

UNIVERSITATEA BABES-BOLYAI BABES-BOLYAI TUDOMÁNYEGYETEM BABES-BOLYAI UNIVERSITÄT BABES-BOLYAI UNIVERSITY TRADITIO ET EXCELLENTIA





WORKING GROUP 2 WORKSHOP OF THE COST ACTION CA18222

BOOK OF ABSTRACTS

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February 17-19, 2021 | Organized on-line



The activity of **WG2** focuses on computational tools for the description of attosecond electron and nuclear dynamics and its goal is the development or adaptation of new theoretical techniques for the description and imaging of ionization and electron dynamics in molecules.

The topic of the workshop: Models and numerical methods for the description of ionization and electron dynamics in molecules.

Local organizer



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Wednesday, February 17, 2021

(All times are in CET)

9.50	Opening	
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10.40	Loïc Joubert-Doriol From low-energy nonadiabatic dynamics to attochemistry	WED-2
11.20	Elke Fasshauer Fano meets Nuclei — How nuclear degrees of freedom influence time-resolved spectroscopy of electronic decay processes	WED-3
12.00	Break	
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(All times are in CET)

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10.40	Vicent J. Borràs The XChem code: molecular-frame photoelectron angular distributions	THU-2
11.20	Karl Michael Ziems Quantum mechanical simulations of attosecond XUV ionisation dynamics using atomic and molecular model systems	THU-3
12.00	Break	
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13.30	Alejandro Saenz A more detailed look into enhanced ionization in intense laser fields	THU-4
14.10	Andrej Mihelič Multiphoton ionization of few-electron systems: amplitudes and cross sections	THU-5
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(All times are in CET)

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12.10	Break	
	Dicuk	
	Chair: Ladislau Nagy	
13.40	Chair: Ladislau Nagy Zdeněk Mašín Localization of Siegert states in multi-electron molecular R-matrix calculations and applications to analysis of dissociative electron attachment in pyrrole	FRI-5
13.40 14.10	Chair: Ladislau Nagy Zdeněk Mašín Localization of Siegert states in multi-electron molecular R-matrix calculations and applications to analysis of dissociative electron attachment in pyrrole András Csehi Probing strong-field two-photon transitions through dynamic interference	FRI-5 FRI-6
13.40 14.10 14.40	Chair: Ladislau Nagy Zdeněk Mašín Localization of Siegert states in multi-electron molecular R-matrix calculations and applications to analysis of dissociative electron attachment in pyrrole András Csehi Probing strong-field two-photon transitions through dynamic interference Torsha Moitra Theoretical Description of Photoionization Observables	FRI-5 FRI-6 FRI-7



The time-dependent two-particle reduced density matrix method

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We present a new method that is able to describe the correlated electron dynamics of strongly driven multi-electron atoms. The fundamental object propagated in time is the two-particle reduced density matrix (2RDM) [1, 2]. Compared to wavefunction-based methods, a reduced object such as the 2RDM bears the advantage that we avoid the exponential growth of configuration space with particle number, a problem that restricts highly accurate methods such as multi-configurational time-dependent Hartree-Fock (MCTDHF) to systems with just a few particles [3]. As compared to other methods that use even more reduced objects such as the particle-density within time-dependent density functional theory (TDDFT), two-particle correlations are fully accounted for within our theory. We will present essential components of the theory, show benchmark calculations for high-harmonic generation in multi-electron atoms, and demonstrate the accuracy of the new method by comparing to fully converged MCTDHF results. Marked differences between the fully correlated spectrum and the spectrum obtained from TDDFT and time-dependent Hartree-Fock are found.



Figure 1: The high harmonic spectrum of neon when driven by a two-cycle IR laser pulse with $\lambda = 800$ nm and $I = 10^{15}$ W/cm². Comparison between different theoretical approaches.

