



## Workshop on Frontiers in Excited State Electronic Structure Methods: from Spectroscopy to Photochemistry | (SMR 3836)

16 May 2023 - 19 May 2023  
ICTP, Trieste, Italy

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# Excitation Channels in Bulk Germanium under the Influence of Intense Laser Pulse

Understanding and manipulation of out-of-equilibrium quantum states is a growing area of scientific and industrial research. Modern experimental techniques are able to probe the dynamics of electrons on attosecond time scales, and time-dependent density functional theory (TDDFT) simulations allow to follow the electronic structure in real time in materials subject to intense laser pulses and assist in interpreting and understanding the experimental data. For intense laser fields, non-linear effects open new intriguing questions and novel opportunities, which are beyond the seminal yet oversimplified analytical Franz-Keldysh model. In this work, we apply TDDFT to simulate pump-probe experiments in narrow-gap bulk semiconductor Germanium (Ge). The semi-core d-levels of Ge add extra dynamical features as well as extra computational challenges compared to earlier investigations for Silicon and Diamond. We determine the transient reflectance spectra for moderate and strong laser fields and compare our results to novel experimental findings. We also present an analysis of the excited charge and follow its time evolution resolving it in its band and k-point contributions. One- and two-photon transitions and excited-to-excited charge transitions can thus be resolved, which is seen to be crucial for rationalizing the optical response of materials with multiple excitation channels.

# Stability of moving solitons in trans-polyacetylene in an electric field

In this work we study the dynamics and stability of charged solitons in trans-polyacetylene (tPA), and revisit the issue of the stability of these non-linear excitations under the effect of an external electric field applied parallel to the polymer. Using the formalism of the Su-Schrieffer-Heeger (SSH) model, we solve the coupled dynamical equations for electrons and classical nuclei at the mean-field level and in the regime of low external electric field  $E$ , where the dynamics of the moving soliton is adiabatic. Analyzing observable quantities in real space and frequency space, we identify the microscopic mechanisms triggering the dynamical instabilities of the soliton. In addition, we put forward the definition of a proper quantitative measure of its stability, an issue which to the best of our knowledge has remained an open question. Besides its intrinsic interest from the fundamental point of view, our work might be relevant for the design of novel organic electronic devices based on soliton-mediated transport.

## DFT prediction of new possible halide superconductors

Halides have been explored as potential high-temperature superconductors since the discovery of superconductivity in hydrogen sulfide (H<sub>2</sub>S) under high pressure. In particular, the combination of light elements, such as hydrogen and fluorine, with heavier elements such as La, has been shown to enhance superconductivity. LaH<sub>10</sub> represents the highest T<sub>c</sub> superconductor discovered in this class of materials, and has sparked renewed interest in the search for new high-T<sub>c</sub> superconductors based on halides. Understanding the mechanism of superconductivity in LaH<sub>10</sub> and other halide-based superconductors remains an active area of research, with many questions yet to be answered. However, the discovery of LaH<sub>10</sub> has opened up exciting new avenues for exploring the properties of halides and their potential as high-T<sub>c</sub> superconductors.

## Benchmarking the excited-state methods in DFTB+

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In this poster we divulge the results of our recent publication: “Data-driven approach for benchmarking DFTB-approximate excited state methods” [1]. In that article we proposed a chemically-informed data-driven approach to benchmark the approximate density-functional tight-binding (DFTB) excited state (ES) methods then available within the DFTB+ suite [2]. We compared the first singlet–singlet vertical excitation energies ( $E_1$ ) predicted by the DFTB-approximate methods with predictions of less approximate methods from the reference machine learning (ML) dataset, QM8 [3]. For the nearly twenty-two thousand organic molecules in the GDB-8 chemical subspace, we were able to identify clear trends in the  $E_1$  prediction error distributions, showing a strong dependence on chemical identity. This allowed us to extract valuable insights regarding the limitations of the DFTB-approximate ES-methods in terms of the approximations made to the parent formalism, density-functional theory (DFT). As a result, we were also able to provide recommendations to the user community on how to overcome the encountered limitations and also suggested a possible direction for improvement to the developer community.

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## Exploring radiative decay in electron dynamics with CEED, a novel semiclassical approach: applications and limits.

Radiative decay is a fundamental process in quantum systems that is difficult to model accurately. Coherent Electron Electric-field Dynamics (CEED) is a novel semiclassical approach that can include radiative decay in electron dynamics without the need for empirical or fitted parameters. This approach has shown remarkable properties in Tight Bindings systems and ab initio calculations. In this work, we share our latest results using CEED to study radiative time decay, black body radiation, fluorescence, and super- and sub-radiance. Our findings shed light on the scope of the model and show its potential as a powerful tool in quantum dynamics.

