Acceptance type: Invited

40

Identification of collective variables and metastable states of protein dynamics

Gerhard Stock

Biomolecular Dynamics, Institute of Physics, Albert Ludwigs University, Freiburg, Germany

Abstract

The statistical analysis of molecular dynamics simulations requires dimensionality reduction techniques, which yield a low-dimensional set of collective variables x = x that in some sense describe the essential dynamics of the system. Considering the distribution P(x) of the collective variables, the primal goal of a statistical analysis is to detect characteristic features of P(x), in particular, its maxima and their connection paths. This is because these features characterize the low-energy regions and the energy barriers of the corresponding free energy landscape, and therefore amount to the metastable states and transition regions of the system. In this perspective, we outline a systematic strategy to identify collective variables and metastable states, which subsequently can be employed to construct a Langevin or a Markov state model of the dynamics. In particular, we account for the still limited sampling typically achieved by molecular dynamics simulations, which in practice seriously limits the applicability of theories (e.g., assuming ergodicity) and black-box software tools (e.g., using redundant input coordinates). We show that it is essential to use internal (rather than Cartesian) input coordinates, employ dimensionality reduction methods that avoid rescaling errors (such as principal component analysis), and perform density based (rather than k-means-type) clustering. Finally we discuss a machine learning approach to dimensionality reduction, that highlights the essential internal coordinates of a system and may reveal hidden reaction mechanisms.

F. Sittel and G. Stock, Perspective J. Chem. Phys 149, 150901 (2018)

Advanced Techniques for the Computer Simulation and Analysis of Bimolecular Systems

Johannes Dietschreit

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Abstract

The talk will give an overview of three major topics: First, the computation and partioning of the free energy as a fundamentally important quantity. We developed the density of states integration (DSI) which allows to detect the subsystems that contribute most significantly to a free energy difference. The method utilizes the velocity density of states function (VDoS) of each atom to calculate its contribution to the vibrational free energy. In this way, large local changes can be identified, which is crucial for the understanding of free energy differences.

Second, we focused on the reaction mechanism of SIRT5. The relationship between the configuration of the enzyme's active site and the height of the reaction barrier was studied by computing minimal energy paths starting from many different reactant configurations. Using the power of machine learning, atomatom distances influencing the activation barrier were identified, allowing for a comprehensive understanding of the active site of SIRT5. Subsequently, we set out to compute the free energy profile of the reaction instead of a minimum energy path.

Third, a further theme was the computation of spectroscopic observables in a cost-effective manner while simultaneously including important features of the experimental setup. In this context, we highlight the importance of sampling atomic configurations (with and without explicit solvent) and the non-negligible influence of electron correlation on the accuracy of computed observables. Simulation strategies were developed that enable sampling, the inclusion of correlation methods, and large quantum mechanical subsystems at a low computational cost.

Chemical Bonding and the Atomic Valence Space

Gernot Frenking

Philipps-Universität, Marburg, Germany. Nanjing Tech University, Nanjing, China

Abstract

The lecture discusses essential features of covalent bonding. The concept of atomic valence space and electron counting rules developed 100 years ago by Irving Langmuir on the basis of Gilbert Lewis' model of electron-pair bonding are connected with quantum chemical approaches and with recent results of bonding analyses of unusual molecules.

DMRG-tailored CC method: towards transition and heavy metal compounds

Andrej Antalik¹, Jiri Brabec¹, Jan Brandejs¹, Ondrej Demel¹, Jakub Lang¹, Libor Veis¹, Jakub Visnak¹, Ors Legeza², Frank Neese³, Jiri Pittner¹

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Abstract

In the last decade, the quantum chemical version of the density matrix renormalization group (DMRG) method has established itself as the method of choice for calculations of strongly correlated molecular systems. Despite its favourable scaling, it is in practice not suitable for computations of dynamic correlation.

We present the DMRG-based tailored coupled cluster (DMRG-TCC) method, which is a ``post-DMRG'' treatment of dynamic correlation,

in which the DMRG method is responsible for the proper description of non-dynamic correlation, whereas the dynamic

correlation is incorporated through the framework of the CC theory.

In order to overcome the computational scaling bottleneck of traditional CC methods, we have developed an implementation of the DMRG - tailored coupled cluster method based on the domain-based local pair natural orbital formalism (DLPNO).

We illustrate the capabilities of our implementation on the

oxo-Mn(Salen) molecule and iron-porphyrine model complex, for which we have performed the first ``post-DMRG'' computations in order to shed light on the energy ordering of the lowest spin states.

We present also the relativistic version of the DMRG-tailored coupled cluster

method (4c-DMRG-TCC), aimed at calculations of strongly correlated systems containing heavy atoms. The lower rows transition metal compounds, lanthanides and actinides with open d or f shells combine the complexity of realtivisitc effects and non-dynamic/dynamic electron correlation and present thus a particular challenge.

The 4c-DMRG-TCC method allows to include dynamical correlation at lower computational costs with respect to DMRG in a very large active space, as we

demonstrate on the TIH, SbH and AsH molecules.

Get the point right: Nuclear structure and fundamental physics with molecules

Robert Berger

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Abstract

In electronic structure theory, the atomic nucleus is often treated as an infinitely heavy point with just some positive electric charge. But there is much more to this little object that can be revealed in particular from precision spectroscopy of well-chosen, heavy-elemental molecules with the help of quantum chemical approaches. Besides conventional electromagnetic moments of the nucleus like magnetic dipole moment and electric quadrupole moment [1] as well as finite nuclear size effects that cause isotope shifts [2], one can aim to extract exotic, symmetry-violating nuclear moments such as anapole moment [3], magnetic quadrupole moment and Schiff moment [4]. Moreover, fundamental interactions between electrons and nuclei are much richer than what electromagnetic theory provides. The fundamental weak force leads, for instance, to electron-nucleus interactions that are no longer symmetric with respect to spatial inversion and thus violate parity. And various models that go beyond the current standard model of particle physics predict sizeable parity and time reversal symmetry violating interactions between electrons and nuclei as well as static electric dipole moments of elementary particles that can be favourably enhanced in heavy-elemental molecular systems [5]. In this talk, I will present some of the recent experimental and theoretical activities with molecules that aim to improve our understanding of nuclear structure and the fundamental interactions in nature [1-6].

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2. Udrescu et al., Phys. Rev. Lett., 2021, 127, 033001.

3. Isaev, Berger, *Phys. Rev. A*, **2012**, *86*, 062515; Isaev, Hoekstra, Berger, *Phys. Rev. A*, **2010**, *82*, 052521.

4. Gaul, Berger, J. Chem. Phys., 2020, 152, 044101.

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New avenues in laser based photoelectron circular dichroism

<u>Thomas Baumert</u> Institut für Physik, Universität Kassel, Kassel, Germany

Abstract

Exploiting an electric dipole effect in ionization [1], photoelectron circular dichroism (PECD) is a highly sensitive enantioselective spectroscopy for studying chiral molecules in the gas phase using either single-photon ionization [2] or multiphoton ionization [3]. In the latter case resonance enhanced multiphoton ionization (REMPI) gives access to neutral electronic excited states. The PECD sensitivity opens the door to study control of the coupled electron and nuclear motion in enantiomers. A prerequisite is a detailed understanding of PECD in REMPI schemes. In this contribution I will report on our recent experiments devoted to unravel different aspects of this effect on the fenchone prototype by addressing the range from impulsive excitation on the femtosecond time scale to highly vibrational state selective excitation with the help of high resolution nanosecond laser techniques [4]. The reflection of the number of absorbed photons in the PECD will be discussed as well as subcycle effects in bichromatic fields [5].

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[3] C. Lux, M. Wollenhaupt, T. Bolze, Q. Liang, J. Köhler, C. Sarpe, T. Baumert, Angew. Chem. Int. Ed. 2012, 51, 5001–5005.

[4] A. Kastner et al., Phys. Chem. Chem. Phys., 2020, 22, 7404.

[5] P. V. Demekhin, A. N. Artemyev, A. Kastner and T. Baumert, Physical Review Letters, 2018, 121, 253201.

From light harvesting to quenching in plants: an atomistic description through quantum chemistry and molecular dynamics

<u>Benedetta Mennucci</u> University of Pisa, Pisa, Italy

Abstract

Light-harvesting in pigment-protein complexes of plants is accompanied by photoprotective processes: in specific light conditions the energy absorbed by the chlorophylls cannot be transferred to the reaction center and has to be dissipated into harmless heat through processes collectively called nonphotochemical quenching (NPQ). Here, we characterize the quenching mechanisms through an integrated approach combining enhanced-sampling techniques, dimensionality reduction schemes and electronic calculations. Our analysis reveals that the mechanism is more complex than previously thought as many pigments are simultaneously involved through a diffuse mechanism controlled by conformational changes in the protein.

A Two-dimensional View on the Exciton Dynamics in the LH2 Complex of Purple Bacteria

<u>Oliver Kühn</u>

University of Rostock, Rostock, Germany

Abstract

Frenkel exciton delocalization and ultrafast relaxation in the light-harvesting complex 2 (LH2) of purple bacteria has been a hot topic ever since the publication of the highly symmetric crystal structure in 1995 [1]. Recently, coherent photon echo type two-dimensional electronic spectroscopies provided rather detailed insights into the quantum dynamics of various forms of LH2s [2,3,4]. In addition two-dimensional action spectroscopies such as fluorescence detected two-dimensional spectroscopy (FD2DS) delivered details complementary to that of well-established photon echo setups. FD2DS in particular has been shown to give direct access to the early time evolution of weakly coupled chromophores thus unraveling the role of quantum delocalization. Here, it benefits from an intricate cancelation of ground state bleach and excited state absorption contributions to the cross-peak signals. Details depend on the interplay between time scales for exciton-exciton annihilation, exciton relaxation, and radiative decay [5,6]. FD2DS enabled, for instance, the observation of the initial exciton delocalization between the B800 and B850 pigment pools in the LH2 complex [7]. Viewed from the traditional concept of Förster excitation energy transfer, FD2DS provides a glimpse at the transient regime directly following excitation.

In this contribution I will discuss different approaches to the exciton quantum dynamics of coupled multichromophoric systems in the context of the LH2. This will cover perturbative and non-perturbative regimes with respect to the exciton-vibrational interaction as well as multi-time response functions for the light-matter interaction.

- [1] G. McDermott et al., Nature <u>374</u>, 517 (1995).
- [2] M. Schröter et al., J. Phys. Chem. Lett. 9, 1340 (2018)
- [3] E. Thyrhaug et al., J. Chem. Phys. <u>154</u>, 045102 (2021)
- [4] X. Liu et al., Chem. Phys., <u>527</u>, 110476 (2019)
- [5] M. Schröter et al., J. Chem. Phys. <u>149</u>, 114107 (2018)
- [6] O. Kühn et al., J. Phys. Chem. Lett. <u>11</u>, 838 (2020)
- [7] K. J. Karki et al.,, Chemical Science <u>10</u>, 7923 (2019)

Regulation and signaling in proteins: challenges to multi-scale modelling

<u>Ricardo A. Mata</u> University of Göttingen, Göttingen, Germany

Abstract

Although we recognise proteins as incredibly complex machines, we tend to think about the chemistry of its basic components as somewhat less exciting. We dedicate our time to cofactors, metal-binding sites, etc... and the residues that make up for the bulk of proteins are usually just that, a sort of bulk. The residues will twist, turn, and in the end provide conformations surrounding our site of interest, but do not take center stage when it comes to chemistry.

In this talk I will review some of our most recent multiscale modelling studies of proteins which place this view in question. Combining high-level quantum mechanics/molecular mechanics (QM/MM) calculations with proton dynamics, I will highlight how acid-base chemistry is expertly used by enzymes not only in their catalysis[1] but also for communication[2], and how QM calculations provide a glimpse into molecular evolution mechanisms. Furthermore, I will discuss the finding of a new protein crosslink and its relevance in well-known pathogens[3]. All of these examples paint a much colourful picture of aminoacids and their role as active chemical entities. They are also humbling in that they show how hard it is to simplify such systems, how we need to push for larger size and time scales in our simulations without compromising the use of quantum mechanics.

[1] J. Schrader, F. Henneberg, R. A. Mata, K. Tittmann, T. R. Schneider, H. Stark, G. Bourenkov and A. Chari, *The inhibition mechanism of human 20S proteasomes enables next-generation inhibitor design*, <u>Science 353, 594-598 (2016)</u>

[2] S. Dai, L.-M. Funk, F. R. von Pappenheim, V. Sautner, M. Paulikat, B. Schröder, J. Uranga, R. A. Mata and K. Tittmann, *Low-barrier hydrogen bonds in enzyme cooperativity*, <u>Nature 573, 609-613 (2019)</u>

[3] M. Wensien, F. R. von Pappenheim, L.-M. Funk, P. Kloskowski, U. Curth, U. Diederichsen, J. Uranga, J. Ye, P. Fang, K.-T. Pan, H. Urlaub, R. A. Mata, Viktor Sautner and K. Tittmann, *A lysine-cysteine redox switch with an NOS bridge regulates enzyme function*, <u>Nature 593, 460-464 (2021)</u>.

Correlated calculations in molecules and solids

<u>Sandeep Sharma</u> University of Colorado,, Boulder, USA

Abstract

In the first part of the talk I will describe an algorithm that can be used to systematically improve the accuracy of non-mean field wavefunctions such as CCSD without having to go to higher order cluster expansions. Instead, we start with the coupled cluster wavefunction and use imaginary time propagation to rapidly project out high energy contributions. With several examples, I will demonstrate that this algorithm is able to deliver near-exact energies for strongly-correlated systems that are difficult to treat using any other method.

Time permitting, I will also talk about our recent efforts to obtain Gaussian integrals for use in periodic systems. Once such integrals are available any quantum chemistry package should be able to treat periodic systems using exactly the same algorithms that are used for molecules.

Machine learning for excited-state molecular dynamics simulations

<u>Julia Westermayr</u>¹, Leticia González², Philipp Marquetand² ¹University of Warwick, Coventry, United Kingdom. ²University of Vienna, Vienna, Austria

Abstract

Excited-state molecular dynamics simulations have proven powerful in deciphering fundamental mechanisms of light-induced reactions. However, photodynamics simulations are not only restricted to short time scales by the high computational costs of accurate *ab initio* excited state methods, they are often also limited by the difficulty of finding a suitable reference method [1]. In this talk, we will show how machine learning (ML) can overcome both bottlenecks by providing analytical expressions of multiple excited-state potential energy surfaces of different spin multiplicities, which can be obtained by combining different levels of theories. Our method, termed the SchNarc approach [2,3], offers an efficient training set generation to minimize the costs of the reference calculations and a phase-free training algorithm to enable the fitting of excited-state properties that are arbitrary with respect to their sign.

The accuracy of the SchNarc framework is demonstrated on the example of the full (66)-dimensional photodynamics of excited tyrosine. By further utilizing unsupervised ML to analyze and interpret our results, we discover roaming atoms in tyrosine - a reaction that was never considered before in biology and opens a new perspective on the photochemistry of biological systems [4].

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[3] J. Westermayr, M. Gastegger, M. Menger, S. Mai, L. González, P. Marquetand *Chem. Sci.* 10, 8100-8107 (2019).

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Bending the rules of classical mechanics to simulate quantum dynamics

Jeremy Richardson ETH, Zurich, Switzerland

Abstract

Quantum mechanics is hard - hard to simulate and often hard to interpret. Classical mechanics is much more computationally efficient and intuitive but fails to describe many fundamental aspects of molecular processes. I will describe ways in which we can slightly modify the classical algorithms such that they give reasonably accurate predictions of the quantum result while retaining the inherent efficiency and leading to simple mechanistic insights. In particular, golden-rule instanton theory allows us to study quantum tunnelling in nonadiabatic reactions using upside-down classical trajectories computed via on-the-fly ab initio electronic-structure theory. By introducing concepts of particle-antiparticle creation and annihilation and negative temperatures, we can tackle the Marcus inverted regime and find that in this case, even carbon atoms give massive tunnelling effects at room temperature. Applications include absorption and emission spectroscopy, intersystem crossing, electron transfer and bridge-mediated electron transfer, molecular polaritons and QED cavity-enhanced reactivity, and practically anything else where Fermi's golden-rule would traditionally be applied.

Geometric magnetism and new enantio-sensitive observables in photoionization of chiral molecules.

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Abstract

Chiral molecules are instrumental for molecular recognition in living organisms. Distinguishing between two enantiomers, the mirror twins of the same chiral molecule, is both vital and challenging. Photoelectron circular dichroism (PECD) is an extremely sensitive probe of molecular chirality, which outperforms standard optical methods by many orders of magnitude. We show that the emergence of PECD can be linked to the concept of geometric magnetism, which enables a broad class of phenomena in condensed matter systems including the anomalous electron velocity and the Hall effect and related topological phenomena. Following this link, we uncover geometric magnetic field in photoionization of chiral molecules and show that PECD is only a tip of the iceberg, the iceberg being a new class of efficient enantio-sensitive observables emerging in non-linear photoionization. We formulate the fundamental principles which allow one to predict new enantio-sensitive observables. Crucially, the emergence of these new observables is associated with ultrafast excitation of chiral electronic or vibronic currents prior to ionization and can be viewed as their unique signature. To illustrate our concept, we introduce a new phenomenon - enantio-sensitive orientation of chiral molecules via photoionization, opening a way to efficient enantio-separation and molecular imaging on ultrafast time scales. New enantio-sensitive observables associated with chiral geometric fields are messengers of charge directed reactivity in randomly oriented chiral molecules. Imaging of chiral geometric fields and of the associated new ultrafast enantio-sensitive observables is a new frontier in non-linear photoionization.

Deep learning for molecular kinetics and electronic structure

<u>Frank Noe</u> Freie Universität Berlin, Berlin, Germany

Abstract

Machine learning and specifically deep learning has recently had profound impact on helping to answer basic questions in the molecular sciences. Here I will summarise some of our work on two how deep learning can help to address two fundamental problems in Computational and Physical Chemistry: (i) finding highly accurate solutions for the ground state in the electronic structure problem, and (ii) strategies to alleviate the sampling problem of macromolecules by leveraging variational principles of molecular kinetics and generative deep learning.

Related literature:

[1] Hermann, Schätzle and Noé: Deep-neural-network solution of the electronic Schrödinger equation. Nature Chemistry 12, 891-897 (2020)

[2] Mardt, Pasquali, Wu, and Noé: VAMPnets for deep learning of molecular kinetics. Nature Communications 9, 1-11 (2018)

[3] Noé, Olsson, Köhler and Wu: Boltzmann generators: Sampling equilibrium states of many-body systems with deep learning. Science 365 eaaw1147 (2019)

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25

Alchemical Enantiomers Simplify Inverse Materials Design Problems

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Abstract

Chemical Compound Space (CCS) is so vast, that even simple enumeration is unfeasible, let alone systematic property estimation. Therefore, molecule or materials design requires approaches which implicitly assess multiple compounds at once. Perturbative approaches like Alchemical Perturbation Density Functional Theory (APDFT) [1] treat a change in elemental composition as a perturbation to the system Hamiltonian and allow to estimate properties of millions of compounds at once rather than enumerating them one-by-one. We show that this perturbative treatment allows to simplify material design problems by identifying alchemical enantiomers [2] which are compounds that need to be degenerate in their electronic energy up to third order of the perturbative expansion. Most interestingly, this new and fundamental constraint on chemical space is independent of bond topology, which simplifies material design problems due to the effectively reduced dimensionality of the search space.

Furthermore, alchemical enantiomers define approximate energy ranks for fixed lattices, more accurately so than some semi-empirical quantum chemistry methods. We use alchemical enantiomers to obtain new rules for electronic energy contributions to chemical bonding and for ranking over 2000 and 400 million BN-doped naphthalene and picene derivatives, respectively. We thus demonstrate how alchemical chirality deepens our understanding of CCS and enables the establishment of trends without empiricism for any materials with fixed lattices.

[1] Alchemical Perturbation Density Functional Theory, GF von Rudorff, OA von Lilienfeld, Phys.Rev.Research 2020, 2, 023220.

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A new perspective on the calculation of photoelectron spectra: Giving the photoelectron its physical source

Tobias Marx, <u>Sergey I. Bokarev</u> Universität Rostock, Rostock, Germany

Abstract

This contribution proposes a novel theoretical approach for computing molecular photoelectron spectra, representing an alternative to the commonly used Fermi's Golden Rule expression for the cross-section and offers several advantages. Instead of constructing a continuum state as a solution to the usual, homogeneous Schrödinger equation together with scattering boundary conditions, e.g., in the form of partial wave expansion, the new method solves an inhomogeneous equation with outgoing boundary conditions. The new approach gives a single solution for every kinetic energy and thus avoids the in general slowly converging expansion series. The solution represents an outgoing wave, and the gradient of the Dyson orbital (initial state) serves as a source of probability. The cross-section computation is performed directly as the probability density current at the infinitely distant point (detector). Hence, it provides an intuitive physical picture of the process. The novel method is implemented within the finite/infinite element framework. Its peculiarities and advantages are demonstrated on atoms and small molecules.

Accurate Thermochemistry and Structures from Second Order PerturbationTheory: The OO-REMP Hybrid Perturbation Theory

Stefan Behnle, Reinhold Fink

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Abstract

We present an open shell generalization and an orbital optimized variant of the REMP hybrid perturbation theory that reproduces non-multireference atomization

energies with a mean absolute deviation of 1 kcalmol⁻¹[1]. The underlying

REMP approach emerges as a constrained mixture of the unperturbed Hamiltonians $H^{(0)}$ of the Møller-Plesset perturbation theory (MP) and the "Retaining the Excitation Degree Perturbation Theory" (RE) as

 $H^{(0)}_{REMP} = (1 - A) H^{(0)}_{RE} + A H^{(0)}_{MP}$

REMP builds on complementary errors in the parent methods and results in a systematic internal error compensation leading to an improvement upon both parent methods.

Analogous to OO-MP2 and OO-CEPA(0), an orbital-optimized variant termed OO-REMP was implemented and benchmarked. Orbital optimization is achieved by minimizing the second order energy functional

E⁽²⁾_{REMP} w.r.t. amplitudes and orbital coefficients of the single-determinantal reference wavefunction.

OO-REMP systematically outperforms the parent methods OO-MP2 and OO-RE as well as REMP based on canonical orbitals. For both closed and open shell thermochemistry

benchmark sets, mean absolute deviations below 1 kcalmol⁻¹ are achieved. Equilibrium bond lengths for closed- and open shell molecules are predicted with mean absolute errors of about 0.3 pm. In general, the performance of OO-REMP is near to that of CCSD(T)

while having a more favorable formal computational scaling. It will be shown

that regardless of the considered property, a REMP mixing parameter of $A \approx 0.25$ represents a reliable and robust choice.

[1] Behnle, S. and Fink, R. F. J. Chem. Theory Comput. 2021 17, 3259



Integrating Electronic Structure Theory and Machine Learning

<u>Johannes T. Margraf</u> Fritz-Haber-Institut, Berlin, Germany

Abstract

Recent years have seen an explosion of work related to machine-learning (ML) models trained on electronic structure data. To push the boundaries of what can be done with physics-based ML, we have explored how ML can be directly incorporated into electronic structure calculations. This dispenses of the separation between electronic structure theory as a mere data generation device on one hand, and ML as a mathematical fitting framework on the other. In this case, the ML model is used to predict more fundamental physical relationships, rather than the full structure-property mapping. This has the advantage of making the model more transferable and data-efficient, since the mathematical framework of the electronic structure calculation is retained.

To this end, we recently reported a size-extensive and rotationally invariant ML representation based on the atomic decomposition of the electron density obtained from mean-field electronic structure calculations.[1] This was used to develop so-called Kernel Density Functional Approximations (KDFAs), trained on coupled cluster correlation energies. Importantly, KDFAs are pure functionals of the electron density that are nonetheless able to capture the non-local nature of the correlation energy. Currently, we are further developing this concept to obtain a self-consistent version of KDFA. This enables the prediction of electronic properties like the dipole moment and the density on the same footing as the energy and thus offers a route to CC-quality electron densities for systems of unprecedented size.

[1] Margraf, J. T.; Reuter, K. Nat. Commun. 2021, 12, 344.

The Independent Gradient Model: a new tool for the extraction, identification and quantification of chemical interactions

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¹Institute of Condensed Matter and Nanosciences - Catholic University of Louvain, Louvain-la-Neuve, Belgium. ²Molecular Chemistry Institute of Reims - University of Reims Champagne-Ardenne, Reims, France

Abstract



A new concept relying either on promolecular densities or quantum electron density is presented there : The Independent Gradient Model (IGM). This methodology is able to accurately extract the signature of each chemical interaction from a whole molecular system only from a cartesian or a wavefunction file. For the first case, IGM allows for visualizing regions of weak interactions between user-defined fragments in large systems encountered in material and biological science. And so, within an automatic workflow it is possible to separate covalent from non covalent interactions without applying any user threshold. Beyond this simple visualization, an atomic decomposition scheme has been developed to access the contribution of each atoms in a given molecular interaction. It provides to the chemist a fast and easy manner to locate most importants atoms involved in a given interaction. In the second case (electrondensity coming from QM calculations), besides the visualization of region of desired interactions (with a natural separation between covalent and non-covalent interactions), physically-grounded indexes have been developped : Intrinsic Bond Strength Index (IBSI) and Bond Asymmetry Factor (BAF). These two descriptors concomitantly enable a rapid screening of a molecular system to unveil the most sensitive bonds to disturbances (electrical, photochemical). Use of IGM is implemented in IGMPlot software (http://igmplot.univ-reims.fr/) free and multiplatform available.

A Quantum Chemical and Microkinetic Study to Combine Theory and Experiment in Catalysis

Juliane Heitkämper, Johannes Kästner

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Abstract

In this work, we combined microkinetic modelling to extract reaction barriers from experimental kinetics data and quantum chemical calculations to investigate the hydroboration of acetophenone with a highly active cooperative Lewis acid-ammonium salt catalyst. We have shown that such an approach allows bridging the gap between theory and experiment, revealing detailed insight into the elementary steps of the reaction mechanism. We gained consistent free enthalpy barriers for the quantum chemical and kinetic model. Further, a microkinetic sensitivity analysis was used to determine the rate-limiting steps to discuss the states that are relevant for enantioselectivity.

