_0}^{\text{res}}(E) \propto \frac{\Gamma_{ICD}^2}{4(E - E_{L_1 R_0})^2 + \Gamma_{ICD}^2}. \quad (29)$$

Despite the maximized energy-resolved flux at the overlay of the Gaussian and the Lorentzian, in our investigations this was not necessarily the case with the largest ICEC probability. And indeed there is a second effect determining the

wavepacket-independent quantity RP: it is the definition of the initial wavepacket. It enters the RP (equation (28)) through the denominator that incorporates division by $|\Delta E_{WP_i}(E_T)|^2$, the energy widths. This means that all the contributions of the flux that are exactly in the range of initial wave packet give a reduced RP even when the two ICEC peaks perfectly overlay [86]. This signifies that ICEC from a wavepacket is not only sensitive to confinement sizes, but likewise to the incoming wavepacket. In contrast, if the large Lorentzian contribution is located at the tail of ΔE_{WP_i} , the RP experiences an enhancement even though the electronic structure is unfortunate in the sense that the direct and the resonance-enhanced ICEC channels do not overlay inside the width of the wavepacket.

4.5. Interplay of direct and resonance-enhanced ICEC

If different QD energy levels are to be compared, then it is advisable to use an energetically wide wave packet. This was done in a study where the quantum-size effect [56, 88, 89] was explored to determine the overall largest possible RP in a PQD. To this end a scan over about 8000 QD geometries (b_L, V_L, R) was undertaken, which resulted in an empirical understanding of the interdependence of the ICEC probability on single-electron level energy relations useful for the *a priori* decision on whether a certain atomic, molecular, or nano-sized system is capable of ICEC or not [72].

Several conditions were set up and probed in the given parameter space. Of the trivial ones, one is the boundary conditions $E_{L_1} = 0$, which determines whether there is a second energy level L_1 in the left dot that could be available to resonance-enhanced ICEC or not. Following directly on that is the condition that $L_1 R_0$ is a resonance (and no bound) state given through $E_{L_1 R_0} = E_{R_0}$. The existence of the resonance gives rise to another three conditions that determine the position of the largest RP, each at least on a distinct area of the total (b_L, V_L) parameter plane. One of these conditions is $E_{L_1 R_0} = E_{L_0} - E_{R_0}$, which reflects the coincidence of the direct (accelerating) and the resonance-enhanced ICEC channel. As in this scan, the direct (slowing) ICEC via occupation of the L_1 level is not excluded, also the coincidence of that channel and resonance-enhanced ICEC leads to high rates following the energy condition $E_{L_1 R_0} = E_{R_0} - E_{L_1}$. Last, but not least, also the two direct channels can occur simultaneously even without the resonance pathway involved. Then $E_{L_1} - E_{R_0} = E_{R_0} - E_{L_0}$ must hold.

The efficiency can be explored by scanning the maximum RP (colour bar in figure 14) for each configuration on the (b_L, V_L) planes for different R 's. The above conditions can be confirmed from areas of zero RP and a branching line of maximal RP (close to a Y shape). The largest RP exceeds 50% for $R = 88.14$ nm as shown in figure 14. It occurs when the conjunction of three conditions is synergistic and enables the stronger increase of the ICEC probability. The three conditions for the largest RP can be evaluated *a priori* from single-electron energies alone [72]. This prediction is applicable to all possible systems beyond models and can apply to atom and molecule pairs as well.

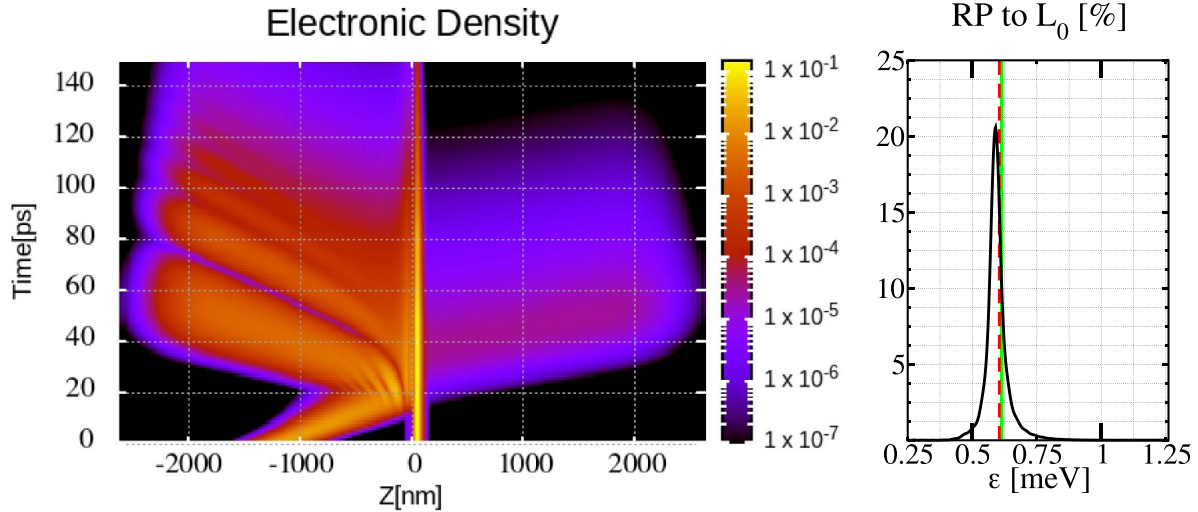


Figure 13. Time dependent electronic density for a resonance-enhanced ICEC process in a PQD and its corresponding reaction probability. Note that the reaction probability shows a Lorentzian shaped energy dependence in this case and has peak value of 20%, this is 40 times larger than direct ICEC. The time-energy uncertainty allows to obtain a resonance decay time of $\tau_{\text{ICEC}}^{\text{GaAs}} = 14.26$ ps, which is ten times slower as direct ICEC. Hence, an interesting trade off between a slower, selective and highly probable process (resonance enhanced) and a faster (direct) process is present. Note that the range in this figure is the same as in figure 11 (1 meV). The green solid line indicates the $E_{L_1 R_0}$ resonance energy at $\varepsilon_i = 0.61$ meV. Reproduced from [72]. © IOP Publishing Ltd. All rights reserved.

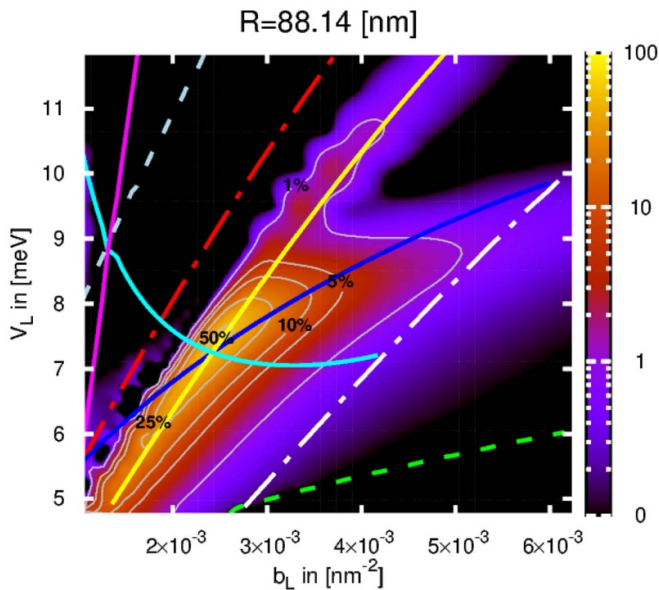


Figure 14. Maximum of the RP as a function of the geometric parameters b_L (inverse of left QD size) and V_L (left QD depth). The contour grey lines indicate the RP level. The coloured lines corresponds to some energy condition that is fulfilled along it. The best geometry is at the crossing of the cyan line ($E_{L_1 R_0} = E_{L_0} - E_{R_0}$, resonance enhanced ICEC to L_0) and the yellow line ($E_{L_1 R_0} = E_{R_0} - E_{L_1}$, resonance-enhanced ICEC to L_1). Reproduced from [85]. © IOP Publishing Ltd. All rights reserved.

4.6. Conclusion and outlook on QD ICEC research

Likewise to atomic and molecular systems, electron capture itself is an emerging topic in QD research. And much like what is found for atoms/molecules, capture happens by redistribution of the excess energy onto other degrees of freedom.

While the energy transfer to the phonons of the system is most prominent [90–95], energy transfer to the electrons can lead to different follow-up settings: Excited states that store multiple excitons [96] or induce Auger relaxations [97], as well as the ICEC process.

The studies on ICEC in QDs were, however, not only driven by the fundamental curiosity on the generality of the process, on its enhancement factors, and on a fundamental understanding of its drivers [52, 72, 83, 85, 86]. One significant aspect is its anticipated application in modern miniature electronic devices. With miniaturization such devices are beyond the regime of classical physics and governed by quantum-mechanical effects [98]. Among the four basic elements of all nano-electronic devices [99]—resistor, capacitor, (light-emitting) diode and transistor—ICEC may be instrumentalized in a transisting one. Certain electrons are blocked while others can enter the device via capture depending on their velocity. If successfully captured, the electronic structure of the device determines if the ICEC electron proceeding through the circuit at the other side is faster or slower than the captured ones. Its speed can be tuned by setting the relative energies in the QD pair, e.g. electrostatically. In the context of miniaturization, the QDs in nanowires [57, 68–71] analysed in the presented works are optimal candidate structures to achieve the recent goal of further miniaturization in nano-electronics, where systems on chips operating different logic functionalities are expected to be as small as 2 nm in 2025 [100].

5. Perspectives

5.1. Experimental demonstration of ICEC

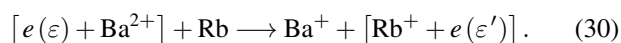
As a first remark, it should be emphasized that there is no experimental observation yet of ICEC processes. Measuring

ICEC is hence an obvious and crucial need. At the time of writing this review, several international groups are working on the development of the techniques necessary for such measurements. One of the simplest systems to demonstrate ICEC might be $\text{Ne}^+ @ \text{He}_n$ (see section 3.2). Indeed, such systems are simple enough to be prepared and, as shown above, ICEC would provide a clear signature in the electron energy loss spectrum. We hope that this topical review will help them in their efforts and will encourage more groups to tackle such difficult but essential tasks.

5.2. ICEC in ultracold atoms

Beyond rare-gas clusters $\text{Ne}^+ @ \text{He}_n$ (see section 3.2) as a possibility of future experimental observation of ICEC, it appears of interest to investigate electron dynamics of ICEC in the domain of ultracold-atom physics. This domain has seen a considerable growth but has not been addressed in the context of non-local continuum energy transfer processes. Of particular interest could be the investigation of a heteronuclear ultracold atom–ion pair [101], where an analogous experiment appears within reach [102–105].

A frozen-core description is therefore proposed as initial venture into atomic assisted electron-capture dynamics in which an ionic Ba^{2+} core could be modelled with an incident electron e of kinetic energy ε in a local subsystem, that is in interaction with an assisting distant subsystem of an ionic Rb^+ core with a reactive outer valence electron initially bound in the rubidium $5s$ level to form a ground state rubidium atom, Rb [101]. The assisting rubidium subsystem can then mitigate electron capture on the barium site through ICEC by emitting its modelled outer valence electron with kinetic energy ε' :



Promising indications of electron capture stemming from interatomic energy transfer are already seen in this quantum-dynamical exploratory work at experimentally relevant macroscopic interatomic distances [106]. This present research project ventures into the first highly-correlated electron dynamics of two free electrons in a three-dimensional continuum. It aims at exploring a complementary research direction within current initiatives in the scientific community of electron dynamics in the context of inter-Coulombic processes. As such, it is expected to yield results that will shed light on findings from other research endeavours.

5.3. ICEC in microhydrated cations

Radiation from the Sun, radioactive substances, or x-rays can cause damage in living organisms. Indeed, it has been recently found that the damage due to radiation can spread exponentially through the human body by a cascade of decay processes of chemical compounds which release numerous slow electrons [38, 39]. Decay processes related to radiation damage include Auger decay, interatomic Coulombic decay, superexchange ICD, and ETMD, which have attracted considerable attention over the last decade [107].

Free electrons are genotoxic agents since they can break up chemical bonds by attaching themselves to neighbouring atoms. This is called DEA [26–28]. As shown above, ICEC leads to a strong enhancement of electron attachment. ICEC might thus be a general process that controls damage of living cells under ionizing irradiation. It is therefore highly relevant to investigate ICEC in biological model systems and thus reveal its potential impact on radiation damage.

Overall, up to 60% of the adult human body consists of water and even the bones contain 31% water [108]. Furthermore, metals [109] are comprised by about 2% in total. In their ionic form they regulate fluid flow into and out of body cells, blood pressure, muscle contractions and nerve signals and heart activity. More importantly, they are the key ingredient to complex chemical structures called coordination compounds, in which a central metal atom is surrounded by groups of non-metal molecular structures, called ligands. An important example for such complexes is haemoglobin, which contains a central iron atom. It gives blood its red colour and carries the vital oxygen through our body to the organs.

Metal cations are biologically abundant and they are expected to be strongly ICEC-active owing to their large electron affinity. As discussed in section 2.2.3, it was indeed shown using the virtual photon approximation that ICEC is very efficient in micro-hydrated cations [36]. To gain more insights, one can/should however go beyond the virtual photon approximation and investigate *ab initio* systems containing a metal cation and few water molecules. The *R*-matrix method, as discussed above in section 3, is the primary choice for these studies and has proven successful in initial proof-of-concept explorations for microhydrated proton (see in particular section 3.3) [37, 46].

5.4. Impact of the nuclear dynamics on ICEC

As shown above, the theoretical approaches employed to describe ICEC range from analytical models to *ab-initio* electronic structure and dynamical calculations. A common assumption in these approaches is that nuclei remain fixed during ICEC. However, based on observations on the related ICD process [110, 111], nuclear dynamics should play an important role changing the efficiency and/or influencing the final state of the system. Investigating the impact of the nuclear dynamics on ICEC is therefore crucial. However, this requires a significant methodological and numerical development. At time of writing this review, the authors are implementing such project which is supported by a German and French collaboration through an ANR-DFG program.

Two kinds of nuclear degrees of freedom should be investigated: in the first, one can focus on the impact of the nuclear motion along the axis between the ICEC donor and acceptor species. As shown above, the ICEC cross sections vary substantially along this distance and a large effect of the nuclear dynamics is therefore expected. A second kind of nuclear motion that can impact ICEC is the intramolecular vibrational motion of the donor and/or acceptor species. For these modes, it is difficult to anticipate the effects on ICEC processes.

Data availability statement

No new data were created or analysed in this study.

Acknowledgments

We thank the ANR-DFG for financial support of the QD4ICEC project. The respective DFG Grants are BA 3770/5-1 and FA 1989/1-1; the ANR Grants are ANR-22-CE92-0071-01 and ANR-22-CE92-0071-02. E F gratefully acknowledges financial support from the research and service facility LISA⁺ of the University of Tübingen. F M P gratefully acknowledges partial financial support of CONICET(PIP-KE311220210100787CO), SECYT-UNC (Res. 233/2020) and ANPCYT-FONCYT, PICT-2018 No. 3431. A B is grateful for the funding received through the Freigeist fellowship (89525) from Volkswagen Foundation. Financial support for the work of A M has been gratefully received from the Research Foundation—Flanders (FWO) within the Junior Postdoctoral Fellowship Mandate 1232922N, and from the Fulbright Schuman-Program Award issued by The Commission for Educational Exchange between the United States, Belgium and Luxembourg. This recognition does not imply that the Government of the United States or any agency representing it has endorsed the conclusions or approved the contents of this publication.

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Ultrafast Resonant Interatomic Coulombic Decay Induced by Quantum Fluid Dynamics

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(Received 3 September 2020; revised 5 January 2021; accepted 19 February 2021; published 12 April 2021)

Interatomic processes play a crucial role in weakly bound complexes exposed to ionizing radiation; therefore, gaining a thorough understanding of their efficiency is of fundamental importance. Here, we directly measure the timescale of interatomic Coulombic decay (ICD) in resonantly excited helium nanodroplets using a high-resolution, tunable, extreme ultraviolet free-electron laser. Over an extensive range of droplet sizes and laser intensities, we discover the decay to be surprisingly fast, with decay times as short as 400 fs, nearly independent of the density of the excited states. Using a combination of time-dependent density functional theory and *ab initio* quantum chemistry calculations, we elucidate the mechanisms of this ultrafast decay process, where pairs of excited helium atoms in one droplet strongly attract each other and form merging void bubbles, which drastically accelerates ICD.

DOI: [10.1103/PhysRevX.11.021011](https://doi.org/10.1103/PhysRevX.11.021011)

Subject Areas: Atomic and Molecular Physics,
Chemical Physics,
Superfluidity

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I. INTRODUCTION

In molecular and condensed-phase systems, interatomic processes offer a means for localized energy or charge to disperse to the surrounding environment. The diversity of these processes often makes it tedious or impossible to obtain a complete picture of the ionization mechanisms and dynamics. Alternatively, free, weakly bound nanosystems, such as van der Waals (vdW) clusters, can be used to study such interatomic interactions in a well-controlled manner. In particular, the study of vdW clusters irradiated by intense extreme ultraviolet (XUV) free-electron laser (FEL) radiation has led to the observation of numerous novel interatomic processes [1–3]. An important type of interatomic process known as interatomic Coulombic decay (ICD) [4] has been widely studied in weakly bound systems [5–7]. In cases where local Auger decay is energetically forbidden, an excited atom or molecule releases its excitation energy by transferring it to a neighboring atom or molecule, which can result in its ionization. In general, ICD is a prominent decay mechanism in a multitude of systems, specifically those of biological relevance [8–11]. A key parameter in determining the importance of ICD in a nanosystem is its decay time, which is directly linked to its efficiency. With the advent of seeded FELs and the availability of intense, tunable XUV radiation [12,13], new types of resonant ICD [14] have been observed in vdW clusters [15–18], where at least two photons are absorbed and energy is exchanged between neighboring excited atoms. More importantly, FELs offer the capability to directly follow the dynamics of ICD in the time domain. So far, ultrafast time-resolved measurements have been limited to ICD in vdW dimers [19,20]. Although vdW dimers, a type of weakly bound molecular system, are of fundamental interest, they can by no means exemplify the complex dynamics occurring in a nanoparticle or condensed-phase system where multiple intermolecular processes can play a critical role.

He nanodroplets serve as model nanosystems in numerous research fields, since they can bridge the gap between simple atomic and molecular systems and extended, condensed-phase systems [21]. Because of their extremely weak interatomic binding, superfluid nature, and simple electronic structure, He nanodroplets are an ideal environment to study interatomic processes in a homogeneous liquid [15,16,18,22,23] or in a well-defined heterocluster, as is the case for doped He nanodroplets [24–29]. When the He environment is excited, a void bubble, or “cavity,” is formed around the excited atom [30,31], which can freely move about the droplet. This phenomenon is a general feature in closed-shell systems where the local environment tends to exert a repulsive force on electrons or impurities with a low electron affinity due to the Pauli exclusion principle. This interaction induces the formation of cavities around the impurities and possible clustering or assembly thereof [32]. A similar, although more complicated, process of cavity formation occurs in classical fluids and is responsible for

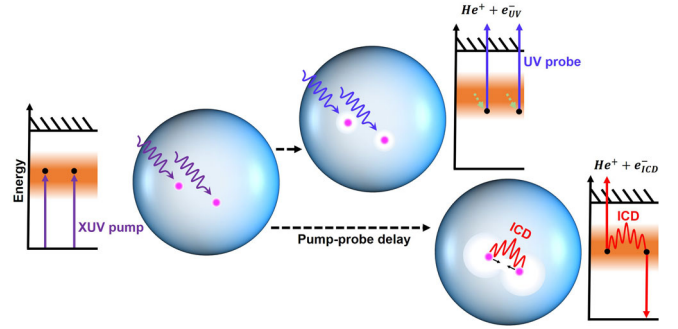


FIG. 1. Atoms in the He droplet are excited to the $1s2p$ droplet band by the XUV pump pulse. After internal relaxation, bubbles are formed around the excited atoms. The two bubbles are accelerated toward each other, leading to a merging of the bubbles and ICD (bottom scenario). A time-delayed UV pulse is used to probe the dynamics of the process. If the UV probe pulse comes before ICD occurs, the pulse ionizes the excited atoms, thereby halting the ICD process (top scenario at short pump-probe delay). The He droplet is represented by the large blue circles, and excited atoms and bubbles are represented by pink and white circles, respectively. The energy-level diagrams illustrate the energetics of processes. Using photoelectron spectroscopy, one can differentiate ICD electrons and UV-ionized electrons as shown in Fig. 2.

molecular solvation. For example, in water, the so-called hydrophobic effect determines whether a molecule is individually hydrated or assembles into a larger structure [33].

Here, we report on time-resolved measurements of resonant ICD in nanoparticles, where He droplets are chosen as a model system. The process is schematically shown in Fig. 1. Atoms are excited by an XUV pulse tuned into resonance with the $1s2p$ droplet band ($h\nu = 21.6$ eV) [34]. The pulse creates multiple excited atoms in the droplet which can decay via ICD; i.e., the energy from one excited He atom, He^* , is transferred to another He^* , which, in turn, is ionized. A second, time-delayed UV pulse can directly ionize the excited atom(s) in the droplet, thereby interrupting and halting any interatomic decay processes. Over an extensive range of droplet sizes and laser pulse energies, the decay mechanism is found to be much faster than predicted by theory [14]. Even more surprisingly, the decay rate is nearly independent of the number of excited atoms per droplet, although theory predicts a very strong dependence on the internuclear distance [14]. To understand these discrepancies, the experimental results are modeled using a combination of time-dependent density-functional theory (TDDFT) [35,36] and *ab initio* calculations of the doubly excited He^*-He^* pair potentials as well as the ICD widths.

We discover that the ICD dynamics are largely determined by the attractive interaction of closely spaced He^* atoms and by the formation of bubbles around them. The latter strongly accelerates the ICD via the merging of overlapping bubbles. Previous experimental work on bubble formation in He droplets [31] focuses on the relaxation

of one excitation in a droplet, which forms a single bubble in the course of its relaxation. In contrast, here, the focus is on ultrafast dynamics between two bubbles, which facilitates the ICD process. Overall, the relevance of our findings is (i) realizing that, in a condensed-phase system, ICD is not only determined by the electronic interaction of the two atoms involved, but it can be crucially influenced by the response of the surrounding medium, and (ii) the resulting ICD time is drastically reduced to the femto-second range, in contrast with previous expectations that this type of ICD is much slower, i.e., tens to hundreds of picoseconds [14,17].

II. EXPERIMENT

This work is performed at the low density matter end station [37] of the seeded FEL FERMI, in Trieste, Italy. The FEL photon energy (21.6 eV) is tuned via the seed laser, undulator gaps, and other machine parameters, yielding a pulse length of approximately 100 fs full width at half maximum (FWHM) [12,13]. The measurements are taken over two separate periods with different experimental conditions. The second set of parameters is given in parentheses. The FEL pulse energy, varied from 0.1 to 50 μJ , is determined upstream by gas ionization, taking the nominal reflectivity of the optical elements in the beam transport system into account. The diameter of the FEL focus is 250 μm FWHM. The UV probe pulse is obtained from a frequency-tripled (-doubled) Ti:sapphire laser [$h\nu' = 4.8$ (3.2) eV] with a pulse energy of 50 (200) μJ and a focus diameter of 250 μm FWHM. A tin filter of 160 nm thickness is used to suppress higher-order harmonic radiation. The cross-correlation between the FEL and the probe laser is 200 fs FWHM, measured by resonant two-photon ionization of He gas. A supersonic jet of He nanodroplets is produced by expansion of high-pressure He gas through a pulsed, cryogenically cooled Even-Lavie nozzle. By varying the expansion conditions (backing pressure and nozzle temperature), the mean cluster size is varied in the range of $\langle N \rangle = 10^2$ – 10^5 He atoms [38]. The nanodroplet beam is perpendicularly crossed by the FEL and UV beams at the center of a velocity map imaging spectrometer [37]. The electron kinetic energy distributions are reconstructed using the maximum entropy velocity Legendre reconstruction method [39].

III. RESULTS AND DISCUSSION

Figure 2(a) shows the distributions of electron kinetic energy E_e emitted by resonantly excited He droplets as a function of the delay between XUV pump and UV probe laser pulses. The mean droplet size is $\langle N \rangle = 76\,000$ atoms, and the XUV intensity is 2.8×10^9 W/cm². At low kinetic energies ($0 < E_e < 2$ eV), the electron distribution is created by resonant two-photon ionization (2PI) in He nanodroplets. At short delays, $\Delta t < 1$ ps, the distribution

shows the droplet-induced relaxation dynamics of He* from the XUV-excited $1s2p$ state to the $1s2s$ state [31]. At higher kinetic energies ($15 < E_e < 18$ eV), resonant multiphoton ICD is observed according to the reaction [14–16,18]



Here, He_{N-2} denotes the He droplet, and e_{ICD} is the ICD electron. A discussion of the electronic states which initiate this type of ICD is given in the Appendix A. Since resonant ICD is a binary process, at least two excited atoms are required per droplet.

The intensities of photoelectrons (red squares) and ICD electrons (blue circles), depicted in Fig. 2(b), display opposing trends in their time evolution: The 2PI signal

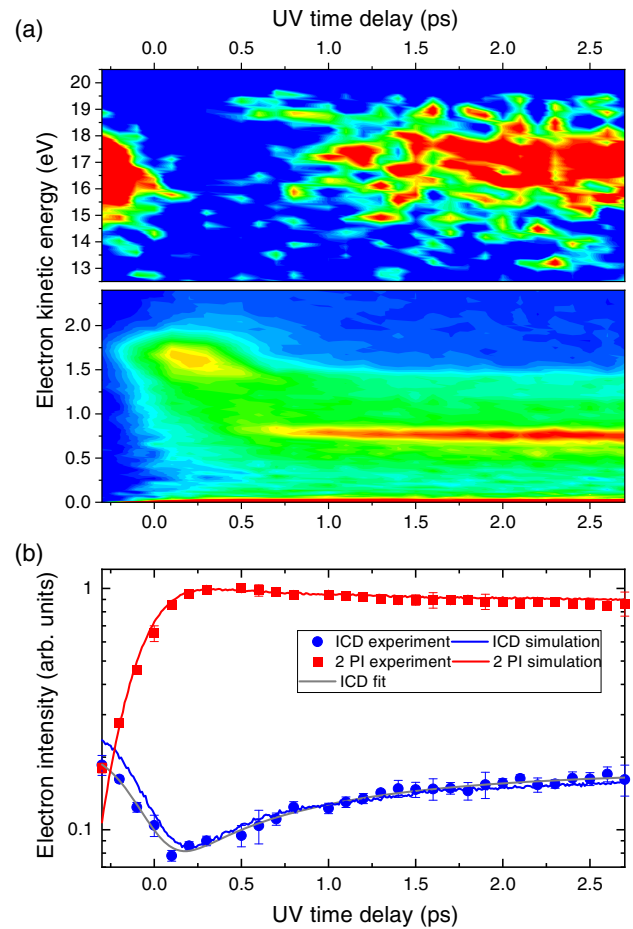


FIG. 2. (a) Time-resolved electron kinetic energy distributions of resonantly excited He droplets centered around the ICD peak (top) and the two-photon ionization (2PI) signal (bottom). (b) Projection of the intensity of the ICD peak (blue circles) and the 2PI signal (red squares) as a function of XUV-UV pump-probe delay. The experimental data are fitted with an exponential decay function convoluted with a cross correlation function (gray line). The red and blue lines show the results of a MC simulation (see the text for details). The droplet size is 76 000 atoms, and the excitation photon energy is 21.6 eV.

is enhanced at delays $0 < \Delta t < 0.2$ ps, whereas the ICD signal is depressed. This result can be rationalized by the depletion of the He^* population through photoionization by the UV probe pulse, thereby suppressing the ICD. As the pump-probe delay is increased, ICD can proceed before the He^* are photoionized and the e_{ICD} yield is replenished. Thus, the rise of the e_{ICD} yield reflects the timescale of the ICD. To quantify this process, the ICD signal is fitted with a function [gray line in Fig. 2(b)] accounting for the exponential rise as well as the pump-probe cross correlation. A thorough discussion of the fitting procedure is given in Appendix B. Figure 2(b) also shows the ICD (blue line) and 2PI (red line) data from a Monte Carlo (MC) simulation as discussed later in the text. Additional data and fits for different experimental parameters are given in Appendix C.