## Simulation of exited states of complex oxides

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Technological development cannot take place without a deep knowledge of materials and their physical properties. Complex Oxides [1-2] constitute a family of materials characterized by specific properties which make them very useful for technological applications. In this work, a study related to the exited states, and magnetic properties of two complex oxides like  $\text{Nd}_2\text{Be}_2\text{GeO}_7$  and  $\text{Gd}_2\text{Be}_2\text{GeO}_7$  compounds is presented. This study is carried out on melilite type structure (see Fig1) by employing “full potential (FP) linearized augmented plane wave plus local orbital (LAPW+lo)”. To describe the electronic structure precisely the modified Becke-Johnson exchange potential in combination with GGA is used. Our obtained results of the electronic properties and exited states are determined with spin-polarized inclusions, where we presented a detailed discussion of different optical parameters, like, dielectric function, absorption coefficient and optical conductivity, reflectivity spectra as well as refractive index and we concluded that both complex oxides  $\text{Nd}_2\text{Be}_2\text{GeO}_7$  and  $\text{Gd}_2\text{Be}_2\text{GeO}_7$  with a non-centrosymmetric tetragonal structure are a negative birefringents, therefore they exhibit the possibility of applying to the birefringent field and non linear optical process. Further, we attempted to examine the layer coating of these compounds utilizing the optical matrix approach, for which we concluded that the studied  $\text{Gd}_2\text{Be}_2\text{GeO}_7$  thin film can be more efficient for applications in the ultraviolet (UV) region of the spectrum as shown in Fig2, and it could be useful for the high frequency UV device applications [2].

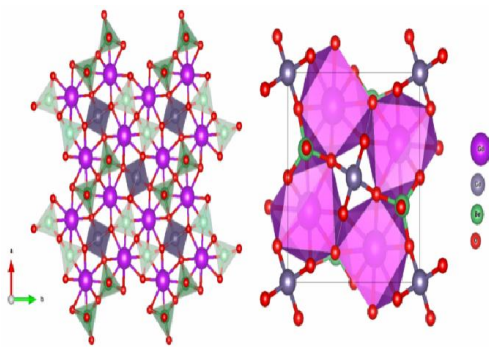


Fig1: The melilite crystalline structure

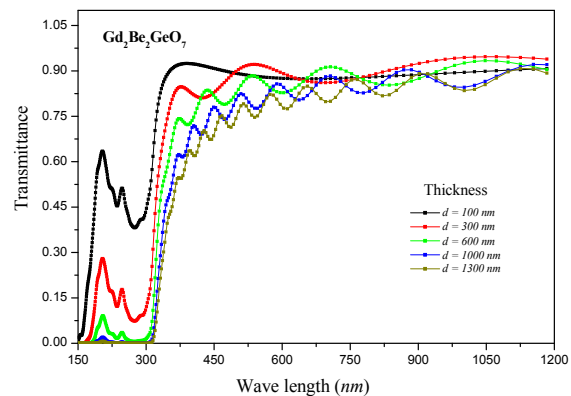


Fig2: Calculated Transmittance at different thicknesses  $d$ .

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## Modelling attosecond x-ray spectroscopy studies

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Resolving the real-time motion of electrons in complex systems is a fundamental step for the understanding of the underlying physics and for the enhancement of the functionality of modern materials. Nowadays, it has been possible to excite materials with attosecond x-ray pulses and with them it opens the way for the possibility of following electron dynamics combined with site specificity. Here we will show our methodology [1] to resolve electron dynamics that accounts for excitonic interactions, based on the time-propagation of the reduced density matrix in quasi-momentum representation. We will present some calculations describing attosecond transient absorption spectroscopy experiments in two-dimensional materials [2].

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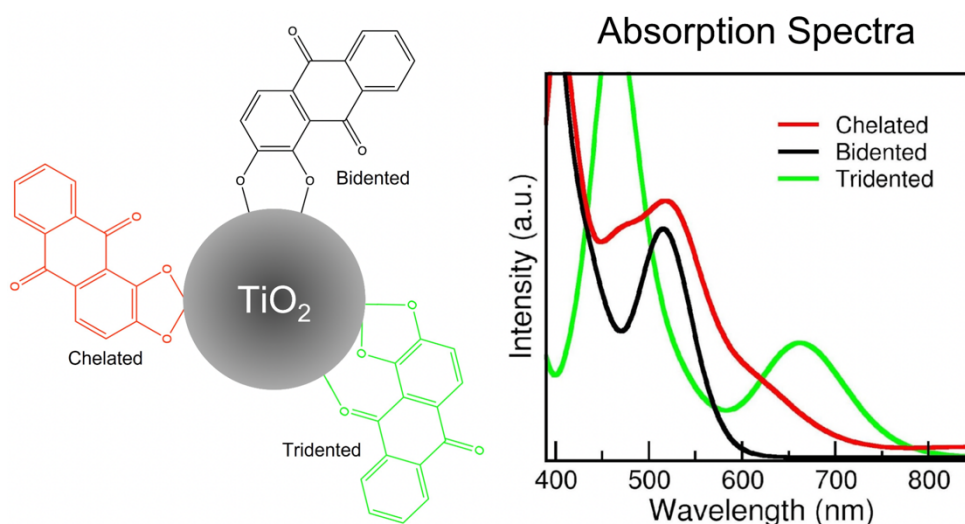
## Tuning the electron injection mechanism by changing the adsorption mode: the case study of Alizarin on $\text{TiO}_2$

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Functionalized  $\text{TiO}_2$  nanoparticles with intense fluorescent dyes is a promising tool for several technological applications ranging from photochemistry, photocatalysis, photovoltaics, photodynamic therapy or bioimaging. Here [1], we present the case study of the Alizarin adsorption on  $\text{TiO}_2$  nanoparticles (NPs) of different shape and increasing size up to 2.2 nm (700 atoms), by means of density functional theory (DFT) calculations. We find that Alizarin can bind in three different ways, depending on the number and type of bonds between Alizarin and  $\text{TiO}_2$ : “tridented”, “bidented” and “chelated”. Next, we investigate the optical properties of these systems by time-dependent density functional theory (TDDFT) calculations. Based on the absorption spectra and the Kohn-Sham orbitals analysis, we discovered that the mechanism of electron injection depends on the Alizarin binding mode to the  $\text{TiO}_2$  surface. While for bidented and chelated adsorption modes a direct charge transfer is observed, for the tridented one an indirect mechanism governs the charge transfer process following the excitation. Our results are in good agreement with existing experimental data [2] and suggest that by tailoring the shape of the  $\text{TiO}_2$  NPs and, thus, determining the type of undercoordinated Ti atoms prevalently exposed at the surface, it is possible to control the predominant injection mechanism.