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From Low-Energy Nonadiabatic Dynamics to Attochemistry

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The exponential scaling of quantum methods prevents the full quantum simulations of large molecular systems. A usual approach employs the adiabatic representation, in which the nuclear problem is solved on potential energy surfaces, but the exponential scaling severely limits this approach since adiabatic states must be evaluated numerically on large grids. Furthermore, the adiabatic representation presents singularities when electronic states intersect, which is commonly the case in ultra-fast photochemistry. It seems that we should depart from the adiabatic representation. However, we can do it in a way that we exploit all the developments associated to this representation.

I will present the moving crude adiabatic (MCA) representation [1], which directly employs the adiabatic states while avoiding singularities. Combined with a basis of moving Gaussians for the nuclei, we can also replace the large dimensional grids by one-dimensional trajectories and use electron-nuclei Gaussian integration to remove the approximations usually associated with potential models [2].

Alleviated from the adiabatic representation, it is possible to abandon adiabatic states completely. This is especially useful in the context of attochemistry, where more than few electronic states interact, and employing electronic stationary states do not bring any advantage. I will show how it is possible to extend MCA for time-dependent electronic states by employing the MultiConfiguration Time-dependent Hartree (MCTDH) method for the electrons.

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Fano meets Nuclei — How nuclear degrees of freedom influence time-resolved spectroscopy of electronic decay processes

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Electronic decay processes like the Auger-Meitner process [1, 2] and the Interparticle Coulombic Decay (ICD) [3] are omnipresent and occur in areas like metallurgy, analysis of surfaces, semi-conductors, water, solvents, noble gas clusters and even in the active centers of proteins. These processes are initated by removal or excitation of a sub-outervalence electron, which can be achieved by, e.g., light in the XUV to x-ray range. These energies allow the creation of ultrashort laser pulses and hence time-resolved measurements with high time resolutions.

So far, electronic decay processes were described by Fano's theory [4]. However, this theory considers only the involved electronic states while neglecting the nuclear parts of the wavefunction. Especially in the case of ICD, though, the nuclear dynamics are required for an accurate description. We therefore present an analytical ansatz for the inclusion of the nuclear wavefunction within the Born-Oppenheimer approximation into Fano theory and use the results for an analytical discussion of time-resolved kinetic energy spectra of electronic decay processes. [5, 6]

We will show:

- 1. How the electronic width of the short pulse influences the spectra.
- 2. How several vibrational states influence the spectra.
- 3. Characteristic interference patterns created by simultaneously decaying vibrational states.
- 4. Explain, why theoretically simulated lifetimes, which are based on purely electronic wavefunctions underestimate experimentally determined effective lifetimes.

Due to the general nature of the analytic ansatz, it can straightforwardly be extended to different experimental techniques such as, e.g., RABBIT.

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Promises of Auxiliary DFT to investigate radiation chemistry problems

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The transient collision of high-energy-transfer particles (e.g. MeV H⁺ or He²⁺ ions) with biological matter results in the ionization or the excitation of its constituent molecules. Huge amounts of energy are deposited locally, typically several tens of eV. These early physical events produce a myriad of reactive radical species that are at the source of cascades of chemical processes spanning several spatial and temporal scales. The physical-chemistry of these ultrafast processes is not well understood at the present time and computer simulations are prone to play a key role in this research field [1].

We have devised a dedicated methodology relying on Real-Time Time-Dependent Density Functional Theory relying and Auxiliary DFT (RT-TD-ADFT) to deal with large and inhomogeneous molecular systems comprising hundreds of atoms[2]. RT-TD-ADFT affords promising computational performances on HPC architectures (scaling, memory demand), and still offering much room for future improvements (Figure 1). We combined RT-TD-ADFT to polarizable classical force fields to handle even larger systems. Our implementation includes time delays in electric field propagation between quantum and classical regions (retardation effects). The promises but also the current limitations of our methodology to embrace the physics at play in radiation chemistry will be discussed.

I will finally show applications to current radiation chemistry problems. I will show for instance that deposition of energy into condensed phase is not an additive property and investigate the physical stage of irradiation of solvated DNA, with a particular focus on so-called secondary electrons[3].