A fragment diabatisation technique applied to the excitonic modelling and quantum dynamics of DNA

<u>James A. Green</u>¹, Haritha Asha¹, Martha Yaghoubi Jouybari², Fabrizio Santoro², Roberto Improta¹ ¹Consiglio Nazionale delle Ricerche, Istituto di Biostrutture e Bioimmagini, Naples, Italy. ²Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organo Metallici, Pisa, Italy

Abstract

In this work we describe a fragment based technique for obtaining diabatic electronic states from ab initio data for multi-chromophoric systems, and use it for two applications within DNA. Firstly, we use it to parameterise an excitonic model including charge transfer states for a guanine quadruplex, and calculate electronic circular dichroism spectra [1]. We illustrate the importance of including charge transfer states on the spectral shape for such a closely stacked system. Furthermore, we show that the local excitations are perturbed by the surrounding guanine bases, and are not simply equivalent to the local excitations of an isolated guanine, as in a standard excitonic model. Both of these features are able to be captured and demonstrated with the fragment diabatisation technique. Secondly, we apply the method to parameterise a linear vibronic coupling model for the quantum dynamics of a guanine-cytosine Watson Crick base pair [2]. We investigate the competition between the intra-chromophore processes of excitation energy transfer and charge transfer. We find that by initial excitation on either base, there is fast (<100 fs) and effective transfer to the guanine->cytosine charge transfer state, whilst the involvement of excitation energy transfer and nπ* states is minimal. We believe the method may be generally applicable to other systems, and will soon be distributed in a code.

[1] J. Chem. Theory. Comput., 2021, 17, 405-415

[2] J. Chem. Theory. Comput., 2021, in press, DOI: 10.1021/acs.jctc.1c00416

Hole-hole Tamm-Dancoff-approximated density functional theory: an efficient electronic structure method to simulate photochemical reactions

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Abstract

The study of photochemical reaction dynamics requires accurate as well as computationally efficient electronic structure methods for the ground and excited states. While time-dependent density functional theory (TDDFT) is not able to capture static correlation, complete active space self-consistent field (CASSCF) methods are deficient in their ability to describe dynamic correlation.

In this contribution, we demonstrate that the hole-hole Tamm-Dancoff approximated (*hh*-TDA) density functional theory, which is derived from the particle-particle random phase approximation, is an inexpensive method that encompasses both static and dynamic electron correlation. Here, the *N*-electron electronic states are obtained through double annihilations starting from a doubly anionic (*N*+2 electron) reference state. This way, *hh*-TDA treats ground and excited states on equal footing, allowing for conical intersections to be correctly described.

We show that this DFT-based *hh*-TDA scheme is a promising candidate to efficiently treat the photochemistry of molecules with multiple low-lying excited states – particularly those with $\pi\pi^*$ and $n\pi^*$ states. Its performance is demonstrated in the simulation of the wavelength-dependent photochemistry of azobenzene.

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Chiral-induced spin selectivity as a challenge for first-principles methods

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Abstract

When electrons are moving through helical molecules, one spin orientation has a larger chance of making it through than the other, despite the helices being diamagnetic. This effect is termed chiral induced spin selectitivity (CISS) [1], and it has been observed in electron transport and in electron photoemission through biomolecules, organic molecules and also in inorganic solids. Besides its fundamental importance, it is highly promising for applications ranging from enantiomer separation and electrochemical hydrogen evaluation to quantum materials [2]. The magnitude of the effect is not yet understood, and first-principles simulations [3-5] can be a valuable tool to gain insight into the underlying mechanisms and into structure-property relationships. We will discuss the status and current developments in the first-principles description of CISS, in the light of recent exeriments.

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Pushing the limits of the Density Matrix Renormalization Group: from vibrational spectroscopy to quantum dynamics

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Abstract

Simulation methods based on tensor factorizations, such as the density matrix renormalization group

(DMRG),¹ are currently reshaping the limits of wave function-based quantum chemical algorithms. Tensor-based methods provide very compact parameterizations that can encode many-body wave functions by taming the high computational cost of Full Configuration Interaction and, therefore, enable large-scale exact quantum chemical simulations.

Quantum chemical applications of DMRG have focused so far on time-independent electronic problems. In the present contribution, we show the potentiality of DMRG beyond this application field, by focusing on three simulation targets.

We first introduce the vibrational DMRG theory² to calculate the exact anharmonic vibrational energies of large molecular systems.

Then, we apply DMRG to solve the time-dependent (TD) Schrödinger and show that the resulting

algorithm, namely TD-DMRG,^{3,4} can accurately simulate ultrafast molecular processes occurring on multiple time-scales.

Finally, we present an explicitly correlated DMRG variant, the transcorrelated DMRG (tc-DMRG),⁵ that relies on the transcorrelated method and enhances the accuracy of conventional DMRG for strongly-correlated molecules.

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³ Baiardi, A., Reiher, M., *J. Chem. Theory Comput.* **2019**, 15, 3481–3498.

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Non-adiabatic quantum dynamics without potential energy surfaces based on second-quantized electrons: Application within the framework of the MCTDH method

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Abstract

A first principles quantum formalism to describe the non-adiabatic dynamics of electrons and nuclei based on a second quantization representation of the electronic motion combined with the usual representation of the nuclear coordinates is introduced. This procedure circumvents the introduction of potential energy surfaces and non-adiabatic couplings, providing an alternative to the Born-Oppenheimer approximation. An important feature of the molecular Hamiltonian in the mixed first quantized representation for the nuclei and the SQR representation for the electrons is that all degrees of freedom, nuclear positions and electronic occupations, are distinguishable. This makes the approach compatible with various tensor decomposition Ansätze for the propagation of the nuclear-electronic wavefunction. Here, we describe the application of this formalism within the multi-configuration timedependent Hartree framework and its multilayer generalization, corresponding to Tucker and hierarchical Tucker tensor decompositions of the wavefunction, respectively. The approach is applied to the

calculation of the photodissociation cross section of the HeH⁺ molecule under extreme ultraviolet irradiation, which features non-adiabatic effects and quantum interferences between the two possible

fragmentation channels, He + H⁺ and He⁺ + H. These calculations are compared with the usual description based on ab initio potential energy surfaces and non-adiabatic coupling matrix elements, which fully agree.

Accelerating the Computation of Fock-exchange with Seminumerical Integration: Linear-scaling, GPU-acceleration, and Adaptive Numeric Precision

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Abstract

The evaluation of Fock-exchange represents the major computational bottleneck in Hartree-Fock or hybrid density functional theory, due to its formal N^4 scaling, which quickly becomes unfeasible for large molecules and basis sets. Seminumerical integration, i.e., integrating one electronic coordinate analytically and one numerically, alleviates this problem by reducing the formal scaling to N^3 .

In this presentation, we show how this scaling can be further reduced to an asymptotic O(N) scaling by exploiting the locality of the exchange-interaction,^[1] which requires novel integral bounds^[2] for the necessary 3-center-1-electron integrals to be combined with information of the density matrix to preselect significant contributions.

Furthermore, the contribution from each grid point can be trivially processed in parallel, ideally suited for execution on GPUs.^[3] Moreover, we show that most of the significant integrals may be computed with reduced numerical precision with no measurable deterioration of the overall accuracy.^[4]

Overall, these developments lead to nearly 100x speedups. E.g., the execution time for one exchange build of (DNA)₁₆/def2-TZVP (1052 atoms, 22742 basis functions) is reduced from 320 minutes (conventionally) to <3.5 minutes (seminumerically).

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Electronic Structure as an Energy Landscape: An Orbital-Free Perspective

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Abstract

Multiple solutions in electronic structure theory are increasingly being targeted as state-specific approximations to difficult electronic excitations or representations of dominant electron configurations in the presence of strong correlations. In a departure from the molecular orbital perspective, these

multiple solutions can be identified as stationary points of a parametrised energy surface.^[1] However, the underlying structure of this energy surface for approximate methods, or even exact electronic structure, is still not fully understood. In this presentation, I will show how exact and approximate

electronic structure theory can be understood as an energy landscape.^[2] Starting with exact full configuration-interaction, I will describe the fundamental properties of the electronic structure landscape and explain how exact ground and excited states emerge from this representation. I will then show how approximate methods form constrained subspaces of the exact energy landscape and introduce a set of guiding principles for locating higher-energy excited-state approximations. Finally, I will show how the properties of the underlying exact energy surface can be used to develop an orbital-free interpretation of topics such as configuration interaction singles, spin-symmetry breaking, and divergent perturbation theory.

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On the photochemistry and photophysics of azobenzene in an aggregated state

<u>Evgenii Titov</u>¹, Anjali Sharma², Marek Bekir², Nino Lomadze², Svetlana Santer², Peter Saalfrank¹ ¹Theoretical Chemistry, University of Potsdam, Potsdam, Germany. ²Experimental Physics, University of Potsdam, Potsdam, Germany

Abstract

Azobenzene is arguably the most famous molecular switch, which is widely employed in numerous applications at the nanoscale. The photochemistry of azobenzene has been a topic of numerous experimental and theoretical investigations. Yet, in many systems employing azobenzene-containing molecules, azobenzene units may associate with each other, which, in turn, may affect their photophysical and photochemical properties. One example is micellization of azobenzene-functionalized surfactants. It has been observed that the micelle formation leads to a slowdown of the photoinduced *trans* \rightarrow *cis* isomerization.

The first part of this contribution will be devoted to nonadiabatic, surface hopping dynamics simulations for the surfactant molecules within the micelles. We utilize a quantum mechanics/molecular mechanics (QM/MM) scheme whereby internal conversion and isomerization of azobenzene is treated with a semiempirical configuration interaction method of Granucci and Persico. Our simulations reveal a decrease of isomerization quantum yields for molecules inside the micelles. We also observe a reduction of extinction coefficients upon micellization. These findings explain the deceleration of the switching in micelles. [1]

In the second part of this contribution, we will present a transition density matrix analysis of exciton states of azobenzene dimers. We find that the transitions to the lowest exciton states are dominated by local excitations, but charge transfer contributions become sizable for some of the $\pi\pi^*$ transitions in stacked and slip-stacked dimers at short intermolecular distances. In addition, we assess different ways to partition the transition density matrix between fragments. [2]

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Surface Hopping Meets Vibronic Coupling Theory: Efficient Simulation of Excited-State Dynamics of Transition Metal Complexes in Full Dimensionality on Picosecond Time Scales

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Abstract

The study of excited-state dynamics of transition-metal complexes is challenging due to their large number of vibrational degrees of freedom and many close-lying electronic states. When using quantum dynamics to simulate transition-metal complexes, this imposes the use of truncated models with typically only few degrees of freedom and electronic states, where the electronic potentials are often described in parameterized vibronic coupling models. An alternative to quantum dynamics that can include all degrees of freedom and large number of electronic states is given by on-the-fly surface hopping (SH) methods. However, the repeating cost of the underlying electronic structure calculations restricts the range of possible simulation times for molecules the size of transition-metal complexes severely.

By using SH on vibronic-coupling potentials, we can now lift the simulation-time restriction in SH and enable full-dimensional nonadiabatic dynamics simulations of transition-metal complexes on picosecond time scales.[1] This is demonstrated for two examples. First, using CASSCF-derived linear vibroniccoupling (LVC) potentials, we can unravel the relaxation mechanism to the phosphorescent singlet state of a near-infrared emitting vanadium(III) complex with an open-shell triplet ground state, allowing us to establish a clear model to improve luminescence.[2] Second, combining SH on LVC potentials with SH on ab initio potentials, we can capture both ultrafast bond breaking as well as long-time dynamics populating emissive states of a closed-shell rhenium(I) carbonyl diimine complex used in photoactivated redox reactions.

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Molecular photodynamics and its manifestation in UV-Vis and X-ray timeresolved spectra. Insights from quantum chemistry and quantum dynamics

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Abstract

Computational strategies are illustrated, which combine quantum chemistry and quantum dynamics to investigate which aspects of photochemical processes can be unambiguously inferred from time-resolved spectroscopic signals.

The first example presented is the excited-state intramolecular proton transfer of 10hydroxybenzo[h]quinoline (HBQ), for which pump-probe spectroscopies revealed several multimode coherences that, according to the most recent investigations, are a signature of a nonadiabatic reaction. Nuclear quantum dynamics on *ab initio* potential energy surfaces show that the reaction after $S_1 \leftarrow S_0$ photoexcitation actually proceeds on a single Born-Oppenheimer surface, and the coherences are formed by mode-mixing along the reaction path. The mechanism following the $S_2 \leftarrow S_0$ excitation is instead nonadiabatic, involving a $n\pi^*$ state stabilized at the photoproduct geometry.

The second example is the gas-phase photophysics of 2-thiouracil, which involves three singlet and triplet states, and is studied in a joint experimental-theoretical collaboration using time-resolved X-ray photoelectron spectroscopy (XPS) at the sulphur edge. The dynamics are disentagled by comparing the time-dependent shift of the XPS signal with the core ionization potential calculated at the coupled-cluster level for different electronic states and molecular geometries. The excited molecules relax from S₂ to S₁ and T₁ on a time scale faster than 100 fs, a 200 fs relaxation channel to S0 is found, and the coherent electronic population exchange is observed. The quantum chemical data allow us to formulate a "potential model" to invert the XPS band to the partial charge at the probed atom: a key quantity to understand excited state chemistry and photoreactivity.

Quantum dynamics of electron-hole separation in stacked perylene diimidebased self-assembled nanostructures

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Abstract

Charge separation at donor-acceptor interfaces is a fundamental process in organic photovoltaics. Yet, the theoretical description beyond the standard Onsager-Braun model is challenging. Here, we present high-dimensional quantum dynamical simulations of electron-hole (e-h) separation in self-assembled mesomorphic nanostructures [1] composed of conjugated co-oligomers of perylene diimide (PDI) type acceptor units and fluorene-thiophene-benzothiadiazole type donor units. These form highly ordered, stacked structural motifs upon self-assembly [2], whose local electrostatic properties we characterized using micro-electrostatics calculations [1]. Based on this, a full quantum dynamical picture of e-h separation is developed for a first-principles parametrized model lattice of 20 stacked PDI units under the effects of an applied external field and temperature. The Thermofield Dynamics (TFD) approach [3] is employed in conjunction with the Multilayer Multiconfiguration Time-Dependent Hartree (ML-MCTDH) method [4] with nearly 800 vibrational degrees of freedom and 20 electronic states. From

these simulations, e-h dissociation rates in the range of 1 to 10 ns⁻¹ are obtained from a flux-overpopulation analysis, showing that charge separation occurs even at 0 K and exhibits a moderate field and temperature dependence. These results are employed as a benchmark to calibrate the parametrization of Kinetic Monte Carlo (KMC) simulations applied to much larger lattice sizes.



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Electron correlation with magnetic fields - a voyage from astrophysics to larger systems

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Abstract

Magnetic fields play an important role in quantum chemistry. They are for example employed in nuclear magnetic resonance (NMR) and routinely used for structural elucidation. Quantum-chemical predictions often enable the assignment of complicated spectra, thereby treating the magnetic field perturbatively. When increasing the field considerably, the assumption that it constitutes a small perturbation crumbles. Eventually, only finite-field (ff) approaches suitably describe the complicated emerging electronic structure. Fields of up to 100000 Tesla occur in White Dwarf (WD) star atmospheres and lead to complicated spectra.

In this talk, the assignment of WD spectra via ff predictions is presented. Transition wavelengths and intensities of alkaline and alkaline earth metals are computed at the ff equation-of-motion coupledcluster (EOM-CC)¹⁻⁴ level of theory. We will then turn to small molecules investigated at the ff CC2 and CC3 levels⁴, thereby discussing their usefulness in the ff context. We also address larger molecules: For the weak-field case, we present a scheme employing Cholesky decomposition (CD) for the efficient computation of NMR shieldings at the level of second-order Møller-Plesset perturbation theory (MP2)⁵. For the strong field case, we treat systems with up to 2000 basis functions by employing CD on two-electron integrals over London orbitals together with ff second-order Møller-Plesset perturbation theory.⁶

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Acceptance type: Poster

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Chemoton 2.0: Automated Exploration of Reaction Networks

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Abstract

In recent years, much algorithm development was devoted to the computer-based automated exploration of reaction networks.[1] In parts, this can be attributed to the potential role in the automation and acceleration of Design-Make-Test-Analyze (DMTA) cycles for new materials and chemical processes. All of these reaction network based methods aim at establishing a sufficiently complete reaction network in order to allow for reliable predictions, detailed understanding, and eventually, the design of chemical processes. A complete reaction network consists of all thermodynamically and kinetically relevant intermediates and all reaction paths that connect them. Already due to conformational diversity, the reaction network generated for relatively simple chemical processes can be vast if they are to be complete. This poses a set of challenges for methodology and software, which we have analyzed and discussed recently.[2]



Here, we will present the current developments of our mechanism exploration automaton, called Chemoton[3], in its latest version 2.0.[4]

We will touch upon software, data and database structure of the project, resource estimates for the exploration, network visualization and benchmark networks.

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Investigation of CO_2 Orientational Dynamics through Simulated NMR Line Shapes

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Abstract

The dynamics of carbon dioxide in third generation (i.e., flexible) Metal-Organic Frameworks (MOFs) can be experimentally observed by ¹³C NMR spectroscopy. The obtained line shapes directly correlate with the motion of the adsorbed CO₂, which in turn are readily available from classical molecular dynamics (MD) simulations. In this work, we implement an algorithm to calculate NMR line shapes from MD trajectories in a matter of minutes on any current personal computer. We apply the methodology to study an effect observed experimentally when adsorbing CO₂ in different samples of the pillared layer MOF Ni₂(ndc)₂(dabco) (ndc = 2,6-naphthalene-dicarboxylate, dabco = 1,4-diazabicyclo-[2.2.2]-octane), also known as DUT-8(Ni). In ¹³C NMR experiments of adsorbed CO₂ in this MOF, small (rigid) crystals result in narrower NMR line shapes than larger (flexible) crystals. The reasons for the higher mobility of CO₂ inside the smaller crystals is unknown. Our ligand field molecular mechanics simulations provide atomistic insight into the effects visible in NMR experiments with limited computational effort.

Resonance Effects in the Raman Optical Activity Spectrum of [Rh(en)₃]³⁺

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Abstract

Raman optical activity (ROA) denotes the effect that all chiral molecules show a small difference in the intensities of Raman scattered left and right circularly polarized light. ROA spectroscopy is a very sensitive structural probe and, therefore, has a great potential for molecular structure elucidation [1], in particular when the incident laser beam resonates with one or more electronically excited states of the molecule.

Today, ROA spectroscopy is routinely applied in the study of biomolecules, but ROA spectra of transition metal compounds are largely missing [2]. However, several studies have demonstrated the great potential ROA spectroscopy can offer for the structural investigation of such metal complexes.

We present ROA spectra of Λ -tris(ethylenediamine)-rhodium(III) {[Rh(en)_3]³⁺} calculated at 16 on-, near-, and off-resonant wavelengths between 290 and 800 nm [3, 4]. This complex is a very interesting example case, because some intriguing resonance effects are observed originating in its complex electronic structure. We analyzed the spectra focussing on these resonance effects and could explain the molecular origins of the Raman optical activity intensity for selected normal modes by means of group coupling matrices.

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Toward absorption and fluorescence spectroscopy for large-scale applications

<u>Anna Hehn</u>¹, Beliz Sertcan¹, Sergey Chulkov², Matthew Watkins², Jürg Hutter¹ ¹University of Zurich, Zurich, Switzerland. ²University of Lincoln, Lincoln, United Kingdom

Abstract

State-of-the-art computational approaches to describe photochemical processes in extended materials often rely on time-dependent density functional theory, representing a feasible and robust tool to enable broad applications. However, when aiming for high-throughput screening on the large scale, the computation of excited-state properties becomes tedious, being in comparison to ground-state properties theoretically more challenging requiring an accurate description of exact exchange, as well as computationally more demanding with a less favorable scaling and higher computational cost. We therefore propose a combined hybrid functional and semi-empirical tight binding scheme exploiting the concepts of the auxiliary density matrix method (ADMM)[1] and the simplified Tamm-Dancoff approximation (sTDA)[2]. Among the existing techniques to improve the unfavorable basis-set dependence of exact Hartree-Fock exchange, ADMM has proven to be a reliable approach to achieve significant speedups without significant accuracy loss, being based on the idea of constructing an auxiliary density matrix and correcting the thereby introduced error by a density functional contribution. The setup for the ground-state treatment is complemented by employing the sTDA ansatz for the excited state: sTDA relies only on global parameters requiring no bond-specific parameterizations while being computationally cheap and physically reasonable using semi-empirical electron-repulsion operators. Benchmarks and applications of the combined hybrid-ADMM and sTDA approach in CP2K [3] are presented regarding the description of absorption and fluorescence spectra.

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Fast prediction of correlation energies for Møller-Plesset perturbation theory: atomic contribution model and machine learning

<u>Ruocheng Han</u>, Sandra Luber University of Zurich, Zurich, Switzerland

Abstract

Various post-Hartree-Fock methods have been adopted to calculate correlation energies of chemical systems, but time complexity usually prevents their usage in large scale. We propose a density functional approximation, based on an artificial neural network consisting of recursive layers, on a newly introduced descriptor "orbital energy weighted electron density", which can be readily employed to produce results comparable to 2nd order Møller-Plesset perturbation (MP2) ones. Various systems have been tested and the transferability across basis sets, structures, and nuclear configurations has been evaluated. Moreover, a concise and fast model for the fast estimation of dynamic correlation energy is introduced. Dynamic correlation energy calculated by up to 4th order Møller-Plesset perturbation (MP4) theory can be predicted with 0.16 % error using only 1.3 % of the dataset as reference/training data.

Deterministic quantum mechanics: Simulation of chemical reactions

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Abstract

The Born-Oppenheimer approximation can be replaced by a better approximation in a very simple way. The consideration starts from the notion that it is problematic to describe the nuclei and the electronic cloud in a similar way, hoping that the Schrödinger equation will generate meaningful results for both of these two completely different types of objects. In the end of the simulation of a chemical reaction one wants to have an electronic cloud and well localized nuclei which clearly define the product state. A nuclear cloud extending over scales that do not agree with the Rutherford picture of the nuclei is not acceptable. The only consistent way to achieve this, is by treating the motion of the nuclei classically right from the beginning. The immediate result is ab-initio molecular dynamics (AIMD). Movies of chemical reactions generated with AIMD show clearly that this approach is working well. The talk will make the connection to recent publications which claim to prove that nuclear motion must be treated quantum mechanically. The observation of kinetic isotope effects is not an argument for nuclear tunneling, because also Newton dynamics depends on mass, F = m a. If the differences are so small compared to the error of density functional theory, why switch to deterministic quantum mechanics? The reasons are obvious: We have the simpler approach, our results are easier to interpret, and we get rid of all paradoxa.

Coarse-graining all-atom molecular dynamics into free energies and friction profiles: accessing dynamics of the multisecond time scale

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Abstract

Fully atomistic simulations of processes with rates longer than milliseconds are still far beyond the scope of current all-atom molecular dynamics (MD). To access such time scales and elucidate the microscopic processes governing substrate diffusion in biological systems, we have developed the dissipation-corrected targeted MD approach [1], which combines a Markovian Langevin equation framework with the Jarzynski equality. We enforce a molecular process along a reaction coordinate x and use the resulting bias force to calculate the free energy $\Delta G(x)$ and friction profile $\Gamma(x)$. Analysis of $\Gamma(x)$ allows insight into system dynamics not encoded in free energies. For example, this analysis elucidates position-dependent friction coming from hydration shells, and how these shells mediate important dynamics in ion solutions, protein-ligand systems as well as in ion channels. With $\Delta G(x)$ and $\Gamma(x)$ as input for a temperature-boosted integration of the Langevin equation [2], we readily simulate dynamics far beyond the limits of fully atomistic MD methods. The massive acceleration of dynamics facilitates the calculation of experimental observables such as I-V-characteristics in ion channels [3]. Last, I will give an outlook on what we have learned from the comparison of friction profiles between different molecular systems, and how we use this approach to enforce conformational changes of full proteins.

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Optimized effective potentials for density functional theory studies of excited-state properties

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Abstract

In various systems, acidic properties emerge when the system is electronically excited. Although the time scale attributed to the dynamics of the electrons is usually on the order of femtoseconds, the electronic excitations can in general trigger much slower processes.

Here, we propose and benchmark a novel approximate first-principles molecular dynamics simulation idea for increasing the computational efficiency of density functional theory-based calculations of the excite states. We focus on obtaining proton transfer energy at the S₁ excited state through actual density functional theory calculations at the T₁ state with additional optimized effective potentials. The potentials are optimized such as to reproduce the time-dependent density functional theory energy surface, but can be generalized to other more accurate quantum chemical methods. We demonstrate the applicability of this method for several photoacids, namely phenol, 2- and 4- cyanophenol, 1- and 2-naphthol, and finally 7-hydroxyquinoline. We show that after optimizing the additional effective potentials for the photoacidic, both thermodynamics and kinetics of proton dissociation reaction can be well reproduced as compared to reference excited-state calculations. It is also found that a reasonable agreement with the reference values can be reached even by optimizing one additional effective potential only for the acidic hydrogens.

Enantiomer superpositions from matter-wave interference of chiral molecules

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Abstract

Molecular matter-wave interferometry enables novel strategies for manipulating the mechanical motion of complex molecules [1,2]. In this presentation, I will argue how chiral molecules can be prepared in a quantum superposition of two enantiomers by far-field matter-wave diffraction and how the resulting tunnelling dynamics can be observed [3]. I will discuss the impact of ro-vibrational phase averaging and propose a setup for sensing enantiomer-dependent forces and environment-induced superselection of handedness [4].