**Figure 1.** Left: Alizarin binding modes to the  $\text{TiO}_2$  surface. Right: Absorption spectra of bidented, chelated and tridented complexes of Alizarin on the  $(\text{TiO}_2)_{40} \cdot 2\text{H}_2\text{O}$  cluster.

[1] F. Soria, C. Daldossi, C. Di Valentin, *Mater. Today Energy* **28**, 101085 (2022).

[2] R. Huber, S. Spörlein, J. E. Moser, M. Grätzel, J. Wachtveitl, *J. Phys. Chem. B* **104**, 8995 (2000).

# Laser-induced symmetry breaking in energy absorption of silicon induced by ultrafast laser pulse irradiation

The absorption of light by a crystal is critically influenced by the symmetry of its lattice. However, the modification of crystals by ultrashort laser pulses routinely employs intensities of the order of  $10^{14}$  W/cm<sup>2</sup> at which the band structure of the material can be modified by various phenomena such as laser-dressing [1], band-gap renormalization and structural modifications. In this report, we performed measurements of laser-induced damage threshold of (100) c-Si as a function of the angle between sample's <100> direction and the laser polarization (laser wavelength: 800 nm, pulse duration: 37 fs). The results were compared to those obtained with time-dependent density functional theory (TDDFT). In intensity regime close to materials modification, the damage threshold well correlates with the 4-fold symmetry of Si cubic lattice, consistently with the TDDFT simulations. At higher intensity, the TDDFT simulations predicts unexpected features in the angular distribution of the energy absorbed by silicon. This prediction may have an important impact on the understanding of the transient optical response of solids [2], on the generation of high harmonics [3, 4], and on the study of electron-phonon coupling [5]. [1] Derrien, T. J.-Y. et al. Phys. Rev. B 104, L241201 (2021). [2] Yamada, S. & Yabana, K. Phys. Rev. B 101, 165128 (2020). [3] Apostolova, T. & Obreshkov, B. Eur. Phys. J. D, 75, 267 (2021). [4] Suthar, P. et al. Commun Phys 5, 288 (2022). [5] Sentef, M. A. Phys. Rev. B 95, 205111 (2017).

## Reorganization Energies of Photosynthetic Pigments with Vibrational and Electronic Corrections

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Photosynthesis begins when pigments are excited by absorbing light, which creates excitons. When these quasiparticles suffer charge separation, a region is populated with holes and electrons that move through different molecules[1]. Charge transport in such conditions is highly affected by molecular-dependent properties such as the reorganization energy ( $\lambda$ ) and the associated free energies[2]. These quantities are typically estimated via density functional theory (DFT) applied to optimized geometries. However, most of the pigments in photosynthesis are conjugated, making delocalization and vibrational effects relevant. In this work[3], we calculated the reorganization energy of 15 molecules present in photosynthesis using a reliable DFT-based approach suitable for conjugated molecules. Tuning of the functional's long-range parameter is applied to prevent the over-delocalization of the molecular orbitals while the molecules' vibrational character is taken into account via the nuclear ensemble method. Results show that correcting the long-range parameter can lead to significant drops in  $\lambda$  compared to standard calculations. On the other hand, vibrational effects give rise to distributions of  $\lambda$  that may change the charge hopping rate by up to one order of magnitude. Finally, our calculations of Gibbs' free energy variation suggest that hole and electron transfers among chlorophylls tend to occur through opposite reaction paths, potentially reducing energy loss over recombination. Our results shed light on how the vibrational and orbital's delocalization affects the charge transfer mechanism, providing a more realistic picture for photosynthesis.

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# High-throughput DFT for NEW spintronic materials

Based on high-throughput density functional theory calculations (DFT), we have performed systematic research of other new semiconductors with tailored physical properties to the desired applications. The goal is to complete and/or modify the optoelectronic properties of conventional semiconductors in order to improve their yield and performance. Using Wien2k code, we have carried out a stability investigation of 32 compounds. Phonon frequencies, elastic constants, and enthalpy formation are three necessary criteria to validate the chemical, thermodynamical and mechanical stability of each compound. In this study, we have selected five compounds as potential candidates for spintronics as DMS materials.