Figure 1: computational performances of RT-TD-ADFT as implemented in deMon2k on a 200 as electron dynamics simulation of a solvate peptide (top-right corner).

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Implementation and validation of the relativistic attosecond transient absorption theory within the dipole approximation

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Attosecond transient absorption spectroscopy (ATAS) is used to study electron coherence and motion in atoms and molecules [1]. Typically, an intense laser field is used to prepare an electron wave packet in the target system and a XUV pulse is used to probe the dynamics. All studies so far are based on *non-relativistic* ATAS theory [2], althought the importance of spin-orbit coupling was demonstrated already by the first ATAS experiment which targeted Krypton [3]. Numerical calculations including spin-orbit effects have been done by few authors (i.e. Pabst *et al* [4] and Baggesen *et al* [5]) but without a fully relaticistic approach. In the present work, a *relativistic* ATAS theory is derived, implemented and validated within the dipole approximation based on the time-dependent Dirac equation. In the nonrelativistic limit, it is found that the absorption agrees with the well established non-relativistic theory based on the time-dependent Schrödringer equation. Time-dependent simulations have been performed using the Dirac equation and the Schrödringer equation for the Hydrogen atom in two different attosecond transient absorption scenarios. These simulations validate our relativistic theory. The present work can be seen as a first step in the development of a more general relativistic attosecond transient absorption spectroscopy method for studying heavy atoms, but it also suggests the possibility of studying relativistic effects, such as Zitterbewegung [6], in the time domain.

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Control of electron-nuclear dynamics with IR pulse: simulation with Quantum-Ehrenfest

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The advent of attosecond spectroscopy has opened the door to monitoring ultrafast phenomena occurring at the timescale of electronic motion. An ultrashort pulse has a photon in the energy range of the extreme ultraviolet which leads to formation of cationic species. The photoionization will excite the molecule onto multiple electronic states at the same time. Thus, the resulting dynamics involve motion of electrons and nuclei that are heavily coupled. Subsequent control of the dynamics can be achieved by the use of a short IR pulse.¹

To unravel the mechanism behind the coherent superposition of electronic states and the effect of the pulse on the electron and nuclear dynamics, the Quantum-Ehrenfest² method was employed to simulate the time evolution of the molecular wavefunction within a full quantum approach. The effect of the pulse is included in the simulation by implementing it directly within the electronic structure method and an initial application of the algorithm is done on the allene cation.³ A more thorough investigation is performed on the ethylene cation by direct comparison with previous experimental results where an IR pulse was used to change the outcome of the photofragmentation.⁴

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Laser-field induced channel closings in molecular excitation

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The experimental verification of frustrated-tunneling ionization has lead to increased interest on electronic excitation without ionization [1]. While the occurrence of neutral excited states of atoms and molecules that survive within the adopted intense laser fields is surprising in itself, it was demonstrated that in the case of atoms the excitation yield plotted as a function of the laser peak intensity shows very pronounced steps due to channel closings, much more pronounced than is seen in the ionization yield [2].

In view of the results for atoms it is an interesting question whether the excitation yield of molecules shows a comparable behaviour, as molecules possess vibrational degrees of freedom, which may lead to a blurring of the effect or in the extreme case to the disappearance of the sharp channel-closing structures.

In this talk, the results from a combined experimental and theoretical investigation of the intensitydependent excitation yield for the diatomic hydrogen molecule will be presented.



Figure: Averaged (black) and vibrationally-resolved (blue, red) excitation yields of H_2 for 40 fs laser pulses with varying intensity. Solid lines indicate a full (six-dimensional) two-electron calculation, while dash-dotted lines are retrieved by applying an effective single-electron potential [3].

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Many-electron effects of strong-field ionization described in an exact one-electron theory

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A central problem in the theoretical description of an ionization dynamics induced by an ultrashort and ultrastrong laser pulse is to simulate the many-electron dynamics at the nuclei together with the voyage of the ionized electron. It is challenging to treat these two parts both accurately, as in principle a many-electron dynamics over a very large spatial region needs to be modeled.