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The road to exascale quantum chemistry

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Abstract

Progress in computational quantum chemistry is deeply connected to the most recent advances in hardware technology. As larger and more powerful computers are built, the more complex and challenging problems in *ab initio* quantum chemistry open up: heterogenous catalysis, polymer chemistry, biomolecules, among others. The GAMESS software package has been at the edge of high-performance computing by implementing a diverse set of parallel methods and implementing several methods on GPUs. Now, as the petascale era ends and the exascale one dawns, GAMESS has sought to modernize itself to be able to reach exaflops levels of performance. To address the extreme requirements for exascale computing, the Restricted Hartree-Fock (RHF) and the Resolution of the Identity MP2 (RIMP2) methods have been redesigned for high performance and scalability. The new SCF code is part of the LibCChem library interfaced with GAMESS to provide accelerated quantum chemistry routines. Coupled with a parallel molecular fragmentation framework, the GPU-accelerated SCF code in LibCChem scaled up to the entirety of the Summit supercomputer at ORNL, at the time the most powerful in the world, treating a system with >60k atoms fully *ab initio*. Without using fragmentation, the new implementation is faster by up to 30 than the open-source code QUICK and always outperforms the commercial and well-established code Terachem when using multiple GPUs.

Going Beyond the PT2 Correlation for DSD Double Hybrids: Direct Random-Phase Approximation and Scaled MP3 Corrections

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Abstract

For the revDSD (DOI: 10.1021/acs.jpca.9b03157) double hybrids, the Görling-Levy second-order perturbation theory component is an Achilles' Heel when applied to systems with small band gaps (a.k.a absolute near-degeneracy correlation, type A static correlation). We have explored its replacement by the direct random phase approximation (dRPA), motivated by the SCS-dRPA75 functional of Kállay and coworkers. The addition to the final energy of both a D4 empirical dispersion correction and of a semilocal correlation component, lead to significant improvements, with DSD-PBEdRPA₇₅-D4 approaching the performance of Mardirossian and Head-Gordon's ω B97M(2), and our own revDSD-PBEP86-D4. This form appears to be fairly insensitive to the choice of semilocal functional, but does exhibit stronger basis set sensitivity than the PT2-based double hybrids (due to much larger prefactors for the nonlocal correlation). As an alternative, we explored adding an MP3-like correction term (in a medium-sized basis set) to both global and range-separated DSD-PBEP86-D4 double hybrid. These DSD3 and ω DSD3 functionals, respectively, turned out to have significantly improved the WTMAD2 (weighted mean absolute deviation) for the large and chemically diverse GMTKN55 benchmark suite; the added computational cost can be mitigated through density fitting techniques. The range separated ω DSD3-PBEP86-D4 (WTMAD2=1.76 kcal/mol) is the best fifth-rung functional available to date.

From Orange to Blue to Green: How to Influence the Color of an Aromatic Compound Using Strong Magnetic Fields

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Abstract

Aromatic substances and their optical properties have been thoroughly studied in the past using both experimental and computational methods. The tetracene molecule in particular is known for its characteristic vibrant orange-red color, which is caused by three electronic excitations often referred to as the p-, α - and β -bands of the optical spectrum.

Calculations of molecular properties in strong external magnetic fields have recently become increasingly popular, especially for investigations of excited state properties. However, these computations have so far been limited to either time-dependent Hartree-Fock theory, which is not suitable to accurately predict the optical spectrum of aromatic compounds or, alternatively, time-dependent density functional theory which in the case of external magnetic fields suffers from instabilities in the non-collinear exchange-correlation kernel. We thus report the efficient implementation of both *GW*/BSE and CC2 in strong external magnetic fields into the Turbomole package employing London atomic orbitals throughout in order to guarantee gauge-invariance.

Using *GW*/BSE and CC2, we investigate the optical properties of tetracene in strong external magnetic fields at various field-strengths. Firstly, we assess how the *p*-, α - and β -excitations are affected. Secondly, we thoroughly examine the influence of the field on other excitations such as γ and δ as well as transitions that are no longer forbidden due to symmetry reduction. We aim at understanding the influence of a magnetic field of up to 10,000 tesla on the optical spectrum of aromatic compounds, thereby predicting the color change of tetracene within such an extreme environment.



Atomistic characterization of the tuning mechanisms for chlorophyll excitation energies in photosystem 1

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Abstract

Photosystem 1 (PS1) is one of the most efficient light-harvesting systems found in nature. The 96 chlorophylls in its antenna complex absorb light and funnel energy to the reaction center, where charge separation occurs. It is known that the local environment affects the absorption energy of the individual chlorophylls (site energy), yet characterizing the exact sites of chromophores with red- and blue-shifted absorption energies is challenging due to the complexity of the system. Identifying these chlorophylls can help elucidate the energy transfer mechanisms occuring in PS1 at a microscopic level, paving the way for applications in artificial light harvesting systems.

We therefore built a fully atomistic model of the trimeric PS1 complex, including all cofactors and embedded in a solvated lipid bilayer, to simulate the natural environment as thoroughly as possible. With this extensive structural model at hand, we sampled geometries from classical molecular dynamics trajectories and calculated accurate site energies of all 96 chlorophylls with the high-level DFT/MRCI method in a hybrid QM/MM scheme. Our results identify energy sinks in the antenna complex and reveal a fundamental asymmetry in the reaction center, where the electron transfer chain is initiated, in terms of single-chromophore excitations. Moreover, we are able to distinguish two effects in the environmental influence: The direct electrostatic interaction of the protein with the chromophore and the more subtle structural constraints imposed on the chromophore by its surroundings. Finally, we discuss if and how targeted mutations can tune the energy of individual chlorophylls in PS1.



Diabolical limits of ab initio multiple spawning - nonadiabatic dynamics near conical intersections

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Abstract

Full multiple spawning describes the nonadiabatic dynamics of a system in principle exactly, expressing nuclear wavefunctions by coupled classically-moving trajectory basis functions (TBFs). For molecular systems, the couplings between TBFs can approximated, leading to the more tractable ab initio multiple spawning (AIMS), which provides an accurate description of the photochemistry of larger molecules in full dimensionality. While these approximations have recently been validated for a one-dimensional system (JCP,148,134110,2018), no detailed tests of AIMS have been conducted for dynamics approaching conical intersections.

In this work, we propose to investigate the implications of the AIMS approximations on the dynamics of a molecule through a conical intersection by using a two-state two-dimensional linear vibronic coupling model, parametrised to reproduce the nonadiabatic dynamics of molecules like butatriene cation, bismethylene-adamantyl or pyrazine (JCP,140,214116,2014). We analysed the AIMS-dynamics in comparison with exact quantum-dynamics, for the predicted population decay and the time-evolution of the wavepackets. Additionally, we looked at the influence of neglected contributions to the matrix elements, highlighting the challenges of including second-order couplings and geometric phase effects within the AIMS-framework.

Overall, we show that AIMS not only qualitatively reproduces the exact population decay around a conical intersection but also captures the main features of the nuclear wavepackets. While the approximations in AIMS balance each other, our results show that any attempt to improve over one approximation will unavoidably deteriorate the stability of other ones. The stability of AIMS for dynamics around conical intersections is nevertheless a good omen for the excited-state dynamics of molecular systems.



Roadmap for Designing the Strategy to Mimic the Experimental Turnover Numbers: A Case Study to Artificial Water Splitting Reaction

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Abstract

Computationally finding the efficiency of the catalysts in terms of turnover number (TON) is a challenging task. Although experimentally, the efficiency is determined over the catalytic cycle, no strategy has been reported computationally, to the best of our knowledge, to identify the efficiency of catalysts. To do so, we have computationally designed a roadmap, namely, the Efficiency Conceptualization Model (ECM), to predict the efficiency of the Ru-based molecular water oxidation catalysts (WOC). The bedrock of the ECM model is on the kinetics, thermodynamics, bonding, and reactivity performance of the complexes. The computations with density functional theory were adopted to determine the rate constants using non-variational transition state theory (TST) as a function of the activation barrier recognizing the proton-coupled electron transfer (PCET) to be the rate-determining step (RDS). The classical rate was further corrected by Truhlar, Wigner, and Eckart tunneling methods. The thermodynamic and reactivity studies demonstrate that the proton accepting tendency of the carboxylate group in addition to the π -conjugation and hydrophobicity of the N-heterocyclic isoquinoline ligand was the driving force in constructing the robust and dexterous catalyst. Our calculations were successful in validating the experimental TON of the WOCs and hence may be correlated to the experiment. At present, the ECM is under the validation stage, and the water splitting reaction was our first choice of theoretical validation. We are currently working on organic and inorganic catalysts mediated reactions to establish our Efficiency Conceptualization Model.

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The modulation of substrate binding and catalysis through electrostatics in acetoacetate decarboxylase

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Abstract

Acetoacetate decarboxylase (AAD) is a prominent example in the discussion of p*Ka* shifts in enzymes. The latter promotes the decarboxylation of acetoacetate (AA) and it has long been accepted that the catalyzed reaction takes place through an enamine intermediate, formed by the nucleophilic attack of Lys115. In order for such an intermediate to be formed, Lys115 must be present at its deprotonated form. In this sense, it has been proposed that the necessary p*Ka* shift takes place by desolvation, albeit electrostatics of the neighbouring Glu76 residue have also been discussed. Herein, we show that the negatively charged AA substrate shifts the p*Ka* value of Glu76 which can be present at either the protonated or deprotonated state, whereas Lys115 is a regular protonated residue. The QM reaction path analysis shows that the decarboxylation reaction takes place by direct proton transfer without requiring the formation of any intermediate. This study further underscores how electrostatic potentials are primed by enzymes to effect catalysis as well as the need to consider multiple protonation states along a catalysed process (from binding to product release).

Theoretical studies of Density Functional Models for the Description of Fe(II) Spin-Crossover Complexes

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Abstract

Spin-crossover (SCO) complexes, exhibiting spin transitions under external stimuli such as temperature and pressure, have a wide potential application as molecular switches for use in display, memory and sensing devices [1,2]. Notable examples of SCO materials are based on Fe(II) [3], whereby the transition occurs between the S = 0 (low-spin, LS) and S = 2 (high-spin, HS) states.

However, the *ab initio* simulation of such systems remains not without issues. On the one hand, the widely used general gradient approximation methods tend to over-stabilize the low-spin states. On the other hand, for the more advanced hybrid functionals the HS-LS gap is directly dependent on the admixture of Hartree-Fock (exact) exchange. Thus these methods can not necessarily be used out of the box for the goal of describing the HS-LS gap accurately [4,5].

Our goal in this project was to explore different venues for the parameterization of hybrid functionals to approach wave-function method accuracy by using Bayesian optimization to match benchmark data from pair natural orbitals local coupled cluster methods with explicit correlation [6].

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Probing Dark Matter and Special Relativity with Chiral Molecules

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Abstract

Considering only the electromagnetic force enantiomers of chiral molecules should be degenerate in energy. However, violation of parity (*P*), the symmetry related to space inversion, in the fundamental weak force can induce an energy difference between enantiomers.^[1] In addition, energy differences between enantiomers could be caused by *P*-violation due to so far unknown forces or unexplored

particles. Certain models for dark matter (DM) consider pseudovector cosmic fields.^[2] DM is a obscure substance which has to make up more than 80% of all matter in order to explain the movement of stars

and planets, but so far it could not be detected and its nature is unknown.^[3] Such pseudovector fields can induce *P*-violation and, moreover, appear as sources of local Lorentz invariance violation (LLIV), which is predicted by theories that aim to unify general relativity and quantum theory, like string theory. [4,5]

In this contribution, *P*-odd effects of cosmic pseudovector fields on vibrational spectra of chiral molecules are computed and analyzed with respect to nuclear charge number and multi-mode couplings. The sensitivity of a 20-year-old experiment with CHBrClF^[6] with respect to cosmic *P*-violation is discussed. It is demonstrated that modern experiments with heavy-elemental chiral molecules can improve current best limits by at least two orders of magnitude.^[7,8]

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Computational Investigation of the noncovalent interactions in ditopic receptor host and its complex formation with a benzene metabolite resorcinol molecule

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Abstract

In this work, we explored the noncovalent interactions present in a ditopic receptor host, 1,6-bis(2,6bis(benzothiazol-2-yl) pyridine-4-yloxy) hexane (bbh), and its interaction with a guest molecule, resorcinol, using different quantum chemical methods. We found that non-traditional hydrogen bonding interactions play a prominent role in differentiating the stability of the conformers. However, such interactions are weak and could be disturbed at room temperature through dihedral rotation and exhibit other conformation. Further, the binding energies for the host-guest complex formation were estimated using different functionals of density functional theory (DFT). The intermolecular interactions within the complexes were further analyzed using Quantum Theory of Atoms in Molecules (QTAIM), Natural Bond Orbital (NBO), Reduced Density Gradient (RDG), and Noncovalent Interactions (NCI) methods.

Detailed kinetic study of hydrogen abstraction reactions of PAHs by H atoms

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Abstract

The control of soot particles emission is necessary to minimize their effects on human health and the environment. It requires in particular a better understanding of the formation mechanisms of their precursors, which are polycyclic aromatic hydrocarbons (PAHs). Motivated by the importance of abstraction pathways in PAHs formation and by the crucial lack of experimental information, the main goal of this work is to provide a reliable thermo-kinetic data of hydrogen abstraction reactions on pathways involving bigger/higher-C-number PAHs by H atom over a wide temperature range (250-2500 K).

The potential energy surface of the considered medium and large sized molecules was explored using high-level ab initio approach with highly correlated wave functions within the explicitly correlated UCCSD (T)-F12 method in comparison with the DFT approach. The influence of the system environment on thermodynamic and kinetic properties were examined. The rate constants obtained using the transition state theory with the one-dimensional Eckart approximation are reported over a wide temperature range (250-2500 K). The results show that the kinetic parameters are not affected by PAH size and its structures in flame conditions.

Towards Unraveling Reaction Mechanisms in On-Surface Chemistry

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Abstract

DFT model

STM simulation



On-surface chemistry has evolved into a very promising research area for the construction of novel materials such as functionalized surfaces and two-dimensional covalently bound organic networks, which may serve in nanotechnology and heterogeneous catalysis. [1, 2] However, comparatively little is known about what happens at an atomistic level when organic molecules meet their substrate under ultra high vacuum conditions, and about how and why such polymerization reactions proceed. [3, 4] Density functional theory (DFT) is a powerful tool to characterize and design new materials [5, 6], which has already provided important insights into the interactions between adsorbates and surfaces [1, 2]. Here, we demonstrate how a close cooperation between theory and experiment can elucidate unexpected product structures and shed light onto novel on-surface reaction mechanisms.

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Accurate Receptor-Ligand Binding Free Energies from QM Conformational Chemical Space Sampling

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Abstract

Small molecule receptor-binding is dominated by weak, non-covalent interactions such as van-der-Waals, hydrogen bonding or electrostatics. Calculating these non-covalent ligand-receptor interactions is a challenge to computational means in terms of accuracy and efficacy since the ligand may bind in a number of thermally accessible conformations. The conformation/rotamer ensemble sampling tool (CREST) uses an iterative scheme to efficiently sample the conformational space and calculates energies using the semi-empirical 'Geometry, Frequency, Noncovalent, eXtended Tight Binding' (GFN2-xTB) method. This combined approach is applied to blind predictions of the modes and free energies of binding for a set of 10 drug molecule ligands to the cucurbit[n]urils CB[8] receptor from the recent 'Statistical Assessment of the Modeling of Proteins and Ligands' (SAMPL) challenge including morphine, hydromorphone, cocaine, fentanyl, ketamine and others. For each system, the conformational space was sufficiently sampled for the free ligand and the ligand-receptor complexes using the quantum chemical Hamiltonian. A multitude of structures makes up the final conformer-rotamer ensemble, for which then free energies of binding are calculated. For those large and complex molecules, the results are in good agreement with experimental values with a mean error of 2-3 kcal/mol. The GFN2-xTB energies of binding are validated by advanced density functional theory calculations and found to be in good agreement. The efficacy of the automated QM sampling workflow allows the extension towards other complex molecular interaction scenarios.

Large amplitude motions tunneling splittings made easy

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Abstract

Large amplitude motions (LAMs) in free molecules manifest themselves in the high-resolution spectroscopic measurements via tunneling splittings: the ground vibrational states of the molecules are being split into two states with opposite parity. An accurate theoretical prediction of the tunneling splitting energy usually requires the application of sophisticated computational procedures.

Here, we present an approach for the calculation of the tunneling splitting for a single LAM based on the solution of the 1D Schrödinger equation with effective kinetic and potential energies. Kinetic energy is taken from Meyer – Günthard Hamiltonian [1] and requires the computation of the reaction coordinate-dependent mass. The potential energy includes the zero-point vibrational energy correction from all the other vibrational degrees of freedom, thus the approach is effectively full-dimensional. The procedure is realized as a Python script that works with the Orca [2] output files. This allows for routine estimation of the LAM tunneling splittings by inexperienced users.



We will present benchmark calculations for the double proton transfer in the formic acid dimer (FAD), and in the complex of FAD with the fluorobenzene, which was measured only recently, and for the internal rotation of the -CH₂XH (X=O, S) group with respect to the aromatic ring in the benzyl alcohol, some of its symmetric fluoro-derivatives, and in the benzyl mercaptan.

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The accurate and robust "high-speed" composite DFT method r²SCAN-3c: comprehensive benchmarking including the newly compiled ROST61 open-shell organometallic reactions test set

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Abstract

We present a new efficient "3c" composite DFT method termed r²SCAN-3c.[1] It is constructed from the

 r^2 SCAN meta-GGA functional, a tailor-made triple- ζ Gaussian AO-basis as well as refitted basis-set superposition error and D4 London-dispersion corrections. Extensive testing on molecular and condensed

phase systems demonstrated impressive performance and robustness: r²SCAN-3c reveals one of the best results of all semi-local DFT/QZ methods ever tested and even outperforms commonly applied hybrid-DFT/QZ approaches for conformational energies and non-covalent interactions at up to three orders of magnitude lower cost. This is also true for the newly compiled challenging benchmark set

"Reactions of Open-Shell Single-Reference Transition Metal Complexes" (ROST61),[2] for which r²SCAN-3c is surpassed only by hybrid DFT/QZ methods with small amounts of Fock exchange and significantly more expensive double-hybrid DFT functionals. Hence, it has the potential to replace costly higher-level methods in various standard applications for systems with up to several hundreds of atoms.

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Coarse-grained molecular dynamics simulations of nanoplastics interacting with a hydrophobic environment in aqueous solution

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Abstract

Plastic waste in form of small particles is an emerging threat for marine and terrestrial ecosystems. Little is known about the fate and potential impacts of plastic nanoparticles in the environment. In this work, an attempt for understanding the molecular level interaction behavior between nanoplastics (NPs) and hydrophobic environments in aqueous solution is introduced. Here, NPs are simulated with different polymers, namely polyethylene oxide (PEO), polyethylene (PE), polypropylene (PP) and polystyrene (PS). On the other hand, carbon nanotubes (CNTs) are used to mimic hydrophobic environmental molecular systems. Moreover, hydrophobicity of CNTs is modified by introducing different hydrophobic and hydrophilic functional groups (alkane, phenyl, and carboxylic acid groups) into the inner surface of CNTs. The interaction of the modeled NPs with bare and modified CNTs in the presence of water is investigated via MARTINI force field based coarse-grained molecular dynamics simulations. The results show that hydrophobic polymers have a relatively strong affinity to CNTs, especially PE, which is connected to an increase of the contact area between polymers and CNTs. The hydrophobic functional groups introduced into CNTs increased the interaction between hydrophobic polymers and CNTs. This was observed as an attraction of hydrophobic polymers and reduction of their movement. In contrast, PEO showed the lowest affinity towards CNTs and was nearly not affected by functional groups. Therefore, one can expect that hydrophobic polymers have a higher tendency to accumulate at hydrophobic environmental molecular systems. The chemical nature of present functional groups plays a role in controlling this accumulation process.

Charge and Exciton Transfer Simulations driven by Machine Learned Models

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Abstract

Quantum mechanical (QM) simulations of charge and exciton transfer in molecular materials are a key method to increase our understanding of the processes therein. Our goal is to build an efficient multiscale model to investigate the underlying transfer mechanisms and to predict experimental observables such as charge-transfer mobilities and exciton diffusion constants from non-adiabatic molecular dynamics simulations in a semi-classical approach. Yet, the QM calculations remain computationally demanding compared to the calculations necessary for the classical propagation of nuclei. This motivates the use of machine learned (ML) models for these repetitive calculations. We show that different ML models can be trained to predict electronic and excitonic Hamiltonian elements from semi-empirical density functional tight-binding (DFTB) reference data with very good accuracy, while decreasing the cost of simulations. Using artificial neural networks instead of kernel ridge regression models allows the joint prediction of Hamiltonian elements and their derivatives, which can be used to simulate relaxation as a result of a transfer event and to account for proper energy conservation during the propagation.

Point Charge Variation Analysis (PCVA) - A Simple and Reliable Approach for QM Region Construction in QM/MM Calculations

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Abstract

QM region determination is crucial to obtain accurate and consistent results in QM/MM calculations. Simply including residues by their distance to the active site is generally not sufficient because necessary residues might be missing or unimportant residues included. To identify important residues, the understanding of parameters affecting QM/MM calculations must be improved by quantifying the sensitivity of the results to these parameters and by using this knowledge to develop simple but reliable methods for QM region construction.

Several approaches were reported previously, such as CSA [1] or FSA [2] which perform well in detecting important amino acids but which also require a huge computational effort. Here, we present a less expensive approach based on the variation of MM point charges resulting in a different sensitivity of the QM charges and reaction energies for each residue [3]. This point charge variation analysis (PCVA) allows us to detect important residues which should be included into the QM region in an easy and cheap approach based on calculations with a minimal QM region.

PCVA is applied to the example of the catechol *O*-methyltransferase (see Kulik *et al.* [1]). PCVAconstructed QM regions are evaluated by comparing QM ligand charges and reaction energies as well as determined sensitivities with those calculated for CSA- and FSA-derived QM regions.

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New densities and flux densities derived from momentum expectation values

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Abstract

A time-dependent momentum expectation value can be calculated either directly from his definition or via the Ehrenfest theorem. In the first case, the expectation value can be expressed as an integral over the probability flux density **j**, whereas in the second one, the integral contains another density which we call the translation flux density **j**. Using the continuity equation, the probability flux density is connected to the probability density ρ . In a similar way, a (translation) density $\tilde{\rho}$ can be defined which satisfies the continuity equation containing **j**. Employing a model system for a coupled electron-nuclear dynamics, we investigate the properties of these new quantities. An analysis shows that in this way one arrives at information about electronic and nuclear momenta and dispersion in different spatial directions.

Schaupp, T., Renziehausen K., Barth I., Engel V., J. Chem. Phys. 154, 064307 (2021)

Assessing MP2 frozen natural orbitals for relativistic electronic structure

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Abstract

The O(N⁶) computation cost is a bottleneck preventing performing Coupled-Cluster (CC) on large systems, particularly when employing 4-component based relativistic Hamiltonians, for which in practice one often uses uncontracted basis set generating large virtual molecular orbital spaces.

The canonical Hartree-Fock (HF) orbitals are not the most compact representation for post-HF method. On other hand, using natural orbital is an efficient way to reduce the orbital space and maintains most of the accuracy. We therefore implemented MP2 frozen natural orbital (FNO) method [1] in the Exacorr code [2], with the particularity that our implementation can generate both complex and quaternion FNOs, and express these in AO basis. It also allows us to obtain CCSD natural orbitals on AO basis, which can be subsequently used in analysis.

We have investigated the orbital truncation errors in both correlation energy and molecular properties including dipole, quadrupole moment, electric filed gradient, for hydrogen halides HX (X=F, Cl, Br, I, At, Ts), and parity violation for the H_2X_2 (X= O, S, Se, Te, Po) molecules. We find that FNO indeed

accelerates rapidly the energy convergence. For properties, truncated FNOs seem to slightly outperform canonical HF orbitals, and to provide reliable estimates for the properties obtained for complete virtual spaces.

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Determining core electron binding and excitation energies with fourcomponent based EOM-CCSD approaches

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Abstract

The localized nature of core orbitals makes spectroscopic approaches probing core electrons very selective and sensitive, so that they are capable of providing very accurate information about the chemical surroundings of atoms of interest. At the same time, the complexity of the physical processes taking place in experiment make it very difficult to interpret them without an underlying theoretical framework.

Recent years have seen an interest in accurate molecular electronic structure methods such as coupled cluster with with singles and doubles theory (CCSD) to provide such a framework. These efforts have largely focused on elements of the first and second rows, for which relatively simple treatments of relativistic effects provides very good results [1-3].

In this contribution I will present our implementation of the core-valence separation approach to the 4component relativistic Hamiltonian based equation-of-motion CCSD (CVS-EOM-CCSD) [4], and an initial application to determine core ionization binding energies of halogenated and xenon-containing species, as well as to core excitation energies for xenon-containing species.

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Visualisation of electron dynamics - *Jellyfish* a new program suit able to perform and analyze TDCI calculations

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Abstract

The study of explicitly time-dependent phenomena and processes has gained increasing attention due to its relevance for spectroscopy and nanoelectronics. A state-of-art tool to investigate such processes is the time-dependent configuration interaction method (TDCI)^[1].

Previous programs for performing and evaluating TDCI calculations and related methods are mostly specialized for specific use cases such as atomic strong field processes^[2] or truncated TDCI^[3]. We present the program suit *Jellyfish*^[4], which allows the most flexible execution of TDCI including the underlying electronic structure calculations such as Hartree Fock or CI at any truncation level. Since *Jellyfish* was developed with a modular structure and a node-based graphical user interface the program is extensible for a variety of applications. Examples are electron dynamics in model potentials^[5] or a Hamiltonian simulation of laser-driven ionization dynamics on a quantum computer(simulators)^[6].

In the current phase of program development, a particular focus is on novel routines for evaluating laserdriven TDCI. This includes, for example, graphics modules to visualizing time-dependent electron densities or natural transition orbitals^[7] in real time to literally get a better insight into dynamical processes.