To systematically investigate the dynamics of ICD in He nanodroplets, pump-probe delay dependences over a wide range of He droplet sizes and XUV intensities are recorded. The latter controls the He^* excitation probability (photon flux $\times$ absorption cross section) and thereby the mean distance between He^* in a droplet. Because of the strong coupling between the FEL power, droplet size, and collective autoionization (CAI) effects [18], only a limited range of excitation probabilities (0.1%–1%) show a clearly distinguishable ICD peak, despite the broad range of droplet sizes and FEL intensities available. As the FEL intensity increases, multiple excited atoms may interact, leading to decay by CAI and formation of a nanoplasma [16]. In the transition from ICD to CAI, the ICD peak broadens and shifts to lower energies due to the formation of a collective Coulomb potential and eventually becomes dominated by low-energy thermal electrons from the nanoplasma [18].

Similar to what is shown in Fig. 2(b), each ICD delay dependence is fitted with a function to determine the time constant of the e_{ICD} evolution. The resulting ICD times τ_{ICD} and e_{ICD} yields are, respectively, plotted as red symbols in Figs. 3(a) and 3(b) as a function of the excitation probability. The corresponding MC simulation results are shown as blue dots. The e_{ICD} yield is determined from the total number of detected electrons and the He^* photoionization cross section [40]. It is normalized to the number of He^* atoms in the droplet and multiplied by 2 to account for the fact that two excitations produce one ICD electron. The resulting ICD efficiency rises from 0.09 to 0.32 in the given range of He^* excitation probability, while τ_{ICD} decreases from 1000 to 400 fs. To decouple the effect of the droplet size from the FEL intensity, we additionally perform MC simulations (see Supplemental Material [41] for details) for fixed droplet sizes. The results for small and large droplets are shown in Fig. 3 as black and gray lines, respectively. For small droplets, the ICD time is nearly constant and lower than the ICD decay times for large droplets, which show a weak dependence on the FEL intensity. The ICD efficiency shown in Fig. 3(b) rises from zero as a function

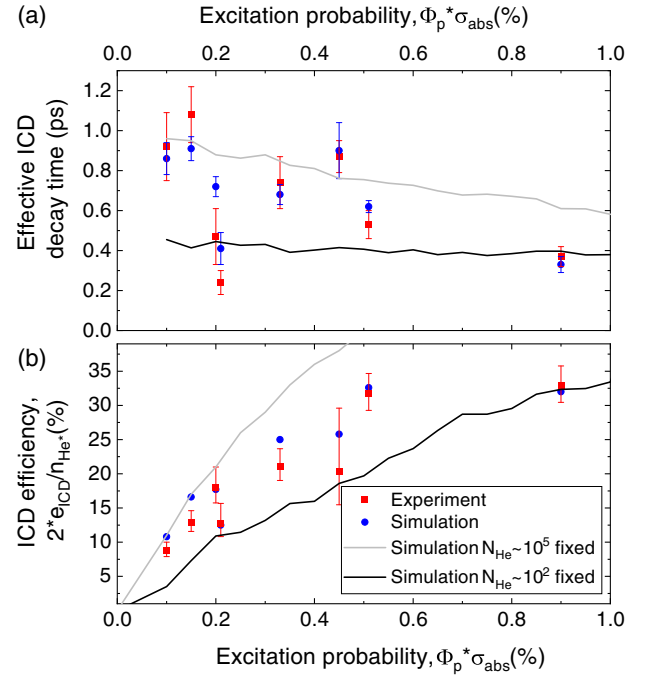


FIG. 3. (a) Effective ICD decay time and (b) ICD efficiency plotted as a function of the excitation probability (red squares). MC simulation results for the specific experimental conditions, droplet size, and FEL intensity are shown as blue dots. Additionally, to show the general trend in the simulations on the FEL intensity, the results for fixed small and large droplets are shown as black and gray lines, respectively.

of the excitation probability with a higher slope for large droplets. Overall, the MC simulations are in excellent agreement with the experimental data.

In general, the measured ICD decay times are surprisingly short ($\tau_{\text{ICD}} < 1$ ps) compared to estimates based on the virtual photon ICD model for this type of decay, which yield 52 ps for the fastest channel [14]. Furthermore, previous static measurements predict this type of ICD to be much slower, in the high picosecond range [17,28]. Further proof of the discrepancy between theory and experimental results can be seen in Fig. 4(c), which shows the ICD decay width Γ as a function of the He^* - He^* distance. $\Gamma(d)$ is calculated by the Fano-CI-Stieltjes method [42] for all possible combinations of electronic states populated during droplet relaxation [28,31] (see Supplemental Material [41] for details). Γ , which is inversely proportional to the decay time τ_{ICD} , shows a very strong dependence on the He^* - He^* distance. On the other hand, the measured τ_{ICD} , in Fig. 3(a), shows only a weak dependence on the He^* excitation probability, which is a measurable quantity proportional to the mean He^* - He^* distance. The observed ultrafast ICD rates, in the femtosecond regime, can be explained only through an additional mechanism that brings the two He^* atoms into close contact. Excitation migration [43,44], excitation

delocalization [45], and hole hopping have been discussed extensively over the years, especially in the context of Penning ionization [44,46]. While fast excitation transfer, akin to exciton hopping, can explain the high efficiency of the Penning process [44], it cannot account for the short ICD lifetime. Delocalization of excitations over an extended region of the He droplet as a consequence of exciton hopping would lead to a reduced local spatial overlap and, thus, to low ICD rates. Besides, the large variation of the interatomic distances between He atoms in the droplets due to the large zero-point motion as well as many-body quantum effects may also limit delocalization [45,46]. Unfortunately, the problem of excitation transfer in superfluid He has not yet been addressed theoretically, despite the numerous experimental Penning ionization studies. That said, an additional mechanism is required that brings two He^* into close contact such that ICD takes place at short distances.

Aside from the fast delay-time dependence of the ICD signal, we observe that the e_{ICD} yield in most cases does not fully rise to the level measured at negative delays within the full range of pump-probe delays; see Appendixes B and C. This result indicates that some of the He^* decay by ICD much more slowly than the experimentally observed asymptotic value from which we deduce τ_{ICD} . Furthermore, the observation that the ICD efficiency never exceeds 35% in our experiments points at a competing

relaxation channel that prevents the majority of He^* from decaying via ICD.

To better understand the response of He nanodroplets to multiple excitations and to rationalize our experimental findings, TDDFT simulations are performed [31,35,36,47] for the motion of He^* pairs. To keep the simulations tractable, we consider bulk superfluid He, which is coupled to the He^* pair self-consistently. Because of the light mass of the He^* “impurities,” they must be treated quantum mechanically with the potential term given by the He^* -droplet interaction. To include the interaction between the two He^* atoms, the He^* - He^* pair potentials are calculated using highly correlated *ab initio* methods (see Supplemental Material [41] for details).

Figure 4(a) shows the time evolution of the 2D cuts of the He density distribution (yellow-red area) when the two excited He atoms are initially separated by $d_0 = 10 \text{ \AA}$ (pink-green dots). Animations of these simulated dynamics for various initial conditions are included in Supplemental Material [41]. Upon excitation, bubbles form around them due to the repulsion between the Rydberg electrons and the surrounding closed-shell He atoms [30,31,47–49]. As the bubbles grow and the two He^* atoms weakly attract each other, the bubbles eventually overlap and merge into one large bubble. The salient feature is that, shortly after the two bubbles coalesce, the two He^* are strongly accelerated toward each other. This process is facilitated by the merging

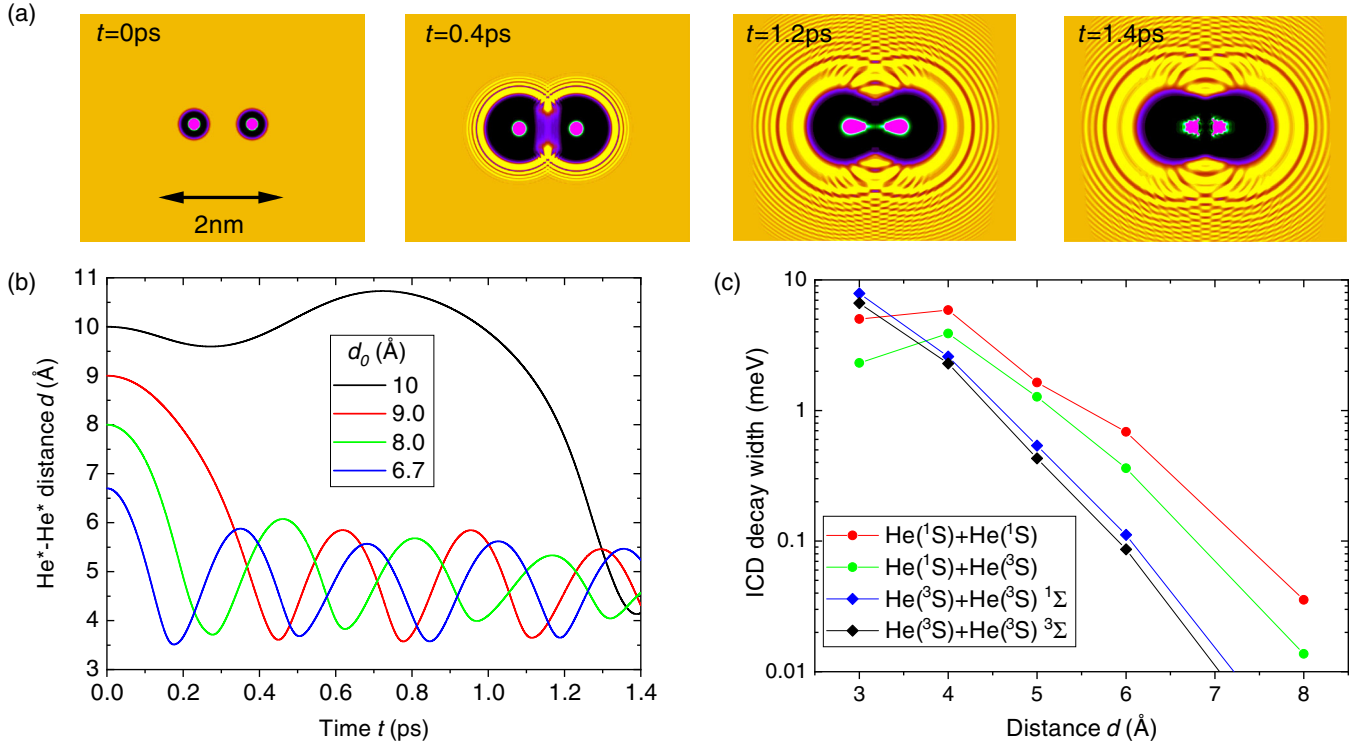


FIG. 4. (a) Snapshots of the He density evolution around two He^* centers separated initially by $d_0 = 10 \text{ \AA}$. The probability distribution of He^* is represented as pink dots, and the black areas show the void bubbles forming. (b) Evolution of the He^* - He^* distance d for various values of the initial distance d_0 . (c) Calculated ICD widths for various combinations of $1s2s$ -excited He^* atomic states.

of the bubbles where the He^* reach interatomic distances $d < 4 \text{ \AA}$ within 400 fs for all initial distances d_0 up to 9 $\text{\AA}$; see Fig. 4(b). As ICD is not explicitly included in the TDDFT simulations, the He^* pair continues vibrating at a short distance due to the attractive He^*-He^* potential. However, within the first half cycle of the vibration, the ICD decay width reaches $\Gamma(d = 4 \text{ \AA}) = 5.9 \text{ meV}$, corresponding to a characteristic ICD time $\tau_{\text{ICD}}^{\text{theo}} = 110 \text{ fs}$ for the $\text{He}^*(^1S) + \text{He}^*(^1S)$ pair, which has the largest branching ratio in the droplet relaxation [28,31]. Thus, all He^* pairs with $d_0 \lesssim 10 \text{ \AA}$ actually decay via ICD within $t \lesssim 1.4 \text{ ps}$ with a probability of near unity. Thus, we conclude that the decay in this particular system is largely determined by the quantum fluid dynamics of the merging bubbles, as well as the pairwise attraction of excited atoms.

For larger initial distances ($d_0 > 10 \text{ \AA}$), the time between He^* excitation and bubble merging quickly increases to $t > 10 \text{ ps}$, and, therefore, ICD becomes very slow. This result explains the observed incomplete replenishment of the e_{ICD} signal at long pump-probe delays. The question remains why not all He^* decay by ICD, in the absence of the probe pulse. It is known that radiative decay is not expected to play a significant role, since the lifetime is in the nanosecond range [30,50]. Previous experimental and theoretical studies show that, following the bubble formation, some of the He^* remain weakly bound to the He droplet surface, where they eventually form He_2^* excimers [51], whereas others are directly ejected from the droplets [31,48,52]. Once a He^* detaches from the droplet, it can no longer decay via ICD, but it still contributes to the photoionization signal. Based on our measurements [Fig. 3(b)], the fraction of ejected He^* is estimated to be larger than 50%. The competition between direct ejection and ICD for initial distances $d_0 > 10 \text{ \AA}$ is strongly dependent on the droplet size.

The ICD dynamics in He nanodroplets are largely governed by the motion of He^* driven by the bubble dynamics and the interatomic He^*-He^* potential, competing against the ejection of surface He^* from the droplet. To account for the aforementioned effects, a simplified MC simulation based on $\Gamma(d)$ is developed. The results are displayed in Fig. 3(b). The He droplet is treated as a homogeneously packed sphere of He atoms represented by equally sized spheres. An initial number of He^* , according to the XUV intensity and the He droplet absorption cross section [34], are placed at random positions within the droplet. Then, for each He^* , the following conditions are tested. If the distance to the droplet surface $d_S < 7.5 \text{ \AA}$ and the distance to the nearest-neighbor He^* $d_0 > 9.5 \text{ \AA}$, then the He^* is ejected. If $d_S > 7.5 \text{ \AA}$ and $d_0 < 15.5 \text{ \AA}$, then the He^* undergoes ICD; the ICD probability is then calculated based on $\Gamma(d)$ according to the trajectory $d(t)$ obtained from the TDDFT simulations. If $d_S > 7.5 \text{ \AA}$ and $d_0 > 15.5 \text{ \AA}$, the He^* does not decay by ICD and only

photoionization is possible. The probe pulse is implemented by converting the He^* into photoelectrons at a rate consistent with the experimental estimate. The values $d_0 = 15.5 \text{ \AA}$ and $d_S = 7.5 \text{ \AA}$, used as criteria for ICD enhanced by bubble merging and He^* ejection, respectively, are deduced from the TDDFT simulations. Additionally, when the same simulation is performed for fixed positions of He^* , the ICD time constants are 1–2 orders of magnitude longer than the experimental values, thus demonstrating the importance of ultrafast bubble dynamics and the attractive He^*-He^* potential. An in-depth discussion of these simulations is given in Appendix D.

Overall, the conceptual leap presented in our results show that resonant ICD in a superfluid nanosystem is predominantly driven by the ultrafast dynamics of the medium surrounding the interaction centers ($\text{He}^* + \text{He}^*$, in this case). Previous work on (nonresonant) ICD considers only the dynamics of the interaction centers, not their environment. While this assumption is valid for small systems like dimers and crystalline clusters, in extended condensed-phase systems such as liquids and superfluids, the response of the local environment has to be taken into account. Our work directly demonstrates that the mesoscopic dynamics may drastically enhance the ICD rate. This result has implications for biological systems where the local aqueous medium surrounding the biomolecules may crucially impact the decay rate when being subjected to radiation damage by ICD [10,11].

IV. CONCLUSIONS

In summary, we have performed time-resolved measurements of resonant ICD in He nanodroplets. Over a wide range of droplet sizes and laser pulse energies, we have found the decay to be as fast as 400 fs and to have little dependence on the density of excited states, in contrast to the strong dependence of the predicted ICD decay width on the distance between excitations. Our simulations have shown that the ICD dynamics are largely determined by the pairwise attraction of excited atoms, as well as the peculiar response of He droplets to multiple resonant excitations. The formation of bubbles around the excitations and their subsequent merging accelerates ICD, whereas the ejection of excited state atoms from the droplet competes with it. Thus, using He droplets as a model system bridging molecular and condensed-phase sciences, we have demonstrated that resonant ICD in the condensed phase is governed by ultrafast relaxation mechanisms that couple electronic and nanofluid translational degrees of freedom. These results pave the way for time-resolved measurements of more complex intermolecular decay processes involving He excited state dynamics in doped He droplets, such as ICD-mediated single or double ionization of molecules and clusters [26–28].

Although He nanodroplets are a unique type of quantum fluid, our findings of the bubble dynamics could have

implications for other classical fluid systems where charge, excitations, or impurities can freely move throughout the medium. The dynamics of bubbles, also known as cavities in water, are responsible for a wide variety of fundamental processes, such as protein assembly into functional complexes in biological systems [33] or the behavior of impurities in metals, relevant to materials science [32]. Although classical fluids are more complex than He nanodroplets, intermolecular electronic decay and bubble dynamics are highly relevant processes in these systems. The range of intermolecular decay mechanisms extends beyond ICD [11] to processes such as electron transfer mediated decay [53], exciton-exciton annihilation [54], singlet fission [55], and Förster resonance energy transfer [56]. The rates of these decay mechanisms could be enhanced through bubble dynamics. In this regard, future time-resolved studies where the electronic decay and bubble dynamics could be controlled by laser excitation are of broad interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Carl-Zeiss-Stiftung, the Deutsche Forschungsgemeinschaft (DFG) under Grant No. MO 719/14-2, within the frame of the Priority Program 1840 “Quantum Dynamics in Tailored Intense Fields” (MU 2347/12-1 and STI 125/22-2), and the Carlsberg Foundation. TDDFT work has been performed under Grant No. FIS2017-87801-P (AEI/FEDER, UE) (M. B. and M. P.). A. C. L. and N. B. acknowledge the support of the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, Grant No. DE-SC0012376. D. R. acknowledges funding from Leibniz Grant No. SAW/2017/MBI4 and NCCR MUST of the Swiss National Science Foundation (SNF). J. E. acknowledges support from the National Science Foundation Grant No. DMR-1828019. J. M. E. acknowledges support from Ministerio de Ciencia e Innovación of Spain through the Unidades de Excelencia “María de Maeztu” Grant No. MDM-2017-0767.

APPENDIX A: HIGH-RESOLUTION ICD ELECTRON KINETIC ENERGY DISTRIBUTION

Information about the electronic states involved in the ICD process is encoded in the kinetic energy distribution of ICD electrons. Figure 5 shows a high-resolution electron spectrum measured at the photon energy $h\nu = 23.7$ eV. At this photon energy, the $1s4p$ excited state of He droplets is resonantly excited [34]. The mean droplet size is set to 5×10^5 He atoms. Besides the large signal component at low kinetic energy resulting from CAI [16], an additional peak is observed around 16 eV with a shoulder near 15 eV, which is due to ICD. For comparison, we add vertical lines showing the expected ICD electron energies, $E_{e,ICD}$, for

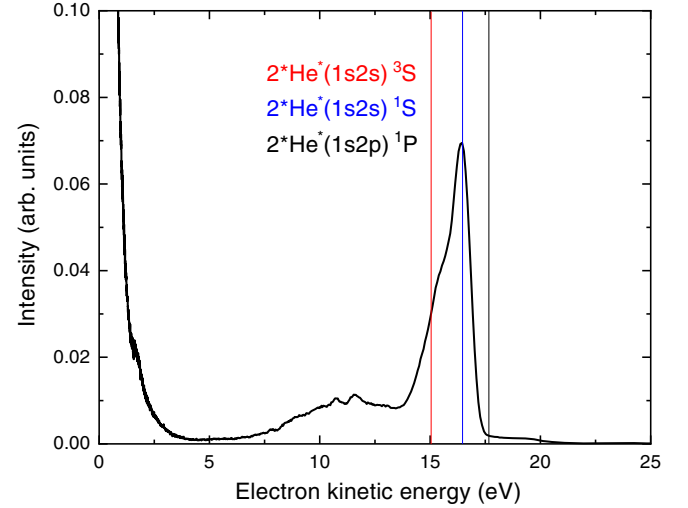


FIG. 5. Static (XUV only) electron kinetic energy distribution measured at $h\nu = 23.7$ eV. The vertical lines depict the nominal values of ICD electron energies for pairs of He* atoms in the three lowest excited states.

pairs of He* in the lowest excited states $2s2s$ 1^3S and $2s2p$ $1P$ according to

$$E_{e,ICD} = 2E_{He(1s2s,p)} - E_{i,He}. \quad (A1)$$

Here, $E_{He(1s2s,p)}$ is the energy of the $1s2s, p$ states of the He atom, and $E_{i,He}$ is the He ionization potential. Clearly, the $1s2s$ $1S$ state is the dominant state producing ICD electrons. The $1s2s$ $3S$ state and He* excimer states (broad feature around $E_{e,ICD} = 11$ eV) also contribute but to a lesser extent. Although this electron spectrum is measured at a different excitation energy than those in the main text, ICD electrons appear to originate mostly from the same He* states. This result is due to fast electronic relaxation, as previously observed in experiments using high-harmonic laser radiation [57], FEL [18,31], and synchrotron radiation [24,28].

APPENDIX B: FITTING OF ICD ELECTRON YIELDS

The time-dependent ICD electron intensities are fitted with a convolution of the pump-probe cross correlation function obtained by resonant two-photon ionization of He gas and an exponential decay leading to the following function:

$$I(t) = I_0 - A \operatorname{erfc}\left\{\frac{\sigma^2 - \tau(t - t_0)}{(\sqrt{2}\sigma\tau)}\right\} \times \exp[-(t - t_0)/\tau] - B \operatorname{erfc}[(t - t_0)/(\sqrt{2}\sigma)]. \quad (B1)$$

This model is the simplest analytic function that reproduces the experimental measurements and is consistent with a more rigorous model of the pump-probe dynamics of ICD processes [58]. The exponential function describes the rise

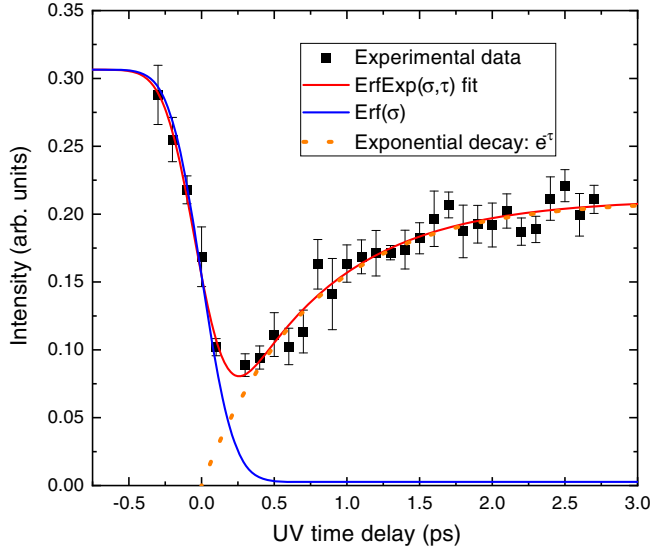


FIG. 6. Fitting of experimental time-resolved ICD data (black squares) with the function from Eq. (B1) (red curve). The components of the fit are illustrated separately: error function (blue curve) and exponential decay (orange dotted line).

of the electron counts for long delay times. Thus, the exponential decay constant τ represents the effective ICD time. The parameter σ represents the cross-correlation width of the two overlapping laser pulses and is fixed to the value measured by resonant two-photon ionization of He gas. The time-zero value t_0 is constrained to 0 ± 15 fs in order to account for possible drifts in the FEL timing. The free parameters I_0 , A , and B reflect the total ICD intensity for $t \rightarrow -\infty$, $t \rightarrow \infty$, and the maximum depletion $I_{\min}$.

Figure 6 displays a fit of a typical experimental measurement. In addition to the full fit curve (red), we show the separate contributions from the error function (blue line) and exponential decay (orange dots).

APPENDIX C: ADDITIONAL EXPERIMENTAL DATA

To give a better overview of the experimental results and systematics, in Fig. 7(a), we show additional pump-probe ICD electron yields measured under different experimental conditions. The red symbols correspond to small droplets with high excitation density. The resulting ICD curve is characterized by a fast time variation, as the mean interatomic distance between excited atoms is small, $d < 10$ Å, and, thus, ICD is fast. The black curve is for an intermediate excitation density and intermediate droplet sizes. The blue curve is for large droplets combined with a low excitation density. Replenishment of the ICD electron signal after depletion is slower, as ICD mostly occurs for pairs of He* with larger initial separation. Figure 7(b) shows the results of the MC simulation for the same parameters as in the experiment. The good agreement

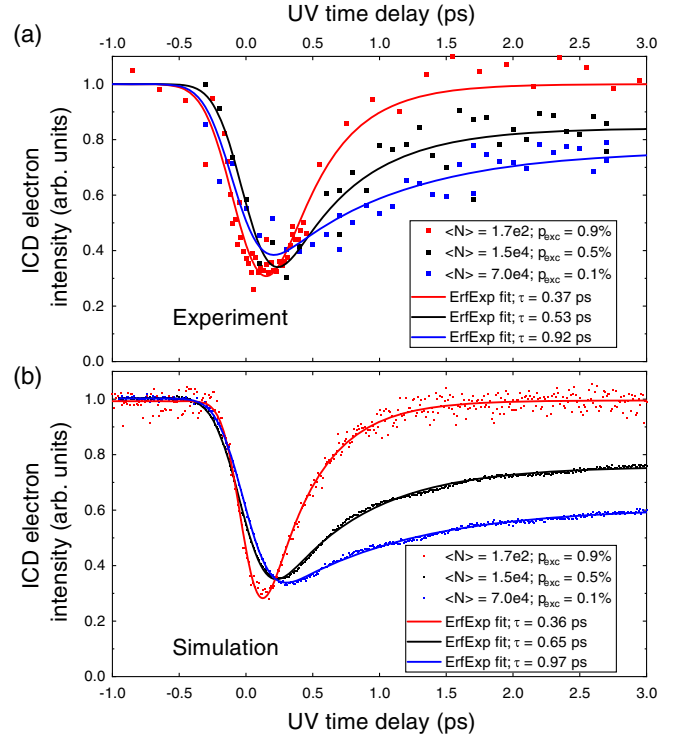


FIG. 7. (a) Experimental ICD electron intensities as a function of XUV-UV pump-probe delay with corresponding exponential fits for three different droplet sizes and excitation densities. (b) Simulated ICD electron intensities and fits for conditions similar to those of the upper panel.

shows that our model captures the main aspects of the pump-probe ICD dynamics.