In the single-active electron assumption, this problem is avoided by assuming that only the simulation of one electron is necessary, but at the cost of neglecting relevant electron interaction effects. However, if one-electron observables of a many-electron problem are of interest, those can in principle be obtained exactly from a one-electron problem. If this one-electron problem would be known, the many-electron problem would also be solved.

The formalism of the exact electron factorization (EEF) achieves the reduction of dimensionality from a many-electron system to a one-electron system formally. In the EEF, the one-electron system is determined by a time-dependent potential v(t) that can have a complicated structure. For numerically solvable models of few-electron systems interacting with a laser field, we investigate the features of v(t)relevant for attoscience and ionization dynamics, and we explain the origin of those features. We find that a simple approximation can already describe the dynamics correctly for some parameter regimes of the laser pulse. In general, however, we find that excitations of bound states of the ion need to be modeled to obtain a useful v(t). Based on these results, we present a possible way for a simulation method based on the EEF beyond the single-active electron assumption.

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The XCHEM code: molecular-frame photoelectron angular distributions.

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Due to the high photon energy of attosecond light sources, the theoretical description of attosecond experiments requires a proper representation of the ionization continuum. For polyelectronic molecules, the description of the ionization process requires the use of electronically correlated wave functions for the molecular bound states as well as the system's ionization continuum. Despite the huge success of state-of-the-art Quantum Chemistry Packages (QCP) for describing molecular bound states, the combination with their ionization continuum at the same level of theory is still challenging.

The XCHEM code, recently developed in our group, overcomes these difficulties by using a hybrid Gaussian-B-Spline (GABS) basis interfaced with existing QCPs via close-coupling scattering methods [1, 2]. The XCHEM approach has produced excellent results in different atomic and molecular systems [2, 3, 4, 5, 6, 7], encouraging us to go one step further.

The inherent anisotropy of molecules makes photoelectron angular distributions (PADs) an interesting observable to study, especially in the presence of Feshbach resonances where PADs are expected to change abruptly with the energy. The PADs, either in laboratory frame (beta asymmetry parameter) and molecular frame (molecular-frame photoelectron angular distribution) have been just incorporated to the XCHEM code, allowing us to study them in more complicated systems such as CO and pyrazine.

In this talk, we will introduce the XCHEM code. For that, we will explain the principles in which it is based and show its performance. We will put especial emphasis on PADs for the CO and pyrazine molecules in the region where molecular Feshbach resonances are expected to appear.

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Quantum mechanical simulations of attosecond XUV ionisation dynamics using atomic and molecular model systems

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Electron dynamics during strong field ionisation have been investigated for a plethora of atomic systems, however, few many-body systems and molecules have been examined. While originally the research focussed on the infrared regime, in recent year this was extended to the high frequency regime and attosecond pulses. Here, we want to provide a systematic in-depth study of the attosecond XUV induced single ionisation dynamics in atoms and molecules by means of solving the time-dependent Schrödinger equation of quantum model systems numerically. Results are compared against various approximations, such as first-order perturbation theory, a (time-dependent) self-consistent field approach, and analytical plane wave approximations.

It is well known that electron-electron and nuclear-electron correlation modifies the ionisation dynamics beyond the single active electron picture resulting in effects such as shake-up/down, knock up/down and non-adiabatic processes. By using a model system with differently bound electrons, a strongly and weakly bound electron, we mimic valence electrons of molecular systems. Time-resolved analysis of the emitted electron's dynamics allows us to distinguish different pathways leading to ionisation. Subsequently, the different pathways are shown to also lead to differences in the electronic and nuclear postionisation dynamics within the parent ion [1].

Moreover, we analyse few-cycle XUV effects and laser induced asymmetries during the ionisation of atomic and molecular systems and their interplay with electron-electron correlation effects.



Figure 1: We theoretically investigate electron-electron correlation effects during attosecond XUV ionization on the extended Shin-Metiu model system. The one-dimensional molecular system consists of two fixed outer nuclei, one movable central nucleus at *R*, and two mobile electrons at *x* and *y*.