## Modeling the Annihilation Coefficient by the Exciton Density Decay: a Kinetic Monte Carlo Study

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Bimolecular effects play a crucial role in describing energy transport in organic optoelectronic devices. In particular, the interaction between two excited molecules can lead to the annihilation of energy carriers, which is the dominant non-radiative loss mechanism for high exciton densities[1]. The decay of exciton density is directly associated with the annihilation coefficient, which measures how relevant the annihilation is in the system[2]. Furthermore, the annihilation radius characterizes the distance at which the annihilation process preferably occurs. However, ascertaining these quantities between singlet states in organic systems has remained a challenge[3, 4]. Here, we seek to investigate and present a methodology for estimating the annihilation coefficient and its associated radius between singlet states in organic molecules. Employing density functional theory (DFT) and its time-dependent extension (TD-DFT), we calculate the electronic properties of the ground and singlet first excited states of typical organic systems. We obtained the photophysical properties of the systems via the nuclear ensemble method, enabling the determination of energy transfer rates by the Förster mechanism. Using the dipole-dipole interaction between singlet excited states and a Förster-type expression to model the annihilation rate, we perform Kinetic Monte Carlo simulations to estimate the annihilation coefficients of various organic materials. Our results reveal a linear dependence of the annihilation coefficient with the exciton diffusion coefficient. In addition, we estimate the annihilation radius of the organic systems. Overall, our work presents an innovative methodology for estimating the annihilation coefficient and therefore the annihilation radius, offering new insights into the energy transport mechanisms as well as improving the description of non-radiative loss processes in relevant organic systems.

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- [2] A. J. Lewis et al. Org. Electron. **7**, 452 (2006).
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# Radiative thermalization in semiclassical simulations of light-matter interaction

Prediction of the equilibrium populations in quantum dynamics simulations of molecules exposed to blackbody radiation has proved challenging for semiclassical treatments, with the usual Ehrenfest and Maxwell-Bloch methods exhibiting serious failures. In this context, we explore the behavior of a recently introduced semiclassical model of light-matter interaction derived from a dissipative Lagrangian [C. M. Bustamante, E. D. Gadea, A. Horsfield, T. N. Todorov, M. C. González Lebrero, and D. A. Scherlis, *Phys. Rev. Lett.* 126, 087401 (2021)]. It is shown that this model reproduces the Boltzmann populations for two-level systems, predicting the blackbody spectra in approximate agreement with Planck's distribution. In multilevel systems, small deviations from the expected occupations are seen beyond the first excited level. By averaging over fast oscillations, a rate equation is derived from the dissipative equation of motion that makes it possible to rationalize these deviations. Importantly, it enables us to conclude that this model will produce the correct equilibrium populations provided the occupations of the lowest levels remain close to unity, a condition satisfied at low temperatures or small excitations.

**Modeling optical properties  
of molecular aggregates from scratch:  
the case of chiral squaraines**

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Hybrid modeling is a powerful tool to compute optical properties of molecular aggregate, starting from reliable structural models. We present here a combined computational and experimental study on aggregates of chiral Proline-derived anilino squaraines (ProSQs) functionalised with alkyl chain of various lengths [1]. Such molecular aggregates feature both blue- and red-shifted spectroscopic signatures in solutions, as observed in both absorption and circular dichroism spectra. An hypothesis for the aggregate structure obtained via Molecular Dynamic (MD) simulations translated into handedness that did not fully corresponded to experimental circular dichroism signatures, suggesting a kinetic control for the experimental aggregation formation and/or non-trivial dependence on the aggregate size. However, by combining sensible geometrical information with two modified essential state models (ESM) it was possible to simulate optical spectra compatible with experiments. In particular, a model accounting for just electrostatic intermolecular interactions (ESM-ES) suggests two concomitant aggregates to explain the simultaneous blue- and red-shifted spectral signatures, while a model including intermolecular charge transfer (ESM-CT) returns both features for a single aggregate. While offering valuable interpretation of the experimental results, we found that the role of disorder and finite-size effects may play a critical role in relation with the proposed modeling strategy. For example, a dimeric model is sufficient to describe linear absorption but fails for chiroptical properties, where an amplification of circular dichroism intensity with increasing aggregate size is found for both models - adding value for the application potential of this family of aggregates.

- [1] D. Giavazzi, M. Schumacher, L. Grisanti, M. Anzola, F. Di Maiolo, J. Zablocki, A. Lützen, M. Schiek, A. Painelli, *submitted*



## Electronic structure and charge transfer of the hetero-interfaces in perovskite solar cells

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The excellent optoelectronic properties coupled with low-cost solution processability make perovskite solar cells (PSCs) the most promising contestant against typical crystalline-silicon solar cells. However, PSCs suffer from insufficient stability problem under real working conditions, which remains a crucial obstacle to be resolved before their commercialization. The PSCs are generally fabricated in a multilayered structure where the perovskite light-absorbing layer is sandwiched between the inorganic electron-transport layer (ETL) and the polymer hole-transport layer (HTL). The stability of the ETL/perovskite and HTL/perovskite interfaces are inherently important for the PSCs performance because the choice of these materials and their microstructures have great effects on the carrier transport and separation and so on. The interfacial structural features, including the atomic arrangements and interactions, are not so clear and require further characterizations. Better understanding of the hetero-interfaces should be obtained to search for new PSCs-engineering routes. Up to now, the performances of PSCs were still limited by the conventional ETL and HTL materials. In this perspective, we focused on finding alternative ETL and HTL materials. With the assistance of software packages like VASP, Quantum Espresso, etc., density functional theory (DFT) calculations were utilized to investigate the electronic, optical, and transport properties of the hetero-interfaces in PSCs. The charge transfer processes, interfacial modification, interface stability and device performance were carefully analyzed. Our research gives clear information on the atomic structure and a direct evidence of interfacial interactions, which could contribute to clarifying the functionalities of the new ETL and HTL materials studied in this study.