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Dispersion forces in chirality recognition - a density functional and wave function theory study of diols

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Abstract

In the discussion of the forces governing chirality recognition, specifically on systems where hydrogen bonding is possible, it is usually assumed that the charge transfer and electrostatics effects are the main forces for the stabilization of the conformation. However, other intermolecular forces of attraction, such as dispersion, are also present to the point that it can have a determining role in chirality recognition. Using several diol molecules, we explore different factors in the formation of homo and hetero-dimers as well as their relative stability. Our results from density functional theory and analysis using local correlation methods, we infer the impact of dispersion not only on the energies but also on the structures of the chiral dimers. A local orbital based scheme is used to calculate wave function dispersion-free gradients and compare to the dispersion corrected and uncorrected density functional structures.

Density functional dependence of the level alignment in DSSC

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Abstract

Renewable energy sources are desperately nedeed today and good potential is realized through solar energy. Intention is to use eco-friendly and cheap dye-sensitized solar cells (DSSC) which have for now the highest recorded efficiency of 14.3%.¹ Density functional theory (DFT) and time-dependent DFT (TDDFT) are the methods which can be used to investigate the efficiency of individual systems. Our work is motivated by the findings of Pastore et al.² about the functional dependence of energetic parameters (level alignments) and excited states of joint dye/semiconductor system for two organic dyes sensitized on TiO₂ surface. These two investigated organic dyes are among the highest-efficient ones with different electron-donor acceptor groups, named JK2 and D102. We present results for these systems of dye@TiO₂ in gas phase and solvent (water) for ground and excited state with different local hybrid functionals. This new family of hybrid density functionals with a flexible exact exchange admixture provides an extension of traditional global hybrids. In order to understand the dependency of the level alignments on the functional, we also apply each functional to the dye and cluster separately and compare to the experimental data. Work is provided through the TURBOMOLE, modular program suite for *ab initio* guarantee.

quantum-chemical and condensed-matter simulations.³ Our results reveal reasonable energy alignments with respect to the experimental data, which confirmed that manipulation of the self-interaction with real-space dependent exact exchange admixture can improve the characterization of DSSC models even qualitatively in comparison to some other, mainly used functionals.

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Dispersion vs. Steric Hindrance: Reinvestigating Classic Steric Factors

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Abstract

London dispersion (LD) interactions, the attractive part of the van-der-Waals interaction hold somewhat of a unique position in the chemical world. Although their role in influencing macroscopic phenomena (such as the higher boiling points of larger alkanes) is well recognized, they are usually overlooked when discussing molecular phenomena. Substituents in reactions are generally considered as a source of "steric hindrance" and not as "steric attractors", better termed dispersion energy donors (DEDs). As such, their influence on reaction outcomes was quantified and presented by classic steric factors such as the A-value.

We have shown, using computational quantum mechanical tools, that these well recognized steric factors have also an attractive LD component that balance part of the steric repulsion. By focusing on the LD component we can explain various non-intuitive trends between substituents, such as the inconsistency between the size of the halogens and their A-values.

In addition, a systematic analysis of both the steric and dispersion interactions of the same molecules allows us to quantify the relative weights of the two effects and form a new DED scale. Such corrected steric and LD factors could later be applied to explore the role of LD interactions also in other reactions. Our computations show that LD interactions have a significant influence on the overall relative stabilities and energetics in cyclohexane chair conformers, and also in related concerted reactions, and must not be ignored in reaction design.

X = F. Cl. Br. I



 $\mathbb{E}^{\mathbb{A}} \to \left[\mathbb{E}^{\mathbb{A}}\right]^{\mathbb{A}} \to \mathbb{N}^{\mathbb{A}}$ (E.E)

Approaching *ab initio* accuracy for excitation energy of huge aggregated system

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Abstract

Recently we proposed a model Hamiltonian method that works for huge aggregated system, which represents the quality of an ab initio excited state method, i.e. TDDFT, CC2, ADC(2). The main idea is by using a diabatization scheme[1] to capture the site energies and the corresponding couplings of dimers in the aggregated system, and then merge these elements into a "complete" coupling matrix for the aggregated system. Followed by a simple diagonalization, we could get the excitation energy of the whole aggregated system at the quality of the used ab initio excited state method, while the computational cost is greatly reduced. The method can also be served in different level of accuracy.

We have tested few sample systems, from thiophene tetramer to Y6 trimer to compare with the full QM results and both result in very good agreement. A more "ambitious" example, a Y6 aggregate of 30 Y6 monomers (2550 atoms), is also tried at first level of accuracy. The calculated excitation energy of the Y6 aggregate has been brought down to 2.0 eV, which is 0.2 eV lower than the ones of a Y6 dimer system and 0.3 eV lower than a Y6 monomer. We believe by applying a higher level of accuracy calculation, the calculated excitation energy will be further close to the experimental value of the Y6 crystal.



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Generation of hydrated electrons with visible light

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Abstract

The hydrated electron is a metastable defect in liquid water which also exhibits an exceptional reactivity. While the hydrated electron is capable of reducing CO_2 and N_2 to CO and NH_3 , respectively, its current generation requires high energy photons. This can be overcome by using the heptazinyl radical (HzH) as a source of electrons. HzH is generated as an intermediate product in the water-splitting cycle catalyzed by heptazine (Hz). Combining the water-oxidation reaction with the generated upon the formation of the hydrated electron. Ab initio methods are employed to explore possible minimum-energy excited-state reaction paths for photoinduced proton-coupled electron transfer from HzH to water. The results suggest an exothermic reaction pathway which is free of barriers and conical intersections for the formation of hydrated electrons by photodetachment from the HzH radical.

Exchange-correlation functionals with balanced description of weak and strong correlation

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Abstract

Based on an established approach of acquiring exchange-correlation functionals for Kohn-Sham density functional theory (KS-DFT) through interpolation between the non-interacting and strongly correlation limit [Y. Zhou, H. Bahmann, M. Ernzerhof, J.Chem.Phys., 143, 124103 (2015)] new methods are developed. Describing strong correlation properly is still a challenge for modern KS-DFT. Even a simply system such as the infinitely stretched H₂ pose a major obstacle for established functionals. In the referenced scheme the exchange-correlation energy in the strongly correlation limit was acquired via the nonlocal-radius model [L.O. Wagner and P. Gori-Girorgi, Phys. Rev. A, 90, 052512 (2014)] while in the non-interacting limit the exchange-correlation energy reduces to exchange energy. These two limits were connected by an interpolation scheme to approximate the adiabatic connection and thus, receive the exchange-correlation energy. To acquire a formula for the adiabatic connection the two limits and the local spin density approximation (LSDA) were used. In this work new approximations are tested based on PBE instead of LSDA. After investigation of the strong correlation limit in PBE the functional is adjusted in order to acquire new interpolation schemes. In addition the shell model [H. Bahmann, Y. Zhou, M. Ernzerhof, J.Chem.Phys., 145, 124104 (2016)] is utilized instead of the nonlocal-radius model for the strong correlation limit. Novel expressions and parameters are also employed to introduce new interpolation formulas. All of the previously referred approaches are assessed by the calculation of atomization energies and total atomic energies.

Development of Equidistant Energy Level Potential Energy Surface Data Sampling for Efficient Neural Network Potential Training

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Abstract



Ab-initio molecular dynamic simulations are often too slow to simulate phenomena on long time scales. In contrast, classical molecular dynamics, while fast, are not readily available for inorganic, organometallic and radical compounds. Furthermore, the accuracy of the calculated energies is often low. Machine learning can be used to create neural network potentials that match the accuracy of electronic structure approaches such as DFT for systems from the whole periodic table, while being fast

enough to describe phenomena on long time scales.^{1,2} However, to achieve high accuracy, large amounts of accurate training data are required.

We present here a normal mode sampling method for creating equidistant energy level potential energy surfaces for the examples of the diastereoselective samarium diiodide induced cyclization of 5-phenylpentan-2-one, and reactions of polyoxometalates. This approach increases the accuracy of the neural network over the entire potential energy surface since all areas are equally represented. In addition, this approach aims to reduce the computational costs for the creation of the data points (by electronic structure methods) by using previous data points to assess the next.

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Incremental vibrational configuration interaction theory, iVCI

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Abstract

The variational solution of the molecular vibrational Schrödinger equation by vibrational configuration interaction theory (VCI) remains the workhorse for calculating highly accurate anharmonic vibrational spectra of small to medium sized molecules. However, VCI calculations can be rather computationally expensive and thus prohibitive for larger systems.

We present the implementation of incremental vibrational configuration interaction theory (iVCl), an algorithm for the determination of vibrational state energies based on a many-body expansion of the vibrational correlation energy [1]. The new algorithm is characterized by an embarrassingly parallel workload and low memory demands, alleviating some of the major bottlenecks of conventional VCl. An iterative configuration selection scheme enables the efficient evaluation of the increments within this approach. Methodologies which have been applied successfully in the determination of potential energy surfaces such as pre-screening (and multi-level schemes) have been incorporated in iVCl. Vibrational resonances present an important challenge in iVCl calculations, since they can lead to poor convergence of the expansion. This issue can be resolved by explicitly accounting for expected resonances in the construction of the bodies. The convergence of the expansion has been studied for a series of small molecules of increasing size, with special attention to the impact of different body definitions. For comparison, benchmark calculations with respect to customary configuration-selective VCl are presented.

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New approach for modelling two-photon absorption spectra of photoactive proteins

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Abstract

Two-photon excitation microscopy is one of the most powerful tools for bioimaging. To fully realize the potential of using two-photon absorption (TPA) of fluorescent proteins, it is important to understand the factors that affect the TPA spectra as compared to those obtained following one-photon absorption (OPA). Here, we develop a sum over states approach employing a two-level model for calculating TPA spectral shapes of fluorescent proteins at a high level of theory.

We simulate the S_0-S_1 TPA and OPA spectral profiles of the GFP chromophore anion inside the protein. The parameters used for modeling vibronic band shapes are obtained using the XMCQDPT2 theory coupled to the EFP method. The TPA and OPA spectra are calculated using the double harmonic parallelmode approximation and include both Franck-Condon and Herzberg-Teller couplings.

By using the two-level model, we show that the TPA cross-section and the contribution from each vibrational mode can be estimated using simple parameters, such as a difference between permanent dipole moments in the ground and excited states, a transition dipole moment, and their derivatives with respect to normal modes. We show that the non-Condon effects are responsible for the observed shift between the TPA and OPA absorption maxima in GFP. The major contribution to the shift comes from those vibrational modes that modulate permanent dipole moments, correlating with IR-active modes. We conclude that the intensity of these modes can be significantly enhanced when switching from conventional one-photon excitation to a non-linear two-photon absorption regime.

The work is supported by RSF №17-13-01276.

Insights into Jahn-Teller Effects and Spectroscopy of Manganese-Oxo Cubane Water Oxidation Catalysts

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Abstract

The active center of the oxygen evolving complex in photosystem II is known to contain a Mn_4CaO_5

cluster, and similar transition metal oxide clusters are also promising candidates for catalysts in artificial photosynthesis. However, these clusters possess a very intricate electronic structure and thus there is still much to be learned about the relevant activation and catalytic mechanisms.

We have computationally characterized the complex $[(Mn_4O_4)(V_4O_{13})(OAc)_3]^{n-}$, which has relevant

oxidation states from [Mn₄^{IV}] to [Mn₄^{III}]. The Jahn-Teller effect leads to an elongated octahedral

coordination of Mn^{III} atoms, which leads to both valence isomerism and orientational Jahn-Teller isomerism in the complex, producing a large number of thermally accessible minima for the different oxidation states. Based on systematic optimizations of all these minima, we propose several heuristic rules to identify the most stable ones for each oxidation state. We also discuss how the combination of inert Mn-O-V bonds, Mn-O-Ac bonds that can be activated via Jahn-Teller elongation, and low barriers to interconvert between valence and orientational isomers contribute to the reactivity of the complex. We also show that in both infrared and UV/Vis spectroscopy, there are clear signals that can be used to track the oxidation state of the complex. In the infrared spectra, isolated bands arising from V=O stretch

vibrations shift consistently with each oxidation equivalent. In the UV/Vis spectrum, Mn^{III} atoms produce

a weak absorption in the red and near-infrared spectral range, whereas ${\rm Mn}^{\rm IV}$ atoms absorb more strongly in the visible range.

How Projected Force Constants Help Revealing the Nature of Chemical Bonding in Functional Chalcogenides

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Abstract



The unusual property portfolio of maingroup IV chalcogenides has made them essential for thermoelectric and phase-change applications but the atomistic origin of their characteristic properties has yet to be fully understood. Over the years, several chemical-bonding models, mostly density-based, have been proposed to model the unique mechanism giving rise to how these materials behave physically.

We demonstrate how projecting the phononic force-constant tensors resulting from *ab initio* thermochemical simulations along interatomic vectors results in a new bonding descriptor that reveals information about the bonding behavior of these functional materials never seen before. The projected force-constant approach provides an explanation for the unusual prevalence of the rock-salt structure among phase-change materials and, also, contextualizes the high probability of multiple emissions in atom-probe tomography (APT) that are so typical for such materials. In addition, the same approach lets us conclude that well-established (molecular) models for multi-center bonding provide a suitable picture of the solid-state bonding mechanism, in good agreement with a recently published hyperbonding proposal for these compounds. This is also reflected in a bonding analysis using the crystal orbital Hamilton population (COHP) and the novel crystal orbital bond index (COBI) allowing for a more complete picture encompassing both lattice-dynamic and orbital-based approaches.

Long-Range Forces in Rock-Salt-Type Tellurides and How they Mirror the Underlying Chemical Bonding, J. Hempelmann, P. C. Müller, P. M. Konze, R. P. Stoffel, S. Steinberg, R. Dronskowski, *Adv. Mater.*, https://doi.org/10.1002/adma.202100163 ⁽⁹⁾

Crystal Orbital Bond Index for the Calculation of Covalent Bond Orders in Solid-State Materials

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Abstract



bond index by Wiberg and Mayer but which has now been generalized to translationally invariant systems such as crystalline matter. The COBI appearance resembles the established crystal orbital overlap population (COOP) and crystal orbital Hamilton population (COHP) but its interpretation is almost trivial as it refers to a concept know to every chemist: the bond order. In addition to two-center bonds, COBI is easily generalized to also quantify multicenter bonding such as the three-center four-electron bond in XeF₂ and CsI₃, so far impossible to cope with commonly used descriptors, at least within the solid state. In addition, the concept of multicenter bonding can be used to explain and understand the quantum-chemical origin of uncommon material properties in, say, functional phase-change materials such as GeTe. COBI has been implemented into the most recent (4.1) version of LOBSTER.

Crystal Orbital Bond Index: Covalent Bond Orders in Solids, P. C. Müller, C. Ertural, J. Hempelmann, R. Dronskowski, *J. Phys. Chem. C* **2021**, *125*, 7959–7970.

Understanding the photochemsitry of *cis*-stilbene with ab initio multiple spawning nonadiabatic dynamics simulations

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Abstract

The photochemistry of *cis*-stilbene proceeds through two pathways: *cis-trans* isomerization and ring closure to 4a,4b-dihydrophenanthrene (DHP). Despite serving for many decades as a model system for photoisomerisation, the photodynamics of *cis*-stilbene is still not fully understood. We use *ab initio* multiple spawning on a SA-2-CASSCF(2,2) potential energy surface to simulate the nonadiabatic dynamics of isolated *cis*-stilbene. We find the cyclisation (to DHP and *cis*-stilbene) and isomerisation (to *trans*- and *cis*-stilbene) reaction coordinates to be orthogonal; branching between the two pathways is determined on the S₁ excited state within 150 fs of photoexcitation. The isomeric form of the vibrationally hot photoproducts is determined within 50 fs of decay to the ground state via one of three avoided crossings. Excess vibrational energy of ground state *cis*- and *trans*-stilbene is channelled into phenyl torsions.

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Homogeneous catalysis under confinement: A QM & MM expedition to the core of a calixarene nanoreactor

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Abstract

C-N coupling methods based on earth-abundant metals represent an area of research of increasing interest. Recently, attention was directed towards systems inspired by biological supramolecular systems, such as metal centre enzymes. In this work we present a multi-scale modelling approach for the investigation of supermolecular complexes. The chosen system consists of Cu(I), anchored to a bidentate phenanthroyl moiety enclosed by calix[8]arene, which exhibits remarkable yields in C-N coupling reactions. As this system is quite complex, a multi-step approach is needed to unravel not only the mechanics behind the reaction, but also characterize the behaviour of the nanoreactor cavity. To this end, density functional theory (DFT) was the tool of choice for determining the reaction pathway, via a scaled down model, but this proves insufficient for the full characterization of the complex. In support of the quantum mechanical approach, molecular mechanics methods such as accelerated molecular dynamics simulations (aMD) help shed some light on the flexibility and changes in the cavity created by the calixarene. Performing the simulations with explicit solvent, as well as a parametrized metal center, allowed us to obtain a good sampling of the calixarene ring conformations. These structures were then used as a starting point for a retro-fitting of the small model. This leads to more accurate estimations of the reaction energies, when the full complex is taken into consideration.

Theoretical Analysis of the Oxygen Reduction Reaction by a 2-electron Mechanism on Ceria Surfaces

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Abstract

The 2-electron pathway of the oxygen reduction reaction has been gaining attention from the scientific community as a promising way of water treatment, specifically for removing emergent pollutants and endocrine disruptors from water bodies - a problem yet to be solved for large-scale implementation. The hydrogen peroxide in situ electrogeneration is also a potential application for this reaction, since a more sustainable and environmentally friendly alternative for its production is needed. In this sense, experimental works show that cerium oxide has remarkable selectivity towards the 2-electron mechanism, even surpassing the commercial reference materials for this application. In this work, we have considered different ceria crystal cleaving directions (100), (110), (221), and (331) to investigate the role of surface orientation on the 2-electron pathway selectivity by first-principles methods, based on density functional theory. According to our results, the (100) surface is the most favorable for this pathway and all considered surfaces promote this reaction in at least one site, with the exception of (110). Our work also sheds light on the favorable role of stepped surfaces for this application, especially (331), which are not usually taken into account. This study provides atomistic information to guide the design or synthesis of novel nanostructures with high catalytic activity and selectivity towards the 2-electron mechanism of the oxygen reduction reaction.

Veni, vidi, modifici: Investigating and adapting the excited state dynamics of a ruthenium photosensitizer

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Abstract

Many novel light-harvesting approaches rely on photosensitizers as intermediaries for the transmutation of light into chemically more accessible forms. A photosensitizer featuring a disulfide bridge has recently been designed, capable of storing energy by interconversion to a dithiole species (*Chem. Eur. J.* **2018**, 24, 19, 4864; *Inorg. Chem.* **2020**, 59, 7, 4972). This $[Ru(S-Sbpy)(bpy)_2]^{2+}$ complex was found to feature two distinct absorption bands, reminiscent of excitation of an electron from the center ruthenium atom to either the standard 2,2´-bipyridine (bpy) or the disulfide featuring S-Sbpy ligand. To investigate the subsequent excited state dynamics following population of these different sets of states, we employed surface hopping dynamics using a linear vibronic coupling model (*Inorg. Chem.* **2021**, 60, 3, 1672). With the help of these simulations, ultrafast intersystem crossing into the triplet manifold is observed in less than 50 fs independent of the initially excited states. At the end of the 250 fs simulations, an increase in the population of states that are either locally excited on the S-Sbpy ligand or

represent charge transfer from the ruthenium to the S-S bpy ligand occurs. The driving feature for the stabilization of these states is the elongation of the S-S bond. Having identified the key points of the excited state dynamics, laser pulses are employed to both model real experimental conditions and to delay the relaxation to the T₁ minimum within the simulated time.

Quantum Molecular Dynamics in Out of Equilibrium Environments: Redfield-Smoluchowski and Hydrodynamic Approaches

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Abstract

The description of quantum molecular dynamics as influenced by a polarizable and dynamically evolving environment is critical to understand the nature of various physical processes, from solvation phenomena to photobiological processes in protein environments, and transport of charge carriers and excitons in nanostructures. However, the typically used dielectric continuum picture for the environment [1-2] is likely to fail when dealing with nonequilibrium solvation effects. On the other hand, fully atomistic first principles quantum calculations are hardly feasible due to the large number of environmental degrees of freedom.

Against this background, we present the effect of a dynamic polar/polarizable environment on a timeevolving molecular system, using two different mixed quantum-classical approaches, namely the Multistate Redfield-Smoluchowski Equation (MRSE) [3] and the Quantum-Classical Reduced Hydrodynamic (QCRH) approach [4-5]. Both approaches can describe molecular relaxation and inertial effects in condensed dynamic phases, complementing typically used dielectric continuum models for the environment.

The Figure shows the electric field created by an electron donor-acceptor organic dye (DANS) (a), its effect on solvent (CH_3CN) density (b), polarization (c), linear (d) and angular momentum (e). Panel (f) shows DANS dipole correlation function in CH_3CN , using both MRSE and QCRH.



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On-the-fly Training of an atomistic potential for flexible and mechanically interlocked molecules

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Abstract

Molecular machines enable to externally control structural and dynamic phenomena at the atomic level. To rationally transfer their tunable properties into designated functionalities, a detailed understanding not only of their intrinsic properties is needed, but also their molecular embedding and their collective and cooperative interplay has to be elucidated. In particular to design hierarchical multi-functional systems – inspired by biological cells – a comprehensive insight with high spatial and temporal resolution is fundamental.

Atomistic simulations are a powerful tool to study these types of responsive materials. However, their quality strongly depends on the applied potentials. Thus, a consistent development of these potentials to accurately and efficiently represent the relevant structural and dynamic properties of the system is fundamental to enable reliable and automated application in atomistic simulations. The development of such potentials is in particular challenging for flexible and mechanically interlocked molecules, which are often utilized to develop molecular machines. These molecules provide due to their flexibility a complex potential energy landscape with multiple thermally accessible structures. To develop a reliable potential for this class of molecules, relevant parts of the phase space must be sampled sufficiently and included in the parametrization. Due to missing physical insights, usually high amount of reference data ist required for parametrization to avoid underrepresenting the phase space. Here, we present an on-the-fly training algorithm to parametrize based on quantum mechanical calculations atomistic potentials describing Rotaxanes. By a guided and non-guided phase space sampling, relevant reference data are automatically and continuously generated and included into the parametrization of the potentials. Together with our recently introduced population swapping genetic algorithm a balanced representation of the energy landscape is ensured. After extensive validation of these potentials, we applied them to perform atomistic simulations, which enabled us to calculate the free energy profile describing the shuttling dynamics of the mechanically interlocked rotaxane molecules.

Electronic and Transport Properties of Fluorinated Graphene Materials

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Abstract

A systematic examination of the electronic and transport properties of 1D fluorine saturated Zigzag graphene nanoribbons (ZGNRs) is presented. The study is motivated by the tunability of the electronic

properties found in 2D fluorinated graphene materials¹ and an experimental publication², where a controlled synthesis of fluorinated graphene via electron beam is reported. The correlation between the conductivity of resulting materials and the width of fluorinated area is revealed in the experimental measurement. In order to understand the detailed transport mechanism, edge fluorinated ZGNRs with different widths and fluorination degrees are investigated. Periodic density functional theory (DFT) is employed to determine their thermodynamic stabilities and electronic structures. Associated transport models of selected structures are subsequently constructed. The combination of Non-Equilibrium Green's function (NEGF) and Landauer Equation is applied to investigate the global transport properties. By

projecting the corresponding lesser Green's function on the atomic orbital basis³, the local current

density maps of selected systems are calculated. Our results⁴ suggest that specific fluorination pattern and fluorination degrees have significant impact on the conductivity. With asymmetric fluorination pattern one can trigger spin dependent transport properties, which shows its great potentials in the spintronic applications.

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Modulation of photoresponsive properties of thin films by designed assembly in metal-organic frameworks

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Abstract

Exceptional sensitivity of stimuli responsive materials is provided by light that by different wavelengths allows for the highly specific phenomena with high spatial resolution used in optoelectronics, photonics, field effect transistors, intelligent sensors and actuators. The optoelectronic responses are modulated by the composition of molecular units, leading to an intricate interplay of packing and function. A precise architecture, which incorporates light-active components at well-defined positions and orientation can be realized by the self-assembly into metal-organic frameworks, MOFs. This may induce various photophysical phenomena, including thermally-activated delayed fluorescence, energy transter, photoconduction or controlled emission. Designing these versatile assemblies enables the upscaling of the functionality of a single molecule to yield functional solid materials or thin films of macroscopic dimensions.

In my talk, I will demonstrate the modulation of diverse photoresponsive properties of MOF thin films (with incorporated porphyrins, perylenes, pentacenes and diphenylamine-tetraphenylethylenes) as a result of an interplay between chemical composition and structuring of chromophores in a material. I will explain observed phenomena via electronic structure calculations based on the density functional theory (DFT) and time-dependent-DFT. I will present new developments of predictive multiscale methods, implemented in automated workflows, to screen libraries of linkers and MOF topologies for the design and tuning MOF scaffolds for a specific light induced functionality of new nanomaterials.

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Modelling Self-Assembled Monolayers of Triptycene-Based Systems

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Abstract

Self-Assembled Monolayers (SAMs) provide an excellent avenue of surface functionalization, with applications across many fields.^[1] Here, we present insights and challenges obtained by modelling triptycene-based^[2] SAMs on (i) crystal, (ii) gold, and (iii) water surfaces.

On a crystal surface, the spacing between adsorbates is completely dictated by the crystal geometry, resulting in coarse arrays which can be modelled using a combination of periodic and nonperiodic (hybrid) DFT, yielding accurate energies and shielding tensors.^[3]

Using the gold surface as a substrate permits the formation of denser SAMs, but also requires careful choice of an anchoring group. Structure of such SAMs will be determined by the interplay of intramolecular interactions and the site-specific adsorption on the rigid gold lattice. We have described these systems by systematic PES scans, which revealed a strong tendency towards bending and tilting of the adsorbate tails. This unusual structure is a product of maximizing triptycene-triptycene interactions, while preserving anchor-gold interactions.^[4]

Finally, structure of SAMs on a water-air interface prepared using a Langmuir-Blodgett trough will be virtually completely determined by external pressure and intermolecular interactions between the adsorbate tails. In order to investigate these systems, we are using molecular dynamics based on tight-binding DFT and modern force fields.