APPENDIX D: THE EFFECT OF ATOMIC MOBILITY ON ICD TIMESCALES

Besides providing a deeper understanding of our experimental findings, MC simulations additionally allow us to ask more fundamental questions about the process, which cannot be directly addressed through experiment. For instance, how important is the mobility of the He* atoms in the ICD process? To benchmark our simulations against a model system where the ICD rate is entirely given by the initial distances between He*, we carry out simulations where the He* positions are held fixed. Figure 8(a) shows the simulated ICD electron intensity for stationary He* atoms as a function of the UV time delay for three different excitation probabilities (blue lines). For comparison, the experimental data are shown as black squares, and the corresponding MC simulation assuming mobile He* atoms is shown as a red line. As can be clearly seen, the simulated dynamics for fixed He* positions proceed on much longer timescales compared to the experimental data, thus showing the critical importance of atomic mobility in the ICD process. To further illustrate this point, Fig. 8(b) shows the relative

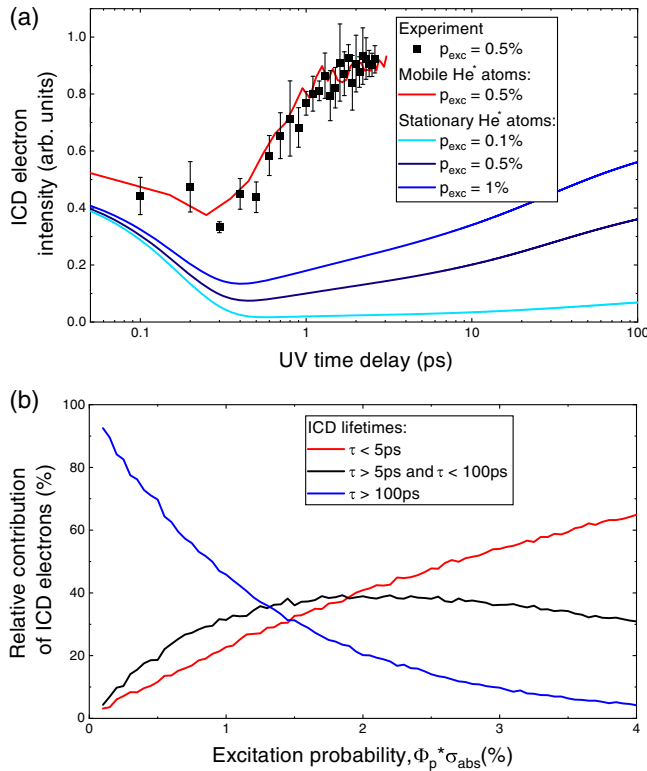


FIG. 8. (a) Simulated ICD electron intensities as a function of the UV time delay for fixed He^* positions with different excitation densities (blue curves). For comparison, the experimental data are shown as black squares, and the corresponding MC simulation assuming mobile He^* atoms is shown as a red line. (b) Relative contribution of ICD electrons broken up into three different ICD lifetime intervals as a function of excitation probability for fixed He^* positions.

contribution of ICD electrons broken up into three different ICD lifetime intervals as a function of excitation probability for fixed He^* positions. For low excitation probability ($\lesssim 1\%$), the ICD lifetime would primarily be $\tau > 100\text{ ps}$, which is dramatically longer than what is shown in Fig. 2 for similar experimental conditions. Only for high excitation probability ($\gtrsim 2\%$) do shorter ICD lifetimes ($\tau < 5\text{ ps}$) significantly contribute. We note that at 2.5% excitation probability the transition from ICD to CAI occurs, in agreement with previous findings [18].

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Cite as: J. Chem. Phys. **152**, 224307 (2020); <https://doi.org/10.1063/5.0002243>

Submitted: 23 January 2020 . Accepted: 21 May 2020 . Published Online: 12 June 2020

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Cite as: J. Chem. Phys. 152, 224307 (2020); doi: 10.1063/5.0002243

Submitted: 23 January 2020 • Accepted: 21 May 2020 •

Published Online: 12 June 2020



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ABSTRACT

Auger–Meitner processes are electronic decay processes of energetically low-lying vacancies. In these processes, the vacancy is filled by an electron of an energetically higher lying orbital, while another electron is simultaneously emitted to the continuum. In low-lying orbitals, relativistic effects can not, even for light elements, be neglected. At the same time, lifetime calculations are computationally expensive. In this context, we investigate which effect spin–orbit coupling has on Auger–Meitner decay widths and aim for a rule of thumb for the relative decay widths of initial states split by spin–orbit coupling. We base this rule of thumb on Auger–Meitner decay widths of $\text{Sr}4p^{-1}$ and $\text{Ra}6p^{-1}$ obtained by relativistic FanoADC–Stieltjes calculations and validate it against Auger–Meitner decay widths from the literature.

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I. INTRODUCTION

Electronic decay processes are initiated by sub-outer valence ionization or excitation. The system relaxes by filling the vacancy with an electron and transferring the excess energy to another electron of the system, which is emitted. One example of electronic decay processes is the well known Auger process. It was first discovered by Lise Meitner¹ and later rediscovered by Pierre Auger.² In order to give credit where credit is due and following the renaming suggestion of Ref. 3, we will refer to it as the Auger–Meitner (AM) process. It is found in a variety of different systems such as atoms, molecules, and solids. As a consequence, Auger–Meitner spectroscopy is used for surface analysis in metallurgy, quality analysis of microelectronics, and basic studies of chemical reaction mechanisms.⁴ Since the advent of short extreme ultraviolet (XUV) pulses, it has been a test process for time-resolved measurements^{5,6} and is often observed as a side product of modern x-ray spectroscopies.⁷ Another relevant and interesting process is the family of Interparticle Coulombic Decay (ICD) processes.^{8–10} A deeper understanding of the effects that determine the decay widths of electronic decay processes, which can lead to rule of thumbs, which do not require expensive lifetime calculations, will be helpful for the interpretation of the observed spectra. This article aims to provide such a rule of thumb for relative Auger–Meitner decay widths of initial states split by spin–orbit coupling. In the following, we will assume processes initiated by ionization.

In order for the Auger–Meitner process to occur, two criteria need to be fulfilled: the energy and the coupling criterion. To fulfill the energy criterion, the final state energy is required to be lower than the energy of the singly ionized initial state. If this is not the case, the channel defined by a certain doubly ionized final state is closed and the corresponding fragments of the channel are not observed after the decay. To fulfill the coupling criterion, the decay process needs to be fast enough to prevail over other energetically accessible decay pathways such as radiative relaxation or coupling to nuclear degrees of freedom. It, hence, contains the information whether an energetically allowed process can be expected to be observed experimentally or not. Therefore, a typical study of electronic decay processes consists of two parts:

- determination of the kinetic energy of the secondary electron and, as a consequence, which decay channels are open.
- calculation of the decay width $\Gamma = \frac{\hbar}{\tau}$, which is proportional to the decay rate $\frac{1}{\tau}$ and inversely proportional to the lifetime τ .

The primary ionization often removes an electron from an atomic core, where relativistic effects are stronger than those for valence electrons. The relativistic effects can, therefore, be expected to play a crucial role for the understanding of the systems' lifetimes. Phenomenologically, the relativistic effects can

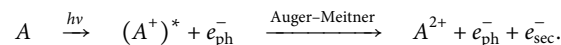
be divided into spin-orbit coupling and scalar-relativistic effects. The spin-orbit coupling requires the system to be described in terms of the total angular momentum j rather than the orbital momentum l and the spin momentum s . Thereby, the non-relativistically degenerate states of one particular l value are split into states characterized by $j = l \pm s$ with two different energies.¹¹ The scalar-relativistic effects result in spatial contractions of all orbitals in one-electron systems. In many-electron systems, however, those orbitals with density close to the nucleus are more strongly contracted than the others. They thereby shield the positive charge of the nucleus from the electrons in other orbitals, which are, therefore, effectively spatially decontracted compared to the non-relativistic solutions. Therefore, as a rule of thumb, s and p are spatially contracted, while d and f orbitals are spatially decontracted.¹¹

The initial and final state energies can be obtained using a variety of quantum chemical approaches. One is known in the literature as the Algebraic Diagrammatic Construction^{12–17} (ADC), which is also available for a fully relativistic treatment.^{18–20} The calculation of the respective lifetimes is a challenging task because it requires the description of both bound and continuum electrons. The bound electrons are best described by wavefunctions with $\mathcal{L}^2$ boundary conditions, while continuum electrons far away from the atom are best described by plane waves. This imposes the technical choice between (a) describing the entire atom using an $\mathcal{L}^2$ basis, (b) describing the entire process using a grid, and (c) describing the bound electrons using an $\mathcal{L}^2$ basis and the continuum electron using a grid. Either of these approaches faces difficulties in either describing the bound or the continuum states or some artificially constructed interface region. Traditionally, most quantum chemical program packages are based on $\mathcal{L}^2$ bases, and we, therefore, choose to describe the electronic decay processes using a large $\mathcal{L}^2$ basis for convenience.

The quantum chemical methods, which have been developed for a relativistic description of the decay widths, are the Multi-channel Multi-Configurational Dirac-Fock (MMCDF)²¹ and the FanoADC-Stieltjes.^{22,23} The MMCDF is limited to atomic systems and strongly depends on the manual selection of CI (Configuration Interaction) components to be included in the description of initial and final states. The FanoADC-Stieltjes is based on the ADC and not limited to spherically symmetric systems. It is furthermore size-consistent and includes terms up to third order in perturbation theory yielding the interaction between the initial and final state without actually calculating the states themselves. It is, therefore, a good compromise between accuracy and computational cost. At the same time, the configurations needed for the accurate description of initial and final states are determined automatically up to the implemented order of the perturbed wavefunction. The FanoADC-Stieltjes approach is implemented in the relativistic quantum chemistry package DIRAC,^{25,26} which allows us to use different Hamiltonians while keeping all other parameters constant. This allows us to computationally consider only scalar-relativistic effects using Dyall's spinfree Hamiltonian²⁶ as well as perform a fully relativistic calculation using the four-component Dirac-Coulomb (DC) Hamiltonian taking both scalar-relativistic and spin-orbit coupling into account. By comparing the results, we can extract the effect caused by spin-orbit coupling. We, therefore, choose the FanoADC-Stieltjes approach for our calculations.

In this work, we focus on the atomic Auger-Meitner process in order to exploit basic knowledge about the influence of

relativistic effects, but we expect the conclusions to hold for the molecular Auger-Meitner process and Interparticle Coulombic Decay (ICD) processes^{8–10,27} as well. The Auger-Meitner decay process initiated by photoionization can most generally be described by



A system A is ionized, while the photo-electron e_{ph}^- is emitted. After this, the actual Auger-Meitner process of the initial state A^+ can occur. An electron from an outer shell fills the vacancy, and the excess energy is instantaneously transferred to another (secondary) electron e_{sec}^- , which is subsequently emitted. The final state of the decay process is to be described by a doubly charged atom A^{2+} and the secondary electron in the continuum. In the special case, when the vacancy filling electron or the secondary electron stems from an orbital of the same shell as the initial vacancy, the process is called Coster-Kronig (CK) decay. When both are from the same shell, the process is referred to as the super-Coster-Kronig decay. These Coster-Kronig decays are characterized by very large decay widths.²⁸ We will discuss these special cases separately from the Auger-Meitner process in this paper.

We have previously shown how scalar-relativistic effects influence the decay widths of the Auger-Meitner process in noble gas atoms.²³ After primary ionization from the $(n-1)d$ orbitals, the noble gas atoms decay to np^{-2} , $np^{-1}ns^{-1}$, and ns^{-2} final states. We observed that the Auger-Meitner decay widths increased by up to 326% for radon by including scalar-relativistic effects in the calculation. This dramatic increase could be explained by the larger spatial overlap of the orbitals involved in the decay compared to non-relativistic calculations due to the contraction of the s and p orbitals of the final states.

However, the fully relativistic calculation resulted in different decay widths for the different $d_{3/2}^{-1}$ and $d_{5/2}^{-1}$ initial states split by spin-orbit coupling (see Fig. 5 of Ref. 23). The aim of this work is, therefore, to investigate the influence of spin-orbit coupling on the decay widths of electronic decay processes. For this purpose, we will study the Auger-Meitner processes of earth alkaline atoms after primary ionization from the $(n-1)p$ orbitals. The earth alkaline elements have the benefit of a single and closed shell ns^{-2} final state. This might allow us to purely observe how the spin-orbit splitting of the different initial states affects the Auger-Meitner decay width. Moreover, in the single particle picture, a Coster-Kronig decay is possible for neither of the earth alkaline elements, and thus, the pure Auger-Meitner process, where the initial states have an equal number of possible decay channels, can be observed. Having only one final state, which is not affected by spin-orbit coupling, reduces the complexity of the analysis of the results significantly.

This paper is structured as follows: in Sec. II, we recapitulate the basics of the FanoADC-Stieltjes method. We then give the computational details for our *ab initio* calculations in Sec. III. We present the results and their interpretation in Sec. IV and conclude in Sec. V.

II. THEORY

Following Wentzel²⁹ and, later, Feshbach^{30,31} and Fano³², the decay width of a decay process initiated by primary ionization is

given by

$$\Gamma = \sum_{\beta} 2\pi |\langle \Phi | \hat{V} | \chi_{\beta,\epsilon} \rangle|^2. \quad (1)$$

Here, $|\Phi\rangle$ and $|\chi_{\beta,\epsilon}\rangle$ denote the initial and final state, respectively. $\hat{V}$ is the interaction operator of the initial and final states, which in Feshbach's definition is known as H_{PQ} . The index β refers to the different decay channels, and ϵ denotes the energy of the final state. Equation (1) thereby connects the metastable initial and the continuum final states. They are constructed by partitioning the Hamiltonian into two subspaces. The initial (final) state is then an eigenfunction of this initial (final) state sub-space Hamiltonian. However, finding proper solutions to both the initial and the final states on an equal footing is a non-trivial task because they adhere to different boundary conditions. Since the final state depends on the energy of the emitted electron, any approach needs to either determine the continuum state or to mimic the final state using $\mathcal{L}^2$ -functions. While the continuum functions are normalized with respect to their energy,

$$\langle \chi_{\epsilon} | \chi_{\epsilon'} \rangle = \delta(\epsilon - \epsilon'), \quad (2)$$

the $\mathcal{L}^2$ approach is based on a discrete set of final states $|\tilde{\chi}_{E_j}\rangle$, which adhere to different boundary conditions and are normalized with respect to space (see, e.g., Ref. 33),

$$\langle \tilde{\chi}_{E_i} | \tilde{\chi}_{E_j} \rangle = \delta_{ij}. \quad (3)$$

Because of this different normalization, the decay widths are not amenable to a direct calculation. As first proposed by Hazi,³⁴ for autoionization processes, such difficulties can be solved by using the Stieltjes–Chebyshev moment theory also called Stieltjes imaging.^{35–37} It relies on the observation that the moments of order k of the projected final state Hamiltonian H_f ,

$$\mu_k = \langle \Phi | \hat{V} H_f^k \hat{V} | \Phi \rangle, \quad (4)$$

calculated from the determined discrete pseudo-spectrum are good approximations to the moments determined from the real continuum states. This can be shown by inserting the resolution of identity for the continuum states,

$$\mu_k = \sum_i \epsilon_i^k |\langle \Phi | \hat{V} | \chi_{i,\epsilon} \rangle|^2 + \int_{E_0}^{\infty} \epsilon^k |\langle \Phi | \hat{V} | \chi_{\epsilon} \rangle|^2 d\epsilon. \quad (5)$$

Since the non-zero contribution to the coupling matrix elements in the Feshbach–Fano approach stems only from an interaction region of finite size, where the $\mathcal{L}^2$ final state functions are nonvanishing, we may replace the expansion $\sum_i |\chi_{i,\epsilon}\rangle \langle \chi_{i,\epsilon}| + \int d\epsilon |\chi_{\epsilon}\rangle \langle \chi_{\epsilon}|$ by its $\mathcal{L}^2$ approximation $\sum_j |\tilde{\chi}_{E_j}\rangle \langle \tilde{\chi}_{E_j}|$ (see Ref. 38),

$$\mu_k \approx \sum_j \tilde{E}_j^k |\langle \Phi | \hat{V} | \tilde{\chi}_{E_j} \rangle|^2. \quad (6)$$

Then, the decay width can be determined through a series of consecutive approximations to the moments of increasing order k .

To achieve this kind of description, we choose the relativistic FanoADC–Stieltjes approach. Here, a proper selection of $2h1p$ intermediate state configurations is used for the description of the

continuum final state, while the rest is used for the description of the initial state. The resulting discrete pseudo-spectrum is then subject to a Stieltjes imaging procedure. An exhaustive description of the method can be found in Refs. 23 and 39.

III. COMPUTATIONAL DETAILS

The Auger–Meitner decay widths were calculated with the relativistic FanoADC–Stieltjes method implemented in the relativistic quantum chemical program DIRAC.^{25,26} We included up to third-order contributions of perturbation theory and additional constant diagrams. For each element, four-component calculations based on the Dirac–Coulomb (DC) Hamiltonian and scalar-relativistic spinfree calculations were performed for both the $(n-1)p_{1/2}$ and $(n-1)p_{3/2}$ initial states. Dylla's cv4z basis sets⁴⁰ were augmented with additional diffuse 5s5p5d3f basis functions following the Kaufmann–Baumeister–Jungen approach.⁴¹ The resulting moments were checked for numerical instabilities. Only those moments without numerical instabilities entered the interpolation scheme for the determination of the decay widths, as described in Ref. 23.

The radial orbital densities of the ions were calculated using GRASP.^{42,43}

IV. RESULTS

In order to analyze the decay processes, we first discuss the energetic accessibility of different decay channels and then present the corresponding Auger–Meitner decay widths. In Fig. 1, we present the computed single and double ionization spectra of strontium obtained by DC–ADC calculations. The main peaks of the ionization from $\text{Sr}4p_{3/2}$ and $\text{Sr}4p_{1/2}$ have single ionization potentials (SIPs) of 28.277 eV and 29.402 eV, respectively. The experimental values of 28.21 eV and 29.17 eV are very close and verify the applicability of the chosen method.⁴⁴ They are characterized by pole-strengths, which in this implementation is defined as the sum of the absolute squares of the $1h$ coefficients,⁴⁵ of 0.76 and 0.80

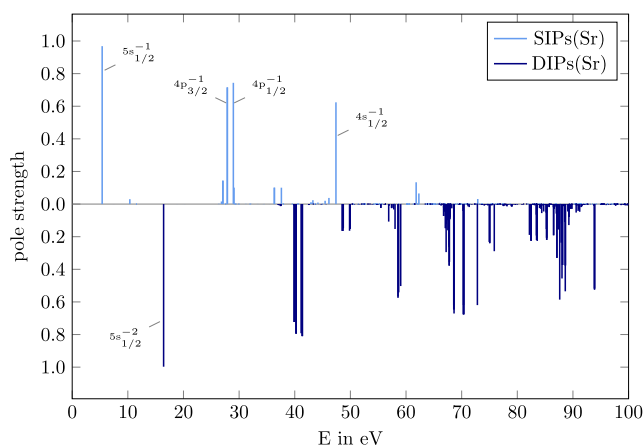


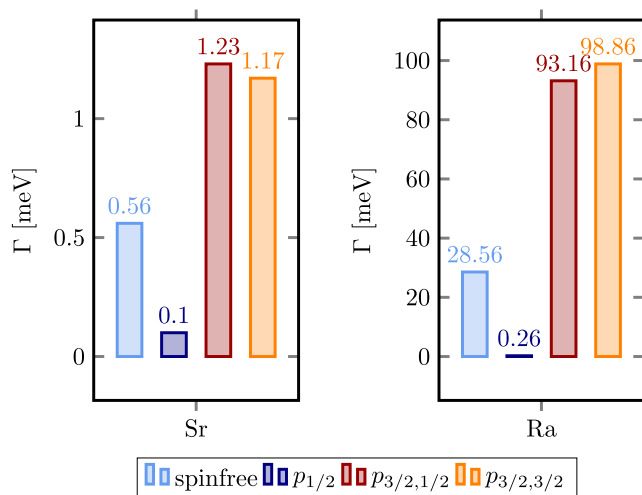
FIG. 1. Comparison of the single (SIP) and double (DIP) ionization spectra of strontium obtained by a DC–ADC calculation.

TABLE I. Ionization energies, pole-strengths P , and decay widths Γ of different Auger–Meitner initial states of strontium and radium obtained by relativistic FanoADC–Stieltjes calculations.

Initial state	Energy (eV)	P	Γ (meV)
Sr spinfree	28.599	0.78	0.56
Sr4 $p_{1/2,1/2}$	29.402	0.80	0.10
Sr4 $p_{3/2,1/2}$	28.277	0.76	1.23
Sr4 $p_{3/2,3/2}$	28.277	0.76	1.17
Ra spinfree	21.836	0.49	28.56
Ra6 $p_{1/2,1/2}$	25.494	0.78	0.26
Ra6 $p_{3/2,1/2}$	19.267	0.50	93.16
Ra6 $p_{3/2,3/2}$	19.267	0.50	98.86

(see Table I). We will at this point treat them as single configurations and analyze them in detail later. These two single ionization energies are higher than only one double ionization potential (DIP) of 16.430 eV, which is to 99.7% characterized by the double ionization from the 5s valence. The Auger–Meitner process is, therefore, energetically accessible and results in a single final state. For radium, the spectra are qualitatively the same and lead to the same conclusion.

We show the corresponding decay widths of strontium and radium obtained by relativistic FanoADC–Stieltjes calculations in Table I for the scalar-relativistic spinfree $(n-1)p^{-1}$ as well as the fully relativistic $(n-1)p_{1/2,1/2}^{-1}$, $(n-1)p_{3/2,1/2}^{-1}$, and $(n-1)p_{3/2,3/2}^{-1}$ initial states. They are illustrated in Fig. 2. To the best of my knowledge, the Auger–Meitner decay widths of these systems have not been presented in the literature so far.

**FIG. 2.** Decay widths of strontium and radium after primary ionization from an $(n-1)p$ orbital obtained by relativistic FanoADC–Stieltjes calculations with different Hamiltonians. The spinfree Hamiltonian includes only scalar-relativistic effects, while the four-component DC Hamiltonian also includes spin–orbit coupling, which gives rise to three possible initial states: the $p_{1/2}^{-1}$ as well as the degenerate $p_{3/2,1/2}$ and $p_{3/2,3/2}$ initial states. The decay width of the $p_{1/2}$ initial state is significantly lower than that for either of the $p_{3/2}$ initial states.

Despite the difference in absolute numbers, the decay widths of the different initial states show the same pattern. The decay width of the $(n-1)p_{1/2,1/2}^{-1}$ initial state is the lowest, while the decay widths of the $(n-1)p_{3/2,1/2}^{-1}$ and $(n-1)p_{3/2,3/2}^{-1}$ initial states are close and significantly higher than those for the $(n-1)p_{1/2,1/2}^{-1}$ initial state. As the atomic $(n-1)p_{3/2,1/2}^{-1}$ and $(n-1)p_{3/2,3/2}^{-1}$ states are degenerate, their complex energies, i.e., the decay widths, should also be equal. It may be possible to estimate the error of the calculations from the observed deviation. However, this concept needs to be proven for a larger set of data points. In case of the strontium atom, the decay width of the $p_{3/2}$ initial state is ~ 12 times larger than the decay width of the $p_{1/2}$ initial state. In radium, the corresponding factor is 380. Furthermore, the decay width average of the $p_{3/2}$ initial state is increased by 114% and 236% for strontium and radium, respectively. We can, therefore, observe an increase in the decay width difference of the $p_{3/2}$ initial state compared to both the $p_{1/2}$ and spinfree initial state for heavier atoms. How can this result be understood?

Considering our previous findings about the role of scalar-relativistic effects on electronic decay widths,²³ we inspect the radial densities of the $(n-1)p$ and ns orbitals of the strontium and radium ions, which we assume to be involved in the decay process (see Fig. 3 and Table II). In the case of the strontium atom, the radial densities of the 4 $p_{1/2}$ and 4 $p_{3/2}$ orbitals are almost identical. However, for the radium atom, the radial density of the 6 $p_{1/2}$ orbital is closer to the nucleus than the radial density of the 6 $p_{3/2}$ orbital. This general property of a stronger contraction of the $l-1/2$ orbital than the $l+1/2$ orbital is already visible in the analytic solutions of the one-electron system^{46,47} and the corresponding radial expectation values $\langle r \rangle$. The differences in the radial expectation values increase with the nuclear charge Z . In many electron systems, where the contraction of the wavefunction decreases with the total angular momentum j , this effect is enlarged. Because the Auger–Meitner decay rates crucially depend on the overlap of the involved orbitals, the decay widths of an $(n-1)p_{3/2}^{-1}$ initial state can be expected to be higher than the decay widths of an $(n-1)p_{1/2}^{-1}$ initial state. These findings are reflected in the decay widths shown in Fig. 2 and Table I and are consistent with the observations of the noble gas Auger–Meitner processes in Ref. 23.

However, the simulations of Auger–Meitner processes in other earth alkaline elements have shown that correlation effects are important for the correct description of these elements' decay widths. Both the investigations of the Auger–Meitner process following primary ionization from the 2 p orbitals of calcium⁴⁸ and from the 4 d orbitals of barium⁴⁹ showed the necessity to include excitations from the valence s orbital to the d orbitals, which are unpopulated in the ground state, in the description of the initial state. In our case, this would require to include the following configurations in our simulations: $(n-1)p^{-1}ns^2$, $(n-1)p^{-1}(n-1)dns$, and $(n-1)p^{-1}(n-1)d^2$. Thereby, a fast Coster–Kronig decay is enabled equally for both the $l-1/2$ and the $l+1/2$ case.

Indeed, the analysis of the ADC eigenvectors of the initial states of both strontium and radium showed that beyond the single and main $1h$ contribution of the respective p orbital, the initial state is mainly characterized by $2h1p$ configurations of the $(n-1)p^{-1}nsd$ kind. The $(n-1)p^{-1}(n-1)dns$ configurations are, therefore, automatically included in our simulations. The relativistic FanoADC–Stieltjes implementation is, however, limited

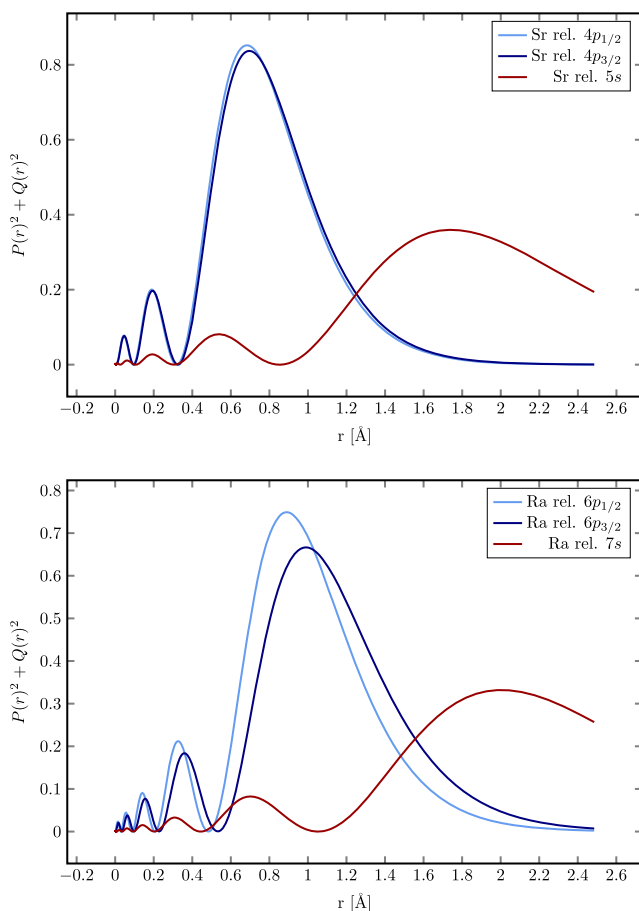


FIG. 3. Radial densities of the orbitals of the $(n-1)p^5s^2$ ions involved in the Auger-Meitner decay. The expectation value of the electron position of the $(n-1)p_{1/2}$ orbital is lower than that of the respective $(n-1)p_{3/2}$ orbitals. The ns orbitals of the ions experience a stronger contraction than those of the atom (not shown here).

to second order perturbations in the wavefunction and, therefore, does not go beyond $2h1p$ configurations. This means that the $(n-1)p^{-1}(n-1)d^2$ configurations are not taken into account in this work.