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A more detailed look into enhanced ionization in intense laser fields

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Enhanced ionization, i. e. a strongly increased ionization probability found for specific internuclear separations of a molecule exposed to an intense laser field, is one of the most paradigmatic molecular strong-field effects. This phenomenon has been investigated experimentally and theoretically for a number of molecules, especially the hydrogen molecular ion and neutral hydrogen molecules. Recently, strong experimental evidence was even found that enhanced ionization can even occur simultaneously, i. e. more than one carbon-hydrogen bond may break in corresponding organic molecules. Besides this plethora of studies, only few investigations have been devoted to heteronuclear systems. Motivated by a combined experimental and theoretical study on HeH⁺ in ultrashort intense laser pulses, we have performed fully correlated calculations of this molecule in intense laser pulses by solving the corresponding time-dependent Schrödinger equation in full dimensionality for fixed, but varying internuclear separation. A pronounced influence of the carrier-envelope phase of the laser is found that can lead to a variation of the products by a factor 50 or more! The detailed analysis reveals an interesting electron dynamics that will be presented and discussed in this talk after a general introduction into enhanced ionization is given.



Multiphoton ionization of few-electron systems: amplitudes and cross sections

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Electronic dynamics in atoms and molecules often unfolds on the femtosecond or attosecond timescales. This is, for example, true of transient states, like autoionizing states, Auger resonances, or dissociative molecular states. Studying the dynamics of these states calls for the use of sources of intense, short light pulses, which can be used to both probe and control the evolution of the system under investigation. When the pulse intensity is high, two or more photons can be absorbed before the atom is ionized or the molecule is fragmented. Theoretical description of multiphoton ionization is especially challenging in the case of the above threshold ionization (ATI), when the number of photons absorbed exceeds the number of photons required to ionize the target, or when the continua involved are resonant (structured). While directly solving the time-dependent Schrödinger equation is usually the preferred way to tackle photoexcitation or photoionization processes, this may, in general, be neither desireable nor achievable, for example, when the pulse duration exceeds ten or a few tens of femtoseconds.

We will summarize our recent work on the theoretical description of multiphoton ionization. We have devised a method for the calculation of multiphoton ionization amplitudes and cross sections, which is applicable to few-electron atoms and molecules [1, 2]. The method is based on an extraction of electron partial wave amplitudes from a solution of a system of driven, time-independent Schrödinger equations. More specifically, it relies on a description of the partial waves in terms of a small number of Coulomb waves with fixed wave numbers. We have demonstrated the applicability of the method by calculating two-, three-, and four-photon ionization amplitudes and cross sections of hydrogen and helium atoms over a wide range of photon energies, both below and above the ionization threshold.

We will also discuss our implementation of the electron wave packet propagation scheme based on exterior complex scaling (ECS) [3, 4], and present some of our recent results obtained by solving the time-dependent Schrödinger equation describing atoms with two active electrons.

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Wave function splitting technique used for the study of interference effects

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During the interaction of few-cycle laser pulses with atomic targets the interference between continuum electronic wave packets occurs [1] and leads to a complex interference pattern in the momentum distribution of the continuum electron. This pattern is composed of substructures, which can be attributed to different interference scenarios: The temporal interference pattern is the result of the interference between electronic wave packets created during different half cycles of the driving laser field [2], while the spatial interference pattern is formed as a superposition of electronic wave packets created at the same time (i.e. during the same half cycle of the driving field), but which follow different spatial paths [3]. In experiments and in *ab initio* calculations the coherent superposition of these substructures is observed, and the physics behind their formation can be understood with the help of approximate analytical models [1]. In our *ab initio* calculations we have employed a wave function splitting technique [4], which allowed us to study the formation of the spatial interference patterns in the continuum wave packets created by each half cycle of the driving laser field. Moreover, with the coherent addition of these partial wave packet we were able to investigate the formation of the temporal interference patterns too.