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Exploring spectra and energy flow in chlorophyll proteins using the new gmx2qmmm package

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Abstract

We have recently devised a Python 2.7/3 package called gmx2qmmm that enables the use of recent Gromacs versions in conjunction with the Gaussian software for additive QM/MM. We use the program to perform simulations on chlorophyll-containing systems, such as LHCII, CP29 and WSCP; however no system-specific restriction for the use of this software exists. The main advantage of gmx2qmmm lies in retaining the strongly user-oriented Gromacs input philosophy, while at the same time enabling the user to describe specific parts of the system with a QM approach of their choice.

In this presentation, we will present the main design principles of the gmx2qmmm approach. This includes the introduction of a correction potential database at the QM/MM junction and a numerical charge shift scheme. This way, we seek to correct the absence of the MM atom/link atom introduction near the QM/MM junction which is a problem for many established QM/MM potentials. Applications will be shown, showing selected results from papers that employed gmx2qmmm so far. We will also present future plans regarding gmx2qmmm development; mostly extending to other QM software such as Turbomole and Orca, as well as possible inclusion/merging with existing QM/MM packages.

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Nuclear Quantum Effects in Electronic Structure Calculations

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Abstract

With modern electronic structure methods converging to an extremely high accuracy, the error introduced by neglecting the quantum character of nuclei is becoming more and more relevant. Methods to include these nuclear quantum effects—especially for light hydrogen nuclei—exist and open a new sub-discipline in computational chemistry, with numerous issues and challenges yet to be addressed. In this contribution, we will focus on the nuclear electronic orbital (NEO) method, in which certain selected nuclei are treated on the same level as the electrons using a multicomponent approach. A brief introduction into the NEO formalism will be given and recent developments regarding the treatment of nuclear spin will be presented. Technical details of such NEO calculations such as the choices for electronic and nuclear basis sets will be discussed.

Molecular hydrogen, which occurs in two nuclear spin isomers—o-H₂ with parallel nuclear spins and p-H₂ with antiparallel nuclear spins—will serve as an example to demonstrate first results. The spin isomers of molecular hydrogen have important implications for experiments and technology. Their distinct properties are relevant for neutron scattering experiments as well as liquefaction and storage of hydrogen gas. Different nuclear spin configurations, their impact on the quantum chemical energy, and their interaction with the electronic structure will be studied by analyzing the nuclear wavefunction which is available from NEO methods.

Finally, unresolved challenges will be outlined as motivation for future work in the field of nuclear quantum effects and nuclear-electronic structure calculations.

Regularizing the MCTDH equations of motion on-the-fly

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Abstract

The multi-configuration time-dependent Hartree method is a general algorithm to solve the timedependent Schrödinger equation, in which the wavefunction is expanded in a direct product of selfadapting time-dependent Single-Particle Functions (SPFs) that are propagated in time according to the Dirac-Frenkel variational principle.^[1] In the current version of this approach, the size of the SPF basis is fixed at the outset so that singularities in the working equations resulting from unoccupied functions

have to be removed by a regularization procedure. Here, an alternative protocol is presented,^[2,3] in which we gradually increase the number of unoccupied SPFs on-the-fly (i.e., spawning) and optimize their shape by variationally minimizing the error made by the finite size of the basis. An initial estimate for the respective new expansion coefficients is also computed, thus avoiding the need to regularize the equations of motion. The advantages of employing the new algorithm are tested and discussed in some illustrative examples.

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Charge transfer in symmetrically bridged mixed-valence compounds: relaxation dynamics and transient absorption spectroscopy

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Abstract

We perform quantum dynamical calculations on the dynamics of optically induced charge transfer processes within symmetrically bridged organic mixed-valence compounds. Models reflecting the most important optical properties of the investigated systems are employed, where the transfer can proceed along a symmetric as well as a symmetry breaking reaction coordinate. In reproducing measured linear absorption spectra [1] the strength of the system-bath coupling is determined. Due to the non-perturbative approach, it is neccesary to directionally decompose the time-dependent polarization to calculate transient absorption spectra. Therefore, we extend a technique for the decomposition proposed by Domcke and coworkers [2]. The time dependence of the spectra are analyzed in terms of the wave packet dynamics, and it is shown that the stronger the involvement of the bridge state in the overall dynamics, the more of the charge is transferred along the symmetric coordinate. It also is found, that the charge transfer in the systems under consideration is dominated by relaxation.

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Spin-Gaps and Reaction Mechanisms of Non-Heme Iron-Oxo Complexes

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Abstract

Heme and nonheme mononuclear iron oxygeneses and their synthetic analogues are known to perform a wide range of catalytic oxidative transformations in chemistry and biochemistry.^[1] The most typical reaction is the C-H hydroxylation which has been proposed to be performed by an iron-oxo $Fe^{IV}=O$ active intermediate. The rate limiting step in these reactions was found to be the hydrogen atom abstraction process. These systems are also known for their multi-state reactivity. We have seen that many methods have problems with accurately calculating this reaction.^[2,3]

Therefore, we have performed an extensive computational study of the quintet-triplet gap ΔE_{TO} of a

series of non-heme Fe^{IV}=O species.^[4] We employed our recently proposed multireference approach CASPT2/CC^[5] to calculate the gaps and subsequently used these results to benchmark two variants of local coupled cluster approaches (DLPNO-CCSD(T) and LUCCSD(T0)). We have showed that current implementations of the local coupled cluster method are not sufficiently accurate. DLPNO-CCSD(T) systematically overstabilizes the quintet state by about 8 kcal/mol, whereas LUCCSD(T0) gives the too stable triplet ground state. Interestingly, we observed a good linear correlation between the ΔE_{TQ} values predicted by CASPT2/CC and DLPNO-CCSD(T).

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Subsampling Quantum Monte Carlo Simulations

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Abstract

Quantum Monte Carlo (QMC) methods use a stochastic approach to solve the Schrödinger equation. Their scaling with the system size considering the computational costs is very favorable and a great flexibility in the choice of the wave function allows to efficiently treat both dynamical as well as static correlation. This makes QMC methods for instance particularly useful for the description of excited states.^{1,2}

Different regions of space exhibit different time scales and contribute to a varying degree to the overall variance in a Variational Monte Carlo algorithm. This leads to large inefficiencies within a regular algorithm as the same computational effort is spend on all regions. We propose a Monte Carlo scheme which exploits that core regions are physically independent in a molecule to almost remove their high

variance contribution to the numerical cost.³ The method relies on efficiently subsampling the core regions using independent sidewalks which can be understood as constructing on the fly an exact stochastic effective core potential. Results are presented on atoms, alkane chains and clusters of silicons which display a gain in numerical efficiency between one and two orders of magnitude.

The extension to more advanced projector Monte Carlo methods is being explored.

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On the Role of Hydrogen Bond Strength and Charge Transfer of a Diels-Alder Reaction On-Water: Semiempirical and Free Energy Calculations.

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Abstract

Accelerated chemistry at the interface with water has received increasing attention. The mechanisms behind the enhanced reactivity On-Water are not yet clear. In this work we use a Langevin scheme in the spirit of second generation Car-Parrinello to accelerate the second-order density functional Tight-Binding (DFTB2) method in order to investigate the free energy of two Diels-Alder reaction On-Water: the cycloaddition between cyclopentadiene and ethyl cinnamate or thionocinnamate. The only difference between the reactants is the substitution of a carbonyl oxygen for a thiocarbonyl sulfur, making possible the distinction between them as strong and weak hydrogen-bond acceptors. We find a different mechanism for the reaction during the transition states and uncover the role of hydrogen bonds along with the reaction path. Our results suggest that acceleration of Diels-Alder reactions do not arise from an increased number of hydrogen bonds at the transition state and charge transfer plays a significant role. However, the presence of water and hydrogen-bonds is determinant for the catalysis of these reactions.

Probability density analysis: a real space valence bond theory

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Abstract

Upon designing and investigating reactions, chemists often use semi-quantitative concepts like resonance structures or electron delocalization. While they are widely taught to students, their theoretical foundation is often limited to certain electronic structure frameworks like valence bond theory.

Here probability density analysis provides a bridge between these concepts on one side and quantum mechanics on the other: resonance structures are rediscovered as most likely electron arrangements, i.e. local maxima of the many-electron probability density $|\psi|^2$. The basins of attraction of these maxima partition the many-electron real space and can be integrated to obtain structure weights that are in good agreement with valence bond theory.

Furthermore, the saddle point between two adjacent local maxima of $|\psi|^2$ is a strong indicator for bonding and directly related to the concepts of delocalization and resonance stabilization. This picture of bonding rationalizes the contribution of ionic structures to non-polar bonds in analogy to reaction intermediates and allows for the generalization of the 4n+2 Hückel rule. This number rule of aromaticity is derived from nothing but the antisymmetry of the wave function without the need of orbitals.

These results demonstrate, that probability density theory, which is applicable to any wave function, is a promising addition to the discussion of chemical bonding.

Towards Modelling Condensed Phase Phenomena with General Effective Fragments

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Abstract

There is a rapidly growing demand to explicitly and rigorously include quantum mechanics in simulations of large and complex molecular systems across all fields of condensed phase chemical physics. Since quantum computing is still in its infancy, [1] currently one rather needs to rely on 'traditional' classical algorithms and methodologies to tackle important challenges in energy conversion and storage devices or unveiling reaction mechanisms occurring in biologically important systems. Unfortunately, a full quantum mechanical description of such systems is typically out of reach, significantly slowing down or even prohibiting certain investigations at the interface of experimental and theoretical chemistry. [2]

Here we present an alternative emerging approach to tackle the electronic structure of large complex molecular systems, which is based on an old idea of effective fragment potentials [3], but revisited to treat mathematically more complex objects such as wavefunctions [4][5] or density matrices. [6] Such a generalized effective fragmentation approach can be particularly useful in two situations where conventional methods face difficulties due to excessive computational demands: i) vibrational properties [7][8] and, ii) electronically excited states from the exciton perspective [5]. We anticipate that our approach will be useful in studies of the structure and dynamics of biomolecules and excitons within biological light-harvesting networks and organic electronics materials.

 $\int d\mathbf{r}_{I} v_{\text{EOP}}(\mathbf{r}_{I}) \rho(\mathbf{r}_{I})$

Nonradiative energy relaxation in 1D molecular wire surfactants modulated by the conformation and length of the system

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Abstract

Thanks to the tunable optical and electronic properties, many organic conjugated materials are excellent candidates for the design of optoelectronic devices and have found wide applications across various technological fields. Complicated excited state electronic structures of such materials have been revealed by optical measurements and theoretical simulations. The dynamics of electronic excitations in such materials is dominated by strong nonadiabatic couplings (NACs) and the Born-Oppenheimer approximation is not valid anymore. Upon photoexcitation, various nonradiative relaxation pathways can produce multiple complex processes, such as internal conversion, energy transfer, charge separation, and spatial localization of excitons. Computational simulation of nonadiabatic excited state molecular dynamics (NAESMD) is an indispensable tool to study the optoelectronic properties and the photoinduced energy transfer dynamics in such materials.

NAESMD studies are conducted in current work to understand the photoinduced dynamics in recently designed and synthesized new classes of 1D molecular wires. Serving as the electronic surfactants, these molecular wires can self-assemble at water-gas interfaces and mechanically stabilize a new class of electronic soap films. Systems with different conformations and lengths are considered in the simulations. The dependence of the photoinduced dynamics on the conformations and lengths of the molecular wires is uncovered by analyzing the transition density dynamics, the NAC distributions, and the relaxation rates. The static and dynamic properties of the molecular wires presented in this study provide an in-depth understanding of energy relaxation in such systems and are of great importance for guiding the design of the materials.

Exciton-exciton annihilation in a molecular trimer: wave packet dynamics and 2D spectroscopy

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Abstract

We theoretically study a molecular trimer MMM, where the focus is on the characterization of excitonexciton annihilation (EEA). The system is treated within a model of electronic states and the coupling to a bath is incorporated using the quantum jump method. We distinguish two cases: In the first one, a twophoton process populates configurations M*M*M and MM*M*, so that two excitons reside on neighboring monomers M. Here, EEA can immediately proceed. In the second case, the trimer is excited to the initial configuration M*MM*. Then, exciton diffusion must occur before the annihilation process can take place. In both cases, wave packets are prepared which show a different quantum dynamics. It is documented how fifth-order coherent two-dimensional spectroscopy can be used to directly map the EEA as a function of time. [1]

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Cholesky decomposition of complex two-electron integrals over GIAOs: Efficient correlated computations for large molecules in strong magnetic fields

<u>Simon Blaschke</u>, Stella Stopkowicz Johannes-Gutenberg Universität, Mainz, Germany

Abstract

In large-scale calculations the electron repulsion integrals (ERI) as a four index tensor rapidly becomes the bottleneck considering virtual memory and disk space. In computations employing a external finite magnetic field this problem is even more pronounced. This is due to the reduction of permutation symmetry and the need to work with complex integrals and wave function parameters. The problem can

be alleviated by employing a Cholesky decomposition^[1,2] of complex two-electron integrals over GIAOs^[3,4]. The Cholesky scheme establishes especially favourable compression rates by selectively discarding linearly dependent product densities from the chosen basis set while maintaining a robust error control without the need of an auxiliary basis set. This error control constitutes the main advantage

over conceptually similar methods such as density fitting^[5]. The Cholesky decomposed representation can in a straightforward manner replace the ERI in various quantum chemical methods. In many cases reordering contractions with amplitudes and density matrices reduces the formal scaling behaviour. In this poster we present the use of the Cholesky decomposition in the framework of Hartree-Fock and the subsequent second-order MØller Plesset perturbation theory (MP2). This enables the correlated treatment of representative systems with more than 2000 basis functions within an external finite magnetic field in a reasonable time span.

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Quantum Cluster Growth: An automated quantum mechanical description of explicit solvation

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Abstract

The description of solvation effects is one of the essential steps to compare computer simulations and experimental findings. Commonly applied implicit solvent models like COSMO-RS and SMD encounter difficulties in describing short-range effects like hydrogen bonding and salt bridges, which may become a key to the success of describing processes in solution. Opposite to this, explicit solvent models suffer from increased computational costs, often allowing only molecular mechanical methods. The newly developed, generally applicable Quantum Cluster Growth (QCG) method combines an explicit cluster growth with an implicit solvent bulk screening similar to other hybrid cluster-continuum approaches [J. Chem. Theory Comput. 2019, 15, 1, 371–381]. The key steps are a fully automated stepwise cluster growth process combining molecular and quantum mechanical methods, an ensemble generation applying multiple molecular dynamics and metadynamics simulations, and the computation of the solvation free energy in a supramolecular fashion. QCG shows reasonable solvation free energies and an improved description of association free energies, IR spectra, and geometries in solution compared to implicit solvation models. The main disadvantages arise due to the statistical approach, resulting in a scattering of the ensemble properties.

Unitary Coupled Cluster theory in finite magnetic fields as a solution to complex energies

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Abstract

Coupled Cluster (CC) theory, based on an exponential parameterisation of the wave function, is considered one of the most accurate methods for the description of electronic structure. However, when placing molecules in finite magnetic fields or when describing conical intersections, which are of particular interest in photochemistry, CC leads to unphysical complex energies [1], because of the non-hermiticity of the Hamiltonian matrix. A unitary formulation of CC is therefore a promising approach in these contexts, retaining real energy values.

Here we employ a perturbative approach, truncating the energy expressions to third order (UCC3) [2]. We adapt this scheme for the treatment of molecules in the context of finite magnetic field methodology. Benchmark calculations on the performance of finite-field UCC3 are compared to other methods in the framework of finite-field CC and EOM-CC theory. We investigate the evolution of ground and excited states for increasing magnitudes and changing orientations of the magnetic field.

To treat conical intersections, an alternative route has been pursued by Koch and co-workers [3], with the similarity constrained CC singles and doubles method (SCCSD). We compare the results given by these approaches by analysing the position of conical intersections on the energy surfaces of HOF.

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Computational Insight to Photoelectron Spectroscopy as a Site-Selective Probe of Glucose Acid-Base Chemistry

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Abstract

A novel approach employing a combination of calculations and photoelectron spectroscopy is utilized to probe acid-base chemistry in aqueous systems. Glucose is a polyprotic acid with five hydroxyl groups and in a basic environment, deprotonation takes place. We show that photoemission spectra of core (energetically low-lying) electrons are specific with respect to the deprotonation site in the molecule. To interpret the observed spectral changes in a basic pH, we simulated photoelectron spectra in an aqueous solution using the maximum overlap method as an efficient tool to describe core-electron holes. The solvent was described by a hybrid (i.e. cluster-continuum) model of solvation. That is, solvent bulk effects were represented using the polarizable continuum model in its non-equilibrium form and specific close-range interactions were modeled by introducing a small number of nearest water molecules explicitly into the calculations. Our results reveal considerable differences among spectra obtained from a glucose molecule deprotonated on different sites. Thus, we are able to assign the correct structure to the spectrum experimentally observed by the collaborating laboratory of Dr. Bernd Winter (Malerz, S. et al., *J. Phys. Chem. A* **2021**. DOI: 10.1021/acs.jpca.1c04695). The presented method provides a tool for probing the site-selective acid-base chemistry of polyprotic molecules in an aqueous solution.

The support by the Czech Science Foundation, project no. 21-26601X (EXPRO) and Specific University Research grant no. A2_FCHI_2021_028 is gratefully acknowledged.

Nonequilibrium aqueous solvation around nascent halogen atoms

<u>Marco Reidelbach</u>, Michaela Schneeberger, Mei Bai, Henning Kirchberg, Christian Bressler, Michael Thorwart, Carmen Herrmann University of Hamburg, Hamburg, Germany

Abstract

Electron transfer is a crucial step in many processes in biology and catalysis. Recent advances in timeresolved spectroscopy made it possible to investigate the nonequilibrium dynamics of the environment affecting, i.e. perturbing and/or modulating, the electron transfer. Here, we study the detachment of an

electron from halide ions (Cl⁻, Br⁻ and l⁻) in aqueous solution as a simple model for nonequilibrium solvent affects, using mixed quantum mechanical / molecular mechanical simulations. Following the electron removal, we observe the formation of halogen-water complexes (the larger the halogen atom, the faster the complex formation) and a rearrangement of the first solvation shell. These results are in good agreement with other experimental and theoretical work.

Improved Simulation of IR Spectra at the Force Field Level by Modifications to the Intensity and Frequency Calculation

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Abstract

Simulation of IR spectra at a low and consequently fast level of theory is an excellent tool for various applications, such as structure determination of large macromolecular systems (e.g., proteins) or prescreenings in high-throughput compound identification studies.

In this work, improvements to the calculation of normal mode intensities and vibrational frequencies at the GFN force field (GFN-FF) level are presented for the "HCNO"-chemical space. The calculation of normal mode intensities was improved by re-fitting parameters of the underlying classical electronegativity equilibration charge model, while vibrational frequencies were adjusted by introducing empirical atomic masses that depend on the coordination number. Theoretical data calculated at the

B3LYP-D3(BJ)^{ATM}-gCP/def2-mSVP density functional theory level as well as experimental gas phase spectra from the NIST data bank served as reference for parameter fitting and evaluation of calculated spectra.

By employing different spectral similarity measures, it could be shown that the modified calculation leads to a significant increase in the quality of vibrational spectra. The atomic mass-based adjustment of vibrational frequencies outperformed the commonly applied global frequency scaling. Overall, the quality of the GFN-FF computed spectra is improved by ~ 24 % without any additional computational costs.



Multiscale Simulations of Spectral Tuning in Phytochrome-like Photoreceptors

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Abstract

Phytochromes constitute a diverse family of photoreceptors and one of its subfamilies are Cyanobacteriochromes (CBCRs), which are composed of a single GAF domain. CBCRs are promising candidates for biotechnological applications, owing to their photochromism, compactness and spectral diversity. In case of the CBCR SIr1393, one isomer absorbs red light and the other one green. These two forms can be interconverted into each other by light illumination. SIr1393 binds phycocyanobilin (PCB) as chromophore and the crystal structures of both forms have been obtained recently [1].

In this contribution, we will present results from hybrid quantum mechanics/molecular mechanics (QM/MM) simulations for both forms of SIr1393 [2]. Also conclusions from a benchmark study for this protein will be discussed [3]. More recently, we have carried out similar simulations of further phytochromes [4-6] and published a review article on computational studies of the photochemistry in phytochromes [7].

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Electronic structure of oxidized transition metal catalysts

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Abstract

In redox induced catalysis the change of the oxidation state of the catalyst molecule can influence reaction barriers and even the reaction path of a reaction. One example is a hydrosilylation reaction catalyzed by the rhodium-ferrocene complex shown in Figure 1. [1] In this respect, the charge distribution of the oxidized catalyst is of interest.

Here, we performed calculations on different binuclear transition metal complexes to obtain the ionization potential and the spin density in the cationic state in different reaction steps. For this purpose, we performed Δ SCF calculations with different DFT functionals and analysed the spin density. However, by this procedure we cannot compare the oxidation potential of the different metal centers in the complex. For this purpose, we performed GW calculations [2] which allow to compare ionization from different orbitals. Furthermore, we constructed model systems where one center was substituted by a large core pseudo potential or mononuclear systems with similar ligand fields.



Figure1. Rhodium-ferrocene complex

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Unravelling heavy-atom quantum tunnelling in spin-crossover reactions

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Abstract

Intersystem-crossing reactions involving the transition between electronic states of different spin are ubiquitous in nature. While there exist multiple highly accurate spectroscopic methods that allow for time-resolved imaging of such reactions, their correct theoretical description still poses a major challenge.

In a study of thiophosgene, a molecule that has drawn much attention from both experimentalists and theoreticians, we employed our recently extended golden-rule instanton theory[1] in conjunction with on-the-fly multiconfigurational electronic structure calculations in order to describe the spin transition taking place. It has been shown that heavy-atom quantum tunnelling speeds up the intersystem crossing by multiple orders of magnitude even at room temperature. The theory does not only provide results in excellent agreement with experiment, but also allows for easily accessible insight into the reaction mechanism by locating the "ideal tunnelling pathway" or instanton. The trajectory on the product surface thereby travels at negative temperature or alternatively in negative imaginary time leading to an interpretation equivalent to that of particle-antiparticle annihilation. A substantial change in the reaction pathway of thiophosgene at low energies due to corner cutting reveals why previous studies of the molecule were unable to capture the full picture of this reaction.

The generality and computational efficiency of the theory enables to describe nuclear tunnelling effects in many scientific fields even for larger compounds as illustrated by the instanton below. The delocalization corresponds to the respective atom's tunnelling in the reaction between the two spin states.



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Chemistry of Hydrogen Peroxide on a Surface of Nanodroplets: Computational Study

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Abstract

Molecular clusters can form a unique nanoreactor for bimolecular reactions. The reactants can concentrate within the volume of the cluster or they can react in the surface of the particles, in analogy to solid state catalysis. Here, we present our investigation of hydrogen peroxide reactivity induce by electrons on the surface of different molecular clusters. We particularly focus on simulating the diffusive motion of hydrogen peroxide molecules on the surface of argon and water clusters consisting of 100 molecules. Apart classical simulations of motion on the cluster's surface we also focus on ab initio non-adiabatic molecular dynamics of electron attachment and ionization. We point out the differences between argon and water clusters in the sense of hydrogen peroxide motion and aggregation on the surface, where argon nanoclusters allow much smoother motion on the surface of the cluster, which can have significant consequences on reaction paths, the cluster takes after either ionization or electron attachment. The post EA and post-ionization reaction paths of small clusters (H₂O₂)₂ or H₂O₂·H₂O are discussed. In small clusters a proton transfer reactions are possible and preferred as a reaction path. Nevertheless, radical species such as OH and HO₂ are produces upon ionization of small clusters as well as isolated hydrogen peroxide molecule. Electron attachment reactions do not differ that much for small clusters and isolated molecule. This work was motivated by recent experiments in collaborating experimental laboratory (Pysanenko, A., et al., Generation of (H₂O₂)_N clusters on argon and ice nanoparticles. IJMS 2021).
Combining single- and multireference methods to describe the dynamics of the excited-state hydrogen transfer mechanism in ortho-nitrobenzaldehyde

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Abstract

Ortho-nitrobenzaldehyde (oNBA) is a well-known photoactivated acid (proton "caged" compound) and represents a good model for similar nitroaromatic compounds [1]. The formation of the first intermediate, the ketene, which irreversibly leads to the photoproduct, is determined already in the first couple of hundred fs after excitation [2]. Due to the multireference nature and complexity of this ketene intermediate, the accurate description of the excited-state relaxation mechanism presents a great challenge. Here, we make use of both single reference (ADC(2)) and multireference methods (MS-CASPT2) to calculate relevant points of the potential energy surfaces and provide a deactivation mechanism for oNBA. Additionally, we carried out excited-state dynamics simulations to validate the mechanism and kinetics of the relaxation process. We found that the intramolecular hydrogen transfer occurs from the lowest singlet excited state, from where two type of conical intersections to the ground state are available and additionally intersystem crossing to the triplet manifold can take place. The combination of the two electronic structure methods (ADC(2) and MS-CASPT2) and the complementary "static" exploration of the important points and "dynamic" simulations allow us to disentangle the relaxation pathway of oNBA and to understand how the ketene intermediate can be formed.