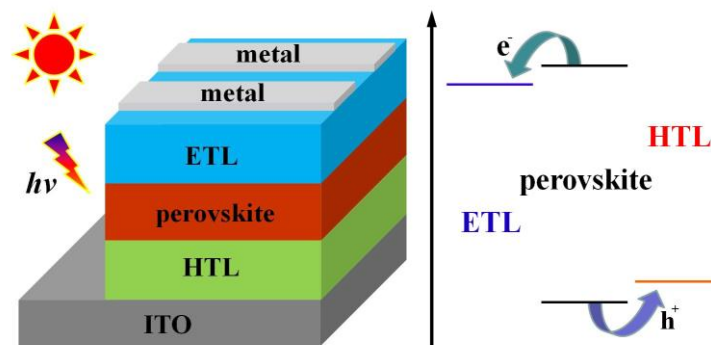


Fig. 1. Device configuration and energy level diagram of PSCs.

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- [5] Y. Guo, *et al.*, *J. Phys. Chem. C*, **123**, 16075(2019).

## Photophysics of self-trapped excitons in perovskites

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We have directly time resolved the lattice and phonon dynamics associated with the formation of the self-trapped exciton in two lead-free double halide perovskites Cs<sub>2</sub>AgInCl<sub>6</sub>, Cs<sub>2</sub>Ag<sub>0.6</sub>Na<sub>0.4</sub>InCl<sub>6</sub>:Bi<sup>3+</sup> [1] using sub 20 fs UV-pumped transient absorption spectroscopy[2]. Following optical preparation of the free exciton state, a strongly damped, low-frequency excited state wave packet modulation at 260 cm<sup>-1</sup> assigned to Jahn-Teller distortions accompanies the formation of the self-trapped exciton (STE) on a 110-140 fs time scale Bi<sup>3+</sup>-doping lengthens the lifetime of the STE by more than 3 folds, thus considerably enhancing the photoluminescence quantum yield of white light emission.

[1] J.Luo et al., "Efficient and stable emission of warm-white light from lead-free halide double perovskites," *Nature* 563, 541–545 (2018).

[2] Borrego-Varillas et al., "Ultraviolet Transient Absorption Spectrometer with Sub-20 fs Time Resolution," *Appl. Sci.* 8, (2018).

## On the role of electronic structure methods in non-adiabatic dynamics

Non-adiabatic dynamics have become a powerful tool for modelling processes in excited states capable of predicting quantum yields, lifetimes and mechanisms with high accuracy. The outcome of any non-adiabatic simulation is determined by the equations of motion for nuclei and the electronic structure method. While a whole range of algorithms for non-adiabatic dynamics has been tested extensively on multiple molecules, usually a single electronic structure method is applied based on inspecting the potential energy surfaces. However, two methods giving the same minima and conical intersections may yield different dynamics due to the huge dimensionality of the configuration space. To what extent the dynamics can differ for similar electronic structure techniques is typically not systematically studied. Therefore, we assess the influence of electronic structure on a test case of a cyclopropanone molecule. Methods from all classes of electronic structure theory (wavefunction-based CASSCF, FOMO-CASCI, MS- and XMS-CASPT2, density-functional REKS, and semiempirical OM3) were compared, together with several algorithms for nuclear evolution (Landau-Zener surface hopping, fewest switches surface hopping and ab initio multiple spawning). In addition to the quantum yields and lifetimes, an advanced statistical technique called multidimensional scaling (MDS) was also applied for enhanced comparison of the transition regions. Furthermore, investigations of effects close to conical intersections are presented. Our results clearly show that electronic structure has a major impact on the quality of non-adiabatic dynamics for cyclopropanone even though the potential energy surfaces are often similar. This indicates that the electronic structure is still the biggest bottleneck of non-adiabatic simulations.

# Stretchable Perovskite Light-emitting Devices

Organometal-halide-perovskites have recently gained tractions for high-performance optoelectronic devices thanks to their high carrier mobility, superior color purity, and tunable emission spectra. The first perovskite light-emitting diode was reported in 2014, which paved the way for a new generation of light-emitting diodes. Unfortunately, applying perovskite in flexible/stretchable electronics remains a significant challenge due to the rigid and brittle nature of perovskite films (Young's modulus  $> 12$  GPa). Furthermore, typical solvents used in the perovskite forming process, such as dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF), can swell or even dissolve organic semiconductor materials and compromise the stretchable substrate. As a result of these hurdles, few stretchable perovskite light-emitting diodes have been reported to date. Here, organometal-halide-perovskite quantum-dots dispersed in a nonpolar solvent are employed to form high efficiency and mechanical robust light-emitting diodes. Ultrathin perovskite quantum-dot light-emitting diode (Pe-QDLED) based on a flexible composite electrode is combined with pre-stretched elastomer to accommodate large external strains. The resulting device can be turned on at 3.2 V and reaches a current efficiency as large as 9.2 cd/A. It can accommodate stretching up to 50% linear strains.

# Linear and nonlinear optical spectroscopy : Atoms, Molecules and Solids

Chemistry and Physics are more and more becoming interdisciplinary fields. Theoretical methodologies that have been well established in one field, starts to become the state of the art of theoretical developments in the other field. I will show different examples of this interdisciplinarity for linear and nonlinear optical spectroscopy (absorption, photoionisation, high-harmonic generation ...) for atoms, molecules and solids.