How do these configurations affect the decay widths? Since the overlap of the orbitals involved in the decay determines the decay

TABLE II. Radial expectation values $\langle r \rangle$ of orbitals involved in the Auger-Meitner process for different configurations given in Ångström.

$\langle r \rangle$	Config.	$(n-1)p_{1/2}$	$(n-1)p_{3/2}$	$(n-1)d_{3/2}$	$(n-1)d_{5/2}$	$ns_{1/2}$
Sr	$4p^55s^2$	0.794	0.809	...	...	1.981
	$4p^54d5s$	0.802	0.818	1.332	1.375	2.062
Ra	$6p^57s^2$	0.996	1.114	...	...	2.244
	$6p^56d7s$	1.001	1.120	1.768	1.821	2.290

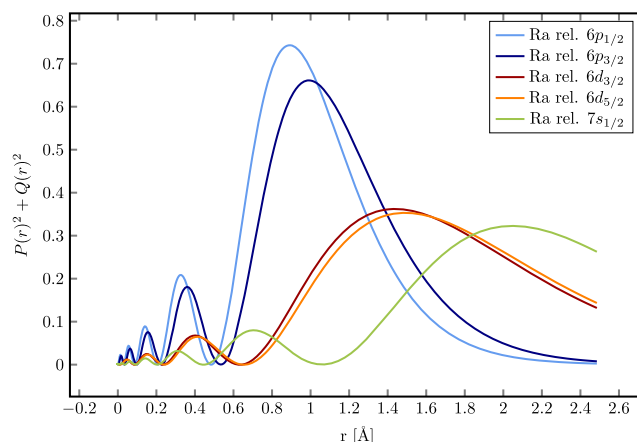


FIG. 4. Radial densities of the radium orbitals of the ionic $6p^56d7s$ configuration involved in the Auger-Meitner decay. The overlap of the radial densities of the $6p$ orbitals with the radial densities of the $6d$ orbitals is more pronounced than that with the radial density of the $7s$ orbital.

widths, we show the radial densities of the orbitals involved in the decay of the $6p^56d7s$ configuration of radium in Fig. 4. The $6p$ orbitals are slightly more contracted than in the $6p^{-1}7s^2$ configuration, while the $7s$ orbital is slightly decontracted by a difference of the electron's distance from the nucleus $\Delta\langle r \rangle$ of 0.046 Å. However, the $6d$ orbitals, which are involved in the Auger-Meitner process of this configuration, show a large overlap with both the $6p$ and the $7s$ orbitals. The corresponding decay width should, therefore, be larger than the decay width of the $6p^{-1}7s^2$ configuration. The prevalence of the $(n-1)p_{3/2}$ decay width over the $(n-1)p_{1/2}$ also holds for this configuration. If the $(n-1)p^{-1}(n-1)d^2$ configurations have non-negligible contributions, the presented decay widths of Table II would be lower bounds to the results of a more accurate decay width calculation.

The observed differences in the decay widths for different initial states and Hamiltonians can, therefore, not only be accounted for by relativistic effects but different contributions of the $(n-1)p^{-1}d\,ns$ configurations may also affect the result. In this case, the required measure of the $(n-1)p^{-1}ns^2$ configuration's contribution to the ionized initial state is the pole-strength, which are listed for the different initial states in Table I. The analysis of the eigenvectors, where the different contributions have been classified according to the main hole, $(n-1)p^{-1}d\,ns$, which includes the $(n-1)p^{-1}(n-1)d\,ns$ configurations, and other, is shown in Table III and illustrated in Fig. 5.

For strontium, the pole-strengths are similar but not identical for all initial states and Hamiltonians. At the same time, both the contribution of the $(n-1)p^{-1}ns^{-1}(n-1)d$ configuration and the manifold of $(n-1)p^{-1}ns^{-1}d$ configurations are similar in all four-component cases. We can, therefore, predominantly attribute the decay width difference between the $p_{3/2}$ and $p_{1/2}$ initial state to spin-orbit coupling rather than the differences in the contributions of the $4p^54d5s$ configuration. For radium, however, the pole-strengths of the initial states differ. The $6p_{1/2}$ initial state has a pole-strength of 0.78, while both the initial state of the scalar-relativistic

TABLE III. Eigenvector analysis of the decaying initial states.

	Configuration	Spinfree	$p_{1/2,1/2}$	$p_{3/2,1/2}$	$p_{3/2,3/2}$
Sr	$(n-1)p^{-1}$	0.782	0.798	0.756	0.756
	$(n-1)p^{-1}ns^{-1}d$	0.050	0.089	0.101	0.084
	$(n-1)p^{-1}ns^{-1}(n-1)d$	0.000	0.002	0.002	0.002
	Other	0.160	0.107	0.140	0.153
Ra	$(n-1)p^{-1}$	0.494	0.777	0.497	0.497
	$(n-1)p^{-1}ns^{-1}d$	0.412	0.011	0.395	0.396
	$(n-1)p^{-1}ns^{-1}(n-1)d$	0.005	0.000	0.005	0.005
	Other	0.086	0.195	0.099	0.086

Hamiltonian and the $6p_{3/2}$ initial state have much lower pole-strengths of 0.49 and 0.50, respectively. The $6p^{-1}7s^2$ configuration is, therefore, predominant for the $6p_{1/2}$ initial state, while it is not for the $6p_{3/2}$ initial state. We can, therefore, not attribute the discrepancy of the decay widths of the $6p_{1/2}$ and $6p_{3/2}$ initial states to spin-orbit splitting alone. However, the initial state determined with the spinfree Hamiltonian has a pole-strength comparable to the $6p_{3/2}$ initial states as well as equal contribution of the $(n-1)p^{-1}ns^{-1}(n-$

$1)d$ configurations and similar contribution of the manifold of $(n-1)p^{-1}ns^{-1}d$ configurations, but the decay width of the $6p_{3/2}$ initial state is increased by 236% compared to the spinfree result. Hence, we can explain the increase in the decay width from the spinfree to the $6p_{3/2}$ initial state by spin-orbit coupling.

Based on these consistent findings, we can formulate the following rule of thumb for the relative Auger–Meitner decay widths:

Two ionized initial states that stem from the same non-relativistic configuration and are split by spin-orbit coupling will have different decay widths, where the decay width of the $l-\frac{1}{2}$ initial state will be significantly lower than the decay width of the $l+\frac{1}{2}$ initial state.

In contrast to the effect imposed by scalar-relativistic effects, this rule of thumb is independent of the angular momentum quantum number l because the $l-\frac{1}{2}$ will always be contracted more strongly than the corresponding $l+\frac{1}{2}$ orbital, and the final state orbitals will be further away from the nucleus than the initial state orbitals. The difference can be expected to increase with the atomic number Z because the difference of orbital contraction increases with Z .

The question is whether this rule of thumb is applicable to the Auger–Meitner processes of other elements. For this, we refer to the Auger–Meitner and Coster–Kronig decay widths of L and M initial states extracted from Refs. 50–52 and presented in Tables IV–VI. We note that these data are limited to comparably heavy elements as simulations of Auger–Meitner decay widths based on relativistic wavefunctions are unavailable in the literature for lighter elements.

TABLE IV. Auger–Meitner (AM) decay widths and Coster–Kronig (CK) widths of L_2 and L_3 shells in eV extracted from Ref. 50.

Z	Element	$\Gamma_{AM}(L_2)$	$\Gamma_{AM+CK}(L_2)$	$\Gamma_{AM}(L_3)$
25	Mn	0.390	...	0.337
30	Zn	0.664	...	0.689
36	Kr	1.101	1.219	1.167
40	Zr	1.373	1.578	1.465
45	Rh	1.705	2.029	1.860
47	Ag	1.832	2.192	2.028
50	Sn	2.016	2.454	2.256
52	Te	2.128	2.614	2.406
54	Xe	2.236	2.767	2.557
56	Ba	2.336	2.912	2.696
60	Nd	2.456	3.060	2.897
63	Eu	2.534	3.146	3.041
67	Ho	2.611	3.233	3.211
70	Yb	2.662	3.285	3.340
74	W	2.753	3.423	3.543
80	Hg	2.877	3.600	3.878
90	Th	3.060	3.877	4.464
92	U	3.082	4.272	4.571
96	Cm	3.126	5.386	4.805
98	Cf	3.146	5.360	4.934
100	Fm	3.168	5.586	5.060

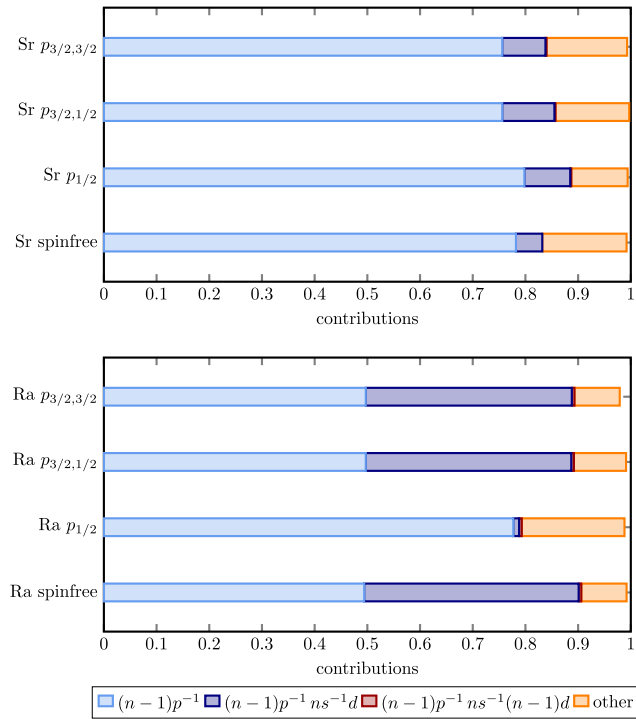


FIG. 5. Illustration of the eigenvector analysis of the different initial states listed in Table III. While the pole strength is similar for all Hamiltonians and initial states for strontium, it differs for different initial states in the case of radium. However, the contributions to the spinfree, $p_{3/2,1/2}$ as well as $p_{3/2,3/2}$ initial state are very similar.

TABLE V. Auger–Meitner (AM) decay widths and Coster–Kronig (CK) widths of M_2 and M_3 shells in eV extracted from Ref. 51.

Z	Element	$\Gamma_{\text{AM}}(M_2)$	$\Gamma_{\text{AM+CK}}(M_2)$	$\Gamma_{\text{AM}}(M_3)$	$\Gamma_{\text{AM+CK}}(M_3)$
67	Ho	0.687	9.484	0.977	9.823
70	Yb	0.277	10.259	1.125	9.949
74	W	0.839	11.870	1.342	10.529
78	Pt	1.257	13.148	1.569	9.735
80	Hg	1.313	13.580	1.673	10.166
85	At	1.403	13.597	1.990	10.879
88	Ra	1.634	14.169	2.170	10.667
90	Th	1.650	14.404	2.264	9.973
92	U	1.727	14.557	2.375	10.235
95	Am	1.836	15.130	2.629	10.850

It is readily seen that the formulated rule of thumb holds for the Auger–Meitner for all cases but one. The latter is the Auger–Meitner process of manganese after primary ionization of a $2p$ orbital (see Table IV). However, the rule of thumb is not correct when Coster–Kronig processes contribute unequally to the decay of the $l + 1/2$ and $l - 1/2$ initial states. The L_3 and M_5 initial states are unable to undergo a Coster–Kronig decay, and they, as well as the M_3 initial state, have one fast decay channel less than their $l - 1/2$ counterpart. One may expect an increasing trend for the ratio of the decay widths with the nuclear charge Z . For the L_2 and L_3 as well as the M_4 and M_5 shells, only few data points contradict this hypothesis, while no clear trend can be seen for the M_2 and M_3 shells.

Based on the above reasoning, one would also expect this rule of thumb to extend to ICD and Electron Transfer Mediated Decay (ETMD) processes. The ICD widths partly depend on the transition dipole moment between the initial and final state of the initially ionized unit, which in return increases with the overlap of the electron densities of the involved orbitals. The ETMD widths are determined by the orbital overlap of two different units, which is larger for orbitals further away from the nucleus. Hence, the same argumentation as for the Auger–Meitner process should be possible in both cases. Validation will be left for future work.

TABLE VI. Auger–Meitner (AM) decay widths and Coster–Kronig (CK) widths of M_4 and M_5 shells in eV extracted from Ref. 52.

Z	Element	$\Gamma_{\text{AM}}(M_4)$	$\Gamma_{\text{AM+CK}}(M_4)$	$\Gamma_{\text{AM}}(M_5)$
70	Yb	1.408	2.445	1.460
74	W	1.758	1.831	1.830
80	Hg	2.259	2.381	2.452
83	Bi	2.512	2.670	2.753
88	Ra	2.923	3.126	3.253
92	U	3.203	3.528	3.611
96	Cm	3.646	4.089	4.075
100	Fm	4.000	4.488	4.583

V. CONCLUSIONS

We have presented lower bounds for decay widths for the Auger–Meitner process initiated by ionization from the $(n - 1)p$ orbitals of strontium and radium. Through analysis of results from different Hamiltonians and initial state eigenvectors as well as radial densities of orbitals involved in the Auger–Meitner process, we were able to show the importance of configuration interaction in this specific case and the effect of spin–orbit coupling on decay widths of electronic decay processes in general. We condensed our findings into the following rule of thumb for the decay widths of electronic decay processes: Two ionized initial states that stem from the same non-relativistic configuration and are split by spin–orbit coupling will have different decay widths, where the decay width of the $l - \frac{1}{2}$ initial state will be significantly lower than the decay width of the $l + \frac{1}{2}$ initial state. We have tested this rule of thumb against Auger–Meitner decay widths available in the literature and could thereby validate it for the majority of cases.

ACKNOWLEDGMENTS

The author would like to thank the audience of the REHE 2017 conference for raising the main question addressed in this article and acknowledges funding from the Villum Foundation.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Cite as: J. Chem. Phys. **152**, 204104 (2020); <https://doi.org/10.1063/5.0004844>

Submitted: 18 February 2020 . Accepted: 22 April 2020 . Published Online: 26 May 2020

Trond Saue , Radovan Bast , André Severo Pereira Gomes , Hans Jørgen Aa. Jensen , Lucas Visscher , Ignacio Agustín Aucar , Roberto Di Remigio , Kenneth G. Dyall , Ephraim Eliav , Elke Fasshauer , Timo Fleig , Loïc Halbert , Erik Donovan Hedegård , Benjamin Helmich-Paris , Miroslav Iliaš , Christoph R. Jacob , Stefan Knecht , Jon K. Laerdahl , Marta L. Vidal , Malaya K. Nayak , Małgorzata Olejniczak , Jógvan Magnus Haugaard Olsen , Markus Pernpointner , Bruno Senjean , Avijit Shee , Ayaki Sunaga , and Joost N. P. van Stralen 

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Cite as: J. Chem. Phys. 152, 204104 (2020); doi: 10.1063/5.0004844

Submitted: 18 February 2020 • Accepted: 22 April 2020 •

Published Online: 26 May 2020



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Note: This article is part of the JCP Special Topic on Electronic Structure Software.

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ABSTRACT

DIRAC is a freely distributed general-purpose program system for one-, two-, and four-component relativistic molecular calculations at the level of Hartree–Fock, Kohn–Sham (including range-separated theory), multiconfigurational self-consistent-field, multireference configuration interaction, electron propagator, and various flavors of coupled cluster theory. At the self-consistent-field level, a highly original scheme, based on quaternion algebra, is implemented for the treatment of both spatial and time reversal symmetry. DIRAC features a very general module for the calculation of molecular properties that to a large extent may be defined by the user and further analyzed through a powerful visualization module. It allows for the inclusion of environmental effects through three different classes of increasingly sophisticated embedding approaches: the implicit solvation polarizable continuum model, the explicit polarizable embedding model, and the frozen density embedding model.

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I. INTRODUCTION

DIRAC is a general-purpose program system for relativistic molecular calculations and is named in honor of P. A. M. Dirac (Program for Atomic and Molecular Direct Iterative Relativistic All-electron Calculations), who formulated¹ his celebrated relativistic wave equation for the electron in 1928. The beginnings of the DIRAC code can be traced back to the four-component relativistic Hartree–Fock (HF) code written by Trond Saue during his master's thesis, defended at the University of Oslo, Norway, in 1991. The original code stored all integrals, provided by the HERMIT code,² on disk, but during Saue's Ph.D. thesis, defended in 1996, the code was extended to direct Self-Consistent Field (SCF) with integral screening³ and a highly original symmetry scheme based on quaternion algebra.⁴ A postdoctoral stay in 1996–1997 with Hans Jørgen Aagaard Jensen at the University of Southern Denmark focused on molecular properties, with the implementation of the calculation of expectation values and linear response functions⁵ at the SCF level. Lucas Visscher, who had written a four-component direct Restricted Active Space (RAS) Configuration Interaction (CI) code for the MOLDIR program system⁶ during his Ph.D. thesis, defended at the University of Groningen in 1993, did a postdoctoral stay with Jens Oddershede in Odense during the years 1996–1997 and joined forces and code with Jensen and Saue to create

the DIRAC program system. Since then, the main author team has been joined by Radovan Bast and Andre Severo Pereira Gomes in addition to almost 50 contributors, and Odense has since 1997 hosted an annual “family” meeting for DIRAC developers. In addition to the above authors, we would like to highlight the contributions to the code infrastructure by Jørn Thyssen and Miroslav Iliáš. The latest version of the code, DIRAC19,⁷ was released on December 12, 2019.

In Sec. II, we give a brief overview of the DIRAC program. Then, in Sec. III, we provide some implementation details, with focus on features that are little documented elsewhere and/or may be a source of confusion for DIRAC users. Throughout this paper, we are using SI units.

II. PROGRAM OVERVIEW

A. Hamiltonians

Within the Born–Oppenheimer approximation, the electronic Hamiltonian may be expressed as

$$\hat{H} = V_{NN} + \sum_i \hat{h}(i) + \frac{1}{2} \sum_{i \neq j} \hat{g}(i, j), \quad V_{NN} = \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}}, \quad (1)$$

where V_{NN} represents the repulsion energy arising from point nuclei fixed in space. Notwithstanding the challenges associated with specific choices of the one- and two-electron operators $\hat{h}(i)$ and $\hat{g}(i, j)$, most quantum chemical methods can be formulated just from this generic form. This becomes perhaps even more evident by considering the electronic Hamiltonian in the second quantized form

$$\hat{H} = V_{NN} + \sum_{pq} h_{pq}^p a_p^\dagger a_q + \frac{1}{4} \sum_{pqrs} V_{pqrs}^{pr} a_p^\dagger a_r^\dagger a_s a_q, \quad \begin{aligned} h_q^p &= \langle p | \hat{h} | q \rangle \\ V_{qs}^{pr} &= \langle pr | \hat{g} | qs \rangle - \langle pr | \hat{g} | sq \rangle \end{aligned} \quad (2)$$

In this form, practical for actual implementations, the Hamiltonian is given by strings of creation and annihilation operators combined with one- and two-electron integrals. In relativistic calculations, the integrals are generally complex, in contrast to the nonrelativistic domain, and contain fewer zero elements, since spin symmetry is lost.

The DIRAC code features several electronic Hamiltonians, allowing for molecular electronic structure calculations at the four-, two-, and one-component levels. Four-component relativistic calculations are sometimes referred to as “fully relativistic” in contrast to “quasirelativistic” two-component calculations. However, a fully relativistic two-electron interaction, which would contain

magnetic interactions and effects of retardation in addition to electrostatics, is not readily available in the closed form, rendering this terminology somewhat misleading. An overview over the most common choices for relativistic molecular Hamiltonians can be found in Ref. 8.

The default Hamiltonian of DIRAC is the four-component Dirac–Coulomb Hamiltonian, using the simple Coulombic correction,⁹ which replaces the expensive calculation of two-electron integrals over small component basis functions by an energy correction. The one-electron part is the Hamiltonian $\hat{h}_D$ of the time-independent Dirac equation in the molecular field, that is, the field of nuclei fixed in space,

$$\hat{h}_D \psi = \begin{bmatrix} V_{eN} & c(\boldsymbol{\sigma} \cdot \mathbf{p}) \\ c(\boldsymbol{\sigma} \cdot \mathbf{p}) & V_{eN} - 2m_e c^2 \end{bmatrix} \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} = \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} E, \quad \begin{aligned} V_{eN}(\mathbf{r}) &= \sum_A \frac{-e}{4\pi\epsilon_0} \int_{\mathbb{R}^3} \frac{\rho_A(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d^3\mathbf{r}' \\ \int_{\mathbb{R}^3} \rho_A(\mathbf{r}) d^3\mathbf{r} &= Z_A e \end{aligned} \quad (3)$$

where c is the speed of light, $\boldsymbol{\sigma}$ is the vector of Pauli spin matrices, $\mathbf{p}$ is the momentum operator, and V_{eN} is the electron–nucleus interaction. The default model of the nuclear charge distribution is the Gaussian approximation,¹⁰ but a point nucleus model is also available. The default two-electron operator of DIRAC is the instantaneous Coulomb interaction

$$\hat{g}^C(1, 2) = \frac{e^2}{4\pi\epsilon_0 r_{12}}, \quad (4)$$

which constitutes the zeroth-order term and hence the nonrelativistic limit¹¹ of an expansion in c^{-2} of the fully relativistic two-electron interaction in the Coulomb gauge. It should be noted, though, that the presence of $\hat{g}^C(1, 2)$ induces the spin–same orbit (SSO) interaction, just as the presence of V_{eN} induces the spin–orbit interaction associated with the relative motion of the nuclei with respect to the electrons.⁸ The spin–other-orbit (SOO) interaction may be included by adding the Gaunt term, which is available at the SCF level. Spin–orbit interaction effects may be eliminated by transforming to the modified Dirac equation and removing spin-dependent terms.¹² In the quaternion formulation of SCF calculations in DIRAC, this corresponds to removing the three quaternion imaginary parts of the Fock matrix.¹³

It is also possible to carry out four-component *nonrelativistic* calculations using the Lévy–Leblond Hamiltonian,^{13,14} which is equivalent to the Schrödinger Hamiltonian within kinetic balance. The Schrödinger Hamiltonian is also available in DIRAC, but due to

its four-component form, the Lévy–Leblond Hamiltonian is better integrated in the code, in particular for the calculation of molecular properties. Contrary to the Schrödinger Hamiltonian, the four-component Hamiltonians are linear in vector potentials. In the *relativistic* case, the calculation of 3×3 second-order magnetic property matrices thus requires the solution of just three linear response equations, contrary to the scalar non-relativistic case that requires the evaluation of at least six diamagnetic expectation values and often solving more than three linear response equations; for example, linear response equations become ten for paramagnetic spin-orbit, Fermi-contact, and spin-dipole (PSO, FC, and SD) contributions to indirect spin–spin coupling between two nuclei.^{15,16} On the other hand, in order to get the diamagnetic contributions converged, special basis set considerations are necessary, usually expressed through (simple) magnetic balance.^{17,18} In the case of the Lévy–Leblond Hamiltonian, the diamagnetic contribution is calculated as an expectation value over the scalar non-relativistic operator.¹¹

A troublesome aspect of the Dirac Hamiltonian is the presence of solutions of negative energy. Over the years, there has been extensive work on eliminating the positronic degrees of freedom of the Dirac Hamiltonian, leading to approximate two-component Hamiltonians, such as the Douglas–Kroll–Hess (DKH)^{19–21} and zeroth-order regular approximation (ZORA)^{22–24} Hamiltonians. Various flavors of the ZORA Hamiltonian have been implemented in DIRAC,¹³ but only for energy calculations. DIRAC features the very first implementation of a two-component relativistic

Hamiltonian for molecular calculations where the one-electron part reproduces *exactly* the positive-energy spectrum of the parent four-component Dirac Hamiltonian.^{25,26} This implementation, presented as the BSS Hamiltonian by Jensen and Iliáš,²⁵ referring to the previous work by Barysz, Sadlej, and Snijders,²⁷ carried out a free-particle Foldy–Wouthuysen transformation²⁸ on the Dirac Hamiltonian, followed by an exact decoupling of positive- and negative-energy solutions. This two-step approach allows for the construction of finite-order two-component relativistic Hamiltonians such as the first- and second-order Douglas–Kroll–Hess Hamiltonians but is unnecessary for exact decoupling. The code was therefore superseded by a simple one-step approach, reported as the Infinite-Order Two-Component (IOTC) Hamiltonian by Iliáš and Saue.²⁹ Due to the equivalence with the exact quasirelativistic (XQR) Hamiltonian reported by Kutzelnigg and Liu,³⁰ it was later agreed³¹ to name such Hamiltonians eXact 2-Component (X2C) Hamiltonians. The X2C decoupling transformation is available in matrix form and is used to transform the matrix of any one-electron operator to the two-component form, hence avoiding picture change errors. For the two-electron integrals, DIRAC employs the uncorrected two-electron operator supplemented with the atomic mean-field approach for including two-electron spin–orbit interactions.^{32,33} Recently, the X2C code in DIRAC was rewritten in a more modular and modern form by Knecht.³⁴

For wave function-based correlation methods, the electronic Hamiltonian is conveniently written in the normal-ordered form

$$\hat{H} = E^{\text{HF}} + \sum_{pq} F_q^p \{a_p^\dagger a_q\} + \frac{1}{4} \sum_{pqrs} V_{qs}^{pr} \{a_p^\dagger a_r^\dagger a_s a_q\}, \quad (5)$$

where E^{HF} is the Hartree–Fock energy, F_q^p are elements of the Fock matrix, and curly brackets refer to normal ordering with respect to the Fermi vacuum, given by the HF determinant. For such calculations, DIRAC features the X2C molecular mean-field approach.³⁵ After a four-component relativistic HF calculation, the X2C decoupling is carried out on the Fock matrix, rather than the Dirac Hamiltonian matrix, whereas the two-electron operator is left untransformed. In combination with the usual approximation of neglecting core electron correlation, this limits the effect of picture change errors to valence–valence electron interactions only: core–core and core–valence electron interactions are treated with the same accuracy as in the 4C approach.

