

ICECream

International Conference on Electron Capture in an environment
- real experiments and models



Tübingen, 23.–26. September 2024

Organizing Committee:

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Funding:



Inter-particle Coulombic electron capture (ICEC) is an environment-enabled process in which an electron can be efficiently attached to an ion, atom, molecule, or quantum dot. The excess energy is simultaneously transferred to a neighboring system which is ionized or excited. ICEC has been predicted by theoretical approaches ranging from analytical models to ab initio electronic structure and dynamical calculations. Their common assumption is that nuclei remain fixed during ICEC. However, given the time scale of ICEC, nuclear dynamics should play an important role in changing the efficiency and/or influencing the final state of the system. The aim of this conference is to gather state-of-the-art research on environment-assisted electron capture and related topics as well as on quantum-dynamical methods and experimental techniques which will provide a complete description of ICEC in the future.

Register at <https://forms.gle/DMVNoQxMZKPgD7CB6>



Confirmed Speakers

Lorenz Cederbaum
Jimena Gorfinkiel
Till Jahnke
Robert Bennett

Venue

Monday:
Rittersaal in Castle Hohentübingen
Museum Alte Kulturen
Burgsteige 11

Tuesday–Thursday:
Geo- und Umweltforschungszentrum
Campus Morgenstelle
Schnarrenbergstr. 94-96

Book of Abstracts

Talks

Monday 23.09.2024

Interparticle Coulombic Electron Capture: an overview and insights from an ab initio scattering approach

Jimena Gorfinkiel
The Open University

During the last decades it was discovered that electronically excited states and even local ground states, which are created through interaction with ionizing radiation, can decay through a variety of interatomic Mechanisms in clusters. Energy and charge can be transferred between the cluster's constituents, resulting in the emission of secondary electrons or photons. The details of such processes determine the final fate of the cluster and in particular its fragmentation into charged or neutral fragments. Here I present multi-electron-photon coincidence spectroscopy as a powerful tool for the experimental investigation of various interatomic decay mechanisms. This method enabled the observation of elusive phenomena like core-level interatomic Coulombic decay in van der Waals clusters and hitherto undiscovered collective processes like electron-transfer-mediated decay with four participants. I will also discuss the capabilities of our experimental approach to detect novel processes such as interatomic Coulombic electron capture.

Scattered thoughts on scattering experiments for ICEC

Juraj Fedor

I will make an overview of experimental approaches available in our laboratory (and in closely collaborating laboratories) and speculate how their combination could lead to ICEC observation. The topics discussed will include:

- Electron-energy loss spectroscopy (for getting information about vibrational [1] and electronic [2] excitation.
- Production of heterogeneous neutral clusters by adiabatic expansion [3].
- Electron collisions with liquid microjets [4].
- Declined (and re-submitted) proposal for ICEC detection at Synchrotron Soleil.

[1] J. Dvořák et al, Phys. Rev. Lett. 2022, <https://doi.org/10.1103/PhysRevLett.129.013401> [2] P. Nag et al., J. Phys. Chem. Lett. 2024, <https://doi.org/10.1021/acs.jpcllett.3c03460> [3] J. Kočíšek et al., J. Phys. Chem. Lett. 2016, <https://doi.org/10.1021/acs.jpcllett.6b01601> [4] P. Nag et al., J. Phys. B 2023, <https://doi.org/10.1088/1361-6455/ad0205>

Correlated wavefunction approaches to laser-driven electron dynamics in molecules and their control

Peter Saalfrank

Institute for Chemistry, University of Potsdam, Potsdam, D-14469 Germany

Progress in generating intense laser pulses has pushed the timescale for probing dynamical processes in atomic and molecular systems down to the attosecond domain. In parallel with experiments, which are more and more applied to *molecular systems*, theoretical methods are being developed to treat explicitly time-dependent electronic motion after photoexcitation. This talk describes our efforts to extend *ab initio* wavefunction based methods of stationary electronic structure theory, to the explicitly time-dependent domain, and their application to molecular systems [1]. In particular, time-dependent configuration interaction (TD-CI) [2] and time-dependent complete active space SCF methods (TD-CASSCF) [3] will be reviewed as systematically improvable, correlated methods for propagating electronic wavefunctions in real time. Extensions towards the treatment of ionization, dissipation, and nuclear motion will be discussed.