## Molecular Mechanism of Primary Charge Separation in the Reaction Center of an LH1-RC Complex

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The bacterio-chlorophylls (BChls) of the light-harvesting complex II of purple bacteria (LH2) absorb solar energy and get electronically excited. The excited pigment molecules then transfer the energy in the form of an exciton to the neighboring pigments inside the LH2 ring. Subsequently, the excitation energy can be transferred to the BChl molecules of the LH1 ring, from where it reaches the reaction center (RC). In the RC, the charge separation of the exciton takes place for further processing in the photosynthesis process chain <sup>[1]</sup>. It has been speculated that the separation of the exciton into electron and hole takes place in the RC's so-called special pair of BChl molecules. In the present study, we have investigated the mechanism of the primary charge separation process in the RC of bacteria using a mixed quantum-classical approach. To this end, we have studied the LH1-RC complex from the bacterium *Tch. tepidum* <sup>[2]</sup> and performed time-dependent long-range corrected density functional (TD-LC-DFT) calculations for the special pairs as well as other chromophore pairs of the RC within a QM/MM framework. Subsequently, natural transition orbitals and density differences between the ground and excited states were extracted with and without the QM/MM couplings to investigate the protein matrix's role in the charge transfer and the excitonic states of the different chromophore pairs.

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## Nonadiabatic processes in condensed phase systems with $\Delta$ SCF

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Nonadiabatic molecular dynamics (NA-MD) enables direct insight into processes taking place after photoexcitation by elucidating mechanistic details at the atomic scale, explaining photoproducts' branching ratios, and mapping all the relevant excited electronic states along the time-evolving NA-MD trajectories. Computing the appropriate observables for the latter, spectroscopic data can be directly obtained, for example, the time-resolved transient absorption spectra by determining the absorbance of all electronic states along the NA-MD trajectories. Accurate calculation of excited electronic state properties in the condensed phase systems represents the main bottleneck for efficient application of NA-MD methods for investigation of nonadiabatic processes in the condensed phase systems. A variational delta self-consistent field ( $\Delta$ SCF) density functional theory (DFT) based method[1,2] represents a potential approach to address the aforementioned constraints in addition to perturbative time-dependent density functional theory (TD-DFT). We applied a restricted-open Kohn-Sham formulation of  $\Delta$ SCF with constrained occupation numbers for the direct construction of singlet and triplet excited electronic states and their corresponding properties.[3] By utilizing the combined Gaussian and plane waves approach with periodic boundary conditions the method is easily applicable to full atomistic DFT simulations of condensed phase and it can be combined with subsystem density embedding to further expand its capabilities.[4] We applied our methodology for the investigation of nonradiative deactivation mechanisms in a number of solvated systems, emphasizing the details of chromophore-environment interactions and their influence on photochemical processes in condensed phase systems.[1,5]

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## A mapping approach to surface hopping

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Fewest-switches surface hopping (FSSH) is a popular approach for simulating ultrafast processes in nonadiabatic systems [1, 2], as it often accurately describes the splitting of a nuclear wavepacket on passing through an avoided crossing. However the main disadvantage of FSSH is that it lacks any formal derivation, meaning that many of its features, such as momentum rescalings, are by definition ad hoc.

In this paper, I will present a mapping approach to surface hopping (MASH) [3], which is a new independent-trajectory surface-hopping approach that is rigorously derivable from the quantum-classical Liouville equation (QCLE). Through application to photoinduced ab initio simulations in molecules, I will demonstrate that MASH provides accurate surface-hopping dynamics without the need for decoherence corrections, exhibiting improved accuracy over FSSH at a comparable computational cost.

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## Thiols' optical sensitivity to contamination by metals: a case study

Plasmonic sensors are an important tool for chemical and biological sensing, and environmental monitoring. Plasmons are excited electrons that move through a metal or semiconductor surface, and they interact with light in a way that can be used to detect changes in the environment. In this work we have modeled several isolated molecules of the thiol group because of their known ability to bind to gold and their potential use for altering the plasmons on this metal's surface. Before functionalizing surfaces with thiols, it is important to study these molecules' stability and optical absorption properties in isolation to establish a baseline. Finally, we incorporate the presence of heavy metals that were selected among those that have been identified in rivers of the northern region of Colombia, such as mercury, Arsenic, and Chrome, to determine changes in the spectra. Structural optimizations were performed with the Quantum Espresso package [1,2] with ultrasoft pseudopotentials and PBE for the exchange-correlation effects with 80 Ry cutoff at gamma, since the system was modeled inside a cubic supercell of 20 Angstrom in its sides. Optical absorption was calculated using Yambo [3,4]. [1] Giannozzi, P. et al., 2009. Journal of Physics: Condensed Matter, 21 [2] Giannozzi, P. et al., 2017. Journal of Physics: Condensed Matter, 29 [3] Marini, A. et al., 2009. Computer Physics Communications, 180(8) [4] Sangalli, D. et al., 2019. Journal of Physics: Condensed Matter, 31(32)