Last but not least, DIRAC features one-component scalar relativistic effective core potentials (AREPs) as well as two-component spin–orbit relativistic effective core potentials (SOREPs).³⁶

B. Electronic structure models

1. Self-consistent field (SCF) calculations

At the core of DIRAC is an SCF module allowing for both Hartree–Fock (HF)³ and Kohn–Sham (KS)³⁷ calculations. These calculations are Kramers-restricted and use a symmetry scheme based on quaternion algebra that automatically provides maximum point group and time-reversal symmetry reduction of the computational effort.⁴ In nonrelativistic quantum chemistry codes, spin-restricted open-shell SCF calculations employ Configuration State Functions (CSFs) $|S, M_S\rangle$ of well-defined spin symmetry. However, in the relativistic domain, spin symmetry is lost, and so the use of CSFs would

require linear combinations of Slater determinants adapted to combined spin and spatial symmetry, which is a challenge for a general molecular code. We have therefore instead opted for the average-of-configuration Hartree–Fock method³⁸ for open-shell systems. Individual electronic states may subsequently be resolved by a complete open-shell CI calculation.³⁹ Open-shell Kohn–Sham calculations use fractional occupation.

SCF calculations are based on the traditional iterative Roothaan–Hall diagonalization method with direct-inversion-in-the-iterative-subspace (DIIS) convergence acceleration. By default, the start guess is provided by a sum of atomic local-density approximation (LDA) potentials, which have been prepared using the GRASP atomic code⁴⁰ and are fitted to an analytical expression.⁴¹ Other options include (i) bare nucleus potentials corrected with screening factors based on Slater’s rules,⁴² (ii) atomic start based on densities from atomic SCF runs for the individual centers,⁴³ and (iii) an extended Hückel start based on atomic fragments.⁴⁴ In each SCF iteration, orbitals are by default ordered according to energy, and orbital classes are assigned by simple counting in the following order: (secondary) negative-energy orbitals, inactive (fully occupied) orbitals, active (if any) orbitals, and virtual orbitals. The implicit assumption of relative ordering of orbital energies according to orbital classes may cause convergence problems, for instance, for f -elements where closed-shell ns -orbitals typically have higher energies than open-shell $(n-2)f$ ones. Such convergence problems may be avoided by reordering of orbitals combined with overlap selection, pioneered by Bagus in the 1970s⁴⁵ and nowadays marketed as the maximum overlap method.⁴⁶ Overlap selection also provides robust convergence to core-ionized/excited states.⁴⁷ Negative-energy orbitals are treated as an orthogonal complement, corresponding to the implicit use of a projection operator.⁴⁸

An extensive selection of exchange–correlation energy functionals, as well as their derivatives to high order, needed for property calculations, is available for Kohn–Sham calculations. These XC functional derivatives are provided either by a module written by Salek⁴⁹ using symbolic differentiation or by the XCFun library written by Ekström^{50,51} using the automatic differentiation technique. By default, Kohn–Sham calculations employ Becke partitioning⁵² of the molecular volume into overlapping atomic volumes, where the numerical integration within each atomic volume is carried out using the basis-set adaptive radial grid proposed by Lindh, Malmqvist, and Gagliardi⁵³ combined with angular Lebedev quadrature. The XC contributions to energy derivatives or Fock matrix elements are evaluated for a batch of points at a time, which allows us to screen entire batches based on values of basis functions at these grid points and enables us to express one summation loop of the numerical integration as a matrix–matrix multiplication step.

2. Correlation methods

a. Four-index transformations. While the AO-to-MO index transformations are subordinate to the correlation approaches described below, some features are worth describing in a separate section. Irrespective of the Hamiltonian that is used in the orbital generation step, the approach always assumes that a large atomic orbital basis set is condensed to a much smaller molecular orbital basis. The result is the second-quantized, no-pair Hamiltonian in molecular orbital basis that is identical in structure to the

second-quantized Hamiltonian encountered in nonrelativistic methods [see Eq. (2)]. The main difference is the fact that the defining matrix elements in this Hamiltonian are in general complex due to the inclusion of spin-orbit coupling in the orbital generation step. As a consequence, integrals will not exhibit the usual eightfold permutation symmetry familiar from nonrelativistic integrals. This is even the case when higher point group symmetry is used to render the integrals real, as they may be a product of two imaginary transition densities. Only for spin-free calculations, is it possible to choose phase factors for the spinors in such a way that eightfold permutational symmetry is recovered. For ease of interfacing with nonrelativistic correlation implementations, such phase factors are inserted in the final stage of the transformation when running in the spin-free mode. The primary interface files that are generated contain the (effective) one-body operator plus additional symmetry and dimensionality information needed to set up the Hamiltonian. The numerous two-body matrix elements are stored in separate files that can be distributed over multiple locations in a compute cluster environment with delocalized disk storage. The program is complemented by a utility program that can convert the MO integrals to formats used by other major quantum chemistry programs, such as the FCIDUMP format,⁵⁴ thus facilitating the interfacing⁵⁵ of DIRAC to other electron correlation implementations, such as MRCC,⁵⁶ or even to quantum computers. With respect to the latter, a four-component relativistic quantum algorithm was reported in Ref. 57. More recently, DIRAC has been interfaced to the electronic structure package OpenFermion through a *Python* interface,⁵⁸ thus allowing for the calculation of energies and energy derivatives on a quantum computer⁵⁹ using either the full Dirac-Coulomb Hamiltonian or the Lévy-Leblond Hamiltonian.

The implementation has been revised several times over the years to account for changes in computer hardware architectures. The current default algorithm for the most demanding transformation of the two-electron integrals uses an MPI type of parallelization in which half-transformed integrals are generated from recomputed AO integrals. If the total disk space is an issue, it is also possible to employ a scheme in which only a subset of half-transformed integrals is stored at a given time. The generation of one-body integrals is less demanding and carried out by calling the Fock matrix build routine from the SCF part of the program, with a modified density matrix that includes only contributions from the orbitals that are to be frozen in the correlation treatment. In the generation of these integrals, it is possible to account for the Gaunt correction to the Coulomb interaction, thereby making a mean-field treatment of this contribution possible.³⁵ Explicit transformation of additional integrals over operators needed for the evaluation of molecular properties, or the inclusion of a finite strength perturbation in only the electron correlation calculation, is also possible and handled by a separate submodule.

The lowest-level correlation method is second-order Møller-Plesset perturbation (MP2) theory, and an early integral-direct, closed-shell implementation was realized by Laerdahl⁶⁰ in 1997. This implementation focuses on efficient, parallel calculation of the MP2 energy for closed-shell systems. A more general implementation that also allows for calculation of the relaxed MP2 density matrix was realized later by van Stralen⁶¹ as part of the coupled cluster implementation discussed below. Both implementations use the conventional MP2 approach; a more efficient Cholesky-decomposed

density matrix implementation was developed by Helmich-Paris.⁶² In this approach, the quaternion formalism, which has been developed in earlier works,⁶³ was used to reduce the number of operations. A production implementation along these lines is planned for the 2020 release.

b. Configuration interaction. The first implementation (**DIRRCI** module) of restricted active space configuration interaction was taken from the MOLFDIR program⁶⁴ and is briefly described in Secs. 3.4 and 4.10 of Ref. 6, with more details on the calculation of CI coupling coefficients given in Chap. 6.5 of Ref. 65. This module is mostly kept for reference purposes as a more powerful implementation of configuration interaction in DIRAC was introduced later by Fleig and co-workers.⁶⁶ A unique feature that makes the DIRRCI module still of some interest is the handling of any Abelian point group symmetry, and not just D_{2h} and subgroups. The implementation is capable of handling every possible Abelian group as long as the respective multiplication table is provided. This feature allows for treatment of linear symmetry (a feature lacking in the MOLFDIR program) by merely changing the dimensions of the arrays that hold the symmetry information. While the DIRRCI code is no longer actively developed, some later extensions beyond the MOLFDIR capabilities have been implemented, such as the (approximate) evaluation of correlated first-order properties using the unrelaxed CI density matrix by Nayak.^{67–69} This implementation allows for the calculation of expectation values of one-electron property operators over the CI wave functions.

The more recent **KR-CI** module is a string-based Hamiltonian-direct configuration interaction (CI) program that uses Dirac Kramers pairs from either a closed- or an open-shell calculation in a relativistic two- and four-component formalism exploiting double point-group symmetry. KR-CI is parallelized using MPI in a scalable way where the CI vectors are distributed over the nodes, thus enabling the use of the aggregate memory on common computing clusters.^{70,71} There are two choices for the CI kernel: **LUCIAREL** and **GASCIP**.

The LUCIAREL kernel^{66,72} is a relativistic generalization of the earlier LUCIA code by Olsen.⁷³ It is capable of doing efficient CI computations at arbitrary excitation levels, FCI, SDCl, RASCI, and MRCl, all of which are subsets of the Generalized Active Space (GAS) CI. The GAS concept⁷⁴ is a central and very flexible feature (described in greater detail in Ref. 75) of the program that can be applied effectively to describe various physical effects in atomic matter. Apart from routine applications to valence electron correlation,^{76,77} it has been used in other modern applications to efficiently describe core-valence electron correlation⁷⁸ and also core-core correlation.⁷⁹ These uses can be combined with excited-state calculations, even when greater numbers of excited states with varying occupation types are required.⁸⁰ In the latter case, typical CI expansion lengths are on the order of up to 10^8 terms, whereas parallel single-state calculations have been carried out with up to 10^{10} expansion terms.⁸¹ If desired, KR-CI computes one-particle densities from the optimized CI wave functions from which one-electron expectation values of any property defined in DIRAC as well as natural orbital occupations can be calculated.

The complete open-shell implementation (**GOSCIP**) of MOLFDIR is used to obtain state energies after an average-of-configuration Hartree-Fock calculation. For other uses, a more

general and efficient **GASCIP** (Generalized Active Space CI Program) module was originally written by Thyssen and Jensen for KR-MCSCF and later parallelized and optimized by Jensen. This very general CI implementation is primarily used for KR-MCSCF and ESR calculations,⁸² but it is also available for KR-CI calculations. Another separate implementation is the spin-free version of LUCIAREL, **LUCITA**, which fully exploits spin and boson symmetry. LUCITA will consequently be faster for spin-free CI calculations than KR-CI using the LUCIAREL kernel. LUCITA has also been parallelized with MPI,⁸³ in the same way as KR-CI.

c. Multiconfigurational SCF. The original **KR-MCSCF** implementation was written by Thyssen, Fleig, and Jensen⁸⁴ and follows closely the theory of Ref. 85. Within a given symmetry sector, it allows for a state-specific optimization by taking advantage of a Newton-step-based genuine second-order optimization algorithm.⁸⁵ The KR-MCSCF module was later parallelized^{70,71} using MPI by Knecht, Jensen, and Fleig by means of a parallelization of the individual CI-based tasks encountered in an MCSCF optimization: (i) generation of the start vector, (ii) sigma-vector calculation, and (iii) evaluation of one- and two-particle reduced density matrices (RDMs). Moreover, its extension to an efficient treatment of linear symmetry (see Sec. III C)—both in the KR-CI part and in the restriction of orbital-rotational parameters—was a central element that allowed for a comprehensive study⁸⁶ of the electronic structure as well as of the chemical bond in the ground- and low-lying excited states of U_2 based on a simultaneous, variational account of both (static) electron correlation and spin-orbit coupling.

d. Coupled cluster. The **RELCCSD** coupled cluster module⁸⁷ is also derived from the MOLFDIR implementation, but in contrast to the DIRRCI module, it is still under active development. The implementation uses the same philosophy as DIRRCI in demanding only a point group multiplication table to handle Abelian symmetry. Furthermore, in some cases, point group symmetry beyond Abelian symmetry can be used to render the defining integrals of the second quantization Hamiltonian real, using the scheme first outlined in Ref. 88, but adjusted to work with the quaternion algebra used elsewhere in DIRAC. The implemented algorithms work in the same way for real and complex algebra, with all time-consuming operations performed by BLAS⁸⁹ calls that are made via a set of wrapper routines that point to the (double precision) real or complex version, depending on the value of a global module parameter. In this way, the need for maintenance of a separate code for real or complex arithmetic is strongly reduced. Due to the dependence on BLAS operations, shared memory parallelization is easily achieved by linking in a multithreaded BLAS library. Parallelization via MPI can be achieved in addition, as described in Ref. 90.

For the description of electronic ground states that can be qualitatively well described by a single determinant, the standard CCSD(T) model is usually the optimal choice in terms of performance,⁹¹ with the code taking the trial CCSD amplitudes from an MP2 calculation. As the RELCCSD implementation does not assume time-reversal symmetry, it is possible to treat open-shell cases as well. This is straightforward at the CCSD level of theory as the specific open-shell SCF approach used to generate the orbitals is then relatively unimportant and the implementation does not assume a diagonal reference Fock matrix. For the implemented perturbative

triple corrections,^{92,93} a larger dependence on the starting orbitals is observed, although performance is usually satisfactory for simple open-shell cases with only one unpaired electron. For more complicated cases, it is often better to use the Fock space coupled cluster (FSCC) model, in which multireference cases can also be handled.

The relativistic use of the FSCC method⁹⁴ has been pioneered by Eliav and Kaldor,⁹⁵ and in the DIRAC implementation,⁹⁶ one is able to investigate electronic states that can be accessed by single or double electron attachment or detachment, as well as singly excited states, from a starting closed-shell reference determinant—that is, states with up to two unpaired electrons. Most calculations done with this method nowadays use their intermediate Hamiltonian^{97,98} (IH) schemes that remove problems with intruder states to a large extent.^{99–102} The IH approach has been recently improved by the very efficient Padé extrapolation method.¹⁰³ As IH schemes often use large active spaces, and the original Fock space implementation⁹⁶ was designed with small numbers of occupied orbitals in mind, these calculations can become rather memory-intensive.

We have also implemented the equation-of-motion coupled cluster approach for the treatment of electron attachment (EOM-EA), ionization energy (EOM-IP), and excitation energy (EOM-EE).¹⁰⁴ EOM-IP and EOM-EE can also be used to obtain core ionization and excitation energies via the core-valence separation approach.¹⁰⁵ This complements the Fock space functionality for treating electronically excited states, especially for species that can be represented by a closed-shell ground-state configuration.¹⁰⁶

e. Range-separated density functional theory. This method allows for grafting of wave function-based correlation methods onto density functional theory (DFT) without double counting of electron correlation.¹⁰⁷ We have explored this approach combining short-range DFT with long-range MP2 theory¹⁰⁸ and CC model.¹⁰⁹

f. Density matrix renormalization group (DMRG). If requested, KR-CI provides a one- and two-electron integral file in the FCIDUMP format,⁵⁴ which allows for, for the active space specified in the KR-CI input, relativistic density matrix renormalization group (DMRG) calculations^{110,111} with the relativistic branch of the DMRG program QCMAQUIS.^{112,113} If desired, the DMRG program computes the one-particle reduced density matrix for the optimized wave function in the MO basis and writes it to a text file that can be fed back into DIRAC. This feature makes it possible to calculate (static) first-order one-electron properties in the same way as described below for SCF calculations. Moreover, this functionality also opens up further possibilities to analyze the resulting wave function and to calculate properties in real-space, as it was shown in Ref. 111 for a Dy(III) complex. For the latter functionality, the visualization module (see Sec. II E) was extended with an interface to wave functions optimized within the KR-CI/KRMSCF framework of Dirac.

C. Molecular properties

A common framework for the calculation of molecular properties is response theory. A less economical, but computationally easier approach is to use a finite-field approach. Implementations for both strategies are available in DIRAC.

The property module of DIRAC has been written in a very general manner, allowing user-defined operators. More precisely, a four-component one-electron operator has the general form

$$\hat{P} = \sum_k f_k M_k \hat{\Omega}_k, \quad (6)$$

where f_k is a scalar factor, M_k is a 4×4 matrix (I_4 , α_x , Σ_y , $\dots$), and $\hat{\Omega}_k$ is a scalar operator. The user can choose between 21 different operators forms, Eq. (6) (for example, $c(\alpha \cdot \hat{\Omega})$ and $f\gamma_5\hat{\Omega}$; for the full list, see the manual on the DIRAC website¹¹⁴). For the definition of specific scalar operators $\hat{\Omega}$, DIRAC benefits from the extensive menu of one-electron operators in the HERMIT module.² For convenience, a number of properties are predefined, as shown in Table I.

1. SCF calculations

At the closed-shell SCF level, both for Hartree–Fock and for Kohn–Sham, DIRAC allows for the calculation of molecular properties corresponding to expectation values as well as linear^{5,116} and quadratic^{131,132} response functions. In addition, first- and second-order residues of the quadratic response function have been programmed, allowing for the calculation of two-photon absorption cross sections¹¹⁸ and first-order properties of electronically excited states,¹³³ respectively.

Linear response functions have been extended to complex response through the introduction of a common damping term that

removes divergences at resonances.¹³⁴ This allows for not only probing of second-order properties in the vicinity of resonances but also simulation of absorption spectra within a selected window of frequencies. In addition, complex response allows for the calculation of properties at formally imaginary frequencies, such as C_6 dispersion coefficients.¹³⁵

Excitation energies are available through time-dependent HF and DFT.¹³⁶ Restrictions may be imposed on active occupied (and virtual) orbitals, hence allowing for restricted excitation window (REW) calculations^{47,137} of x-ray absorption spectra. Another method available for core-excitation processes in molecules is the static-exchange approximation (STEX).¹³⁸ Transition moments may be calculated with user-specified property operators. From DIRAC20 onward, three schemes¹³⁹ to go beyond the electric dipole approximation in the calculation of oscillator strengths will be available in DIRAC. The first is based on the full semi-classical light–matter interaction operator and the two others on a truncated interaction within the Coulomb gauge (velocity representation) and multipolar gauge (length representation). The truncated schemes can be calculated in *arbitrary* order in the wave vector. All schemes allow for rotational averaging.

NMR shieldings as well as magnetizabilities may be calculated using London orbitals and simple magnetic balance.¹⁸ For KS calculations, non-collinear spin magnetization has been implemented¹³² and all required derivatives of exchange–correlation functionals are provided.

TABLE I. Predefined molecular properties in DIRAC. EV is expectation value; LR is linear response; QR is quadratic response.

Keyword	Electric properties	EV	LR	QR	References
.DIPOLE	Electric dipole moment	x			
.QUADRU	Traceless electric quadrupole moment	x			
.EFG	Electric field gradients at nuclear positions	x			115
.NQCC	Nuclear quadrupole coupling constants	x			115
.POLARI	Electronic dipole polarizability tensor		x		5 and 116
.FIRST	Electronic dipole first-order hyperpolarizability tensor			x	117
.TWO-PH	Two-photon absorption cross sections			x	118
<i>Magnetic properties</i>					
.NMR	Nuclear magnetic shieldings and indirect spin–spin couplings		x		15 and 119
.SHIELD	Nuclear magnetic shieldings		x		15 and 119
.SPIN-S	Indirect spin–spin couplings		x		15
.MAGNET	(Static) magnetizability tensor		x		120 and 121
.ROTG	Rotational g-tensor (DIRAC20)		x		122
<i>Mixed electric and magnetic properties</i>					
.OPTROT	Optical rotation		x		123
.VERDET	Verdet constants			x	124
<i>Other predefined properties</i>					
.MOLGRD	Molecular gradient				125
.PVC	Parity-violating energy (nuclear spin-independent part)	x			126 and 127
.PVCNMR	Parity-violating contribution to the NMR shielding tensor		x		128
.RHONUC	Electronic density at the nuclear positions (contact density)	x			129
.EFFDEN	Effective electronic density associated with nuclei (Mössbauer)	x			129
.SPIN-R	Nuclear spin-rotation constants	x	x		130

2. Correlation modules

a. Electronic ground state properties. The implementations for obtaining density matrices for molecular properties are still under development. For the single reference CCSD model, the current available functionality is to obtain the unrelaxed one-particle density matrix.¹⁴⁰ For the MP2 model, for which orbital relaxation effects are more important, the relaxed density matrix can be obtained.⁶¹ After back-transforming to the AO basis, molecular properties can be obtained in the same way as for SCF calculations. Alternatively, one may also obtain matrix elements of property operators in the MO basis and compute expectation values of CI wave functions and/or include property operators as a finite-strength perturbation in the CI or CC wave function determination. This allows for determination of properties that break Kramers symmetry and has, for example, been used for assessing the effect of an electric dipole moment of the electron (eEDM) in molecular systems.¹⁴¹

b. Excited state properties. For properties that depend also on the excited state density matrix, such as transition probabilities, only limited functionality is available in RELCCSD. Transition intensities based on an approximate CI expression and the dipole approximation for the transition moments have been implemented for the Fock space coupled cluster model. Under development, and planned to be available in the 2020 DIRAC release, is an extension to the non-diagonal form of the finite field approach in the Fock space CC. This approach allows for accurate calculations of the dipole moments of electron transitions in heavy atomic and molecular systems.¹⁴² For KR-CI, the range of properties is larger,⁷⁰ and basically the same as for the electronic ground state. These include molecule-frame static electric dipole moments,^{70,143} E1 transition matrix elements,^{70,144} and magnetic hyperfine interaction constants¹⁴⁵ in electronic ground and excited states. Moreover, parity-reversal (P) and time-reversal (T) violating properties are implemented as expectation values over atomic or molecular KR-CI ground- and excited-state wave functions, in particular the electron electric dipole moment interaction,¹⁴⁶ the P,T-odd scalar-pseudoscalar nucleon-electron interaction,¹⁴³ and the nuclear magnetic quadrupole moment electron magnetic-field interaction.⁷⁸

c. Electron propagator. The Algebraic Diagrammatic Construction (ADC) is an efficient, size-consistent post-Hartree-Fock method, which can be used to obtain molecular properties.^{147–150} With DIRAC, the calculation of single¹⁵¹ and double¹⁵² ionization as well as electronic excitation^{153,154} spectra using the RELADC and POLPRP modules is possible. Decay widths of electronic decay processes can be obtained by the FanoADC-Stieltjes method.¹⁵⁵ The ionization spectra can be obtained at the level of ADC(2), ADC(2x), and ADC(3) plus constant diagrams, while the electronic excitation spectra are available at ADC(2) and ADC(2x) levels of accuracy. Technically, the ADC implementation and the RELCCSD code share much of their infrastructure.

d. Quasi-degenerate perturbation theory using configuration interaction. A module is under development for description of properties of quasi-degenerate states as encountered in open-shell molecules. The focus has so far been on calculation of ESR/EPR g-tensors,⁸² hyperfine couplings, and zero-field splitting. It is based on the flexible GASCIP configuration interaction module.

D. Environments

A great deal of information can be extracted from gas-phase electronic structure calculations, even for systems that are studied experimentally in solution or other condensed phases. Nevertheless, the environment can strongly modulate the properties of a system, such as formation/reaction energies and response properties (e.g., electronic or vibrational spectra). It can therefore be important to take into account the influence of the environment on the systems of interest. A straightforward way to include the environment is by performing calculations on large molecular systems or aggregates, but this quickly becomes unwieldy already for HF and DFT calculations, and for correlated electronic structure calculations (Sec. II C 2), this strategy is largely unfeasible.

The alternative to such calculations is the use of embedding approaches,¹⁵⁶ in which the environment is treated in a more approximate fashion with respect to the subsystem of interest, see Fig. 1. Apart from the simplest possible embedding scheme, using *fixed* point charges, DIRAC offers three different classes of increasingly sophisticated embedding approaches: the implicit solvation polarizable continuum model (PCM), the atomistic polarizable embedding (PE) model, and the frozen density embedding (FDE) model; the latter is also referred to as subsystem DFT. In the first two, the environment is treated classically, whereas for the latter, all fragments are treated quantum mechanically, though generally at different levels of theory.

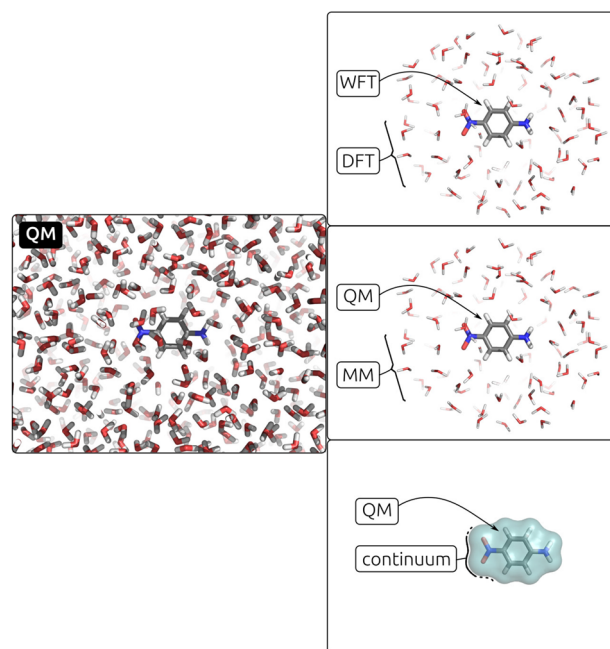


FIG. 1. Pictorial depiction of the transition from the **quantum mechanical** model to one of the **multiscale** models available in DIRAC for the aqueous solvation of *para*-nitroaniline. Leftmost panel: a **fully quantum mechanical** cluster model. Upper central panel: a **frozen density embedding (FDE)** (explicit) model. Middle central panel: a **quantum/classical discrete** (explicit) model. Lower central panel: a **quantum/classical continuum** (implicit) model.

1. Polarizable continuum model (PCM)

The PCM is a quantum/classical polarizable model for the approximate inclusion of solvent effects into quantum mechanical calculations.¹⁵⁷ It is a focused, implicit solvation model: the environment (usually a solvent) is replaced by a dielectric with permittivity ϵ , and the mutual interaction between the quantum mechanical and classical regions is described by the electrostatic polarization. The model cannot describe specific, weak interactions between subsystems, such as hydrogen bonding, but can give the first qualitative estimate of solvation effects on many molecular properties.

The quantum mechanical region is delimited by a *cavity*, a region of space usually constructed as a set of interlocking spheres and hosting the QM fragment, see the lower central panel in Fig. 1. Inside the cavity, the permittivity is that of vacuum ($\epsilon = 1$), while outside, the permittivity assumes the value appropriate for the environment being modeled. For example, in the case of water, the experimental value $\epsilon = 78.39$ would be used. The electrostatic polarization is represented as an apparent surface charge (ASC), which is the solution to the integral formulation of the Poisson equation. The coupling with the QM code at the SCF level of theory is achieved by augmenting the usual Fock operator with an ASC-dependent environment polarization operator. This results in minimal, localized changes to the SCF cycle.

The implementation in DIRAC is based on the PCMSOLVER library,^{158,159} which provides a well-defined interface to a standalone computational backend. The PCM method is available for mean-field (HF and DFT) wave functions. Additionally, static electric linear response properties can also be computed including the effect of the solvent via the PCM.

2. Polarizable embedding (PE)

The PE model is a fragment-based quantum–classical embedding approach for including environment effects in calculations of spectroscopic properties of large and complex molecular systems.^{160–162} The effects from the classical environment on the quantum subsystem are included effectively through an embedding potential that is parameterized based on *ab initio* calculations. The molecular environment is thus subdivided into small, computationally manageable fragments from which multi-center multipoles and multi-center dipole–dipole polarizabilities are computed. The multipoles and polarizabilities model the permanent and induced charge distributions of the fragments in the environment, respectively. For solvent environments, a fragment typically consists of an individual solvent molecule, while for large molecules, such as proteins, a fragmentation approach based on overlapping fragments is used. The resulting embedding potential is highly accurate¹⁶³ and introduces an explicitly polarizable environment that thus allows the environment to respond to external perturbations of the chromophore.¹⁶⁴ The embedding-potential parameters can be conveniently produced using external tools such as the PyFraME package,¹⁶⁵ which automates the workflow leading from an initial structure to the final embedding potential.