Armed with these methods, we seek to describe electronic motion in laser-driven molecular systems, and to control it using shaped, ultrashort laser pulses. In one example, we shall describe High Harmonic Generation (HHG) spectra of molecules with the following purposes: to study the effects of ionization, nuclear motion and non-Born-Oppenheimer effects on molecular HHG spectra [4, 5, 6, 7]; to control HHG by stochastic pulse optimization [9] or by bringing the molecule in a cavity [10]. In a second set of examples we try to enforce selective state-to-state transitions or the creation of specific electronic wavepackets, *e.g.*, to control the electron correlation (or entanglement) in atomic and molecular systems [11].

- [1] P. Saalfrank, F. Bedurke, C. Heide, T. Klamroth, S. Klinkusch, P. Krause, M. Nest, and J.C. Tremblay. *Molecular Attochemistry: Correlated Electron Dynamics Driven by Light*. Advances in Quantum Chemistry: Chemical Physics and Quantum Chemistry **81**, 15 (2020).
- [2] P. Krause, T. Klamroth, and P. Saalfrank, J. Chem. Phys. **123**, 074105 (2005)
- [3] M. Nest, T. Klamroth, and P. Saalfrank, J. Chem. Phys. **122**, 124102 (2005).
- [4] G.K. Paramonov and P. Saalfrank, Phys. Rev. A **97**, 053408 (2018).
- [5] F. Bedurke, T. Klamroth, P. Krause, and P. Saalfrank, J. Chem. Phys. **150**, 234114 (2019).
- [6] F. Bedurke, T. Klamroth, and P. Saalfrank, Phys. Chem. Chem. Phys. **23**, 13544 (2021).
- [7] Ch. Witzorky, G. Paramonov, F. Bouakline, R. Jaquet, P. Saalfrank, and T. Klamroth, J. Chem. Theor. Comput. **170**, 7353 (2021).
- [8] P. Albrecht, P. Saalfrank, and T. Klamroth, J. Phys. Chem. A **127**, 5942-5955 (2023).
- [9] J.B. Schönborn, P. Saalfrank, and T. Klamroth, J. Chem. Phys. **144**, 044301 (2018).
- [10] P. Albrecht, T. Klamroth, and P. Saalfrank, to be published.
- [11] M. Nest, M. Ludwig, I. Ulusoy, T. Klamroth, and P. Saalfrank, J. Chem. Phys. **138**, 164108 (2013).

Tuesday 24.09.2024

Shaking Up ICEC: Exploring Nuclear Dynamics in Inter-Particle Coulombic Electron Capture

Elena Jahr, Elke Fasshauer

University of Tübingen

While existing theoretical approaches for the inter-particle Coulombic electron capture (ICEC) [1] range from analytical models to ab initio calculations of electronic structure and dynamics, they have traditionally assumed static atomic nuclei [2]. Observations of related mechanisms [3] suggest however, that nuclear dynamics may significantly influence efficiency and/or final states.

We develop therefore analytical approaches to gain insights into nuclear dynamics in ICEC and aid in the interpretation of numerical simulations. We will present promising systems and their nuclear dynamics, demonstrating their dominance over simple radiative recombination in our models, with the aim of informing future experiments.

[1] K. Gokhberg K. and L.S. Cederbaum *J. Phys. B: At. Mol. Opt. Phys.* **42** 231001 (2009)

[2] A. Bande et al. *J. Phys. B: At. Mol. Opt. Phys.* **56** 232001 (2023)

[3] T. Jahnke et al. *Chem. Rev.* **20** 11295 (2020)

Wednesday 25.09.2024

Collective emission of real and virtual photons & Energy transfer by light

Lorenz Cederbaum

University of Heidelberg

QED effects in ICD and related processes

Robert Bennett

University of Glasgow

Interatomic relaxation processes are typically described using the tools of ab-initio quantum chemistry. However, subject to certain physical constraints, alternative methods open up the study of these processes to the molecular QED framework. In this talk, I will outline how this applies to interatomic Coulombic decay (ICD) and related processes, discuss the strengths and weaknesses of the alternative approach, and clarify some confusing aspects of the terminology used by both communities.