## Fluorescence Enhancements in Organic Materials: The Impact of Triplet to Singlet Exciton Transfer

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Energy transfer has been in the center of a manifold of optics, photonics and optoelectronic applications. Usually, triplet excitons contribute negatively to device's efficiency, specially in organic light-emitting diodes. Experimental studies have been able to demonstrate simultaneous singlet-singlet (SS) and triplet-singlet (TTS) Förster resonance energy transfer from a single donor material (NPB) [1, 2]. In this work, we performed geometry optimization and normal mode analysis using density functional theory for NPB and the acceptor (DCJTB) molecules. Absorption and emission ( $S_1$ ) spectra for both materials were obtained by means of the nuclear ensemble method. Furthermore, we calculated NPB's intersystem crossing (ISC) rates for the two lowest triplet states ( $T_1$  and  $T_2$ ) as well as their respective phosphorescence spectra. Using the electronic structure parameters, we developed a Kinetic Monte Carlo algorithm to evaluate all energy transferring, internal conversion and non-radiative contributions in exciton dynamics between both materials as we increase acceptor concentration. In agreement with experimental results, our findings indicate that TTS occurs. Nonetheless, our calculated ISC rates from  $S_1$  to  $T_2$  were non-negligible playing an important role on the overall mechanism. Lastly, we analyzed time-resolved photoluminescence spectra for detailed comparison to experimental results. By accounting for all processes involved, our simulations provide a better understanding of simultaneous SS and TTS transfers.

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# Initial conditions in computational photochemistry and their influence on photolysis observables

Nonadiabatic molecular dynamics offers a powerful tool to study the excited-state dynamics of molecular systems beyond the Born-Oppenheimer approximation. The key to any nonadiabatic dynamics simulation is the definition of the initial conditions, ideally representing the initial molecular quantum state of the system of interest. We provide a detailed analysis of how initial conditions may influence the calculation of experimental observables by focusing on the photochemistry of methylhydroperoxide, the simplest and the most abundant organic peroxide in the atmosphere. Following our protocol for the determination of photolysis observables of transient atmospheric molecules,[1] we investigate the outcomes of trajectory surface hopping simulations for distinct sets of initial conditions sampled from different approximate quantum distributions: harmonic Wigner distribution and ab initio molecular dynamics using a quantum thermostat. We show how the choice of initial conditions critically affects photoabsorption cross-sections, photolysis quantum yields, and translational kinetic energy maps, in particular when low-frequency normal modes are coupled to the photophysics of a molecule.[2,3] [1] A. Prlj, L. M. Ibele, E. Marsili, B. F. E. Curchod, *J. Phys. Chem. Lett.* 11, 5418 (2020). [2] A. Prlj, et. al., *ACS Earth Space Chem.* 6, 207 (2022). [3] A. Prlj, D. Hollas, B. F. E. Curchod, in preparation

# Investigating the trans-azobenzene photodynamics with coupled-trajectories trajectory surface hopping (CT-TSH) method

We investigate, in full-dimensionality, the photoisomerization of the trans-azobenzene molecule combining the semiempirical Floating Occupation Molecular Orbitals-Configuration Interaction (FOMO CI) electronic structure method with the coupled-trajectory trajectory surface hopping CT-TSH algorithm. Our preliminary results show that the CT-TSH method, in principle, can capture decoherence effects even at long time scales for the azobenzene molecule.

## Defect controlled deexcitation dynamics in monolayer MoS<sub>2</sub>

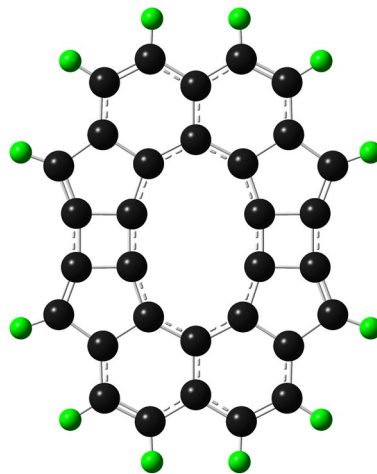
Two-dimensional (2D) materials have gathered enormous attention after the synthesis of graphene. It is highly acknowledged that defects play an important role in manipulating the properties of 2D materials. Here, we have systematically studied the role of point defects in the recombination time of monolayer MoS<sub>2</sub> using time-dependent ab initio nonadiabatic molecular dynamics simulations. Various types of point defects, such as S vacancy, S interstitial, Mo vacancy, and Mo interstitial have been considered. We show that defects strongly accelerate the electron-hole recombination, especially interstitial S atoms by three orders of magnitude higher compared to pristine MoS<sub>2</sub>. Mo defects (both vacancy and interstitial) introduce a multitude of de-excitation pathways via various defect levels in the energy gap. The results of this study provide some fundamental understanding of photoinduced de-excitation dynamics in presence of defects in highly technologically relevant 2D MoS<sub>2</sub>.

## Electrical and optical properties of novel tetra-penta-deca-hexa (TPDH) graphene quantum dot

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Employing state-of-art density functional theory, we have explored 2D quantum dot of tetra-penta-deca-hexa-graphene (TPDH-graphene) 2D sheet[1]. Frequency calculations confirm the stability of pristine, H, and halogen passivated TPDH-graphene qdots are stable. Two different basis sets, namely b3lyp/6-31g(d,p) and b3lyp/6-311g(d,p), have been chosen for computation with Gaussian 16. The electronic structure shows that pristine TPDH-graphene dot has a small bandgap (0.69 eV), however, passivated TPDH-graphene qdots have larger bandgaps (2.066-2.533 eV) which decrease with H, F, Cl, Br and I passivation because of quantum confinement. Optical absorptions of H and halide passivated TPDH-graphene qdots show redshift because of the reduction in bandgaps with increasing mass of halide. Further, we have also studied the size effect of TPDH qdots by considering their twice size. Pristine double sized qdot becomes metallic while H and halide passivated double-sized qdots have half of the bandgaps of smaller qdots and their red-shifting in optical absorptions reduces from 2.3 to 0.7eV because of small contributions of quantum confinement in large qdots.