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Towards Rational Design of Polarity Probes by Noncovalent Functionalization of Phosphorene

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Abstract

Noncovalent functionalization of semiconductors is an effective way to modify their electronic properties. [1,2] We determined the factors that sensitize the band gap of phosphorene, a representative 2D material, to the permittivity of the solvent. This enables an ab initio design approach for polarity sensing devices. Charge transfer to certain cationic conjugated acceptor substrates is highly sensitive to the solvation at the surface, showing the regulation of their acceptor properties by the solvent. This effect turns out to have a large effect on the material's band gap. As a result, we predict that highly electropositive cationic adsorbates, such as aromatic viologens, allow for polarity sensing across a wide range of the permittivity spectrum. Hybrid TD-DFT calculations of their absorption spectra on phosphorene show solvent-sensitive excitations inside the NIR region, as is desirable for high penetration bioimaging. We compare our results to well-established electron acceptors like TCNQ, which do not exhibit significant polarity response. [3]



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CC2 and CC3 methods in finite magnetic-field calculations

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Abstract

Recent developments in finite magnetic-field methods have enabled the investigation of exotic chemistry in extreme environments, where "chemical intuition" does not apply. Such environments occur for example on magnetized White Dwarf stars, whose spectra are challenging to assign. The versatility and accuracy of finite-field Coupled Cluster (CC) and Equation of Motions (EOM)-CC methods make them useful tools for the prediction of the complex electronic structure of atoms and molecules in strong fields.¹ The perturbative CC2 and CC3 methods are particularly promising in order to treat larger systems while retaining predictive capabilities. CC2 scales similarly to MP2 and is the computationally cheapest CC method.² CC3 offers a triples correction for both ground and excited states.³

In this poster, the implementation of finite-field CC2 and CC3 is reported for ground and excited states. Results are presented for atomic Mg, and molecular CH^+ , CH_4 and C_2H_4 . We show that in finite field CC2 exhibits qualitatively wrong behavior for certain electronic states and thus should only be used in "well-behaved" systems. Finite-field CC3 reproduces the CCSDT energy well for ground and singly-excited states. Results for doubly-excited states treated with EOM-CC3 are improved compared to CCSD. Additionally, a somewhat surprising issue with respect to spin contamination in MP2 and CC2 is discussed.⁴

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Embelin-BIR3 binding patterns as revealed by molecular dynamics and Markov State Model

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Abstract

Protein-ligand binding processes are key in developing new drug-like molecules which perform specific biological functions. Identification of active sites and stable binding is thus a desirable step towards discovery of new lead molecules. We present the binding pattern of embelin to baculovirus IAP repeat three (BIR3) domain of the X-linked inhibitor of apoptosis (XIAP) as revealed by molecular dynamics coupled with Markov State model theory. The binding site is shifted by approximately 3 Å compared to the original reported experiment one. A key mechanistic binding pattern, mainly hydrogen donor binding mode, is revealed by Markov state model.

Nanodiamond-Adsorbate Interactions studied by DFT

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Abstract

Nanodiamonds (NDs) are a very recent class of materials with favourable properties such as hardness, inertness, biocompatibility, as well as unique electronic properties. These properties have been exploited in many fields of application, including boimedicine and photocatalysis. For the theoretical investigations, the set of smallest possible NDs, called diamondoids, is used most often. Here, experimental data on the electronic properties (i.e., the optical gap) is available, allowing calibration and verification of the theoretical methods. However, different optical gaps have been obtained from optical absorption experiments in the gas phase and from X-ray emission/absorption studies on diamondoid powders. We clarify the experimental difference by providing density functional theory (DFT) calculations for single diamondoids in vacuum and small diamondoid clusters.

Furthermore, it is known that small NDs have unique frontier orbital shapes. Especially, the lowest unoccupied molecular orbitals (LUMOs) of NDs resemble atom-type orbitals. We show that these orbital shapes are not only obtained for single, spherical NDs, but also for their three-dimensional clusters.

For the application in nanomedicine and photocatalysis the NDs are dispersed in aqueous media. For bulk diamond in contact with water it is known that electrons can leave the diamond surface and move into the aqueous adlayer. This process is known as surface transfer doping and strongly depends on surface configuration and the presence of oxidative adsorbates. We characterize this effect for different small nanodiamonds and four aqueous adsorbates.

The Dance of Diatomic Molecules in Strong Magnetic Fields

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Abstract

Until very recently, the field of molecular dynamics (MD) in strong magnetic fields has remained virtually untouched. Three key components are necessary for an ab initio molecular dynamics approach: Firstly, an efficient gauge-invariant quantum-chemical calculation of molecular properties has to be provided. Such an efficient implementation is present within the Turbomole code for both electronic energies and molecular gradients. Secondly, since Lorentz forces become relevant for the movement of the nuclei, determining the extent of electron shielding is an unavoidable step for such an MD simulation. It can be obtained by calculating the so-called Berry curvature which can be derived from a non-vanishing phase of the electronic wave function within the adiabatic approximation. Thirdly, to propagate the nuclei within MD simulations, two propagation methods have been extended which take both the presence of a magnetic field and the Berry curvature into account while simultaneously conserving the total energy and momentum. The development of the Tajima and ACM (auxiliary coordinates and momenta) propagators thus constitute the last important step.

Using these mothods, we have investigated the dynamics of diatomic molecules for various field strengths of up to 470,000 tesla. Surprisingly, it was found that even for very small molecules such as H_2 and LiH, the presence of an external magnetic field is responsible for a plethora of fascinating effects yet unseen. In order to demonstrate this, we have assessed how nuclear trajectories are influenced and consequently how this affects the rotational and vibrational spectra.





MR-DSRGPT2 as a tool for an accurate description of low-lying excited states in carotenoids

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Abstract

Carotenoids play two important roles in photosynthesis, namely light-harvesting and photoprotection. Two excited electronic states, the optically bright $1B_u^+$ and the dark $2A_g^-$, are crucial for these processes. While these states have very different electronic structures, they both have to be described at a similar level of accuracy to effectively model the energy transfer in photosynthesis. We have recently shown¹ that a novel multi-reference perturbation theory MR-DSRGPT2 combines moderate computational complexity and adequate accuracy for description of low-lying excited states of polyenes.

In this work we expanded a range of model objects to natural carotenoids proving that MR-DSRGPT2 can be used as an effective tool for modeling of their excited states. Vertical and adiabatic excitation energies were calculated for the $1B_{u}^{+}$ and $2A_{g}^{-}$ electronic states of six natural polyenes, three openchain (neurosporene, spheroidene, and lycopene) and three closed-chain (lutein, violaxanthin, and zeaxanthin). Nuclear geometries for the ground and $1B_{u}^{+}$ states were optimized by means of (TD)DFT. We proposed spin-flip DFT for optimization of the $2A_{g}^{-}$ state instead of DMRGSCF used earlier, since the former method successfully accounts for multiconfigurational nature of the $2A_{g}^{-}$ state. State-averaged DMRGSCF with the entire π -system in the active space followed by MR-DSRGPT2 correction was used to calculate electronic state energies for respective nuclear geometries. The proposed approach allowed to achieve the accuracy comparable to that of the previous results for unsubstituted polyenes¹ but with lesser computational complexity allowing to treat larger molecules.

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Development and investigation of implicit quantum chemical solvation models

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Abstract

The importance of solvation in many quantum chemical applications is undisputed. Solvation can have a large impact on the energetic ordering of conformers and various spectroscopic properties. We investigate the accuracy of various implicit solvation models for conformational energies and ensembles.

Furthermore, we developed an advanced composite multi-level workflow, that utilizes extremely fast semiempirical quantum mechanical (SQM) and force-field methods for the initial creation of a conformer ensemble (CE) and more accurate density-functional theory (DFT) methods to reorder and filter the conformers. To be able to use solvation in the early steps of this workflow, we developed a robust and efficient implicit solvation model and parameterized it for extended tight binding (xTB) and density functional tight binding (DFTB) methods, as well as for the GFN-FF general force field.

In combination with even more sophisticated solvation models for the higher (i.e., DFT) theory levels, like the conductor-like screening model for realistic solvation (COSMO-RS), our workflow enables a computationally efficient determination of partition coefficients and other thermodynamic properties for large non-rigid molecules in solution.

NMR Chemical Shift Computations at Second-Order Møller-Plesset Perturbation Theory Using Gauge-Including Atomic Orbitals and Cholesky-Decomposed Two-Electron Integrals

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Abstract

Nuclear magnetic resonance (NMR) spectroscopy plays a major role in molecular structural analysis. The quantum chemical computation of NMR chemical shifts is here of particular interest. Corresponding calculations for larger molecules, however, pose challenges with respect to feasibility and computational cost. This poster¹ reports on the calculation of chemical shieldings and shifts using second order Møller-

Plesset (MP2) perturbation theory and gauge-inclucing atomic orbitals (GIAOs).² In order to considerably

extend the range of application, Cholesky decompositon (CD) of the two-electron integrals is used.³ For the unperturbed integrals we follow Ref. 4, while a new scheme has been devised for the derivatives of

the two electron integrals with respect to the magnetic field.¹ The accuracy of the CD for the derivatives of the two-electron integrals for different Cholesky thresholds as well as the applicability of the CD based GIAO-MP2 scheme is investigated. A comparison of NMR shieldings computed with CD-GIAO-MP2 with those calculated at the standard GIAO-MP2 level shows that the corresponding results for all Cholesky thresholds that have been used have sufficient accuracy. Representative calculations on larger systems with up to one hundred atoms and more than one thousand basis functions demonstrate how the CD-GIAO-MP2 implementation reduces memory usage and computational costs.

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Training set size dependence of residual error of neural network potentials

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Abstract

Neural network potentials (NNPs) are used in molecular dynamics simulations to reproduce potential energy surfaces of electronic structure methods. Using the NNP implementation n2p2 [1], this poster addresses the question of the dependence of the NNP's prediction error on the size of the training data set on the example of liquid water and ice. In addition, we present the same study using NNP-generated training data, for which it is known that at least one configuration of neural network parameters produces exact results and therefore, one can expect a lower prediction error that is purely based on the insufficiency of the training procedure.

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Can neural networks be accelerated using singular value decomposition?

<u>Maximilian Xaver Tiefenbacher</u>, Philipp Marquetand University of Vienna, Vienna, Austria

Abstract

Neural networks are able to provide forces for excited-state dynamics simulations [1] up to a few nanoseconds. Recent developments in the acceleration of neural networks[2] might hold the solution to go to even longer simulation times. Such accelerated networks are able to provide a similar level of accuracy as their non accelerated counter parts. This poster focuses on the acceleration of a neural network called SchNet[3]. The main technique investigated is the so called singular value decomposition, which is a special form of rank reduction. The rank reduction of objects within neural networks has been shown to be a successfully technique in the past. The aim is to use this technique to accelerate the matrix vector product, which is the most common operation in a neural network. The work analyzes mainly the error introduced and the speed up achieved by this technique for different sizes of models and different amounts of reduced ranks.

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Organic-radical metal interaction in molecular junctions

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Abstract



Single molecule-based devices have drawn great attention because bottom-up fabrication processes promise to realize data storage or information processing at the molecular level, which could overcome

barriers on conventional lithography^[1]. As shown in a previous report, the transport characteristics of an individual {4-[{[2,5-bis(4-sulfanylphenyl[eth-1-yn-2-yl])phenyl]carbonyl}(methyl)amino]-2,2,6,6-tetramethylpiperidin-1-yl}oxidanyl (TEMPO-OPE) bridging two gold electrodes in a mechanically controllable break-junction (MCBJ) has been explored. Although the radical part (TEMPO) was well electrically isolated from the OPE backbone, remarkably large magnetoresistance could be observed

compared with non-radical OPE^[2]. From inelastic electron tunneling spectroscopy data, the magnetic field was also able to modify coupling to vibrational modes, which implies a deep connection between spins, phonons, and transport. But this picture neglects the potential impact of multiple adsorbed molecules interacting with each other or with the metal surface.

In this work, non-covalent intermolecular interactions and TEMPO-Au interactions were carefully studied as the primary targets. In the following research, to establish the connection between magnetoresistance and molecular structure, the electronic configurations will be calculated by density functional theory or other alternative electronic structure theory based on the above geometric information.

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Langevin Thermostat implemented in SHARC

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Abstract

Non-adiabatic dynamics based on Tully's surface-hopping approach are traditionally conducted in the NVE ensemble. This is usually a reasonable description for ultrafast photo-dynamics. However, for simulations on longer time scales and where bath effects become important, the NVT ensemble is preferable. Therefore, we have implemented the Langevin thermostat[1] into the SHARC[2,3] program (Surface Hopping in Adiabatic Representation including arbitrary Couplings). This approach allows to control the temperature and it enables possible reaction path discovery through artificial heating, which can be desirable in cases with high barriers and thus rare reaction events. We demonstrate the effect of the thermostat using the Norrish type I reaction of acetaldehyde as an illustrative example.

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Quantum-Chemical Calculation of Two-Dimensional Infrared Spectra

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Abstract

Two-dimensional infrared (2D-IR) spectroscopy is a modern experimental method that allows one to obtain structural information about (bio-)molecules on all relevant time scales. It can be used to detect bond-specific couplings between local oscillators, as well as molecular dynamical processes, such as the changes in the secondary structure or the formation of hydrogen bonds [1].

2D-IR spectra are most commonly calculated by using empirical exciton models that are based on the parametrization of harmonic frequencies of local oscillators as well as the harmonic couplings between them. However, 2D-IR spectroscopy directly probes overtones and combination bands. Therefore, it is necessary to include doubly excited states and an empirical anharmonic shift [2, 3].

Here, we set out to calculate 2D-IR spectra. We employ anharmonic L-VSCF/VCI calculations using our *Vibrations* code [4]. This allows us to directly extract the anharmonic frequencies and transition dipole moments for singly and doubly excited vibrational states. These are used to compute purely absorptive 2D-IR spectra for small molecules, such as dipeptides or nucleic acids, in the frequency range of the carbonyl stretch modes.

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Heterobimetallic lanthanide-coinage metal compounds featuring possible metal-metal interactions in the excited state

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Abstract

Heterometallic compounds exhibiting narrow intermetallic distances have been of rising interest over recent decades. Complexes combining lanthanides(III) (Ln) and coinage metals(I) (M) are scarcely reported, synthetically challenging and highly interesting in terms of their interaction. Previous studies could not show any direct Ln-M interactions so far.^[1]

Here, we use quantum chemical methods, including energy decomposition analysis (EDA) and simplified time-dependent density-functional theory approach to study the interaction in Au/Ag-La complexes in both ground state and excited state.

The results from calculated Wiberg bond order, EDA and a detailed study of dispersion interaction caused by various parts of the molecule have shown that the main contribution to the total interaction in the ground state structure is due to the ligand dispersion interaction, especially from the bridging phenyl rings. However, the transition density of the Au-La complex follows the pattern of a ligand to metal-metal charge transfer (LMMCT), which indicates a possible Au-La interaction in the lowest excited state.

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Implementation of Periodic Boundary Conditions for the Generic GFN Force-Field

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Abstract

We present an implementation of periodic boundary conditions into the general force-field GFN-FF [1]. GFN-FF is designed for fast geometry optimizations and molecular dynamic simulations for large systems, showing excellent performance for various (bio)chemical systems including (transition)metal complexes and related compounds. It is parametrized for all elements up to Radon, which makes it a versatile tool for a large variety of applications. The addition of periodic boundary conditions enables the routine calculation of solid state systems, increasing the applicability of the force field in general. This initial work explains the steps that have to be taken to make GFN-FF applicable to solids and molecular crystals. Because the potential contains some non-standard terms, the implementation is rather involved. The electrostatic interactions are calculated with an electronegativity equilibrium (EEQ) model[2] and Ewald summation. Dispersion is calculated using a modified version of the D4 scheme [3]. For validation, we present preliminary tests on the DMC8 benchmark [4], which shows promising results of the periodic implementation.

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Global Minimum Search of Molecular Adsorption Positions on Metal Surfaces by Combining a Monte Carlo Algorithm and an Extended Tight-binding Approach

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Abstract

For the theoretical investigation of on-surface reactions such as the Ullmann-coupling, the adsorption position of the molecular unit is of great importance, since different positions can lead to different potential landscapes and reaction behavior. Knowledge of the global minimum is therefore necessary, but often difficult to achieve.

In this study, the search for the global minimum consists of a multi-step process involving Monte Carlo simulations with simulated annealing, molecular dynamics simulation, and structure optimizations. Due to the usually large surface systems and the required number of calculations, a fast and reliable method for calculating the structures is required. Thus, the semi-empirical tight binding method (GFN-xTB) [1] was used in this study to describe adsorbed molecules at surfaces, and was reviewed in terms of structural precision.

The investigations were performed on an exemplary Ullmann coupling system of halogenated naphthalene on coin metal surfaces [2]. Further, the search algorithm was applied to 1-bromo-8-phenylnaphthalene and its reaction intermediates at the Cu(111) and Ag(111) surfaces and the results were compared with experimental data from CO-functionalized AFM measurements [3].

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Understanding repulsive forces in non-bonded molecular complexes for $He\cdots Cl_2$, $He\cdots N_2$, and the planar displaced benzene dimer

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Abstract

Exchange-repulsion i.e. the repulsion of the occupied orbitals from two different molecules is known to have a large contribution to the molecular interaction energy. We show that this contribution to the interaction energy has a dominant influence on the intermolecular potential energy surface (PES) and that it can be rationalized in terms of orbital-orbital contributions to the exchange repulsion energy. The later contributions are obtained from an asymptotically correct approximation of the exact quantum chemical interaction between two molecules with their individual Hartree-Fock wave functions. Two example PES (He···N₂ and He···Cl₂) are presented to illustrate that these orbital-orbital contributions to

the exchange-repulsion energy provide an intuitive and pictorial explanation for key features of the PES. Our exchange-repulsion energy contributions are shown to compare well with corresponding terms obtained from the Symmetry-Adapted-Perturbation-Theory (SAPT) approach. We provide evidence that the well-established planar displaced aggregate structure of the benzene-benzene interaction is due to orbital-orbital contributions to the exchange-repulsion energy rather than the often-quoted quadrupole-quadrupole interaction.

Automated fitting of angular overlap model parameters: a case study on tetrahedral halido cobaltates

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Abstract

A characteristic of transition metal complexes is the existence of d-d transitions, resulting in the colours of minerals and solvated complexes. Ligand field theory (LFT) encompasses different approaches to describe the energetic ordering of d orbitals and electronic states. One of these approaches is the Angular Overlap Model (AOM), which describes each metal-ligand interaction separately. [1,2]

By using complete active space self consistent field (CASSCF) calculations, excited d states can be predicted computationally. The ORCA quantum chemistry package contains an *ab initio* ligand field theory (AILFT) module which provides the ligand field energy operators [3] which can then be fitted in order to obtain AOM parameters. [4] Even parameters that are impossible to determine experimentally are accessible via AILFT.

We have developed an automated fitting procedure for AOM parameters which was applied to tetrahedral halido cobaltates. In this contribution, we discuss trends in the halide series and analyze connections between metal-ligand distance and AOM parameters. The results are compared to known concepts, proving their plausibility.

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Excimer formation dynamics in the isolated tetracene dimer

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Abstract

The understanding of excimer formation and its interplay with the singlet-correlated triplet pair state

 1 (TT) is of high significance for the development of efficient organic electronics. Using nonadiabatic dynamics simulations, the photoinduced dynamics of the tetracene dimer in the gas phase are studied to obtain mechanistic insight into the excimer formation dynamics. All trajectories are launched from the bright S₂ state. The simulations are carried out in the frame of the semi-empirical CISD and TD-Ic-DFTB

methods. Both theoretical approaches reveal a dominating relaxation pathway that is characterised by the formation of a perfectly stacked excimer. TD-Ic-DFTB simulations have also uncovered a second relaxation channel into a less stable dimer conformation in the S1 state. Both methods have consistently shown that the electronic and geometric relaxation to the excimer state is completed in less than 10 ps. The inclusion of doubly excited states in the CISD dynamics and their diabatisation further allowed to

observe a transient population of the ¹(TT) state, which, however, gets depopulated on a timescale of 8 ps, leading finally to the trapping in the excimer minimum. Experiments using time-resolved photoionisation and photoion imaging upon excitation into the S₂ state reveal a biexponential time dependence. The obtained time constants are assigned to the relaxation of the excimer on the S₁ surface and to its deactivation to the ground state.

Interplay between Redox Isomerism and Jahn-Teller Effects Enhances Reactivity in a Bioinspired Mn₄O₄ Cubane Water Oxidation Catalyst

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Abstract

In nature, photosystem II catalyzes water splitting as part of photosynthesis to fuel cell growth and produce the oxygen all aerobic life depends on. Within photosystem II, the water oxidation half-reaction is catalyzed by the oxygen-evolving complex (OEC), a highly efficient Mn_4CaO_X cluster that has inspired attempts to develop synthetic catalysts of similar structure.¹ We propose a catalytic cycle for the highly active synthetic water oxidation catalyst (WOC) $[Mn_4V_4O_{17}(OAc)_3]^{3-}$ (1),² a model system for the OEC. Comparison among multiple pathways shows that the pre-catalyst **1** is activated by oxidation and ligand exchange;³ water oxidation then proceeds through a series of proton-coupled electron transfer steps, with a predicted thermodynamic overpotential of 0.71 V.⁴ In-depth investigations of the ligand exchange, O-O bond formation, and O₂ evolution steps reveals the highly dynamic interplay between redox isomerism and Jahn-Teller effects in the catalytic cycle: both serve to enhance catalytic reactivity by redistributing electrons between mixed-valence metal centers and weakening key bonds through Jahn-Teller distortions, introducing flexibility to the otherwise-rigid cubane core of **1**. These results are of general importance both for understanding water oxidation on molecular catalysts as well as advancing the design of Mn-containing WOCs.

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A bosonic perspective on classical mappings forsecond-quantized electronic dynamics

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Abstract

We consider the application of the original Meyer-Miller (MM) Hamiltonian to mapping fermionic quantum dynamics to classical equations of motion. Fermionic and bosonic systems share the same one-body density dynamics when evolving from the same initial many-body state. The MM classical mapping is exact for non-interacting bosons and therefore it yields the exact time-dependent one-body density for non-interacting fermions as well. The MM mapping is compared to different mappings applied to fermionic systems, namely the spin mapping (SM) with and without a Jordan-Wigner transformation, and the Li-Miller mapping (LMM), which is explicitly designed to map fermionic systems. For non-interacting systems, the inclusion of fermionic anti-symmetry through the Jordan-Wigner transform does not lead to any improvement in the performance of the mappings and instead it worsens the classical description. For an interacting impurity model and for models of excitonic energy transfer, the MM and LMM mappings perform similarly, and in some cases the former outperforms the latter when compared to a full quantum description. The classical mappings are able to capture interference effects, both constructive and destructive, that originate from equivalent energy transfer pathways in the models.

Solvation Effects on the Conformational Entropy of Non-rigid Molecules

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Abstract



The absolute molecular entropy is a fundamental quantity for the accurate description of thermodynamical properties. For non-rigid molecules, a substantial part of the entropy can be attributed to a conformational contribution. Systems and properties where this is relevant, e.g., protein-ligand binding affinities or pKa values refer usually to the liquid phase.

In this work, the influence of solvation on the conformational entropy is investigated. Therefore, a recently introduced state-of-the-art computational protocol (CREST) is used in combination with fast and accurate semiempirical quantum-chemical methods and implicit solvation models. A set of 25 commercially available drug molecules and five transition metal compounds is investigated. Computed gas phase conformational entropies are compared with values obtained in implicit *n*-hexane and water.

It is found that implicit solvation can have a substantial effect of several cal/K mol on the entropy as a result of large conformational changes in the different phases. We conclude that for very flexible molecules chemical accuracy for free energies in solution can only be achieved generally if solvation effects on the conformational ensemble are considered.

Adsorption of ammonia on the surface of zinc phthalocyanine

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Abstract

The detection of toxic gases is of great importance for monitoring environmental pollution and industrial emissions as well as for public safety. The detection of $\rm NH_3$ deserves special attention, since the

presence of ammonia in the air exhaled by a person indicates kidney or liver dysfunction. Thanks to advances in nanotechnology, nanoscale devices with promising technical characteristics for developing of appropriate sensors become possible.

It was previously shown that materials based on zinc phthalocyanine

(ZnPc) are sensitive to ammonia and can be successfully

used as active components of devices for its detection. However, interaction between ZnPc and NH₃ at

molecular level is not fully understood. In the present work the most probable channels of interaction of ZnPc with ammonia gases will be systematically studied with the use of advanced methods of quantum chemistry allowing to accurately predict the structural and energy characteristics of such complex chemical system. On the basis of results obtained the possibility of ammonia detection using ZnPc-based materials will be evaluated.

The work was supported by the Russian Science Foundation (project No 21-73-00276).

Combined first principles-statistical mechanics approach to sulfur structure in organic cathode hosts for polymer based lithium-sulfur (Li-S) batteries

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Abstract

The Lithium-Sulfur (Li-S) battery is considered as one of the most viable candidates for next-generation rechargeable batteries. However, several challenges hinder its practical application so far: the insulation of elemental sulfur, the shuttle effect of dissolvable lithium polysulfides, and the volumetric change of sulfur during the charge/discharge processes. One battery class that promises to overcome these drawbacks are polymer-based batteries which utilize organic materials as the active parts within the electrodes [1].

The here proposed cathode is a conductive, flexible, and free-standing polymer poly(4-thiophen-3yl)benzenethiol) (PTBT) as a sulfur host material [2]. By a vulcanization process, sulfur can be embedded into this polymer. We present a characterization of the molecular structure and energetic stability of different sulfurized PTBT dimers as the basic polymer unit within density-functional theory (DFT). Our calculations show that depending on the amount of sulfur that is embedded into the polymer, the main reaction of the vulcanization process leads to either a short sulfur chain crosslinking TBT units belonging to different polymer backbones or a larger sulfur chain connecting adjacent TBT units of the same polymer backbone.

This first-principles study is the first step into a multi-scale approach bridging classical and ab-initio molecular dynamic simulations that will focus on larger solvated polymer structures and spectroscopy calculations, respectively.

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4,4'-bis(carbazol-9-yl)biphenyl (CBP): effects of rotational conformation on excited state properties

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Abstract

Organic light-emitting devices (OLEDs) have been subject of intense research due to their potential applications. Among these, phosphorescent OLEDs (PhOLEDs) are of particular interest as they have shown quantum yields near 100%. Unfortunately PhOLEDs are prone to degradation from normal operation, substantially reducing operation lifetimes [1]. One proposed degradation mechanism is the exciton-polaron-induced aggregation (EPIA), likely caused by interactions between excitons and positive polarons that reside on host molecules during electrical driving [2].