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Quantum dynamics in systems with weak and strong couplings. The special case of Ag_2^-

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Referring to a recent experiment reported by Anderson et al. [1], we theoretically study the process of two-channel decay of the diatomic silver anion (Ag_2^-) , namely spontaneous electron ejection giving $Ag_2 + e^-$ and dissociation leading to $Ag^- + Ag$. The ground state potential curves of the silver molecules of diatomic neutral and negative ions were calculated using proper pseudo-potentials and atomic basis. We also estimated the non-adiabatic electronic coupling between the ground state of Ag_2^- and the ground state of Ag_2 . The relative energies of the rovibrational levels allow the description of the electron emission process, while the description of rotational dissociation is treated with the quantum dynamics method [2]. The results of our calculations are verified by comparison with experimental data. The weakness of the $Ag_2^- \rightarrow Ag_2 + e^-$ process was confirmed, for which the timescale of decay is given in seconds. We also formulate some prospects to control such a process using strong couplings to decrease significantly its timescale.



Figure 1: (left panel) Potential energy curves for the Ag_2^- and Ag_2 ground states: (a) current work; (b) current work with original basis set of Peterson and Puzzarini [3]; (c) Morse potentials generated by experimental and theoretical parameters [1]. (right panel) A map of rovibrational levels of Ag_2^- and Ag_2 : (a) no decay possible; (b) spontaneous electron emission only; (c) fragmentation only; (d) both decay modes possible; (e) rovibrational levels of Ag_2 .

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R-matrix approaches to molecular photoionization

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The R-matrix method is a powerful approach used to study atomic and molecular physics processes for many years. A number of process-specific versions and computational implementations are available, with several of those now forming part of a wider project supported by the UK-AMOR community. Two of these suites are applied to the study of light-molecule interactions. All R-matrix approaches are based on the division of space into an inner and outer regions in which the process is described differently.

The R-matrix with time dependence (RMT) [1] approach has been applied successfully to a variety of processes in atoms subject to ultrashort laser pulses. Recent developments [2] allow the use of arbitrary polarized light and the study of molecules. In the outer region, RMT solves the single-electron time-dependent Schrödinger equation, with the electron subject to the long-range potential of the atom or molecule and the laser field. In the inner region, on the other hand, it uses highly accurate multielectronic wavefunctions to describe correlation.

For molecules, the inner region wavefunctions are generated by the UKRmol+ suite, originally developed for electron/positron - molecule scattering, and also based on the R-matrix approach. In addition to providing the inner region information required by RMT, the UKRmol+ suite can determine (in a time-independent framework) single and multi- photoionization cross sections, asymmetry parameters, Dyson orbitals, etc. This suite has also undergone recent development [3] in order to, for example, use B-splines in the representation of the continuum via the new GBTOlib integral library.

Application of the molecular RMT [4] to strong field ionization of water highlighted the importance of using multielectron approaches to accurately describe these processes: when channel coupling is included in the calculations, the photoelectron angular distributions resembles the HOMO orbital for all final ionic states investigated. The use of both UKRmol+ and RMT to describe weak-field two-photon ionization of H_2 and one-photons will also be discussed in the talk.

The latest versions of all three suites, UKRmol+ (in and out), RMT and GBTOlib, are open access and can be freely downloaded. More recent results will also be presented at the meeting by some of the co-authors of this presentation.

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Ultrafast non-adiabatic dynamics in molecules following ionization

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Due to the electron correlation, the removal of an electron from a molecular orbital can trigger ultrafast, pure electron dynamics [1]. The hole charge created by the ionization can migrate throughout the molecule on a few-femtoseconds timescale even at frozen nuclei [2, 3]. The slower nuclear dynamics is expected to dephase the pure electronic coherence at a later stage and trap the migrating charge. A methodology for performing full-dimensional quantum calculations of the concerted electron-nuclear dynamics following ionization of polyatomic molecules will be presented. Examples on non-adiabatic dynamics initiated by outer- [4] and inner-valence [5] ionization will be shown, and the possibility to trace these dynamics by attosecond transient-absorption spectroscopy [6] will be discussed.