The current implementation of the PE model in DIRAC can be used in combination with mean-field electronic-structure methods (i.e., HF and DFT) including electric linear response and transition properties where local-field effects, termed effective external field (EEF)^{166,167} effects in the PE context, may be included.¹⁶⁸

The model is implemented in the Polarizable Embedding library (PElib)¹⁶⁹ that has been interfaced to DIRAC.¹⁶⁸ The library itself is based on an AO density-matrix-driven formulation, which facilitates a loose-coupling modular implementation in host programs. The effects from the environment are included by adding an effective one-electron embedding operator to the Fock operator of the embedded quantum subsystem. The potential from the permanent charge distributions is modeled by the multipoles, which is a static contribution that is computed once and added to the one-electron operator at the beginning of a calculation. The induced, or polarized, charge distributions are modeled by induced dipoles resulting from the electric fields exerted on the polarizabilities. This introduces a dependence on the electronic density, through the electronic electric field, and the induced dipoles are therefore updated in each iteration of an SCF cycle or response calculation, similar to the procedure used in the PCM.¹⁷⁰

3. Frozen density embedding (FDE)

The FDE approach is based on a reformulation of DFT whereby one can express the energy of a system in terms of subsystem energies and an interaction term (see Ref. 156 and references therein), which contains electrostatic, exchange-correlation, and kinetic energy contributions, with the latter two correcting for the non-additivity between these quantities calculated for the whole system and for the individual subsystems. As in other embedding approaches, we are generally interested in one subsystem, while all others constitute the environment. The electron density for the system of interest is determined by making the functional for the total energy stationary with respect to variations of the said density, with a constraint provided by the density of the environment. The interaction term thus yields a local embedding potential, $v^{\text{emb}}(\mathbf{r})$, representing the interactions between the system and its environment.

The FDE implementation in DIRAC is capable of calculating $v^{\text{emb}}(\mathbf{r})$ during the SCF procedure (HF and DFT) using previously obtained densities and electrostatic potentials for the environment on a suitable DFT integration grid, as well as exporting these quantities. One can also import a precalculated embedding potential, obtained with DIRAC or other codes,¹⁷¹ and include it in the molecular Hamiltonian as a one-body operator.¹⁷² This allows for setting up iterative procedures to optimize the densities of both the system of interest and the environment via freeze–thaw cycles.¹⁷³

At the end of the SCF step, the imported or calculated $v^{\text{emb}}(\mathbf{r})$ becomes part of the optimized Fock matrix and is therefore directly included in all correlated treatments mentioned above^{172,174} as well as for TD-HF and TD-DFT. For the latter two, contributions arising from the second-order derivatives of interaction energy are also available for linear response properties of electric¹⁷⁵ and magnetic perturbations,¹⁷⁶ though the couplings in the electronic Hessian between excitations on different subsystems are not yet implemented. The interaction term for the non-additive kinetic energy contributions is calculated with one of the available approximate kinetic energy functionals that can be selected via input.

E. Analysis and visualization

DIRAC features Mulliken population analysis.¹⁷⁷ However, this analysis should be used with caution due to its well-known basis-set

dependence. An additional complication in the present case is that the analysis distributes density according to *scalar* basis functions, which is incompatible with two- or four-component atomic orbitals. We have therefore introduced **projection analysis**, similar in spirit to Mulliken analysis, but using precalculated atomic orbitals.^{178,179} The reference atomic orbitals may furthermore be polarized within the molecule using the intrinsic atomic orbital algorithm.^{180,181} The projection analysis furthermore allows for the decomposition of expectation values at the SCF level into inter- and intra-atomic contributions, which, for instance, has elucidated the mechanisms of parity-violation in chiral molecules.¹²⁷ It is also possible to localize molecular orbitals, which is favorable for bonding analysis.¹⁷⁹

The **visualization module** in DIRAC makes it possible to export densities and their derivatives, as well as other quantities (such as property densities obtained from response calculations), to third-party visualization software commonly used by the theoretical chemistry community such as Molden,^{182,183} as well as by less known analysis tools such as the Topology Toolkit (TTK),¹⁸⁴ with which we can perform a wide range of topological analyses, including atoms-in-molecules (AIM)¹⁸⁵ with densities obtained with Hartree-Fock, DFT, and CCSD wave functions. DIRAC can export such data in the Gaussian cube file format, or over a custom grid.

DIRAC has been extensively used for the visualization of property densities, in particular magnetically induced currents.^{186,187} More recently, shielding densities have been investigated in order to gain insight into the performance of FDE for such NMR properties.^{173,176}

As an illustration of the visualization module, we start from the observation of Kaupp *et al.*¹⁸⁸ that the spin-orbit contribution to

the shielding $\sigma(H_\beta)$ of β -hydrogen of iodoethane follows closely the Karplus curve of the indirect spin-spin coupling constant $K(H_\beta, I)$ as a function of the H-C-C-I dihedral angle. The DIRAC program makes it possible to isolate spin-free and spin-orbit contributions to magnetic properties;¹¹ this has allowed us to show that this connection is manifest at the level of the corresponding property densities (Fig. 2).

F. Programming details and installation

The source code consists mostly of Fortran 77 and Fortran 90 codes, but some modules are written in C (exchange-correlation functional derivatives using symbolic differentiation, pre-Fortran-90 memory management) and C++ (exchange-correlation functional derivatives using automatic differentiation, polarizable continuum model). *Python* is used for the powerful code launcher pam, which has replaced the previous launcher written in Bash.

The code base is under version control using Git and hosted on a GitLab repository server. The main development line as well as release branches is write-protected, and all changes to these are automatically tested and undergo code review. For integration tests, we use the Runtest library¹⁸⁹ and we run the test set both nightly and before each merge to the main code development branch.

Since 2011, the code is configured using CMake,¹⁹⁰ which was introduced to make the installation more portable and to make it easier to build and maintain a code base with different programming languages and an increasing number of externally maintained modules and libraries. The code is designed to run on a Unix-like operating system, but thanks to the platform universality of the employed *Python*, Git and CMake tools, we have also been able to adapt the DIRAC code for the MS Windows operating system using the MinGW-GNU compiler suite.

G. Code documentation

The code documentation (in HTML or PDF format) is generated from sources in the reStructuredText format using Sphinx¹⁹¹ and served via the DIRAC program website.¹¹⁴ We track the documentation sources in the same Git repository as the source code. In this way, we are able to provide documentation pages for each separate program version, which improves the reproducibility of the code and also allows us to document unreleased functionality for future code versions. In addition to a keyword reference manual, we share a broad spectrum of tutorials and annotated examples that provide an excellent starting point for users exploring a new code functionality or entering a new field.

H. Distribution and user support

The program is distributed in the source code form under a custom open-use license. Traditionally, we have distributed the code to the community upon request, but starting with the DIRAC18 release,¹⁹² we have switched to distributing the source code and collecting download metrics via the Zenodo service.¹⁹³ We plan to transition to an open source license (GNU Lesser General Public License) in the near future to encourage contributions and simplify the derivative work based on the DIRAC package. User support is provided on a best-effort basis using Google Groups, with presently

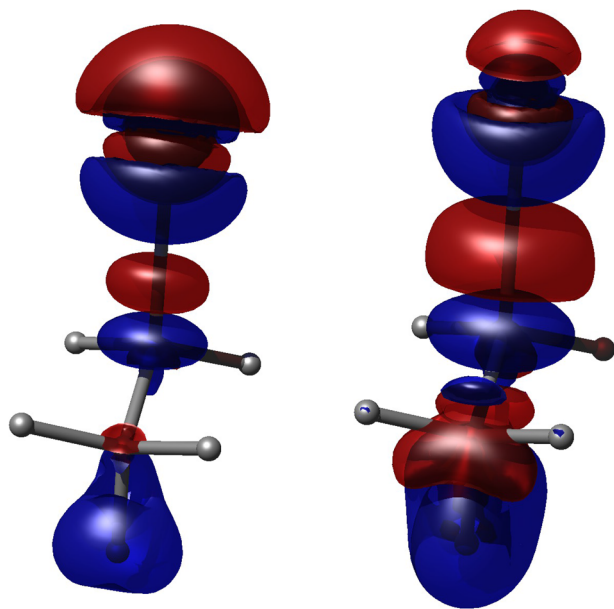


FIG. 2. Visualizing the analogy between the spin-orbit contribution to shieldings and the indirect spin-spin coupling: isosurface plot of the spin-spin coupling density $K(H_\beta, I)$ in iodoethane (left panel; Fermi-contact + spin-dipole contributions), compared with the spin-orbit coupling contribution to the shielding density $\sigma(H_\beta)$ (right panel). The dihedral angle H-C-C-I is 180° .

360 subscribers. Deliberate efforts in community building are also reflected in the social media presence.¹⁹⁴

III. IMPLEMENTATION DETAILS

A. Basis functions

In the nonrelativistic domain, basis functions are modeled on atomic orbitals, but with adaptations facilitating integral evaluation. This has led to the dominant, but not exclusive use of Cartesian or spherical Gaussian-type orbitals (GTOs). Four-component atomic orbitals may be expressed as

$$\psi(\mathbf{r}) = \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} = \frac{1}{r} \begin{bmatrix} P_\kappa(r) \xi_{\kappa, m_j}(\theta, \phi) \\ i Q_\kappa(r) \xi_{-\kappa, m_j}(\theta, \phi) \end{bmatrix}, \quad (7)$$

where P_κ and Q_κ are real scalar radial functions and ξ_{κ, m_j} are two-component complex angular functions. The first four-component relativistic molecular calculations in the finite basis approximation met with failure because the coupling of the large ψ^L and the small ψ^S components through the Dirac equation was ignored. Since the exact coupling is formally energy-dependent, the use of the nonrelativistic limit was made instead, leading to the kinetic balance prescription.^{195–197} However, it is not possible to take this limit for the positive- and negative-energy solutions of the Dirac equation at the same time. Since the focus in chemistry is definitely on the positive-energy solutions, the relativistic energy scale is aligned with the nonrelativistic one through the substitution $E \rightarrow E - m_e c^2$, whereupon the limit is taken as

$$\lim_{c \rightarrow \infty} c \psi^S = \lim_{c \rightarrow \infty} \frac{1}{2m_e} \left[1 + \frac{E - V}{2m_e c^2} \right] (\boldsymbol{\sigma} \cdot \mathbf{p}) \psi^L = \frac{1}{2m_e} (\boldsymbol{\sigma} \cdot \mathbf{p}) \psi^L. \quad (8)$$

In practice, one may choose between one- and two-component basis functions for four-component relativistic molecular calculations. The latter choice allows for the straightforward realization of *restricted* kinetic balance,¹⁹⁷ hence a 1:1 ratio of large and small component basis functions, but requires on the other hand a dedicated integration module. In DIRAC, we opted³ for Cartesian GTOs,

$$G_{ijk}^\alpha(\mathbf{r}) = N x^i y^j z^k \exp[-\alpha r^2], \quad i + j + k = \ell, \quad (9)$$

since this gave immediate access to integrals of the HERMIT integral module,² where the extensive menu of one-electron integrals boosted functionality in terms of molecular properties.

DIRAC provides a library of Gaussian basis sets. The main basis sets available are those of Dyall and co-workers,^{198–210} which cover all elements from H to Og at the double-zeta, triple-zeta, and quadruple-zeta levels of accuracy. They include functions for electron correlation for valence, outer core, and inner core, as well as diffuse functions, in the style of the Dunning correlation-consistent basis sets.²¹¹ In addition, many standard non-relativistic basis sets are available for use with lighter elements. All Dyall basis sets are used uncontracted; however, by default, the non-relativistic basis sets are kept contracted for non-relativistic calculations and otherwise for H–Kr ($Z \leq 36$), for heavier elements, the basis sets are uncontracted to get a better description of the restricted kinetic balance in relativistic calculations. For this reason, the number of basis functions is generally considerably larger than that in non-relativistic calculations; however, this in fact gives better screening

in direct Fock matrix calculations and is therefore generally not a problem in the SCF. For correlated calculations based on HF, the usual procedure is to delete molecular orbitals with high orbital energies.

B. SCF module for HF and KS calculations

The SCF module has some unique features that will be described in the following. In the matrix form, the HF/KS equations read

$$F\mathbf{c} = S\mathbf{c}\epsilon, \quad (10)$$

where F and S are the Fock/KS and overlap matrices, respectively, and $\mathbf{c}$ refers to expansion coefficients. Before diagonalization, the equations are transformed to an orthonormal basis,

$$\tilde{F}\tilde{\mathbf{c}} = \tilde{\mathbf{c}}\epsilon, \quad \tilde{F} = V^\dagger F V, \quad \mathbf{c} = V\tilde{\mathbf{c}}, \quad V^\dagger S V = I. \quad (11)$$

As a simple example, we may take the Dirac equation in a finite basis,

$$\begin{bmatrix} V^{LL} & c\Gamma^{LS} \\ c\Gamma^{SL} & V^{SS} - 2m_e c^2 S^{SS} \end{bmatrix} \begin{bmatrix} \mathbf{c}^L \\ \mathbf{c}^S \end{bmatrix} = \begin{bmatrix} S^{LL} & 0 \\ 0 & S^{SS} \end{bmatrix} \begin{bmatrix} \mathbf{c}^L \\ \mathbf{c}^S \end{bmatrix} E. \quad (12)$$

After orthonormalization, it reads

$$\begin{bmatrix} \tilde{V}^{LL} & c\tilde{\Gamma}^{LS} \\ c\tilde{\Gamma}^{SL} & \tilde{V}^{SS} - 2m_e c^2 \tilde{S}^{SS} \end{bmatrix} \begin{bmatrix} \tilde{\mathbf{c}}^L \\ \tilde{\mathbf{c}}^S \end{bmatrix} = \begin{bmatrix} \tilde{S}^{LL} & 0 \\ 0 & \tilde{S}^{SS} \end{bmatrix} \begin{bmatrix} \tilde{\mathbf{c}}^L \\ \tilde{\mathbf{c}}^S \end{bmatrix} E. \quad (13)$$

DIRAC employs canonical orthonormalization²¹² that allows for the elimination of linear dependencies. However, the orthonormalization step is overloaded as follows:

1. *Elimination and freezing of orbitals:* DIRAC allows for the elimination and freezing of orbitals. Such orbitals are provided by the user in the form of one or more coefficient files. This part of the code uses the machinery of the projection analysis discussed in Sec. II E. The selected orbitals can therefore be expressed either in the full molecular basis or in the basis set of some chosen (atomic) fragment. They are eliminated by transforming them to the orthonormal basis and projecting them out of the transformation matrix V . They may instead be frozen by putting them back in the appropriate position when back-transforming coefficients to the starting AO basis. An example of the use of elimination of orbitals is a study of the effect of the lanthanide contraction on the spectroscopic constants of the CsAu molecule.²¹³ Inspired by an atomic study by Bagus and co-workers,²¹⁴ the precalculated 4f-orbitals of the gold atom were imported into a molecular calculation and eliminated. At the same time, the gold nuclear charge was reduced by 14 units, thus generating a pseudo-gold atom unaffected by the lanthanide contraction. An example of the freezing of orbitals is the study of the effect of the freezing of oxygen 2s-orbitals on the electronic and molecular structure of the water molecule.¹⁷⁹
2. *Cartesian-to-spherical transformation:* As already mentioned, at the integral level, DIRAC employs Cartesian Gaussian-type orbitals (GTOs), Eq. (9), since this allowed the use of a non-relativistic integral code. Cartesian GTOs are particularly suited for integral evaluation due to the separability in

Cartesian coordinates, but in non-relativistic codes, the integrals are typically subsequently transformed to the smaller set of integrals over spherical GTOs,

$$G_{\ell m}^{\alpha}(\mathbf{r}) = N r^{\ell} \exp[-\alpha r^2] Y_{\ell m}(\theta, \phi). \quad (14)$$

However, in relativistic calculations, the situation becomes more complicated due to the kinetic balance prescription. In the atomic case, the nonrelativistic limit of the coupling between the large and small radial functions reads

$$\lim_{c \rightarrow \infty} c Q_{\kappa} = \frac{1}{2m_e} \left(\partial_r + \frac{\kappa}{r} \right) P_{\kappa}, \quad (15)$$

which in the present case implies that if we start from a standard form of the radial function for large components, we end up with a non-standard form for the small component radial function, that is,

$$P_{\kappa}(r) = N r^{\ell-1} \exp[-\alpha r^2] \\ \Rightarrow Q_{\kappa}(r) = N \left\{ (\kappa + \ell - 1) r^{\ell-2} - 2\alpha r^{\ell} \right\} \exp[-\alpha r^2].$$

Rather than implementing the transformation to the non-standard radial part of the small component spherical GTOs at the integral level, we have embedded it in the transformation to the orthonormal basis.

3. *Restricted kinetic balance:* The use of scalar basis functions only allows for *unrestricted* kinetic balance, where the small component basis functions are generated as derivatives of the large component ones, but not in the fixed two-component linear combination of Eq. (8). This leads to the curious situation that the small component basis is represented by more functions than the large component one, e.g., a single large component *s*-function generates three small component *p*-functions. In DIRAC, we do, however, recover RKB in the orthonormalization step. In the first version, RKB was obtained by noting that the extra small component basis functions mean that there will be solutions of the Dirac equation with zero large components. In the free-particle case, these solutions will have energy $-2m_e c^2$. RKB was therefore realized by diagonalizing the free-particle Dirac equation in the orthonormal basis, thus identifying and eliminating (as described above) these unphysical solutions.

It was later realized that RKB could be achieved in a simpler manner by embedding the transformation to the modified Dirac equation^{12,13}

$$Q = \begin{bmatrix} \tilde{T}^{LL} & 0 \\ 0 & \frac{1}{2m_e c} \tilde{\Pi}^{SL} \end{bmatrix} \\ \Rightarrow \begin{bmatrix} \tilde{V}^{LL} & \frac{1}{2m_e} \tilde{T}^{LL} \\ \frac{1}{2m_e} \tilde{T}^{LL} & \frac{1}{4m_e^2 c^2} \tilde{W}^{LL} - \frac{1}{2m_e} \tilde{T}^{LL} \end{bmatrix} \begin{bmatrix} \tilde{\mathbf{c}}^{L'} \\ \tilde{\mathbf{c}}^{S'} \end{bmatrix} \\ = \begin{bmatrix} \tilde{T}^{LL} & 0 \\ 0 & \frac{1}{4m_e^2 c^2} \tilde{T}^{LL} \end{bmatrix} \begin{bmatrix} \tilde{\mathbf{c}}^{L'} \\ \tilde{\mathbf{c}}^{S'} \end{bmatrix}, \quad (16)$$

where

$$\tilde{T}_{\mu\nu}^{LL} = \frac{1}{2m_e} \sum_{\gamma\delta} \tilde{\Pi}_{\mu\gamma}^{LS} \tilde{\Pi}_{\gamma\nu}^{SL} = \left\langle \tilde{\chi}_{\mu} \left| \frac{p^2}{2m_e} \right| \tilde{\chi}_{\nu} \right\rangle, \quad (17)$$

$$\tilde{W}_{\mu\nu}^{LL} = \sum_{\gamma\delta} \tilde{\Pi}_{\mu\gamma}^{LS} \tilde{V}_{\gamma\delta}^{SS} \tilde{\Pi}_{\delta\nu}^{SL} = \left\langle \tilde{\chi}_{\mu} \left| (\boldsymbol{\sigma} \cdot \mathbf{p}) V (\boldsymbol{\sigma} \cdot \mathbf{p}) \right| \tilde{\chi}_{\nu} \right\rangle, \quad (18)$$

where the latter equalities follow from kinetic balance.¹⁹⁶ The metric on the right-hand side of Eq. (16) indicates a non-orthonormal basis. A second canonical orthonormalization transformation $\tilde{V}$ is therefore introduced, so that the total transformation, done in a single step, reads $VQ\tilde{V}$.

4. *Elimination of spin-orbit interaction:* As shown by Dyall,¹² transformation to the modified Dirac equation allows for a separation of spin-free and spin-dependent terms. In the quaternion symmetry scheme of DIRAC, we obtain such a separation by simply deleting the quaternion imaginary parts of Fock matrices in the orthonormal basis.¹³
5. *X2C transformation:* The transformation to the eXact 2-Component (X2C) relativistic Hamiltonian is carried out starting from the modified Dirac equation in the orthonormal basis. Working with a *unit* metric greatly simplifies the transformation.²¹⁵
6. *Supersymmetry:* At the integral level, basis functions are adapted to symmetries of D_{2h} and subgroups. However, for linear systems, we obtain a blocking of Fock matrices in the orthonormal basis on the m_j quantum number²¹⁶ by diagonalizing the matrix of the $\hat{j}_z$ operator in the orthonormal basis and performing the substitution $V \rightarrow VU_m$, where U_m are the eigenvectors ordered on m_j . This provides significant computational savings, in particular at the correlated level. Recently, we have implemented atomic supersymmetry, such that the Fock matrix gets blocked on (κ, m_j) quantum numbers (to appear in DIRAC20).²¹⁷

C. Symmetry considerations

The DIRAC code can handle symmetries corresponding to D_{2h} and subgroups (denoted binary groups) as well as linear and atomic (from DIRAC20) supersymmetries. At the SCF level, DIRAC employs a unique quaternion symmetry scheme that combines time reversal and spatial symmetry.⁴ A particularity of this scheme is that symmetry reductions due to spatial symmetry are translated into a reduction of algebra, from quaternion down to complex and possibly real algebra. This leads to a classification of the binary groups as follows:

- Quaternion groups: C_1, C_i
- Complex groups: C_2, C_s, C_{2h}
- Real groups: D_2, C_{2v}, D_{2h} .

At the SCF level, DIRAC works with the irreducible *co-representations* obtained by combining the above spatial symmetry groups with time reversal symmetry.⁴ A source of confusion for DIRAC users has been that occupations are given for each irreducible co-representation at the SCF level. However, one can show that starting from the binary groups, there are at most two irreducible co-representations, distinguished by parity. This means in practice that a single occupation number is expected for systems without inversion symmetry, whereas occupations for *gerade* and *ungerade* symmetries are given separately otherwise.

At the correlated levels, the highest *proper* Abelian subgroup of the point group under consideration is used and the only *improper* symmetry operation utilized is inversion. For the point groups implemented, this leads to the following group chains:

- $D_2, C_{2v} \rightarrow C_2$
- $D_{2h} \rightarrow C_{2h}$
- $C_{\infty v} \rightarrow C_{64}$
- $D_{\infty h} \rightarrow C_{32h}$

The linear groups $D_{\infty h}$ and $C_{\infty v}$ are special as the number of finite Abelian subgroups that can be used to characterize orbitals is infinite. In practice, we map these groups to a 64-dimensional subgroup, which is more than sufficient to benefit from symmetry blocking in the handling of matrices and integrals and to identify the symmetry character of orbitals and wave functions. The group chain approach²¹⁸ in which each orbital transforms according to the irreps of the Abelian subgroup as well as a higher, non-Abelian group has an advantage that the defining elements of the second quantized Hamiltonian of Eq. (2) are real for the real groups, even though an Abelian complex group is used at the correlated level. The transition between the quaternion algebra used at the SCF level and the complex or real algebra used in the correlation modules is made in the AO-to-MO transformation that generates transformed integrals in the quaternion format, after which they are expressed and stored in a complex (or real) form.²¹⁹

The use of real instead of complex algebra gives a four-fold speed-up for floating point multiplications. In RELCCSD, one generic algorithm is used for all implemented point groups, with the toggling between complex or real multiplications hidden inside a wrapper for matrix multiplications. The LUCIAREL kernel has distinct implementations for real-valued and complex-valued Abelian double point groups.⁷² For linear molecules¹⁴³ and atoms,⁸⁰ axial symmetry is useful and implemented.⁸⁶ For linear groups, an isomorphic mapping between total angular momentum projection (along the distinguished axis) and group irreducible representation is possible for all practically occurring angular momenta using the 64-dimensional subgroups defined above.

IV. CONCLUSIONS

DIRAC is one of the earliest codes for four-component relativistic molecular calculations and the very first to feature eXact 2-Component (X2C) relativistic calculations.²⁶ A strength of the code is the extensive collection of, in part, unique functionalities. This stems in part from the fact that the code has been written with generality in mind. There is a wide range of Hamiltonians, and most program modules are available for all of them. The SCF module allows for Kramers-restricted HF and KS calculations using an innovative symmetry scheme based on quaternion algebra. In some situations, though, for instance, in DFT calculations of magnetic properties, an option for unrestricted calculations would be desirable in order to capture spin polarization.

A number of *molecular* properties, such as electric field gradients,¹¹⁵ parity-violation in chiral molecules,¹²⁶ nuclear spin-rotation constants,^{220,221} and rotational g-tensors,¹²² were first studied in a four-component relativistic framework with DIRAC. The freedom of users to define their own properties combined with the availability

of properties up to the third order means that there are many new properties waiting to be explored. Such properties may be further analyzed through the powerful visualization module.

Another strength of DIRAC is the large selection of wave function-based correlation methods, including MRCI, CCSD(T), FSCCD, EOM-CCSD, ADC, and MCSCF. As already mentioned, the latter allowed for a detailed study of the emblematic U_2 molecule, demonstrating that the spin-orbit interaction reduces the bond order from five²²² to four.⁸⁶ The MRCI and CC methods implemented in DIRAC that account for more dynamic correlation have, combined with the experiment, provided reference values for properties such as nuclear quadrupole moments,^{223,224} hyperfine structure constants,²²⁵ and Mössbauer isomer shifts.²²⁶ DIRAC also provides theoretical input for spectroscopic tests of fundamental physics, within both the standard model of elementary particles²²⁷ and tests of Beyond Standard Model (BSM) theories that give rise to electric dipole moments of fermions.^{141,143,228}

In recent years, DIRAC has been extended to include several models for large environments: PCM, PE, and FDE, which opens new perspectives. For instance, recently, EOM-CC was combined with FDE to calculate ionization energies of halide ions in droplets modeled by 50 water molecules.¹⁷⁴ Another interesting development for large-scale applications is that DIRAC in 2015 was one of the 13 scientific software suites chosen for adaption to the SUMMIT supercomputer²²⁹ at the Oak Ridge Leadership Computing Facility (OLCF). As of November 2019, SUMMIT was the world's fastest supercomputer, and DIRAC production runs are currently being carried out on this machine.

ACKNOWLEDGMENTS

T.S. would like to thank his former advisors Knut Fægri, Jr. and the late Odd Gropen for putting him on an exciting track.

L.V. acknowledges support of the Dutch Research Council (NWO) for this research via various programs. He also likes to thank his former advisors Patrick Aerts and Wim Nieuwpoort for introducing him to the wonderful world of relativistic quantum chemistry.

A.S.P.G. acknowledges support from the CNRS Institute of Physics (INP), PIA ANR Project No. CaPPA (ANR-11-LABX-0005-01), I-SITE ULNE Project No. OVERSEE (ANR-16-IDEX-0004), the French Ministry of Higher Education and Research, region Hauts de France council, and the European Regional Development Fund (ERDF) project CPER CLIMIBIO.