4,4'-bis(carbazol-9-yl)biphenyl (CBP) is a popular and efficient hole-transport host material, composed by two carbazoles joined by a biphenyl moiety.Within devices CBP occurs as an amorphous material, where confinement introduces restrictions to the rather rotationally-flexible molecule. This work aims to study the the properties of the gas-phase, free-rotating CBP as a means to investigate purely geometrical effects on its electronic properties, ignoring any additional interactions with its environment. This is achieved through excited-state calculations of 1.6 k CBP rotamers using the Bethe-Salpeter equation (BSE) based on the GW approximation. As a follow-up, the average absorption and emission spectra were obtained by weighting individual oscillator strengths, taking into account structural degeneracy and through a temperature-dependent Boltzmann factor [3].

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QM/MM and TD-DFT of blue light pathways in complexes with respect to effects of protein matrix

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Abstract

We are investigating the blue light pathways of strongly coupled chromophores in the antenna complex CP29 (LHCII B4.1) of PSII and to what extent they compete with common internal conversion processes. [1,2] We employ a novel hybrid QM/MM interface [3], TD-DFT and analyse the coupling with a simplified Förster model. To get an idea of the conformational space and the intermolecular interaction we apply molecular dynamics (MD) to the system beforehand. The method strongly depends on the number of snapshots along the MD simulation but is a good approach for testing the environmental effects on optical spectra and on energy transfer processes caused by the protein or specific solvents. While we rely on a less elaborate coupling scheme, the excitation level order of the coupled chlorophylls leads to a better agreement with experiments [4] compared to previous work [5,6]. We identified not only the energetic position of the individual chromophores to be tuned by the protein matrix, but also the orientation of the transition dipole moments. We find that both control levels regulate the flow of the energy towards the PSII core complex.

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Advances in understanding and characterization of the P binding at the mineral/water interface

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Abstract

The phosphorus (P) immobilization process in soil is controlled by several factors and especially the strong interaction of P with soil mineral surfaces. The reactions of P with common P-fixing minerals such as Fe- and Al-hydroxides have been studied extensively. However, a systematic molecular-level picture of the P binding mechanism at mineral surfaces and its dependence on the environmental system conditions has not yet been established. Therefore, our main target is to explore the molecular binding mechanism for the P adsorption at mineral surfaces at different environmental conditions. We have simulated the binding of different inorganic and organic P compounds at goethite (-FeOOH) and diaspore (-AlOOH). Here, different surface planes with different degrees of surface unsaturation and different possible binding motifs at several pH values have been modeled. Molecular simulations for all P-surface models have been performed at different levels of theory involving DFT, multi-scale QM/MM and/or MM. All possible interactions taking place at the surface/water interface such as formation of covalent bonds and H-bonds, proton transfer, and water dissociation and the competition

reactions among H_2O , P compounds, and OH^- groups at the mineral surfaces have been

investigated. Furthermore, the applied approaches were able to reasonably calculate and interpret IR spectra that match well with the experimental ones. Moreover, assignments of the calculated IR spectra introduce a benchmark for characterizing experimental IR data for the adsorbed P species at mineral surfaces. Our work presents a step toward resolving the debate about the P binding motifs formed at mineral surfaces.

On the electron transfer chain in Photosystem I and photoreactive chlorophyll clusters

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Abstract

Modern photovoltaic materials can be seen as biomimetics of photosynthesis taking place in photoautotrophic organisms. Photosystem I (PS1) has one of the highest conversion efficiencies of 88%

(in sunflower leaves) from absorbed guanta to the reduction of NADP⁺. We investigated the electron transfer via charge-transfer states in the reaction center and in dimensionality reduced systems of the antenna complex of PS1. In our work we compared several electronic structure methods, namely semiempirical approximations, density-functional-theory and ab initio methods, to overcome common struggles regarding excited state chemistry of non-periodic supramolecular systems. We analyzed sets of relevant internal coordinates to construct significant conformers from molecular dynamics simulations data. Therefore we developed a general-purpose method based on an efficient workflow with unsupervised data projection tools like the principal component analysis, implemented in a self-written program. This approach can be used for other systems and complements the analytical tools for MD simulations. Screening the full atomistic MD simulation of the PS1 elucidated significant configurations of chlorophyll pairs. These discretized configurations were used to model the exciton and electron transfer chains. We assigned an excited state reaction pathway to the electron transfer in the full-dimensional reaction center with these considerations at hand. The same approach approximates the exciton transfer through the antenna complex to the so-called special pair. Due to the reduced dimensionality of the discrete pairs model, we consider our approach to be an effective method to investigate the potential of mutations and artificial photosynthesis in the future.



Are cluster calculations suitable to assign the peaks in thin-film absorption spectra of OSCs?

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Abstract

Acenes are known as archetype of organic semiconductors. Therefore, they have extensively been used as model systems for theoretical investigation on processes after optical excitation, for example exciton transport and singlet fission. Additionally, extensive spectroscopic work has been done on acene thin films. Their absorption spectra were theoretically modelled previously using the Frenkel-Holsteinapproach by Beljonne et al.

In this work, the acenes pentacene, its fluorinated derivate perfluoropentacene (PFP) and tetracene have been examined, mainly by time-dependent density-functional theory. A known fault of this method is the absence of the low lying excited states which are observed in experimental works. This can be amended by tuning the used functionals so that they obey Koopmans' theorem. Until recently, this tuning process was only used on monomers. Tuning whole oligomers has been shown to lead to even lower excited states in Pentacene. This approach has been adapted in the following work. To mimic the crystal environment of thin films, PCM and acene clusters of variable size were used. Using tetramer calculations, the peaks in the thin film spectra of pentacene, PFP and tetracene could be assigned to electronic transitions with errors less than 0.1 eV.

Relativistic DFT Calculations of 119 Sn NMR Chemical Shifts – The *SnS51* Benchmark Set

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Abstract

Being one of the most valuable and commonly used analytical techniques for molecular structure elucidation, nuclear magnetic resonance (NMR) spectroscopy rises great research interests for both experimental and computational chemists. Especially for heavy nuclei such as ¹¹⁹Sn, accurate computational predictions are highly desirable due to the wide measuring range and long scan times.

Following up our previous work on ²⁹Si NMR chemical shifts,^[1] we composed the new *SnS51* benchmark set featuring 50 very diverse tin-containing compounds and their 51 experimentally obtained ¹¹⁹Sn NMR chemical shifts (shown in the figure below with some examples in detail). The recently optimized CREST and CENSO tools^[2] enable us to generate a conformer ensemble for each molecule and compare the ensemble-averaged value with the single-structure one. The present study includes medium-sized complexes with various binding motifs and sheds light on linear scaling corrections as well as relativistic approaches for the chemical shift calculation and the geometry optimization. By assessing a total number of 15 density functional approximations in conjunction with three relativistic approaches we are

able to provide researchers a detailed and profound method suggestion for the prediction of 119 Sn NMR chemical shifts.



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CC2 response method using local correlation and density fitting approximations for the electronic g-tensor of extended molecules

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Abstract

A local CC2 response method for the calculation of electronic g-tensors of extended molecules is presented. Two-electron spin-orbit contributions are accounted for via effective one-electron operators. Calculated g-shifts for small molecules agree well with CCSD results obtained using exact two-electron spin-orbit integrals. Local and density fitting approximations lead to significant computational savings for larger molecues with only negligible impact on the quality of the results. The presented approach provides a viable alternative to density functional theory for the quantitative prediction of electronic g-tensors of extended systems and constitutes an important step towards a low-scaling hierarchy of higher order coupled-cluster methods for this type of problem.

Atomistic Simulations of Laser-controlled Exciton Transfer and Stabilization in Symmetric Double Quantum Dots

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Abstract

Our atomistic modelling sheds light on exciton transfer in coupled quantum dots. We show that with careful choice of pulse parameters the excitonic dynamics in dipole coupled nanocrystals can be controlled [1]. The hybrid CI/TDDFT methodology [2] -- time-dependent configuration interaction singles (TD-CIS) approach with a Kohn-Sham orbital space -- was utilized to simulate the multi-electron dynamics.

In an atomistic treatment of reduced-size, stacked, coupled germanium/silicon quantum dots the creation, transfer, and stabilization of localized excitations is studied in a donor-acceptor Frenkel exciton model. The poster summarizes how laser-controlled hole trapping can be achieved by a pump-dump pulse sequence



First a UV excitation creates an exciton localized on the top QD, then after some coherent transfer time an IR dump pulse localizes an exciton in the bottom QD. While hole trapping is observed in each excitation step, we show that the stability of the localized electron depends on its multi-excitonic character. The influence of size and geometry variations of three Ge/Si nanocrystals on the transfer times and thus the efficiency of laser-driven populations of the electron-hole pair states is presented.

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Vertical excitation energies in periodic systems: embedded-fragment Configuration Interaction Singles

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Abstract

We present an embedded-fragment approach for calculation of vertical excitation energies in periodic systems. The goal is a wave-function-based hierarchy of local post-Hartree-Fock models, which goes beyond the very common one-electron picture of the band gap and offers a way for systematic improvability of the results. The use of local occupied and virtual orbitals allows for a seamless embedding model for the fragment and becomes especially effective in studying defects in solids. As a first step in the hierarchy we present a Periodic-Hartree-Fock-Embedded Configuration Interaction Singles model.
Landau-Zener Approach for Excited State Dynamics Including Inter-system Crossing

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Abstract

Excited-state molecular dynamics simulations involving non-adiabatic transitions have gradually become a mainstream tool in computational photochemistry. Arguably the simplest approach is the surface hopping algorithm based on the extension of Landau-Zener transition formula into multidimensional space. The original Landau-Zener formula, which provides the probability of diabatic transition between two states, dates back to 1932. Recently, Belyaev and coworkers have adapted the approach for surface hopping simulations in terms of adiabatic electronic states. Its simplicity was preserved since the sole requirement of the method is knowledge of potential energy surface shape in points of crossing.

In this work, we present a pragmatic approach to photodynamical simulations with intersystem crossing based on Landau-Zener formula. We make use of combined adiabatic-diabatic representation, treating transitions within the same multiplicity with adiabatic formula, while employing the diabatic formula for states of distinct multiplicity. Our benchmarks show multiple benefits over standardized methods like fewest switches surface hopping, mainly due to the computational efficiency while maintaining high accuracy. We further compare our results with different existing approaches on model molecules, such as thiophene and cytosine.

Tailored anharmonic-harmonic vibrational profiles for fluorescent biomarker

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Abstract

Computational spectroscopy is a powerful tool in chemical structure determination and bioanalytical applications. To obtain accurate band shapes of fluorescent spectra the inclusion of vibrational effects, including anharmonic and quantum-mechanical effects can be required. However, due to the high computational demands, such accurate methods are only applicable to small molecules [1]. The current challenge is therefore to account for the anharmonic effects for large molecules while maintaining the accuracy obtained for the smaller ones. Fortunately full anharmonic treatment is often not necessary for the correct interpretation of experiments as e.g. shown in reduced-space models [2]. We propose a hybrid model, which is a combination of Franck-Condon factors calculated by anharmonic vibrational wavefunction methods (VCI) and the so-called independent mode displaced harmonic oscillator (IMDHO) model. In contrast to purely anharmonic models, the novel approach allows to include the vibronic effects of all vibrational degrees of freedom of medium-sized molecules, while focusing the effort on the important ones. With this approach, we evaluated the vibrational spectroscopy of trans-oligothiophene molecules of different lengths, and found a good agreement with experiment. We also concluded that both the consideration of anharmonicities for selected modes and a resolution measure can be beneficial for convergence of the vibrational profile with increasing number of modes treated on rigorous footings.

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Electron and nuclear correlation effects in ultrafast XUV single ionization dynamics assessed by a molecular model system

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Abstract

The attosecond ultrafast ionization dynamics of correlated two- or many-electron systems have, so far, been mainly addressed investigating atomic systems. It is well known that electron-electron and nuclearelectron correlation modify the ionization 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 arbitrary molecules and distinguish different pathways leading to ionization, be it direct ionization or ionization involving elastic and inelastic electron scattering processes. We find that different pathways result in a difference in the electronic population of the parent molecular ion, which, in turn, involves different subsequent (non-adiabatic) postionization dynamics on different time scales.



Reference

Nuclear-Electronic All-Particle Density Matrix Renormalization Group

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Abstract

We present the nuclear-electronic Hartree--Fock Density Matrix Renormalization Group (NEHF-DMRG) method that aims at solving the molecular time-independent Schr{\"o}dinger equation without invoking the Born--Oppenheimer (BO) approximation. By treating nuclei and electrons on the same footing, the method includes nuclear quantum, anharmonic, and non-adiabatic effects exactly. Moreover, we show how to extend the concepts of orbital entanglement and mutual information to nuclear-electronic wave functions to identify strong correlation between nuclear and electronic orbitals. By comparing NEHF-DMRG ground- and excited-state energies and nuclear densities with state-of-the-art data for the HeHHe\$^+\$ molecular ion, we demonstrate that NEHF-DMRG can compete with other nuclear-electronic multireference methods.

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Replica-Exchange Molecular Dynamics of photocaged circular DNA

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Abstract

Photocages offer a highly selective way to control biological systems like proteins, RNA and DNA. In this study, the duplex stability of a photocaged 32-mer DNA strand was investigated, complementary to earlier experiments [1]. A coumarin photocage was introduced in multiple positions to form a circular, caged DNA. The resulting duplex destabilization, which was previously analyzed experimentally by determination of melting points T_m [1], is here characterized by enhanced sampling techniques, notably replica-exchange molecular dynamics (REMD). An ensemble of various starting structures was created, including small, medium and large-sized loops. These structures were simulated with 110 parallel replicas in a temperature range from 300 to 450 K. The behavior of the systems along the temperature gradient was tracked by using different stability parameters, i.e., the number of Watson-Crick hydrogen bonds describing base pairing and distance/tilting parameters describing base stacking. From these stability parameters, predicted T_m values are obtained which are in good qualitative agreement with experiment.

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Investigation of Structural Anomalies and Properties of μ_2 -oxo-Bridged *bis*-Tetrel Porphyrinic Sandwich Complexes

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Abstract

The structural properties of μ_2 -oxo-bridged *bis*-tetrel porphyrinic double-decker complexes are investigated applying density functional theory (PBEh-3c, B3LYP-D4) [*J. Chem. Phys.* **2015**, 143, 054107] and state-of-the-art semiempirical quantum-mechanical methods (GFN2-xTB) [*J. Chem. Theor. Comput.* **2019**, 15, 1652–1671]. The influence of the metals Si, Ge, Sn, Pb and the ligands porphyrin (P), phthalocyanine (Pc) and naphthalocyanine (Nc) on the stacking and bridging angles, rotational barriers and conformational shapes is elaborated in depth. Rotation around the central M-O-M unit results in two distinct minimum structures. The extent of energetic favoring of the ecliptic (14°) conformation in contrast to the staggered (46°) conformation (a) strongly depends on the ligand and the metal. The calculations yield insight in the structural dependencies of ligand type and element combinations (b,c) and the counteracting role of attractive dispersion interactions and *Pauli* exchange repulsion investigated using orbital analysis and electronic decomposition analysis (EDA).



Reaching high for accuracy magnetic properties of 3d transition metal compounds: Limitations of mean-field spin-orbit operators

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Abstract

Transition metal complexes exhibit an interesting behavior with a lot of possible application fields, for example as single molecule magnets concerning their magnetic properties. Here, quantum chemistry methods are very important to help understand the complexity of those systems.

The inclusion of relativistic effects like spin-orbit (SO) interaction is often treated in a mean-field manner $[\underline{1},\underline{2}]$. In this work $[\underline{3}]$ we present the problems arising in calculations for transition metal complexes using mean-field spin-orbit operators and take a look at the reasons and complications.

We investigated a number of complexes used in current single molecule magnet and quantum bit research and calculated their magnetic properties (D and E values) with various SO operators, namely the full two-electron Breit-Pauli spin-orbit operator, the one-center approximation, the atomic mean-field approach^[4,5] and the mean-field spin-orbital approach^[1,2] using different one-particle densities. We noticed deviations of 5-10 cm⁻¹ for zero-field splittings and 10 to 40 cm⁻¹ for individual SO coupling matrix elements for all mean-field methods. These short-comings cannot be disregarded in high accuracy calculations such as employing multireference CC in an embedding approach^[6] and need to be treated as a limiting factor. Our results suggest that the one-center approximation is a still cost-effective but more accurate alternative to the mean-field approximation.

Applications of second-order approximate internally contracted multireference coupled cluster singles and doubles (icMRCC2) theory

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Abstract

The new second-order approximate internally contracted multireference coupled cluster singles and doubles method¹ (icMRCC2) was developed as the multireference analogon to the single-reference second-order approximate coupled-cluster theory² (CC2).

The accuracy and the interesting features of icMRCC2 were tested. For this purpose, the new method

was benchmarked using a subset of the Thiel database³, and the spectroscopic properties of ground and excited states of diatomic and triatomic molecules were calculated. In addition we show, using the examples of ethylene and cyclobutadiene, that even for a small CAS(2,2), the method is able to reproduce a rich excited state manifold and is thus an interesting candidate for applications in photochemistry.

First insights into nitrogen photoactivation

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Abstract

Ammonia derived from N_2 and fossil H_2 the Haber-Bosch process represents the main source of nitrogen compounds. In order to access a more diverse range of N-containing chemicals without relying on NH_3

as an intermediate, it is of high interest to develop tailored nitrogen-activating catalysts.^[1]

One way of achieving nitrogen activation via synthetic nitrogen fixation is selective light-driven N_2 cleavage. All known complexes for N_2 photoactivation have a linear core of the form M-N-N-M which undergoes geometric and electronic changes during the light excitation process, however the nature of the responsible excited state is presently ill-defined.^[1]

With a relaxed DFT surface scan along the N-N coordinate we provide first insights into possible geometric and electronic changes for the rhenium and tungsten complexes of Schneider and coworkers. Studying the obtained structures on a TDDFT level, we analyse the productive excitations within the M-N-N-M core.^[2,3] However, the complexity of the electronic structure requires the use of multideterminantal methods. For the rhenium complex we present a preliminary electronic structure analysis based on DMRG that will in future permit an appropriate treatment of spin-orbit coupling effects.

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Understanding the optical properties of complex organic high-dipole chromophores

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Abstract

The ever-lasting search for materials with efficient optoelectronic properties has led to numerous discoveries and advancements in the fields of organic semiconductors, non-linear optics, and bioimaging just to name a few. In this context, diaminodicyanoquinones (DADQs) are a class of high-dipole fluorescent dyes with remarkable versatility. DADQs display a fascinating range of intriguing features thoroughly studied in this account. Our short series of papers essentially follows a bottom-up approach of DADQs as optoelectronic building blocks.

Our combined experimental and theoretical approach employs various types of optical measurements and the DFT/MRCI method to elucidate the photophysical behaviour of our DADQ compounds. Our first study concerned DADQ monomers, which could be shown to exhibit substitution-pattern controlled nearperfect fluorescence quantum yields. Second, DADQ aggregates were investigated which displayed unusual optical properties reminiscent of both H- and J-type complexes. We propose an unprecedented mechanism involving nonfluorescent J-aggregates to rationalise our experimental findings. And third, we employed the concept of aggregation-caused quenching (AQC) and aggregation-induced emission (AIE) to solid-state DADQs for which we observed unexpected emission properties explained by a theoretical approach invoking a combination of monomers and H-type dimers polarised by their crystal environments.

Full-dimensional quantum mechanical calculation of thermal rate constants for the Cl + $CH_4 \rightarrow CH_3$ + HCl reaction

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Abstract

Reaction rates are probably the most prominent observables used to characterize chemical reaction processes. Especially in low-temperature regimes as well as when studying hydrogen transfer reactions, thermal rate constants show significant contributions from quantum effects, like tunneling. The reaction of methane with atoms (e.g. H, F, O and Cl) and its isotopic analogues are prototypical examples of polyatomic reactions benefiting from quantum mechanical treatment and were studied intensively both experimentally and theoretically.

Full-dimensional quantum mechanical studies employing these reactions are very challenging. Mainly the reaction $H + CH_4 \rightarrow H_2 + CH_3$ and its isotopic analogues were studied. Thermal rate constants as well as quantum-state resolved reaction probabilities were calculated in full dimensionality. These calculations employ an intuitive and rigorously correct quantum transition state concept. Within this approach, flux correlation functions are employed to obtain thermal rate constants. Employing the ML-MCTDH (*multi-layer multi-configurational time-dependent Hartree*) approach, accurate calculations can be performed for six atom systems in full dimensionality.

This work aims to extend the current framework by studying the title reaction. Flux correlation functions were calculated by propagating wave packets for about 40 fs using an accurate ab initio PES (*potential energy surface*). The computed thermal rate constants obtained from these are in excellent agreement with experimental data.

Dependence of spin polarization on structural parameters in Chiral Induced Spin Selectivity(CISS) : A first principles approach

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Abstract

Spintronics refers to employing the electron's spin and its magnetic moment, which emerges in device applications[1]. Gaining knowledge on controlling and modifying electrical conductance using spin is one of the significant challenges in this field. There are experimental observations of spin-polarized electron transport in closed-shell helical molecules due to the chiral-induced spin selectivity (CISS) effect [2,3], whose mechanism is not fully understood yet. However, considerable theoretical progress has been made in the last few years to unveil a mechanism, which involves chirality, the breaking of time-reversal symmetry, and the inclusion of spin-orbit interaction in the Hamiltonian.

Spin polarization in molecular junctions made of a model helix of 20 carbon atoms has been evaluated employing first-principles methods combined with a coherent tunneling approach to electron transport [3]. The effect could be described qualitatively[4-5]. To gain further insight into the spin polarization magnitude and electronic circular dichroism (CD) spectra (found to correlate with CISS in the experiment) on helical molecules with different pitch, equidistant, and alternating C-C bond lengths were obtained to check the molecular-structure dependence of CISS as described by first principles, and a first approach to the connection between this effect and CD.



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(Active) Learning Physicochemical Properties Based on Gaussian Moments

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Abstract

Machine-learned interatomic potentials are gaining in importance in computational chemistry due to their efficiency comparable to empirical force fields and accuracy on par with the reference ab-initio methods. Here, we elaborate on the methodology developed in our group for constructing efficient and accurate interatomic potentials, referred to as Gaussian moment neural network (GM-NN) [1, 2].

The GM-NN uses neural networks (NNs) to map novel symmetry-preserving local atomic descriptors, Gaussian moments (GMs), to auxiliary atomic quantities and includes both the geometric and alchemical information about the atomic species of both the central and neighbor atoms. Recently, to allow for efficient training on properties such as zero-field splitting tensors we have introduced a novel approach for the encoding of relevant invariances into the output of the respective machine learning model [3]. Besides the conventional property prediction, we introduce the uncertainty estimate for NN-based machine-learned potentials in the framework of the optimal experimental design [4].

As a final remark, we demonstrate the broad applicability of the presented approaches ranging from the conventional modeling of high-dimensional potential energy surfaces to the description of spin-phonon relaxation processes.



Figure 1: Schematic representation of the structure-property mapping employing the GM-NN model.

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Electronic Excitations from GW-BSE in Large Molecular Systems via hybrid embeddings

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Abstract

Many-Body Green's Functions Theory in the GW approximation with the Bethe-Salpeter Equation (GW-BSE) is post-DFT method to obtain accurate energies of charged and neutral electronic excitations. However, the computational cost of GW-BSE calculations scales, depending on implementation details, with the fourth power of the system size, which is a limiting factor for the application to large molecular systems, such as polymers, polymer composites, or complex supramolecular assemblies. We will present several theoretical and computational strategies based on hybrid embedding techniques aiming at a reduction of these computational costs, available in our VOTCA-XTP package. Strategies include, e.g., the evaluation purely classical corrections based on polarizable electrostatic interactions (MM/MM), explicitly coupled GW-BSE/MM, and GW-BSE embedded in DFT calculations. We will discuss the technical details and showcase the applicability of the various method with examples from polymer-fullerene systems.

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Exchange-Correlation Functional Dependence of Spin-Splitting Energies of Trisdiimineiron(II) Complexes

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Abstract

To enhance electron transfer processes and thereby improve the catalytic activity of base-metal catalysts, redox-active ligands are a promising tool. Approximate density functional theory (DFT) calculations are used to support experimental results and to help understand reactivities to improve catalysts. Redox-active ligands such as α -diimines can accept electrons from the metal center. This property influences the oxidation state of the metal center as well as the ground spin state and makes their experimental determination challenging. Therefore, first principle calculations with a proper choice of exchange-correlation (xc) functionals are crucial. To determine their influence, common xc-functionals were tested on a simple model system of homoleptic octahedral trisdimineiron(II) complexes. The spin-splitting energies for most of these complexes show the expected linear dependence on the amount of exact exchange a(HF) included in the xc-functionals with high spin states favored at a higher a(HF). Nevertheless, there are hints that this dependence is changed when the ligands are present in reduced form. This suggests that the redox-activity in the ligands influences the best choice of a xc-functional.

Possible Pitfalls in the Investigation of Covalent Inhibitors

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Abstract

Since cysteine protease Rhodesain plays a major role in the course of the sickness Human African Trypanosomiasis, it has been identified as an attractive drug target. One possible inhibitor, that has already been evaluated in preclinical trials, is vinylsulfone K11777, which inhibits Rhodesain irreversibly. For K11777 two reaction paths were obtained by starting in the reactant conformation and scanning towards the product conformation and *vice versa*. However, these reaction paths show strongly differing energetics. To evaluate where these differences stem from, QM/MM Umbrella Sampling simulations with varying QM regions (DFTB3-D3) were performed and the resulting geometries analysed. It was shown that the applied QM region strongly influences the reaction paths. Additionally, it was observed that the enzymatic conformation and especially the orientation of Asp161 impacts the simulations. By introducing a fluorine atom in alpha-position of the SO₂Phe warhead a reversible inhibitor (compound 1)

is obtained. Our calculations show that the differences between K11777 and 1 are mainly due to the interaction between the fluorine atom and the oxyanion hole, which induces a flip of the warhead olefin group within the active site. As a result, for inhibitor 1, a two-step mechanism is favoured, which contains a torsional movement from the F- to the H-orientation before the actual covalent reaction can take place, yielding a considerably reduced exothermicity. With these findings it is possible to explain the switch from the irreversible (K11777) to the reversible (1) inhibition mode. ^[1]

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Subsystem-Based GW/Bethe-Salpeter Equation

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Abstract

The GW and the Bethe--Salpeter Equation (BSE) methods have gained a lot of popularity in the molecular quantum chemistry community in recent years [1,2,3]. The main reason is the good accuracy-to-cost ratio offered by these approaches. Nevertheless, even the beneficial scaling prohibits the applicability to chromophores in complex biological or chemical environments. Subsystem-based methods are ideally suited to overcome this problem.