Investigation of charge and energy transfer processes in clusters by multi-electron-photon coincidence spectroscopy

Andreas Hans

University of Kassel

During the last decades it was discovered that electronically excited states and even local ground states, which are created through interaction with ionizing radiation, can decay through a variety of interatomic Mechanisms in clusters. Energy and charge can be transferred between the cluster's constituents, resulting in the emission of secondary electrons or photons. The details of such processes determine the final

fate of the cluster and in particular its fragmentation into charged or neutral fragments. Here I present multi-electron-photon coincidence spectroscopy as a powerful tool for the experimental investigation of various interatomic decay mechanisms. This method enabled the observation of elusive phenomena like core-level interatomic Coulombic decay in van der Waals clusters and hitherto undiscovered collective processes like electron-transfer-mediated decay with four participants. I will also discuss the capabilities of our experimental approach to detect novel processes such as interatomic Coulombic electron capture.

Interatomic Coulombic decay in excited pure and doped large He nanodroplets

Ltaief Ben Ltaief, Keshav Sishodia, Sudha Mandal, Subhendu De, Sivarama Krishnan, Cristian Medina, Nitish Pal, Robert Richter, Thomas Fennel, and Marcel Mudrich

Ionization of matter by energetic radiation generally causes complex secondary reactions which are hard to decipher. In this talk, I will show how a full chain of processes ensuring primary photoionization of a condensed phase model system—superfluid helium nanodroplets—can be deciphered using high-resolution electron spectroscopy and electron-ion coincidence detection technique. I will mainly report on observation of an indirect ionization process—Interatomic Coulombic Decay (ICD) [1]—in large He nanodroplets irradiated by weak synchrotron radiation. This indirect ICD process is based on the formation of two excited He atoms in the He nanodroplets following absorption of EUV photons of high $h\nu$ energies lying above the He photoelectron impact excitation threshold— $h\nu \geq 44.4$ eV. The responsible mechanisms behind the formation of the two excited He atoms are photoelectron impact excitation and electron-He⁺ recombination [2]. While the first excited atom is formed just via impact excitation driven by the primary photoelectron, the second excited atom is a result of electron-atom collisions and friction-induced slowdown of the inelastically scattered electron until it gets re-captured by the original residual ion (See Fig. 1). The correlated decay—ICD—of the pair of these two excited He atoms produces a very unusual and characteristic ICD electron signal. It is observed for both pure and doped large He nanodroplets with radius ≤ 40 nm. Furthermore, this indirect ICD is found to be the dominant process of electron emission in a broad range of photon energies $h\nu \geq 44.4$ eV up to the soft x-ray range. It likely plays an important role in other dense systems exposed to ionization radiation as well, including biological matter.

1. T. Jahnke et al. Chem. Rev. 120, 20, 11295–11369 (2020) 2. L. Ben Ltaief et al. Phys. Rev. Lett. 131, 023001 (2023)

Electron beam induced ICD in dimers of organic molecules

Alexander Dorn
University of Tübingen

Thursday 26.09.2024

Now and then: Interatomic Coulombic Decay and related phenomena

Till Jahnke
MPIK Heidelberg

First experiments on Interatomic Coulombic decay were conducted more than 20 years ago. Since then, almost 450 articles on ICD and related phenomena have been published indicating that these non-local processes are omnipresent in nature.

The Frankfurt Atomic Physics group contributed with many works to this large body of literature by using Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) to gather detailed insight into the processes. The talk will revisit some of these studies from the early days of ICD, drawing a line towards more recent experiments that provide an intuitive understanding of the Electron Transfer Mediated decay (ETMD(3)).

The Born-Oppenheimer approximation from a mathematician's point of view

Stefan Teufel
University of Tübingen

The Born-Oppenheimer approximation gives an effective equation for the motion of nuclei in which the electrons no longer appear as degrees of freedom. It is an approximation to the full molecular Schrödinger equation, and in my talk I report mathematical results concerning quantitative bounds on the quality of this approximation. I will also explain how one can improve this approximation by using so-called super-adiabatic approximations and explicitly discuss the second-order corrections to the Born-Oppenheimer approximation. In their most general form, the latter were computed in a joint work with Edit Matyus (J. Chem. Phys. 151, 014113 (2019)) and used by Edit to compute, e.g., rovibrational intervals of the $4\text{He}+2$ molecular ion (Phys. Rev. Lett. 125.21 (2020): 213001).

Posters

Different tastes of ICEC(ream): Large scale investigation including vibrational modes

Fabian Hofmann, Elena Jahr, Elke Fasshauer
University of Tübingen

Interparticle Coulombic Electron Capture (ICEC) is an environment assisted electron capture process. In this process, the capturing species transfers excess energy to a neighbouring species, which subsequently is ionized.