M.I. acknowledges the support of the Slovak Research and Development Agency and the Scientific Grant Agency, APVV-19-0164 and VEGA 1/0562/20, respectively. This research used resources of the High Performance Computing Center of the Matej Bel University in Banská Bystrica using the HPC infrastructure acquired in Project Nos. ITMS 26230120002 and 26210120002 (Slovak Infrastructure for High Performance Computing) supported by the Research and Development Operational Programme funded by the ERDF.

R.D.R. acknowledges partial support by the Research Council of Norway through its Centres of Excellence scheme, Project No. 262695, and through its Mobility Grant scheme, Project No. 261873.

M.O. acknowledges support of the Polish National Science Centre (Grant No. 2016/23/D/ST4/03217).

I.A.A. acknowledges support from CONICET by Grant No. PIP 112-20130100361 and FONCYT by Grant No. PICT 2016-2936.

J.M.H.O. acknowledges financial support from the Research Council of Norway through its Centres of Excellence scheme (Project No. 262695).

E.D.H. acknowledges financial support from the European Commission (MetEmbed, Project No. 745967) and the Villum Foundation (Young Investigator Program, Grant No. 29412).

A.S. acknowledges financial support from the Japan Society for the Promotion of Science (JSPS) KAKENHI Grant No. 17J02767, and JSPS Overseas Challenge Program for Young Researchers, Grant No. 201880193.

S.K. would like to thank Markus Reiher (ETH Zürich) for his continuous support throughout his time at ETH Zürich.

M.P. gratefully acknowledges financial support by the Deutsche Forschungsgemeinschaft (DFG).

T.F. acknowledges funding by the Deutsche Forschungsgemeinschaft (DFG) and the Agence Nationale de la Recherche (ANR) through various programs.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Time-resolved spectroscopy of interparticle Coulombic decay processes

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(Received 12 April 2019; revised manuscript received 6 March 2020; accepted 17 March 2020; published 24 April 2020)

We report the theory for time-resolved spectator resonant interparticle Coulombic decay (ICD) processes. Following excitation by a short extreme ultraviolet pulse, the spectrum of the resonant ICD electron develops. Strong-field ionization is imagined to quench the decay at different time delays and to initiate regular ICD. In this latter process, the ICD electron signal can be measured without interference effects. The typical lifetimes of ICD processes allow for the observation of oscillations of the time- and energy-differential ionization probability. We propose to utilize this oscillation to measure lifetimes of electronic decay processes.

DOI: [10.1103/PhysRevA.101.043414](https://doi.org/10.1103/PhysRevA.101.043414)

I. INTRODUCTION

Interparticle Coulombic decay (ICD) [1,2] is an electronic decay process of ionized systems consisting of at least two weakly bonded units, be it atoms, molecules, or clusters. ICD has been observed in multiple systems like noble gas clusters [3–11] and clusters of different solvent molecules like water [4,5,12] or ammonia [13–16]. It allowed one to explain the repair mechanism of the enzyme photolyase [17] and was used to establish a more efficient double ionization strategy [18]. ICD is furthermore discussed as a source of slow electrons, which are most efficient in damaging the DNA after exposure to high energy radiation or radioactive materials in the human body [19–24]. In this work, we shed light on this fundamental process by offering a time-resolved perspective directly of the electron dynamics.

Due to developments in creating short pulses in the extreme ultraviolet (XUV) and x-ray domain [26] a time-dependent investigation of ICD processes should be within reach. Fano profiles of a much faster autoionization (AI) process were recently measured [27,28]. A few time-resolved investigations of ICD have already been performed theoretically and experimentally, where the ions produced in the process were measured [29–36]. However, electrons can be measured with higher energy resolution than ions and grant direct access to the electron dynamics and interference effects during the process. In this work, we will therefore focus on the evolution of the time- and energy-differential ionization probability, propose how it might be possible to measure this quantity in experiment, and discuss how decay lifetimes can be determined from the time-resolved signal.

In brief, the ICD process starts from a unit *A*, which is ionized in the inner valence shell. This vacancy is filled by an electron from the same unit and the excess energy is simultaneously transferred to a neighboring unit *B*. The latter is consequently ionized by emission of the ICD electron. The two positively charged units undergo a Coulomb explosion

(see Fig. 1). A related process is initiated by an excitation of unit *A*. This resonant ICD (RICD) can be characterized by the behavior of the excited electron: it either participates in the decay process or not. The respective processes are called participator RICD (pRICD) [37] and spectator RICD (sRICD) [37–42]. In this work, we will focus on the sRICD signal: Unit *A* is excited from the inner valence. The vacancy is then filled by an electron from the valence and the excess energy is used to ionize the neighboring unit *B* (see Fig. 1). This process is usually characterized by lifetimes of several tens to hundreds of femtoseconds. After the sRICD process, the excited unit *A* decays via fluorescence within a few nanoseconds. AI and pRICD are competing decay channels and their effect on the sRICD signal is taken into account in the theory developed below.

We propose to initiate an sRICD process by exciting with a short XUV pulse. The system will then decay under emission of an sRICD electron. This is illustrated in Fig. 1 for electronic energies and resonance parameters corresponding to the neon dimer after an excitation to the Ne $2s^{-1}5p$ state. At a later time t_s , a second short and intense infrared (IR) laser pulse quenches the sRICD process by ionization. By varying the time delay t_s one should be able to observe the time-dependent formation of the sRICD signal, as illustrated to the right in Fig. 1 before the second laser pulse, by pump-probe spectroscopy similar to the AI process measured in Ref. [27]. At the same time, the proposed quenching would initiate an ICD process involving the excited ion A^{+*} . Due to the strong-field ionization initiating this latter process, the signals are well separated in energy. In this paper we provide the basic formulation for a purely electronic solution upon which more complex scenarios, including nuclear dynamics, will be built in future work.

II. THEORY

The relevant property for the description of the time evolution of the ICD processes is the time- and energy-differential ionization probability obtained from the time-dependent wave function $|\Psi(t)\rangle$ by $P(E_{\text{kin}}, t) = \sum_i |\langle E_i | \Psi(t) \rangle|^2$. Here $|E_i\rangle$

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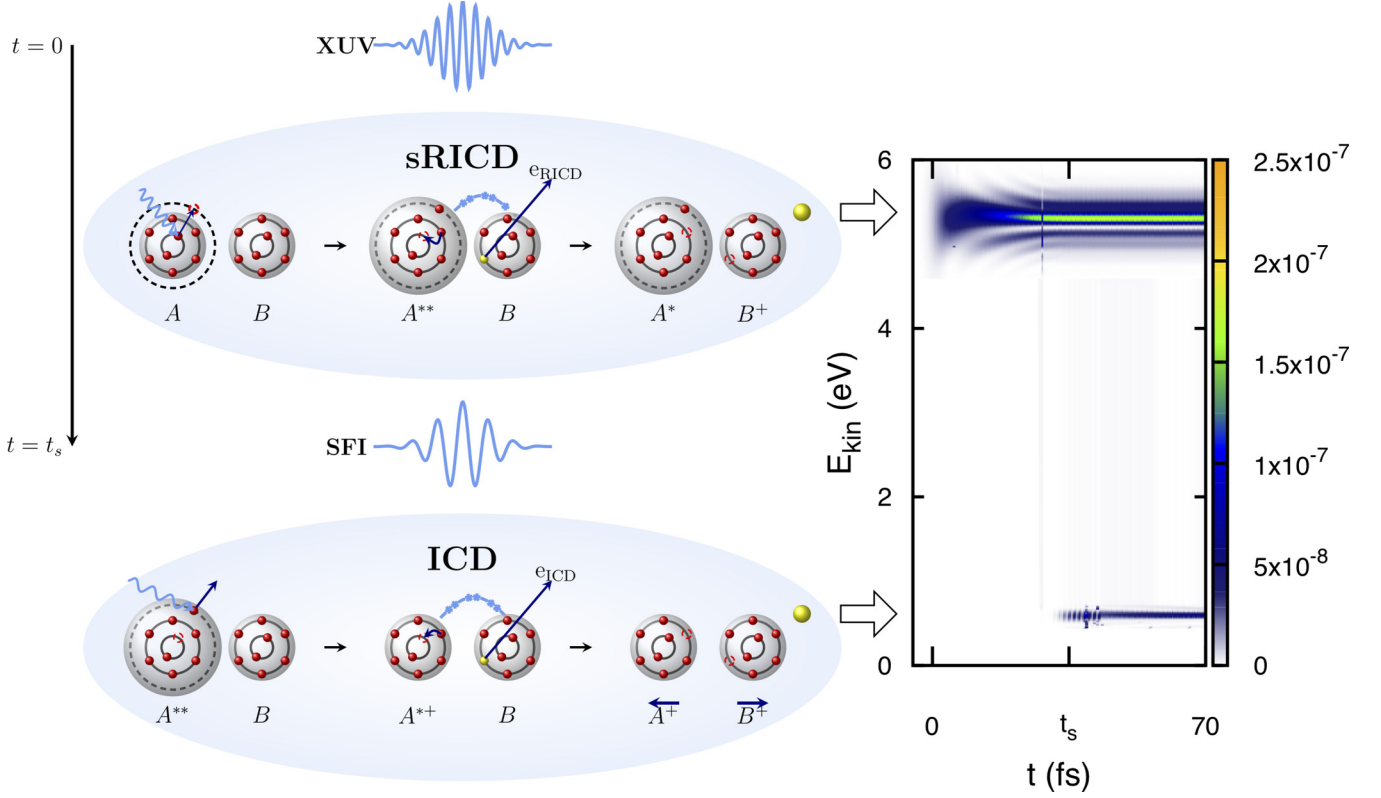


FIG. 1. Illustration [25] of the considered process. At $t = 0$, a spectator resonant interparticle Coulombic decay (sRICD) is initiated by XUV excitation. At a later time t_s , which in this example plot is 35 fs, a second strong infrared laser pulse quenches the sRICD process by ionization and thereby initiates ICD. The signals of the respective electrons with kinetic energies E_{kin} are well separated. While the sRICD appears from the start of the XUV pulse centered at $t = 0$, the ICD signal appears after the second pulse. This approach allows for a time-resolved measurement of the sRICD signal and an interference free measurement of the ICD signal. sRICD: unit A is excited from the inner valence shell. The created vacancy is filled with an electron from the outer valence and the excess energy is simultaneously transferred to B, which emits the sRICD electron. ICD: The initial state is created by removing the excited electron in A. It is then filled by an electron of the outer valence of A while the excess energy is transferred to B, which consequently emits the ICD electron. The two units are both positively charged and therefore undergo Coulomb explosion. The panel to the right illustrates typical time and energy resolved traces of sRICD and ICD electrons (see text).

denotes a continuum state with energy E_i , which entails both the kinetic energy E_{kin} of the emitted electron and the energy of the final cationic state i . These continuum states are orthogonal to all bound states of the system and amongst each other. Because the signals of the competing decay channels do not overlap, we can and will focus on the sRICD signal. Atomic units are used throughout unless stated otherwise.

We obtain the wave function of the system by solving the time-dependent Schrödinger equation $i\partial_t |\Psi(t)\rangle = H(t) |\Psi(t)\rangle$ for a model system consisting of the ground state $|G\rangle$, the resonant state $|R\rangle$ for the sRICD, and the resonant state $|I\rangle$ for the ICD process, as well as three sets of continuum states characterized by the respective final state energy of the decay process. All parameters describing a general resonant state are designated by the index r . The Hamiltonian consists of the single configuration Hamiltonian H_0 , the residual configuration interaction operators V_{RICD} and V_{ICD} as well as V_o for the competing autoionization and pRICD decay channels, and the operator $H_X(t)$ of the exciting XUV pulse:

$$H(t) = H_0 + V_{\text{sRICD}} + V_o + V_{\text{ICD}} + H_X(t). \quad (1)$$

The effect of the ionizing infrared pulse is modeled by terminating the sRICD and starting the ICD process at the time of the second pulse t_s . We will come back to this point below.

A. Description of the RICD process

The sRICD process we intend to describe in a fully time-dependent manner is schematically illustrated in Fig. 2. Starting from the ground state $|G\rangle$ we excite the system with an XUV pulse with a mean photon energy Ω into the resonant state $|R\rangle$ with the corresponding energy E_R . This resonant state can then under emission of an electron either decay to the continuum state characterized by a final state of the sRICD $|E_{\text{sR}}\rangle$ with a partial lifetime of τ_{sR} or to a continuum state characterized by the shared final state of pRICD and autoionization (AI) decay $|E_o\rangle$ with a different partial lifetime τ_o . The continuum state of the sRICD couples to other continuum states under emission of a photon. This fluorescence process is usually several orders of magnitude slower than the electronic decay process and is therefore ignored in this work. Alternatively to arriving in the continuum via the decaying resonant state, a simultaneous direct excitation and ionization

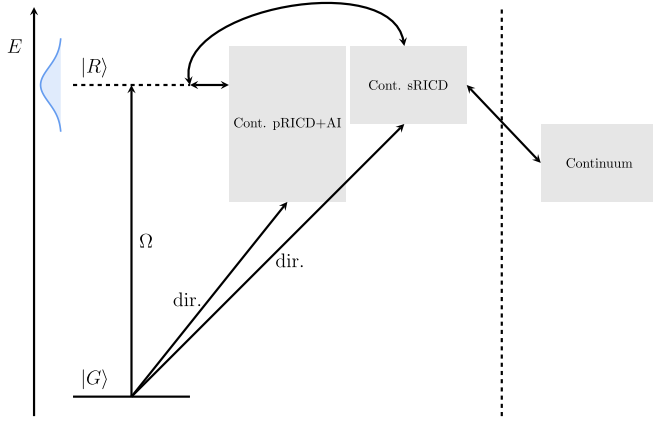


FIG. 2. Schematic illustration of the energy levels involved in the RICD process. The laser pulse with mean photon energy Ω excites the system into the resonant state $|R\rangle$ with energy E_R . The resonant state couples to two continua (denoted Cont. in the figure), one characterized by the sRICD final state and the other characterized by the pRICD and AI final state. Both channels have partial lifetimes in the order of femtoseconds. The continuum state of the sRICD process can then couple to other continuum states by emission of a photon. This fluorescence process has a lifetime τ_{fl} , which typically is in the order of nanoseconds and therefore much larger than the timescales of interest here. Alternatively, all continuum states can be reached directly by simultaneously ionizing and exciting in the case of the sRICD or single ionization in the case of the pRICD and AI. All couplings to the continuum via spontaneous radiative transitions are ignored in this work.

in the case of sRICD or a direct ionization in the case of the pRICD and AI channel, is also possible, which is denoted “dir” in the figure.

We assume low field strengths of the XUV pulse and therefore use first-order perturbation theory to describe its interaction with the system. Hence the wave function evolves according to

$$|\Psi(t)\rangle = \tilde{U}(t, t_0) |G(t_0)\rangle - i \int_{t_0}^t dt' \tilde{U}(t, t') H_X(t') |G(t')\rangle. \quad (2)$$

Here, $\tilde{U}(t, t_0)$ is the time evolution operator from a time t_0 until time t of the unperturbed system pertaining to the first four terms on the right-hand side of Eq. (1).

We are free to choose an energy reference and therefore set $E_G = 0$. This conveniently removes the time dependence from the ground state, since $|G(t_0)\rangle = \exp\{-iE_G t_0\} |G\rangle = |G\rangle$.

We introduce approximations for the time-evolution operator $\tilde{U}(t, t')$ appearing in the last term of Eq. (2). After the system has interacted with the XUV via $H_X(t')$ at time t' , the system decays via the configuration interaction V . In this general discussion, V refers to the sum of all configuration-interaction terms of Eq. (1). We will specify the explicit form of V for the different cases below. In the continuum we neglect the Coulomb interaction for simplicity, which leads to the time-evolution operator

$$\tilde{U}(t, t') = U_0(t, t') - i \int_{t'}^t dt'' U_0(t, t'') V \tilde{U}(t'', t'), \quad (3)$$

where $U_0(t, t')$ is the free-particle time-evolution operator.

By inserting Eq. (3) into Eq. (2) we arrive at

$$\begin{aligned} |\Psi(t)\rangle &= \tilde{U}(t, t_0) |G\rangle \\ &- i \int_{t_0}^t dt' U_0(t, t') H_X(t') |G\rangle \\ &- \int_{t_0}^t dt' \int_{t'}^t dt'' U_0(t, t'') V \tilde{U}(t'', t') H_X(t') |G\rangle. \end{aligned} \quad (4)$$

The time-evolution operator $\tilde{U}(t'', t')$ in the last integral describes the contribution of the Hamiltonian $H_0 + V$. This is equivalent to the Hamilton operator used in Fano’s description [43] of a decaying resonant state and below we therefore add the subscript F to the time-evolution operator and remove the tilde.

We now project on a continuum state $|E_{sR}\rangle$ characterized by the sRICD final state energy of the ionized system and the kinetic energy of the emitted electron. The first term vanishes, because of the orthogonality between bound and continuum states, and we obtain

$$\begin{aligned} \langle E_{sR} | \Psi(t) \rangle &= -i \int_{t_0}^t dt' \langle E_{sR} | U_0(t, t') H_X(t') | G \rangle \\ &- \int_{t_0}^t dt' \int_{t'}^t dt'' \langle E_{sR} | U_0(t, t'') V \\ &\times U_F(t'', t') H_X(t') | G \rangle. \end{aligned} \quad (5)$$

The time-evolution operator $U_0(t, t')$ solves the time-dependent Schrödinger equation for the Hamiltonian $\vec{p}^2/2$. The corresponding wave functions with wave vector $\vec{k}$ are $|\Psi_{\vec{k}}^0(t)\rangle = |\vec{k}\rangle \exp[-i \int_{-\infty}^t dt' \frac{1}{2} \vec{k}^2]$. Another way of formulating a time-evolution operator is by a projection from basis functions at time t' to such of time t :

$$U_0(t, t') = \int d\vec{k} |\Psi_{\vec{k}}^0(t)\rangle \langle \Psi_{\vec{k}}^0(t')|. \quad (6)$$

At this point we only consider the kinetic energy of the emitted electron and can therefore write the projection of a general continuum state $\langle E|$ on the free-particle time-evolution operator in the following way:

$$\langle E | U_0(t, t') = \langle E | \exp[i\Phi_0(E, t, t')] \quad (7)$$

$$= \langle E | \exp\left[-i \int_{t'}^t \left(\frac{k^2}{2} + E_{\text{fin}}\right) dt''\right], \quad (8)$$

where $k^2/2$ is the kinetic energy relative to the final state E_{fin} . The interaction V between a general resonant state $|r\rangle$ coupling to one of the continuum states is given by

$$V = \int dE' |E'\rangle V_{E'r} \langle r| + \int dE' |r\rangle V_{rE'} \langle E'|. \quad (9)$$

For two different final states, and therefore two continua, it reads

$$\begin{aligned} V &= \int dE'_1 |E'_1\rangle V_{E'_1 r} \langle r| + \int dE'_1 |r\rangle V_{rE'_1} \langle E'_1| \\ &+ \int dE'_2 |E'_2\rangle V_{E'_2 r} \langle r| + \int dE'_2 |r\rangle V_{rE'_2} \langle E'_2|. \end{aligned} \quad (10)$$

This case is, e.g., relevant for systems that cannot only decay via sRICD but also via autoionization or pRICD, which both yield a singly ionized system, which is the case that we investigate. At the same time, the initiating energy of the XUV laser pulse will be chosen too low to initiate an ICD process. Hence $V = V_{\text{sRICD}} + V_o$ in our case.

We also insert the resolution of the identity between the Fano time-evolution $U_F(t'', t')$ operator, to be specified below, and the Hamilton operator of the XUV field

using

$$\mathbb{1} = |R\rangle \langle R| + \int dE'_1 |E'_1\rangle \langle E'_1| + \int dE'_2 |E'_2\rangle \langle E'_2| \quad (11)$$

$$= |R\rangle \langle R| + \int dE'_{sR} |E'_{sR}\rangle \langle E'_{sR}| + \int dE'_o |E'_o\rangle \langle E'_o|. \quad (12)$$

By suppressing all dependences on angular momentum and using Eqs. (5), (10), and (12) we arrive at an amplitude of the sRICD process for the resonance $|R\rangle$ consisting of four terms:

$$\begin{aligned} \langle E_{sR} | \Psi(t) \rangle = & -i \int_{t_0}^t dt' \langle E_{sR} | U_0(t, t') H_X(t') | G \rangle - \int_{t_0}^t dt' \int_{t'}^t dt'' \langle E_{sR} | U_0(t, t'') | E_{sR} \rangle V_{ER} \langle R | U_F^R(t'', t') | R \rangle \langle R | H_X(t') | G \rangle \\ & - \int_{t_0}^t dt' \int_{t'}^t dt'' \int dE'_{sR} \langle E_{sR} | U_0(t, t'') | E_{sR} \rangle V_{ER} \langle R | U_F^R(t'', t') | E'_{sR} \rangle \langle E'_{sR} | H_X(t') | G \rangle \\ & - \int_{t_0}^t dt' \int_{t'}^t dt'' \int dE'_o \langle E_{sR} | U_0(t, t'') | E_{sR} \rangle V_{ER} \langle R | U_F^R(t'', t') | E'_o \rangle \langle E'_o | H_X(t') | G \rangle. \end{aligned} \quad (13)$$

In these expressions, $U_0(t, t')$ is the free particle time-evolution operator, whose action was specified in Eq. (8). $V_{ER} = \langle E | V | R \rangle = \sqrt{\Gamma_{sR}/(2\pi)}$ is related to the partial sRICD decay rate of the resonant state Γ_{sR} and $U_F^R(t'', t')$ is the Fano time-evolution operator, which is specific to the resonant state $|R\rangle$. The variables of the other, competing, processes are designated with the index o . The total decay width of the RICD resonant state is given by $\Gamma_R = \Gamma_{sR} + \Gamma_o$.

The terms of Eq. (13) are linked to the different pathways shown in Fig. 2 as follows. The first term of Eq. (13) describes the direct excitation and ionization to the continuum state, while the second term describes the excitation from the ground state to the resonant state followed by a decay to the continuum state. The third, indirect, term describes the direct excitation and ionization to the continuum state related to the sRICD final state, which couples to the resonant state, which then again decays into the continuum state. The last term is similar to the indirect term, but couples to the continuum of the competing pRICD and AI channels. Due to a different model system including only one final state, the latter term is not present in Eq. (11) of Ref. [44]. The interference of these different terms leads to the characteristic Fano profile [43].

We describe the interaction between the system and the exciting XUV field in the dipole approximation. Therefore, the corresponding Hamilton operator in the length gauge is given by $H_X(t') = -\mu E_X(t') = -\mu \frac{d}{dt'} A_X(t') f_X(t')$, where $E_X(t')$ denotes the time-dependent field strength of the XUV laser, while μ denotes the dipole operator, $A_X(t') = A_{0X} \cos(\Omega t')$ is the vector potential of the laser field in the direction of the linear polarization, and $f_X(t')$ is the Gaussian pulse envelope. Over the energy range of interest, we assume the transition dipole matrix element from the ground state to the continuum to be independent of the energy of the continuum state. To indicate these assumptions, we change the notation as $\langle E_i | \mu | G \rangle = \langle C_i | \mu | G \rangle$. We furthermore assume the coupling elements between the resonant and the continuum state to be real and independent of the continuum energy and therefore change the notation $V_{E_1R} \rightarrow V_R$ and $V_{E_2R} \rightarrow W_R$. Then, the Fano matrix elements, i.e., $\langle R | U_F^R(t'', t') | R \rangle$ and

$\langle R | U_F^R(t'', t') | E' \rangle$ of Eq. (13), can be solved using the projection formulation of the Fano time-evolution operator and solving the resulting integral by contour integration. Hence we write the Fano time-evolution operator as

$$\begin{aligned} U_F(t'', t') &= \int d\bar{E} |\Psi_{\bar{E}}(t'')\rangle \langle \Psi_{\bar{E}}(t')| \\ &= \int d\bar{E} |\Psi_{\bar{E}}\rangle \langle \Psi_{\bar{E}}| \exp[-i\bar{E}(t'' - t')]. \end{aligned} \quad (14)$$

The evaluation of these Fano matrix elements is given in the Appendix and for the sRICD signal we finally arrive at

$$\begin{aligned} \langle E | \Psi(t) \rangle = & i \langle C_{sR} | \mu | G \rangle \int_{t_0}^t dt' \exp[i\Phi_0(E_{sR}, t, t')] E_X(t') \\ & + (V_R \langle R | \mu | G \rangle - i\pi V_R^2 \langle C_{sR} | \mu | G \rangle \\ & - i\pi V_R W_R \langle C_o | \mu | G \rangle) \\ & \times \int_{t_0}^t dt' \int_{t'}^t dt'' \exp[i\Phi_0(E_{sR}, t, t'')] \\ & \times \exp\{-i[E_R - i\pi(V_R^2 + W_R^2)](t'' - t')\} E_X(t'). \end{aligned} \quad (15)$$

The first integral corresponds to the direct ionization process. The second integral is identical for the resonant and the two indirect terms. They have, though, different prefactors. For the case of a slowly varying envelope function [$\frac{d}{dt'} f_X(t') \approx 0$] and only considering the absorption of an XUV photon these two integrals are solved analytically for times after the exciting pulse. The direct term is given by

$$\begin{aligned} & - \frac{A_{0X} \Omega \langle C_{sR} | \mu | G \rangle}{4} \exp[-it(E_{\text{kin}} + E_{\text{fin}})] \\ & \times \exp\left[-\frac{\sigma^2}{2}(E_{\text{kin}} + E_{\text{fin}} - \Omega)^2\right] \\ & \times \text{Re}\left\{\text{erf}\left[\frac{1}{\sqrt{2}\sigma}\left(\frac{T_X}{2} + i\sigma^2(E_{\text{kin}} + E_{\text{fin}} - \Omega)\right)\right]\right\}, \end{aligned} \quad (16)$$

where Re denotes the real value and erf denotes the error function. The resonant and indirect ionization terms without their respective prefactors are given by

$$+ \frac{A_{0X} \Omega}{4[E_R - i\pi(V_R^2 + W_R^2) - E_{\text{kin}} - E_{\text{fin}}]} \exp[-it(E_R - i\pi(V_R^2 + W_R^2))] \exp\left[-\frac{\sigma^2}{2}(E_R - \Omega)^2\right] (\text{erf}(\tau_{1,\text{max}}) - \text{erf}(\tau_{1,\text{min}})) \\ - \frac{A_{0X} \Omega}{4[E_R - i\pi(V_R^2 + W_R^2) - E_{\text{kin}} - E_{\text{fin}}]} \exp[-it(E_{\text{kin}} + E_{\text{fin}})] \exp\left[-\frac{\sigma^2}{2}(E_{\text{kin}} + E_{\text{fin}} - \Omega)^2\right] (\text{erf}(\tau_{2,\text{max}}) - \text{erf}(\tau_{2,\text{min}})), \quad (17)$$

with $\tau_{1,\text{max}} = \frac{1}{\sqrt{2}\sigma}(\frac{T_X}{2} - i\sigma^2[E_R - i\pi(V_R^2 + W_R^2) - \Omega])$, $\tau_{1,\text{min}} = -\frac{1}{\sqrt{2}\sigma}(\frac{T_X}{2} + i\sigma^2[E_R - i\pi(V_R^2 + W_R^2) - \Omega])$, $\tau_{2,\text{max}} = \frac{1}{\sqrt{2}\sigma}(\frac{T_X}{2} - i\sigma^2(E_{\text{kin}} + E_{\text{fin}} - \Omega))$, and $\tau_{2,\text{min}} = -\frac{1}{\sqrt{2}\sigma}(\frac{T_X}{2} + i\sigma^2(E_{\text{kin}} + E_{\text{fin}} - \Omega))$. Here, σ is the standard deviation of the Gauss distribution in time and T_X is the duration of the exciting XUV pulse.