**Fig.** H-passivated TPDH-graphene qdot. Black and green color atoms represent carbon and hydrogen atom, respectively.

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## Ab-initio study of acetone sensing mechanism by photocatalytic WO<sub>3</sub> and SnO<sub>2</sub> chemiresistors

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Sensitivity and selectivity are the two major parameters that should be optimised in chemiresistive devices with boosted performances towards Volatile Organic Compounds (VOCs). In many cases an excellent UV light responsivity with a high chemical sensitivity at RT is found [1-3].

Despite a plethora of metal oxides/VOCs combinations that have been investigated so far, a close inspection based on theoretical models to provide guidelines to enhance sensors features has been scarcely explored.

In this work, we measured experimentally the sensor response of WO<sub>3</sub>- and SnO<sub>2</sub>-based chemiresistors towards acetone adsorption. In the latter case the role of a Zn-porphyrine (ZnTPP) in the composite nanostructure is investigated.

In order to shed light on these experimental results, we modelled both a defective  $\gamma$ -WO<sub>3</sub> [4] and a SnO<sub>2</sub> surfaces by means of ab initio density functional theory calculations [5]. Adsorption of acetone and ZnTPP has been also considered and the derived spectral properties in terms of ground state density of states (worked out within the LDA- $\frac{1}{2}$  approach) are reported.

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## Exploring light frequency conversion with quantum dynamics in a semiconductor model

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One of the main difficulties to study relaxation processes in electronically excited states lies in the fact that, to obtain a reliable picture of these phenomena, a quantum description of not only the electrons but also of the nuclei is usually needed. This already challenging task is compounded by the significant differences in temporal scales between the involved pathways taking place simultaneously, as is the case with internal conversion and fluorescence.

We investigated the light-matter interaction of a simplified one-dimensional semiconductor model under continuous laser irradiation, to find a mechanism of frequency conversion, i.e., the emission of frequencies different to the excitation one. We performed quantum dynamics simulations using a semi-empirical minimal model consisting of a periodic linear chain, giving a band structure with two bands separated by a gap. The effect of the laser vector potential was introduced via Peierls substitution<sup>1</sup>, and the interaction of the lattice vibrations with the electronic degrees of freedom was included by coupling them with a phonon bath of harmonic oscillators, using the equation of motion derived from the Redfield formalism<sup>2</sup>.

The system reached a stationary state after an induction period upon turning on the laser, with the density matrix populations and coherences remaining constant. The system then emitted a spectrum of frequencies, of lower energy than the excitation one, due to thermal relaxation. The spectrum obtained was dependent on the laser frequency. The total emission was analyzed in terms of two components: one obtained using a semiclassical mean-field approach<sup>3</sup>, and the other containing the remaining terms of a full quantum electrodynamics treatment for the photons. Our results indicated that, for most cases, the mean-field result was only a small contribution to the total emission, but in certain particular cases, it was the dominant one. In particular, we show how the laser excitation frequencies and intensities can be tailored with the goal of tuning a desired frequency range of emission.

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## Molecular Engineering for Optoelectronic Device Design Through Computational Analysis of Excited States

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Organic materials are pushing numerous breakthroughs in materials science. Uncovering comprehensive methodologies to determine photophysical properties and characterizing said materials may be essential to further reduce costs and optimize the design processes. Understanding how light absorption and light emission takes place in these materials is of paramount importance. In that sense, the employment of computational methods to simulate the aforementioned spectra is of major interest. The nuclear ensemble method is often used to simulate molecular spectroscopy and consists on the excitation of an ensemble of geometrical conformations around the optimized energy for a certain electronic state[2]. It also makes use of the normal mode frequencies obtained from the same geometries. Nevertheless, some normal modes may provide more important vibrational contributions to the formation of the spectrum. In this work, we investigated how each isolated normal mode affects the energy range, absorption and emission intensities and spectral profile of a group of small organic molecules. Employing density functional theory and its time dependent extension[2], we analyzed the vertical transition energies and the associated oscillator strengths when normal modes are individually activated. We used an ensemble of 200 geometrical conformations for each normal mode. Our results indicate spectrum intensity may remain unaltered if certain normal modes are made inactive. For instance, naphthalene's absorption spectrum less than 20% of the normal modes show a variation of more than 26 meV ( $1 k_bT$ ) in its vertical transition energy. Our findings indicate a new path to engineering UV-Vis spectra, potentially inspiring innovative technologies in organic electronic.

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## Room temperature electron-hole liquid phase in monolayer $\text{MoSi}_2\text{Z}_4$ ( $Z = \text{pinctogen}$ )

Photo-excited electrons and holes in insulators, above a critical density and below a critical temperature, can condense to form an electron-hole liquid (EHL) phase. However, observing the EHL phase at room temperature is extremely challenging. Here, we introduce the monolayer  $\text{MoSi}_2\text{Z}_4$  ( $Z = \text{N, As, P}$ ) series of compounds as a promising platform for observing the EHL phase at room temperature. The higher impact of the Coulomb interactions in two dimensions helps these monolayers support the EHL phase with an increased EHL binding energy and transition temperature, along with strongly bound excitons. Our findings motivate further exploration of the  $\text{MoSi}_2\text{Z}_4$  monolayers for realizing the EHL phase at high temperatures to harness collective phenomena for optoelectronic applications.