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Macroscopic Modeling of Attosecond Pulse Generation

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We present a 3D non-adiabatic model [1] and its implementation in a computer code designed to model: (a) the propagation of ultrashort laser pulses in ionizing gas medium; (b) the interaction at single-dipole level between the ultrashort laser pulse and atom; (c) the macroscopic build-up and propagation of the generated attosecond pulses in the gas medium.

Several challenges are discussed and solutions are proposed. During propagation in noble gas medium the strong laser pulse suffers serious distortions both at optical cycle level (self-phase modulation) and in its spatial distribution (intensity decrease, self-guiding) [2]. These modifications of the driving pulse will be transferred to and amplified in the generated dipole radiation during the highly nonlinear laser-atom interaction [3]. The way how these successive attosecond emissions can build up constructively in order to yield strong and coherent XUV radiation at the exit of the interaction volume is a central question to be solved for all attosecond pulse generation beamlines [4].

Another challenge comes together with the increase of the available laser pulse intensity. The proper choice of one (or combination of more) ionization model(s) is crucial because the instantaneous free electron density in the interaction medium directly affects the refractive index "seen" by the driving pulse. As the laser intensity increases, multiple ionization of the noble gas atoms has to be included. We propose a sequential ionization model for this case [5].

It is highly recommended to combine the pulse propagation code with the calculation of the dipole response of the laser-atom interaction at reasonable accuracy and at affordable computational cost. Therefore, we use the strong-field approximation extended with the quantitative rescattering theory for the calculation of the single dipole response.

The propagation of the driving field is described by the Maxwell wave equation at carrier wave level. This is solved in frequency domain in the reference frame moving together with the pulse; we assume cylindrical symmetry and use the paraxial approximation. The Crank-Nicolson method is used in a self-consistent iterative algorithm to obtain the solution. The propagation of the generated attosecond pulses is treated with a similar equation.

The main quantities obtained as results of the calculations are: the driving field temporal and spatial profile at the beginning and at the end of the propagation; the power spectrum of the generated harmonics and the temporal profile of the generated attosecond pulses; the spatial build-up of selected harmonic orders together with the time-dependent phase-matching spatial maps.

Examples for the simulation of existing experimental beamlines are presented.

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"Molecular delay" is Wigner delay

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In this talk we present a detailed analytic and numerical theoretical study of time-delays in molecules, largely based on the newly developed multi-photon molecular R-matrix method. We further show that the first-order "molecular delays" introduced in [1] are identical to Wigner delays.

As the main core of this talk we present a general time-independent method for calculation of multiphoton ionization amplitudes of arbitrary (perturbative) order, for any number of photon absorptions below and above threshold, as recently implemented and scheduled for next release of the UKRmol+ molecular scattering suite [2]. This method, applicable to both atomic and molecular targets, is based on the molecular R-matrix approach, taking advantage of its splitting of the configuration space to inner region and outer region. In the inner region, the photoionization problem is solved in its full multi-electron complexity, while in the outer (asymptotic) region, only the photoelectron is allowed and all necessary contributions of this region—including the many-dimensional free-free dipole integrals—are treated analytically. We apply our method to calculation of multi-photon ionization cross sections for several atomic and molecular targets (H, He, H₂), for which reference results are available in the literature.

Finally, we use the time-independent photoionization amplitudes for interpretation of RABITT experiments in H_2 and N_2 ; we also compare them to results from time-dependent calculations using the "molecular R-matrix with time dependence" (MRMT) approach [3], directly demonstrating the separability into the first-order (Wigner) delay and the Coulomb laser coupling part. We classify the structures in time delays into *resonance* and *interference* kinds and discuss their origin: relation to resonances and to deep minima in differential cross sections.



Figure 1: Left: Generalized cross section of two-photon ionization of He with Gaussian basis set. Right: Attosecond (RABITT) delays for ionization of H_2 in static exchange model.