To identify systems suitable for experimentally verifying the existence of ICEC, we employed the asymptotic approximation to calculate ICEC cross-sections. We analyzed over 600 systems, which included 23 different atoms as either the capturing or ionized species, and six different dimers as the ionized species. To evaluate the results, we introduced a criterion based on the ratio between the ICEC cross-section and the Photorecombination (PR) cross-section at low incoming kinetic energies. This criterion was chosen to highlight systems where ICEC significantly dominates over PR.

For systems where dimers act as the ionized species, we used vibrationally resolved Photoionization (PI) cross-sections. This allowed us to calculate the first ICEC cross-sections that account for vibrational modes within the ionized species.

We present the ICEC cross-sections for the best-performing atom-atom and atom-dimer systems, along with a theoretical electron spectrum to illustrate the impact of vibrational degrees of freedom on ICEC.

Simon Elias Schrader
University of Oslo

A linear combination of Explicitly Correlated Gaussians (ECGs) is a very flexible and compact parameterization of multidimensional wave functions and has been extensively used for very accurate calculations of atomic and molecular properties [1]. While uncorrelated, frozen Gaussian wave packets can be effectively propagated variationally, giving rise to the variational multi-configurational Gaussian (vMCG) method [2], propagating ECGs using a time-dependent variational principle is extremely challenging due to ill-conditioning of the Gramian matrix that needs to be inverted at every time step. This problem can be evaded by using Rothe's method, where time evolution is rephrased as an optimization problem [3]. We show that Rothe's method can be used to propagate linear combinations of ECGs, illustrated by calculating the spectrum of the multidimensional Henon-Heiles potential using only 10-20 Gaussians; and electronic wave functions in strong fields, illustrated by calculating the High-Harmonic Generation (HHG) spectrum of the Hydrogen atom in a strong electric field, using only 50-180 Gaussians [4]. This paves the way for the inclusion of continuum contributions into real-time, time-dependent electronic-structure theory with ECGs for strong fields, and eventually accurate simulations of the time evolution of molecules without the Born-Oppenheimer approximation.

[1] J. Mitroy et al. (2013). *Rev. Mod. Phys.* 85, 693.

[2] G.W. Richings et al. (2015). *Int. Rev. Phys. Chem.* 34(2), 269–308.

[3] S. Kvaal et al. (2022). [arXiv:2207.00271v3](https://arxiv.org/abs/2207.00271v3) [quant-ph].

[4] S. Schrader et al. (2024). *J. Chem. Phys.* 161, 044105.

Describing Time-Resolved Electronic Decay Spectra Including Nuclear Degrees of Freedom Analytically

Alexander V. Riegel, Elke Fasshauer
University of Tübingen

The mutual influence of electronic and nuclear motion can be observed in ultrafast, yet measurable photoinduced electronic decay processes like Auger–Meitner decay or Interparticle Coulombic Decay (ICD) [1,2]. Interpreting such observations, though, requires reliable theoretical models.

We already established an analytical framework for the calculation and analysis of time- and energy-resolved spectra for electrons emitted during such decay processes [3] focussing solely on the electronic states. Now we significantly advance our approach by the inclusion of nuclear dynamics [4]. Combining Fano’s theory of resonances [5], the Born–Oppenheimer approximation and time-dependent perturbation theory yields improved analytical expressions. These permit a deeper understanding of the interaction between electronic and nuclear motion in these processes and enable us to extract characteristic energy spacings and lifetimes from complex spectral features.

To illustrate the merits of our improved description, we examine several systems with known eigenstates undergoing (resonant) ICD by calculating time-resolved kinetic-energy spectra and analyzing signal distributions, peak shapes and oscillation patterns. The selected cases encompass different bound states and also final states with a repulsive potential, which become important for ICD processes that result in a Coulomb explosion.

[1] L. S. Cederbaum, J. Zobeley, F. Tarantelli, *Phys. Rev. Lett.* 79, 4778–4781 (1997). [2] T. Jahnke, U. Hergenhahn, B. Winter, R. Dörner, U. Fröhling, P. V. Demekhin, K. Gokhberg, L. S. Cederbaum, A. Ehresmann, A. Knie, A. Dreuw, *Chem. Rev.* 120, 11295–11369 (2020). [3] E. Fasshauer, L. B. Madsen, *Phys. Rev. A* 101, 043414 (2020). [4] A. V. Riegel, E. Fasshauer, *Phys. Rev. A*, under review (2024). [5] U. Fano, *Phys. Rev.* 124, 1866–1878 (1961).