The time- and energy-differential ionization probability of the RICD process is the absolute square of the amplitude given in Eq. (15) and therefore a sum over 28 different terms (seven absolute squares and 21 mixed interference terms). Their relative contributions are determined by the Fano parameter $q = \frac{\langle R|\mu|G \rangle}{\langle C|\mu|G \rangle \pi V_R}$.

B. Transition from the resonant state of the RICD process to the initial state of the ICD process

We propose a time-resolved measurement of the RICD process, where the quenching of the RICD process by strong field ionization with an IR pulse at time t_s entails the initiation of an ICD process. Technically, this means a population transfer from the resonant state of the RICD process to the initial state of the ICD process. We assume the transition in time to be Gaussian shaped and that the ICD signal is unaffected by pulse shape effects. The transition is modeled as follows.

We determine the remaining population of the resonant state of the RICD process N_0 at the beginning of the second pulse $t = t_s - \delta t$ as

$$N_0 = \frac{|\langle R|\mu|G \rangle|^2}{4} \exp[-\sigma^2(\Omega - E_R)^2] \times \exp[-(\Gamma_{sR} + \Gamma_o)(t_s - \delta t)]. \quad (18)$$

Here, δt is chosen as $\frac{5}{2}\sigma_{\text{IR}}$ with σ_{IR} being the standard deviation of the IR pulse in time. We assume the decrease of the population $N_R(t)$ in the resonant state of the RICD process $|R\rangle$ to have a Gaussian shape $f_{\text{IR}}(t)$ centered around the time of the second pulse:

$$\frac{dN_R(t)}{dt} = -f_{\text{IR}}(t)N_R(t) \quad (19)$$

and therefore

$$N_R(t) = N_0 \exp\left[-\frac{\alpha}{2} \text{erf}\left(-\frac{\delta t}{\sqrt{2}\sigma}, \frac{t - t_s}{\sqrt{2}\sigma}\right)\right]. \quad (20)$$

Correspondingly, the population of the initial state $|I\rangle$ of the ICD process $N_I(t)$ is increased:

$$N_I(t) = N_0 - N_R(t). \quad (21)$$

The square roots of the time-dependent populations are then updated in every time step and used instead of $\langle r|\mu|G \rangle$ in the calculation of the amplitude of the ionization probability. In order to allow for a complete depopulation of the resonant state, we have chosen $\alpha = 8$.

Since we assume a direct population of the resonant state of the ICD process $|I\rangle$ from the resonant state of the sRICD process $|R\rangle$ induced with a short and intense laser pulse, we assume that the terms of Eq. (13), which are mediated by the continuum, can be neglected. After the end of the ionizing pulse the amplitude of the ICD process associated with resonance $|I\rangle$ therefore reads

$$\langle E|\Psi(t) \rangle = - \int_{t_0}^t dt_s \int_{t_s+\delta t}^t dt'' \langle E|U_0(t, t'')|E \rangle \times V_{EI} \langle I|U_F^I(t'', t_s)|I \rangle \sqrt{N_I}. \quad (22)$$

III. COMPUTATIONAL DETAILS

In our model system, where the nuclei are kept fixed, we evaluated Eq. (13), and simulated the time-dependent buildup of the Fano resonance for the sRICD process for parameters corresponding to those of the neon dimer at the equilibrium distance of 3.08 Å [47] after an excitation to the $\text{Ne}2s^{-1}2p^65p_z$ state. The parameters are given in Table I. All simulations were performed with ELDEST [48–52], where only the outer integral over t' in Eq. (15) is solved numerically. We use the Fano parameter $q = 10$. The exact q value is unknown to us, but we expect it to be larger than unity due to the low probability for direct single photon ionization and excitation. Since the exact q values are unknown, we assume equal values for the two continua. We have performed calculations for a range of q parameters, of which a cut is shown in Fig. 3. The time of $t = 93$ fs after the initiating excitation

TABLE I. Energies and lifetimes for the excited states $\text{Ne}2s^{-1}2p^6np\text{-Ne}$ ($n = 4, 5$) undergoing RICD. The resonant energies are taken from Ref. [45], the final-state energies of the sRICD $\text{Ne}2s^22p^5(P_{3/2,1/2})np\text{-Ne}2p^5(P_{3/2,1/2})$, of the pRICD and AI $\text{Ne}2s^22p^5(P_{3/2,1/2})\text{-Ne}$ and the ICD process were averaged to give approximations of nonrelativistic energies. The lifetimes, τ , of the sRICD and pRICD+AI are from Ref. [40] and the ICD lifetime are from Ref. [46].

	$n = 4$	$n = 5$	pRICD + AI	ICD
E_r [eV]	47.1230	47.6930		48.4750
E_{fin} [eV]	41.8391	42.4138	21.6290	47.8688
$\tau[2s^{-1}(np_z)^1\Sigma_u^+]$ [fs]	112	106	206	98

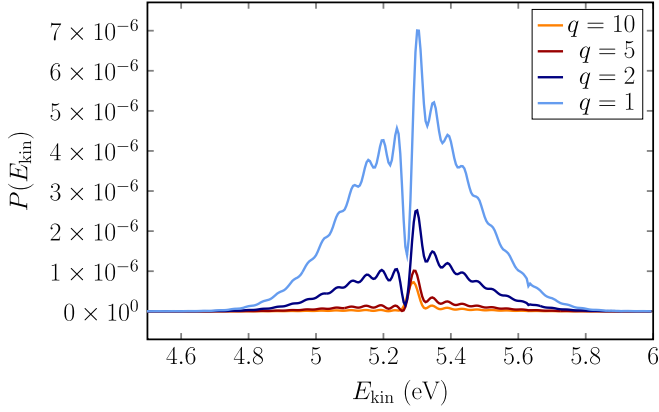


FIG. 3. Peak shape of the spectator RICD electron spectrum for 50 cycles of the exciting pulse with different values of the Fano q parameter at time $t = 93$ fs after the excitation at time $t = 0$. The Fano profile is modified by an oscillation in energy. This oscillation stems from the interference terms of the direct term with the resonance terms of $P(E_{\text{kin}}, t)$ and is described by Eq. (24). The larger q , the less likely the direct path and therefore, for increasing q , the signal is damped for a given transition dipole moment into the resonant state.

was chosen to illustrate a typical behavior. It becomes evident that the basic features of the spectra are identical, even though the width and the amplitude of the signal differ. Therefore, the conclusions of this paper are independent of the choice of the q parameter.

The exciting pulse for the main results in Figs. 1 and 5 has $A_{0X} = 5 \times 10^8$ W/cm², $\Omega = 47.6930$ eV, and a FWHM = 6.1 fs corresponding to 50 cycles. This duration ensures that the bandwidth is so small that only the $\text{Ne}2s^{-1}2p^65p_z$ state in the neon dimer is resonantly excited.

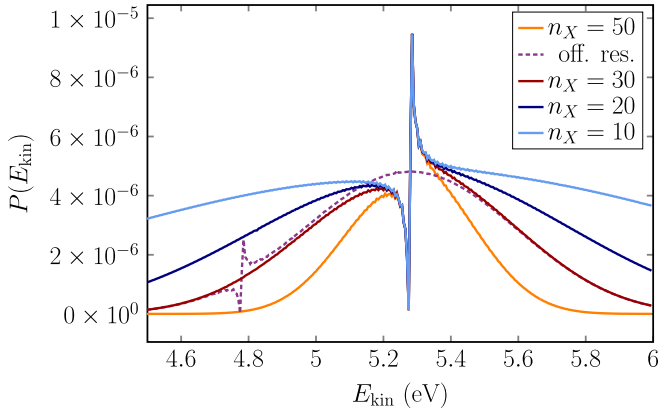


FIG. 4. Peak shape of the sRICD electron spectrum for late time $t \gg \frac{1}{\Gamma_R}$ after excitation of our system with electronic parameters corresponding to those of the $5p$ state in the neon dimer depending on the number of cycles of the exciting pulse n_X . The shape can be explained by folding the Fourier transform of the exciting pulse in time with a Fano profile. In this example, the Fano parameter is $q = 10$. Around the resonance energy, the peaks are identical. The width of the peak is decreased for an increased number of cycles n_X and therefore determined by the duration of the exciting pulse. The dashed line illustrates an excitation 0.5 eV off resonance for $n_X = 30$.

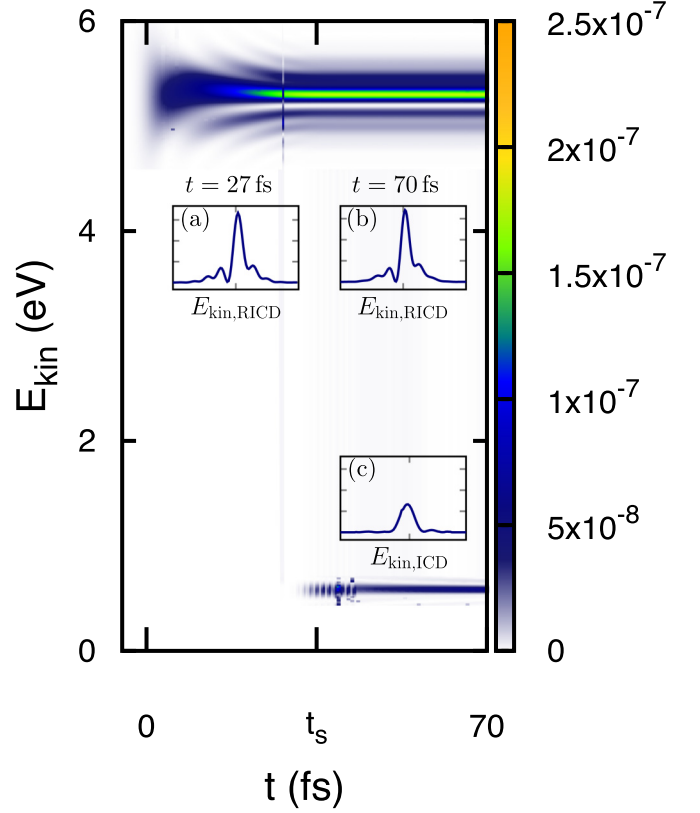


FIG. 5. Time-resolved sRICD and ICD spectrum after initial excitation at $t = 0$ and quenching the sRICD at $t = 35$ fs. The sRICD signal centered around 5.3 eV before the second pulse shows the buildup of a Fano profile, with an additional oscillation in energy $\cos[(E_{\text{kin}} + E_{\text{fin}} - E_r)t]$ [see (a) and text]. After depopulation of the sRICD resonant state around t_s , the signal shape remains constant [see (b)]. For the ICD signal centered around 0.6 eV shown in (c), only the resonant term of Eq. (13) contributes, which has the shape of a Voigt profile. A pump-probe spectrum can be obtained by varying t_s .

We assumed a complete population transfer from the resonant state of the sRICD process to the resonant state of the ICD process during the second ionizing pulse over a time of 15 fs as realized experimentally [27].

IV. RESULTS AND DISCUSSION

In the investigation of decay processes with short laser pulses, the shortness comes with the cost of an energy broadening. As a consequence, the kinetic-energy spectrum of an sRICD electron is given by a Fano profile centered around the kinetic energy, that corresponds to the energy of the resonant state, convoluted with a Gaussian centered around the kinetic energy, that would correspond to a direct excitation and ionization into the final state. Here, we show the Voigt profile part inherent to most terms of the absolute square of Eq. (15):

$$P(E_{\text{kin}}, \infty) \propto \frac{\exp[-\sigma_t^2(E_{\text{kin}} + E_{\text{fin}} - \Omega)^2]}{(E_{\text{kin}} + E_{\text{fin}} - E_R)^2 + \frac{\Gamma_R^2}{4}}. \quad (23)$$

The shapes of the spectra are illustrated for different numbers of cycles n_X for the exciting pulse in Fig. 4 for a late time $t \gg \frac{1}{\Gamma_r}$. There, the mean pulse energy was chosen to be on resonance and, therefore, the Fano profile is centered on the maximum of the Gaussian. It is clearly seen how the peak is narrowed with an increased number of laser cycles in the exciting pulse. In order to only excite into a single state we choose $n_X = 50$, such that other excited states are outside $3\sigma_E$ of the energy distribution of the exciting pulse. In future investigations of the interaction between several decaying resonant states, a smaller number of cycles will be appropriate.

For the case of an off-resonant excitation, the Fano profile and the Gaussian will not be centered around the same kinetic energy of the sRICD electron and the sRICD electron peak will be damped accordingly as illustrated by the dashed line of Fig. 4 for $n_X = 30$.

By using the parameters for the neon dimer (see Table I), we simulated the time evolution of an initial excitation at $t = 0$ and quenching of the decay processes by ionization with a second laser pulse centered at the time $t = 35$ fs. The results are presented in Fig. 5. We will discuss its different characteristics separately.

The time-resolved spectrum shows two energy-separated signals within the chosen kinetic-energy range. The signal of the sRICD process is initiated with the first and the signal of the ICD process by the second laser pulse, which at the same time reduces those contributions of the sRICD signal that involve a population of the resonant state. Due to the fast depopulation of the resonant state, the signal before and after the second pulse are effectively the same [compare Figs. 5(a) and 5(b)]. This allows one to generate a full pump-probe spectrum. The competing autoionization and pRICD process would result in much higher kinetic electron energies of about 26 eV and can therefore unambiguously be distinguished from the sRICD and ICD electrons shown in Fig. 5.

While the sRICD signal shows the buildup of a Fano profile [see Fig. 5(a)], and therefore interference effects, the ICD signal is an interference free Voigt profile [see Fig. 5(c)], because only the resonant term [see Eq. (22)] significantly contributes to it. This can be explained by the initiating process being ionization rather than excitation. In case of the ICD process, the final state is characterized by a doubly ionized system. A single photon double ionization with low laser intensities is very unlikely compared to a single ionization. Hence the corresponding Fano parameter would be very large and interference effects would have low amplitudes. At the same time, the kinetic-energy distribution of the two emitted electrons can be expected to be wide and not necessarily to peak at the energy of the ICD electrons, which would further marginalize the contribution of the direct pathway. As a result, the signal shape is described by the absolute square of Eq. (22), i.e., the terms of Eq. (17).

We now turn our attention from the variation of the signals in energy to their variation in time. During the buildup of the signals over time, they show oscillations in both energy and time, which are easiest seen for the ICD in the video of the Supplemental Material [53]. For the sRICD process, the variation in time can be obtained by solving the dominant part of the absolute square of Eq. (15) analytically. For the ICD

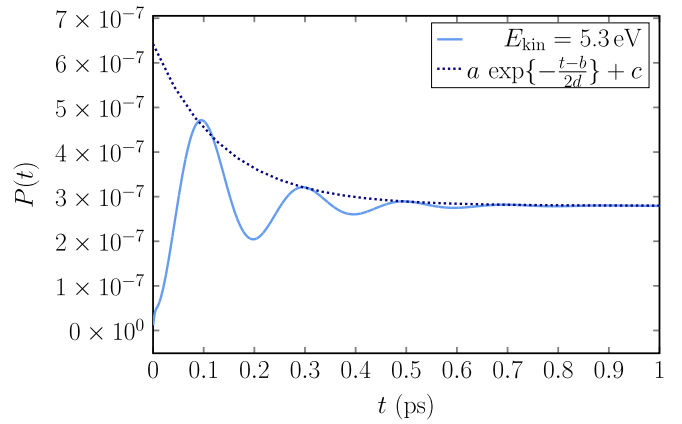


FIG. 6. Oscillation in time for observing the sRICD electron with a kinetic energy of 5.3 eV, for $n_X = 50$ and $q = 10$. This oscillation can be described by $\cos[(E_{\text{kin}} + E_{\text{fin}} - E_r)t]$. Its period is therefore dependent on the kinetic energy of the electron. It is damped in time by the decay of the resonant state $\exp(-\Gamma_r t/2)$. While the oscillations in energy are known and have been observed in energy, the oscillations in time require a process with a long enough lifetime to be observed around the resonance energy.

process, the dominant part of the absolute square of Eq. (22) needs to be solved. In both cases, it can be shown that the signal is proportional to

$$\cos[(E_r - E_{\text{kin}} - E_{\text{fin}})t] \exp\left(-\frac{\Gamma_r}{2}t\right). \quad (24)$$

This equation is not specific to the decay process and therefore valid for both the sRICD and the ICD signal ($r = R, I$). The variation in energy, illustrated in Fig. 5(a), is in agreement with Ref. [54]. As can be seen from Eq. (24), the oscillation is also visible in time as shown in Fig. 6 for a fixed kinetic energy of the sRICD electron of $E_{\text{kin}} = 5.3$ eV.

In order to be observed, such an oscillation requires long enough lifetimes of the resonant state. The comparably slow sRICD process offers the opportunity to observe and utilize it. An oscillation in time has recently been observed experimentally for an AI process [55]. In both the latter and in our case, a discrepancy between the actual and the fitted lifetime is observed. Given the analytical expressions of this work, we are able to understand this discrepancy. The kinetic energy in Fig. 6 is slightly higher than the kinetic energy corresponding to the resonant state. The further away from the resonance this energy is chosen, the shorter the period of this oscillation. The oscillation is exponentially damped by the lifetime of the decaying state. However, the dynamics of the system are more complex than shown in Eq. (24), because some terms of the resonant and indirect contributions are damped by $\exp(-\Gamma_r t)$ while others are damped by $\exp(-\Gamma_r t/2)$, which can be seen by evaluating the time dependence of the absolute square of Eq. (15). This behavior is effectively only observed in the beginning of the decay, because its contribution becomes small within a short time. Therefore, a fit of the maxima at longer times, where the parts damped by $\exp(-\Gamma_r t)$ can be neglected, to the function $a \exp[-(t-b)/2d] + c$ gives a good estimate of the lifetime $d \approx \tau_r$. The fit in Fig. 6, where the first maximum was omitted, yields a lifetime of

68 fs. The effective overall lifetime of the excited resonant state used as input parameter for the simulations is given by $\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{sRICD}}} + \frac{1}{\tau_o}$ and $\tau_{\text{eff}} = 70$ fs using the parameters given in Table I. The value determined from the fit is slightly lower than this effective lifetime but still matches it very well. This kind of fit can therefore be used to determine the lifetime of the electronic decay process.

V. SUMMARY

We have presented a time-dependent theoretical description of the sRICD and ICD processes investigated with short laser pulses for a model system with frozen nuclei. We suggest sRICD as the primary process. We then imagine that it is possible to quench the sRICD process by a strong laser pulse and thereby initiate the ICD process interference free. We

have shown an oscillation of the ionization probability in time, which is general for electronic decay processes. For processes with comparably long lifetimes, such as the ICD processes, this oscillation allows for a new way of measuring the lifetime of the underlying processes. Moreover, the basic formulation opens the door for future investigations in controlling the decay processes and to guide time-resolved experimental studies.

ACKNOWLEDGMENTS

The research of E.F. was supported by the Villum Foundation. The research of L.B.M. was supported by the Villum Kann Rasmussen Centre of Excellence QUSCOPE—Quantum Scale Optical Processes.

APPENDIX: FANO MATRIX ELEMENTS

1. One continuum final state

The time-independent wave function $|\Psi_{\underline{E}}\rangle$ is a solution to the same Hamiltonian as considered in Ref. [43]. We therefore have the same solution

$$|\Psi_{\underline{E}}\rangle = a(\underline{E})|r\rangle + \int dE' b_{E'}(\underline{E})|E'\rangle, \quad (\text{A1})$$

with coefficients

$$\begin{aligned} a(\underline{E}) &= -\frac{V_r}{\sqrt{[\underline{E} - E_r - F(\underline{E})]^2 + \pi^2 V_r^4}}, \\ b_{E'}(\underline{E}) &= \frac{V_r a(\underline{E})}{\underline{E} - E'} \\ &\quad - \frac{\underline{E} - E_r - F(\underline{E})}{\sqrt{[\underline{E} - E_r - F(\underline{E})]^2 + \pi^2 V_r^4}} \delta(\underline{E} - E'). \end{aligned} \quad (\text{A2})$$

Here, $F(\underline{E})$ is a small shift in the energy position of the resonant state $|r\rangle$, which is of second order in V and which we neglect in the following.

The Fano matrix elements of Eq. (13) involving the Fano time-evolution operator can now be solved by contour integration in the negative complex half-plane, where a_{-1} is the first-order residue and we use that $\langle r|r\rangle = 1$, $\langle E|E'\rangle = \delta(E - E')$, and $\langle E|r\rangle = 0$:

$$\langle r|U_F(t'', t')|r\rangle = \int d\underline{E} \exp[-i\underline{E}(t'' - t')] |a(\underline{E})|^2 \quad (\text{A4})$$

$$= V_r^2 \int d\underline{E} \frac{\exp[-i\underline{E}(t'' - t')]}{(\underline{E} - E_r)^2 + \pi^2 V_r^4} \quad (\text{A5})$$

$$= V_r^2 \int d\underline{E} \frac{\exp[-i\underline{E}(t'' - t')]}{(\underline{E} - E_r + i\pi V_r^2)(\underline{E} - E_r - i\pi V_r^2)} \quad (\text{A6})$$

$$= V_r^2 \exp[-iE_r(t'' - t')] \int d\tilde{E} \frac{\exp[-i\tilde{E}(t'' - t')]}{(\tilde{E} + i\pi V_r^2)(\tilde{E} - i\pi V_r^2)} \quad (\text{A7})$$

$$= 2\pi i V_r^2 \exp[-iE_r(t'' - t')] a_{-1} \quad (\text{A8})$$

$$= \exp[-i(E_r - i\pi V_r^2)(t'' - t')], \quad (\text{A9})$$

$$\int dE' \langle r|U_F(t'', t')|E'\rangle = \int d\underline{E} \int dE' \exp[-i\underline{E}(t'' - t')] a(\underline{E}) b_{E'}^*(\underline{E}) \quad (\text{A10})$$

$$= V_r^2 \int d\underline{E} \frac{(\underline{E} - E_r) \exp[-i\underline{E}(t'' - t')]}{(\underline{E} - E_r)^2 + \pi^2 V_r^4} \quad (\text{A11})$$

$$= V_r^2 \int d\underline{E} \frac{(\underline{E} - E_r) \exp[-i\underline{E}(t'' - t')]}{(\underline{E} - E_r + i\pi V_r^2)(\underline{E} - E_r - i\pi V_r^2)} \quad (\text{A12})$$

$$= V_r^2 \exp[-iE_r(t'' - t')] \int d\tilde{E} \frac{\tilde{E} \exp[-i\tilde{E}(t'' - t')]}{(\tilde{E} + i\pi V_r^2)(\tilde{E} - i\pi V_r^2)} \quad (\text{A13})$$

$$= 2\pi i V_r^2 \exp[-iE_r(t'' - t')] a_{-1} \quad (\text{A14})$$

$$= -i\pi V_r \exp[-i(E_r - i\pi V_r^2)(t'' - t')]. \quad (\text{A15})$$

2. Two continuum final states

The time-independent wave function $|\Psi_E\rangle$ is a solution to the same Hamiltonian as considered in Ref. [43]. After neglecting $F(E)$ as before we therefore have the same solutions

$$|\Psi_E\rangle = a(E)|r\rangle + \int dE' b_{E_1}(E)|E'_1\rangle + \int dE' b_{E_2}(E)|E'_2\rangle, \quad (\text{A16})$$

with coefficients

$$a(E) = - \frac{\sqrt{V_r^2 + W_r^2}}{\sqrt{(E - E_r)^2 + \pi^2(V_r^2 + W_r^2)^2}}, \quad (\text{A17})$$

$$b_{E'_1}(E) = \frac{V_r a(E)}{\sqrt{V_r^2 + W_r^2}(E - E'_1)} - \frac{E - E_r}{\sqrt{(E - E_r)^2 + \pi^2(V_r^2 + W_r^2)^2}} \delta(E - E'_1), \quad (\text{A18})$$

$$b_{E'_2}(E) = \frac{W_r a(E)}{\sqrt{V_r^2 + W_r^2}(E - E'_2)} - \frac{E - E_r}{\sqrt{(E - E_r)^2 + \pi^2(V_r^2 + W_r^2)^2}} \delta(E - E'_2). \quad (\text{A19})$$

The Fano integrals can now be solved by contour integration in the negative complex half-plane, where a_{-1} is the first-order residue and we use that $\langle r|r\rangle = 1$, $\langle E|E'\rangle = \delta(E - E')$, and $\langle E|r\rangle = 0$:

$$\langle r|U_F(t'', t')|r\rangle = (V_r^2 + W_r^2) \int dE \exp[-iE(t'' - t')] |a(E)|^2 \quad (\text{A20})$$

$$= (V_r^2 + W_r^2) \int dE \frac{\exp[-iE(t'' - t')]}{(E - E_r)^2 + \pi^2(V_r^2 + W_r^2)^2} \quad (\text{A21})$$

$$= (V_r^2 + W_r^2) \int dE \frac{\exp[-iE(t'' - t')]}{[E - E_r + i\pi(V_r^2 + W_r^2)][E - E_r - i\pi(V_r^2 + W_r^2)]} \quad (\text{A22})$$

$$= (V_r^2 + W_r^2) \exp[-iE_r(t'' - t')] \int d\tilde{E} \frac{\exp[-i\tilde{E}(t'' - t')]}{[\tilde{E} + i\pi(V_r^2 + W_r^2)][\tilde{E} - i\pi(V_r^2 + W_r^2)]} \quad (\text{A23})$$

$$= 2\pi i (V_r^2 + W_r^2) \exp[-iE_r(t'' - t')] a_{-1} \quad (\text{A24})$$

$$= \exp\{-i[E_r - i\pi(V_r^2 + W_r^2)](t'' - t')\}, \quad (\text{A25})$$

$$\int dE' \langle r|U_F(t'', t')|E'\rangle = \int dE \int dE' \exp[-iE(t'' - t')] a(E) b_{E'}^*(E) \quad (\text{A26})$$

$$= V_r \int dE \frac{(E - E_r) \exp[-iE(t'' - t')]}{(E - E_r)^2 + \pi^2(V_r^2 + W_r^2)^2} \quad (\text{A27})$$

$$= V_r \int dE \frac{(E - E_r) \exp[-iE(t'' - t')]}{[E - E_r + i\pi(V_r^2 + W_r^2)][E - E_r - i\pi(V_r^2 + W_r^2)]} \quad (\text{A28})$$

$$= V_r \exp[-iE_r(t'' - t')] \int d\tilde{E} \frac{\tilde{E} \exp[-i\tilde{E}(t'' - t')]}{[\tilde{E} + i\pi(V_r^2 + W_r^2)][\tilde{E} - i\pi(V_r^2 + W_r^2)]} \quad (\text{A29})$$

$$= 2\pi i V_r \exp[-iE_r(t'' - t')] a_{-1} \quad (\text{A30})$$

$$= -i\pi V_r \exp\{-i[E_r - i\pi(V_r^2 + W_r^2)](t'' - t')\}. \quad (\text{A31})$$

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