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Localization of Siegert states in multi-electron molecular R-matrix calculations and applications to analysis of dissociative electron attachment in pyrrole

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In this talk I will describe a recent implementation and application of a method to localize all S-matrix poles (resonances, virtual states, bound states) in electron scattering and photoionization for a multielectron target molecule using the ab initio molecular R-matrix codes [1]. Knowledge of the positions and properties of the S-matrix poles significantly improves physical interpretation of the results.

The method is based on direct solution of Schrödinger equation in the complex plane [2]. Positions of the S-matrix poles coincide with complex energies where solutions obeying the Siegert outgoing-wave boundary conditions at infinity exist. These solutions are exponentially increasing in the lower-half complex momentum plane which makes them difficult to handle using common numerical methods. These problems are avoided in the R-matrix approach which uses a division of space and treats the asymptotic part of the wavefunction as a one-electron problem for which analytical methods can be used.

We have applied our method to analysis of calculations of low-energy (< 10 eV) electron collisions with the ring molecule pyrrole. We have found a large number of Siegert states deep inside the complex plane in agreement with studies of simple model systems [3]. Our Siegert calculations have surprisingly shown that the broad feature in the cross section at energies around 8 eV actually comprises of two broad resonances, see Fig. 1. Additionally, we have clearly shown that this system does not possess a broad σ^* resonance which has been assumed in some previous works to form in strongly dipolar systems and used to explain the dissociative electron attachment process. Instead, we show how the resonant-like effect arises as a consequence of formation of a virtual state.



Figure 1: Electron scattering cross section and S-matrix poles in pyrrole for a bent geometry.

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Probing strong-field two-photon transitions through dynamic interference

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We demonstrate how strong-field multiphoton transitions between dynamically shifted atomic levels can be traced in the energy spectra of emitted photoelectrons [1]. Applying an ultrafast and intense laser pulse, two-photon Rabi oscillations are induced between two bound states of an atom. A third photon from the same pulse directly ionizes the atom, thus the emitted photoelectrons coherently probe the underlying dynamics. As the instantaneous energy of photoelectrons follows the pulse intensity envelope, modulated by the ac Stark shifts, electrons emitted with the same energy but at different times - at the rising and falling edge of the pulse - will interfere leading to pronounced dynamic interference pattern in the spectra (Fig.1).

We investigate this phenomenon both numerically and analitically by developing a minimal threestate model that incorporates two-photon coupling and dynamically shifted atomic levels. On the example of atomic lithium ($2s \rightarrow 4s \rightarrow \text{continuum}$) we show how the individual ac Stark shifts and the two-photon Rabi frequency are reflected through the asymmetry, shifting and splitting of the interference structure of the computed photopeaks [1].



Figure 1: Photoelectron spectra of atomic Li after 2+1 photon resonance-enhanced multiphoton ionization, induced by a single Gaussian laser pulse. Owing to the atomic level Stark shifts, the spectrum is shifted from its nominal position and becomes asymmetric. Furthermore, the splitted spectra exhibit pronounced dynamic interference pattern which carries important information about the underlying dynamics.

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Theoretical Description of Photoionization Observables

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The last couple of decades have witnessed a remarkable boost in the study of sophisticated lightmatter interactions, due to enormous advancements in synchrotron and laser facilities. This has lead to high demands for reliable theoretical and computational methodologies [1]. The objective of my presentation is to give an overview of our development on theoretical models for the calculation of dynamical parameters for photoionization. This requires an accurate description of both initial and final bound states of the system, as well as of the outgoing electron. Our studies show that using a linear combination of atomic orbitals (LCAO) B-spline density functional (DFT) method to describe the ejected electron, in combination with correlated equation-of-motion coupled cluster singles and double (EOM-CCSD) Dyson orbitals, gives good agreement with experiment and outperforms other simpler approaches, like plane wave (PW) and Coulomb waves (CW), used to describe the photoelectron [2, 3]. However, simple DFT based approach fails to precisely capture more intricate phenomenon like Cooper minima. LCAO B-spline time-dependent density functional (TD-DFT) method alleviates this problem.



Figure 1: Partial cross-section for photoionization from 3s orbital of Argon. EOM-CCSD Dyson orbitals are used to describe the bound state.

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