In this contribution [4], we show the derivation of working equations starting from a subsystem-based partitioning of the screened-Coulomb interaction for an arbitrary number of subsystems. We show that by applying certain approximations environmental screening contributions are included for each subsystem, leading to a parameter-free purely quantum mechanical fragmentation scheme. We demonstrate the applicability of these approximations by comparing quasi-particle energies and excitation energies from subsystem-based GW/BSE calculations to the supermolecular reference. Furthermore, we demonstrate the computational efficiency and the usefulness of this method for the description of photoinduced processes in complex chemical environments.

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Excited State Dynamics of the Q-Bands in Chlorophyll a

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Abstract

Conversion of sunlight to chemical energy via photosynthesis is one of the most central processes for life on earth. Here, the pigment chlorophyll adopts different functions depending on the environment: absorption of light in the visible range, excitation energy transfer in the antenna complex, primary charge separation in the reaction centre of the photosystems and subsequent electron transfer to other redox-active cofactors. Thus, nonradiative relaxation of high-energy excited states to the lowest excited state in chlorophylls is central for the understanding of photosynthesis.

In this work, we simulate the ultra-fast relaxation process in the Q-bands of chlorophyll a with grid-based wave packet quantum dynamics in several reduced-dimensional coordinate spaces. The excited state energies and non-adiabatic couplings are computed at CASPT2 level of theory. A number of studies point to the importance of "active" vibrational modes in assisting internal conversion processes. In the case of chlorophyll they are characterized through a high overlap with the corresponding non-adiabatic coupling vectors. Continuing this approach, we discuss the relaxation process in coordinate spaces spanned by a range of relevant normal modes.

In order to corroborate the choice of the reduced coordinates, we also investigate collective coordinates derived from a principal component analysis of semi-classical dynamics. The extracted decay time constants from this combined approach are in agreement with experiments.

Moreover, we show how coordinating ligands can tune the Qx/Qy energy gap and thus influence the relaxation dynamics. This sheds further light on the unsure role of the solvent during the non-radiative decay process.

Multi-State Formulation of the Frozen-DensityEmbedding Quasi-Diabatization Approach

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Abstract

We present a multi-state implementation [1] of the recently developed FDE-diab methodology [2] into the Serenity program package [3, 4]. The new framework improves the original approach such that spindensity distributions and corresponding properties can be reliably calculated coupling any number of charge-localized quasi-diabatic states.



We show that it is possible to obtain similar results compared to correlated wave function approaches like the complete active space self-consistent field method at much lower computational effort. Additionally, we present different approximate strategies the user can employ depending on the system under study. Those approximate approaches all converge to the full FDE-diab result. The newly implemented methodology opens the possibility to calculate spin-density distributions and corresponding properties from a subsystem densityfunctional theory based active space of quasi-diabatic states and can, thus, be used for extensive studies on large biomolecular systems.

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Modeling Human Skin Oil Oxidation and its Impact on Indoor Air Chemistry

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Abstract

We use atomistic molecular dynamics simulations to study the transport of ozone and human skin oil ozonolysis products through skin and the surrounding gas phase, as well as their partitioning between these phases.

Being members of the modeling consortium for the chemistry of indoor environments (MOCCIE), our results feed into kinetic models describing the macroscopic transport of all involved species and subsequently into computational fluid dynamics simulations. By using this multiscale modeling approach, we are able to provide a comprehensive picture of this complex multiphase chemistry with atomistic to roomscale resolution.

We find, among others, surprisingly low barriers against skin permeation of certain nonvolatile reaction products as well as significantly enhanced breathing zone concentrations of primary volatile reaction products.

Direct Orbital Selection within the Domain-based Local Pair Natural Orbital Coupled-Cluster Method

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Abstract

Domain-based local pair natural orbital coupled cluster [1, 2] (DLPNO-CC) has become increasingly popular for the calculation of relative energies. It can be applied within in a multi-level DLPNO-CC-in-DLPNO-CC ansatz to reduce the computational cost and focus the available computational resources on a specific subset of the occupied orbitals [3].



We demonstrate how this multi-level DLPNO-CC ansatz can be combined with the direct orbital selection [4, 5] (DOS) approach to automatically select orbital sets for any multi-level calculation. We find that the parameters for the DOS procedures can be chosen conservatively such that they do not need adjustment between reactions. The resulting automatic multi-level DLPNO-CC method requires no user input and is extremely robust and accurate. The computational cost is reduced significantly without sacrificing accuracy.

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Strain induced direct-indirect transition in III-V semiconductor materials from *ab-initio* approach

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Abstract

In the interest of a deep and thorough understanding of the effect of strain on the electronic properties of III-V semiconductor materials, we presented a systematic analysis of 'strain effect on bandgap' from modern *ab-initio* point of view. Using the density functional theory calculation we showed that depending on the nature and the strength of applied strain in the system the material behavior can change substantially; such as the otherwise conventional direct bandgap semiconductor can transform to an indirect bandgap semiconductor or vice versa. Unlike binary, although the requirement of relatively large supercell and multiple random structures (SQS) result in the band folding and large project size, respectively, complicated the direct-indirect transition (DIT) analysis in ternary system; however, using the idea of 'Bloch spectral density' [1] we developed a recipe for analyzing the DIT in ternary III-V semiconductor materials with fairly good accuracy enabling us to construct the so-called 'bandgap phase diagram'. With the possible future extension to the higher-order system, we believe that this new way of mapping the effect of strain will significantly improve the future development in terms of strategic choice of certain applications-oriented most suited material systems or vice versa.



Fig-1: GaAs isotropic strain DIT



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Theoretical Nonlinear Vibrational Spectroscopy of Water in Slit Pores

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Abstract

Water exhibits surprisingly different properties when it is confined between two parallel walls at nanometer distances with reference to bare interfaces, where the interfacial region is connected with a bulk like region. Although water under confinement has great importance in the biological as well as technological realm, its properties are being disclosed only recently due to breathtaking advances in the fabrication of ultranarrow slit pore confinement systems with different environments, geometries and sizes. Unlike interfacial water, nanoconfined water has not yet been probed using vibrational sum frequency generation (VSFG) spectroscopy – a technique that can efficiently probe interfacial water. This might be due to the fact that most nanoconfined systems used in experiments, such as graphene (GRA)-based nanodevices, are centrosymmetric in nature and hence VSFG inactive. In an effort to explore the VSFG technique to study confinement effects of aqueous solutions, we have modeled an asymmetrically nanoconfined system in a slit pore geometry where water is being sandwiched between GRA and boron nitride sheets, which can be considered as a slightly perturbed form of GRA-GRA slit pores that breaks their centrosymmetry. Using an electronic structure-based parameterized approach within force field-based molecular dynamics simulations, VSFG spectra of such confined water have been computed from the monolayer limit up to thick water lamellae where the confining walls are largely decoupled.

QM/MM molecular dynamics of the antenna complexes in Photosystem II

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Abstract

Light-harvesting complexes (LHCs) collect energy from sunlight and transfer it to reaction centers with the help of intermediate antenna complexes. Lately, the quest for mechanisms of efficient excitation energy transfer (EET) in LHCs of plant systems is an attractive area of research. Excited state calculations of LHCs using the long-range corrected time-dependent Density Functional tight binding (LC-TD-DFTB) approach have recently been shown to be rather accurate and efficient [1, 2]. The present study focuses on the EET in the antenna complexes CP29 and LHCII of the photosystem II (PSII) where we employed quantum mechanical/molecular mechanical molecular dynamics (QM/MM MD) for the ground state dynamics of the systems. The excited state calculations were performed using LC-TD-DFTB in a QM/MM framework. From the excitation energy fluctuations, the spectral densities of the systems have been calculated and can be used as an input in density matrix propagation schemes to obtain spectroscopic properties and population dynamics. The spectral densities of LHCII and CP29 show a good agreement especially in the high-frequency region with experimental spectral densities [3]. Furthermore, the absorption spectra of CP29 and LHCII have been calculated and compared to their experimental counterparts. These results based on QM/MM MD widen the scope for investigating EET mechanisms in large light-harvesting systems.

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Employing pseudopotentials to tackle excited-state electron spillout in Frozen Density Embedding Calculations

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Abstract

In frozen-density embedding (FDE), the properties of a target molecule are computed in the presence of an effective embedding potential in which all attractive and repulsive contributions of the environment molecules are contained. The formally exact embedding potential, however, is calculated using explicit kinetic-energy functionals in practice, for which the resulting potentials are in many cases not repulsive enough to account fully for Pauli repulsion by the electrons of the environment and to compensate thereby the strong electron-nuclear attraction. Using diffuse basis functions for excited states on the target molecule then leads to charge spillout when valence electrons are excited to those regions of the environment where the strong nuclear attraction is not compensated sufficiently by repulsive contributions. To reduce this insufficiency, we propose the inclusion of atomic all-electron pseudo potentials on top of the conventional embedding potential. In presented work the pseudo potentials are applied for computing vertical excitation energies of local excited states in complex systems employing the second-order algebraic diagrammatic construction (ADC(2)) scheme. The proposed approach leads to significantly reduced charge spill out and an improved agreement of FDE and supermolecular calculations in the frozen solvent approximation. In particular when employing diffuse functions the mean absolute deviation (MAD) is reduced from 0.27 eV to 0.05 eV for the investigated cases when using diffuse functions in the orbital basis.

Multiscale modelling of the graphene growth mechanism via chemical vapour deposition

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Abstract

Graphene, a promising material for many industrial applications, is commonly produced via chemical vapour deposition on the Cu(111) surface. However experimental investigations of the growth mechanism are rather difficult due to the growth conditions. Therefore theoretical simulations are important to gain more insights into the graphene growth mechanism. For this purpose we operate on three different scales. We combine a kinetic Monte Carlo model with a kinetic model for nucleation and growth, while we use DFT to study the elementary processes and calculate the required rate constants. With this approach we want to relate theoretical results to experimental findings.

Our DFT calculations show that the decomposition of the carbon precursor methane is the rate-limiting step, the energy needed for the decomposition can directly be related to the experimentally observed activation energy of the graphene growth. Furthermore we figured out from our kinetic Monte Carlo model that the carbon monomer and dimer are the dominant species on the surface and both species play an important role in the nucleation stage. Moreover we are able to predict the distribution of the graphene nucleus size for different growth conditions with the kinetic model of nucleation and growth.

Substitution Effects on the Dinitrogen Photocleavage of an Re-Based Pincer Complex

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Abstract

It is a major challenge to synthesize many N-containing compounds without relying on ammonia

produced by the Haber-Bosch process.^[1]Synthetic nitrogen fixation may circumvent this problem by enabling the direct chemical conversion of N2 gas, which makes up 78% of Earth's atmosphere, into these compounds. Therefore, it is of interest to develop molecular catalysts capable of direct nitrogen transformation.

Schneider and coworkers synthesized dimeric rhenium complexes with a pincer platform that are capable of photochemically spitting the nitrogen triple bond. The resulting rhenium nitride complexes produce benzamide and benzonitrile.^[2] The dimers contain a linear core of the form Re-N-N-Re that can undergo electronic and geometric changes which facilitate the photocleavage process.^[2] However, the role of the organic substituents on the pincer ligands in this reaction is not known yet.

Here we use DFT to examine the electronic and geometric structure changes of a series of dimers and the resulting monomers with different organic substituents on the pincer ligands. Using TDDFT calculations, excited states with metal-ligand charge transfer (MLCT) character were evaluated. While substitution patterns do not have a clear effect on the nitrides, they influence the geometry and MLCT transitions of the Re-N-N-Re core in the dimeric complexes.

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Implementing the r²SCAN-3c Composite DFT Method with Slater Type Orbitals

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Abstract

The recently published "Swiss army knife" composite method r^2 SCAN-3c^[1] yields excellent results for the calculation of conformational energies and thermochemical properties at a moderate computational cost. While the original approach uses a Gaussian type atomic orbital (GTO) basis, Slater functions have essential advantages such as the accurate representation of the core region and a correct long-range behavior. Therefore, we present an r^2 SCAN-3c implementation with a Slater type orbital (STO) basis in the ADF program from the prominent Amsterdam Modeling Suit AMS. We composed a triple- ζ STO basis set in analogy to the original mTZVPP GTO set and adjusted the geometrical counter-poise correction gCP for basis set superposition errors accordingly. Both are used in combination with the unchanged London dispersion correction D4. In contrast to the originally used effective core potentials, relativistic effects are treated with the scalar relativistic approach of the zeroth-order regular approximation (ZORA) as this is the default in ADF. The performance is assessed on a comprehensive database with over 1500 data points containing the whole GMTKN55 test set as well as additional benchmark sets of non-covalent interactions and organometallic reactions such as MOR41 or IONPI19.

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Computational Chemistry Research Lab

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Abstract

Studying chemistry most often concludes in doctoral studies with the goal to obtain a PhD.[1] Here, the students are expected to work independently on a current research project. Therefore, apart from expert knowledge and practical skills the students have to learn how to do research as early as possible in their studies. However, this qualification is lacking in most current chemistry study programs, particularly in Bachelor courses.

Here, we developed a research lab in computational chemistry where students have the opportunity to work on their own chosen research topics and present their findings.[2] Computational chemistry represents an ideal discipline to encourage independent research as the variety in topics is almost unlimited and no (possibly) harmful chemicals are involved.

The course starts with (self-)instructed theoretical learning sessions and a guided tutorial of the used software package.[3] The main part of the semester then consists of (time-)independent working on the research project with some milestone meetings in between. The final presentation is then held as a scientific poster session with an audience from the whole chemistry faculty.

Within our research lab the students pass through the whole circle of research-based learning. They acquire the necessary knowledge and tools to successfully start their PhD studies, not only in computational chemistry.

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Dissecting the polarization contribution in explicit embedding models for local optical spectra

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Abstract

To comprehend the environmental effects on electronic excitation properties of a molecule in solution or embedded in a protein embedding schemes have been devised. These schemes offer an efficient alternative when supermolecular calculations are inaccessible. A variety of different embedding schemes have been established independently, and they mainly differ in whether they include quantummechanical effects and/or polarization.

On the one hand classical embedding via electrostatic quantum mechanics/molecular mechanics (QM/MM) approaches have been extended to account for polarization effects including differential polarization, as for instance the so-called polarizable embedding (PE) model.[1]

On the other hand density-functional theory (DFT) has been reformulated in terms of subsystems from which approximate density-based embedding schemes have been composed. Frozen-density embedding (FDE)[2] accounts for ground-state polarization as well as quantum-mechanical effects. Despite their different origin, PE and FDE target the same effects.

Herein we investigate the influence of different approximations made in the description of polarization effects and the importance of quantum-chemical effects of the FDE scheme in comparison to the PE model on fluorescent dyes. The necessity of (differential) polarization in the determination of excitation energies and oscillator strengths is examined.

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Gold does not care: The impact of relativistic effects on the melting and boiling points of the coinage metals

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Abstract

Few manifestations of relativistic effects are as evident and well-known as the color of metallic gold. Anomalies in the periodic trends of melting and boiling points (MPs and BPs) of Group 11 elements copper, silver, and gold (also coinage metals) are presumably due to the impact of relativity^[1]. It has been argued that a hypothetical non-relativistic gold would behave similar to relativistic silver^[2].

To put those hypotheses to the test, we calculated the MPs and BPs for Group 11 elements in the relativistic and non-relativistic limit, applying a first-principle density-functional theory (DFT) based Gibbs energy approach^[3] using VASP. It combines thermodynamic integration (TI) with thermodynamic perturbation theory (TPT) and an empiric λ -scaling, which corrects for systematic errors of the chosen density functional for the interaction energies, based on molecular dynamics simulations to pin down the phase transition temperatures. At a spin-orbit relativistic level, the employed approach recovers the experimentally known MPs reasonably well (10%), while the predicted BPs are spot-on (1%). Calculations in the non-relativistic limit reveal large relativistic effects for the BP of gold, leading to strong similarities with relativistic silver. The impact of relativistic effects in Group 11 is discussed in the background of recently published results for Group 12.

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A generalized scheme for hybrid multireference methods

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Abstract

Multireference methods are indispensable tools for the investigation of open-shell molecules. These range from the popular complete active space perturbation theory [CASPT2] to the accurate, yet expensive, internally contracted multireference coupled cluster [icMRCC] method, amongst many others. Each of these multireference correlation methods have specific advantages and disadvantages. In order to create a method with an optimal trade-off of accuracy and computational efficiency, we generalized

an idea put forward by Saitow and Yanai to create multireference hybrid methods.¹ These new methods using this scheme are constructed by defining internal and external excitation spaces which are then evaluated on different levels of theory, respectively. Using this scheme, hybrid methods based on icMRCC, unshifted multireference coupled electron pair [MRCEPA(0)] and multireference perturbation methods like the n-electron valence perturbation theory [NEVPT2] have been created. A new separation of the excitation space, which evaluated all single and pair excitations to the virtual orbitals into the external space, is also presented and tested. In general, all hybrid methods created by this scheme improve upon their non-hybrid parent methods and offer a good trade-off between computational expense and numerical accuracy.

Exchange spin coupling in transition-metal doped perovskite nanocrystals

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Abstract

In recent years, lead-halide perovskite (LHP) nanocrystals (NCs) have attracted attention in the science community due to their high defect tolerance and photoluminescence, with quantum yields of up to 100%, making them promising candidates for light emitting diodes and solar cells. Experimentally, it has been demonstrated that LHP NCs and bulk materials can be doped with open-shell transition-metal cations in order to modify their optical properties, and to incorporate new magnetic properties into these materials. However, for many potential applications, NCs are more attractive than bulk materials, due to their unique size variety and behaviour in solution or applomerates. This is the reason why we undertake the first steps to investigate if similar magnetic properties can also be observed in LHP NCs. Since there are no systematic studies on the exchange spin coupling between metal dopant atoms in LHP NCs, the first goal was to evaluate the spin coupling in small doped and co-doped LHP NCs as a function of the choice of transition metals, the relative doping positions, the number of dopant atoms, and also addressing the effects of defects by means of density functional theory employing total energy differences and a Green's-function approach to exchange spin coupling. Among others, we find that the spin coupling in the Mn(II)-doped LHP NCs is antiferromagnetic, while ferromagnetic coupling has been experimentally found in bulk materials, suggesting that the spin coupling mechanism is not maintained when going from bulk to the NCs.
An implementation of Nuclear Velocity Perturbation Theory using a combined Gaussian and plane wave basis set

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Abstract

Infrared spectroscopies are invaluable tools for characterizing structure and composition of molecular systems. Using the Born-Oppenheimer (BO) approximation in a density functional theory framework, the electric dipole moment derivatives (the atomic polar tensors (APTs)) can be recovered by a perturbative treatment in which the solution of a set of coupled perturbed equations is required. In this way the dipole strengths of vibrational modes and hence IR absorption spectra can be computed. An alternative approach for calculating the APTs and further properties that are not accessible in the BO approximation is given by the complete adiabatic (CA) approximation.

In this case the Hamiltonian operator includes the perturbation of nuclear velocities leading to the exact factorization of the nuclear and electronic wave functions. These CA wave functions can be combined with the velocity representations of the electric dipole operators in order to compute APTs. We implemented the nuclear position and velocity perturbations in the CP2K code package, which allows for efficient and accurate electronic structure calculations. The calculations combine an atom-centered (velocity-dependent) Gaussian basis set with a basis of plane waves. Additionally, non-local pseudo potentials are used for the description of core electrons. We present our implementation and its application.

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Benchmark for Boron Containing Compounds

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Abstract

Boron compounds are increasingly being used in practice - among other things, they play a crucial role in the development of cancer therapies. With Boron Neutron Capture Therapy (BNCT), boron atoms can be

selectively incorporated into molecules to enrich ¹⁰B in cells and destroy active cancer cells more selectively than with conventional cancer therapy. So that the method can provide good applications, appropriate boron compounds must be synthesized and classified using Nuclear Magnetic Resonance (NMR) Spectroscopy. In order to confirm or support the results, quantum chemical calculations are usually added. Especially for molecules where experimental values in the literature are not available or not fully understood, theory can help to exclude possible isomeric forms of the products. For carbon and nitrogen centers, detailed benchmarks already exist, but for boron NMR shifts there are hardly any studies and a simple transfer has been found to be complicated due to the often unusual binding situations of boron. For this reason, we built a benchmark with molecules in which boron occurs in a wide variety of bonding situations, from boron-boron triple bonds to cyclic boron systems. In the benchmark,

we focused on the methods that can be used to effectively describe the ¹¹B NMR shifts, whether the bulky substituents of the molecules can be neglected for geometry optimization and/or for NMR calculations to reduce computational costs. Finally, we investigate whether the results of smaller model calculations can be transferred to the full systems. The influence of solvents and vibrational effects were also investigated.



Locally range-separated hybrid functionals from a gradient expansion of the exchange energy density

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Abstract

Locally range-separated hybrid (LRSH) functionals^[1] are a relatively recent class of hybrid functionals, in which the constant range-separation parameter of conventional range-separated hybrid (RSH) functionals is replaced by a real-space-dependent range separation function (RSF). Despite providing a higher flexibility regarding the exact-exchange admixture, in particular by an intrinsically system-dependent range-separation, LRSH functionals are still far less developed than their conventional RSH functional counterparts and received more attention just recently.^[2] Especially, the development of suitable RSF models and exploring the capabilities of the LRSH approach, in general, are tasks that require further investigations and are thus addressed in this work.^[3]

First, we show that, based on a detailed scaling analysis, LRSH exchange is best seen as exchange rather than correlation functional, which suggests the exploitation of exact constraints on the exchange functional. In particular, we employ a short-range expansion of the range-separated exchange energy density to derive new RSF models from the gradient expansion of the exchange energy density. The resulting second- and fourth-order RSF models, which are extended by a small set of empirical parameters to enhance their flexibility, are evaluated with respect to atomic exchange energies, atomization energies, and transition barrier heights.

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Light-heavy scattering in the Effective Relativistic Coupling by Asymptotic Representation (ERCAR) framework

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Abstract

To treat light-heavy scattering quantum dynamically at cold temperatures, a high accuracy is required and hence an accurate analytic potential energy surface (PES) is needed. Especially, the long range interaction region has to be treated physically correctly since this region is the most decisive for the quantum dynamics.

To achieve this high accuracy, non-adiabatic coupling and relativistic coupling effects, particularly spinorbit coupling induced by heavy atoms have to be described properly. Therefore, the Effective Relativistic Coupling by Asymptotic Representation (ERCAR) approach was developed, which combines a fullycoupled diabatization of asymptotic states and a static spin-orbit matrix, which is added to the diabatic model.[1]

In the ERCAR framework many states must be included, so the major task is the construction of an accurate fully-coupled diabatic PES. After generation of *ab initio* data, a non-linear fitting problem remains.

In the long range interaction region no coupling of diabatic states occurs because the diabatic reference states are defined at the asymptote. This region is fitted for every state using a physically motivated ansatz. The remaining coupled interaction region is fitted using a simple model, which includes energy and wave function information (hybrid diabatization fit).[2] An artificial neuronal network-based fit is used to improve the remaining region.[3] Finally, both fitted models for the different regions are combined. In the present work, the above scheme is demonstrated for hydrogen iodide.

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Calculations for high harmonic generation in vibrating molecules using Gaussian-type basis sets.

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Abstract

The process of High Harmonic Generation (HHG) has been intensively studied in the last decades, because it gives rise to new light sources ranging from attosecond pulses to soft X-ray photons. For polyatomic molecules this process is often simulated using time-dependent configuration interaction singles together with Gaussian-type basis sets (GBS), the fixed nuclei approximation and approximate ionization models.[1],[2],[3],[4] In order to estimate the errors introduced by these three additional approximations, we simulate the response of the hydrogen molecular ion H2+, to few-cycle laser pulses of different intensities. We employ different types of approximate dynamics with GBS, i.e., the solution of the time dependent Schrödinger equation within the fixed nuclei approximation, within the Born-Oppenheimer approximation and finally with approximate inclusion of non-adiabatic couplings. We compare our calculations to all-grid based solutions as a reference in order to benchmark GBS approaches. We get excellent agreement of GBS dynamics with all-grid solutions for low laser intensities, i.e., for not too high harmonics and small ionization probabilities for HHG. For the chosen system, non-Born-Oppenheimer effects are small.

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Understanding repulsive forces in non-bonded molecular complexes in terms of orbital-orbital contributions to the exchange repulsion energy

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Abstract

We demonstrate that the repulsive part of intermolecular interactions can be expressed in terms of orbital-orbital interactions which provides a pictorial explanation reminiscent of Frontier Orbital theory. In analogy to prior work [Hayes&Stone, Jensen&Gordon] we derive different approximations to the exchange-repulsion energy which are asymptotically correct to the exact quantum chemical interaction between two molecules with Hartree-Fock wave functions. Calculations of the Pauli repulsion for a small test system validate the quality of the various approximations as a function of the distance and the basis set. A simple form of the approximate exchange-repulsion energy is obtained if canonical orbitals of the individual molecules are used which allowsto partition the exchange repulsion energy into orbital-orbital contributions. This intuitive picture of the exchange-repulsion is illustrated with the example of the interaction of a nitrogen molecule and a neon atom. We conclude that relevant contributions to the exchange repulsion energy stem from orbitals with significant overlap.

Toward the investigation of electrocatalysis with grand-canonical cluster models and implicit solvation

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Abstract

Electrocatalytic reactions on metallic surfaces are often modelled with density functional theory (DFT) in a plane-wave basis and employing periodic boundary conditions. With this approach, the electronicstructure calculation is mostly limited to DFT with generalized gradient approximation functionals.

In contrast, the reduced number of explicit atoms in embedding approaches allow us to use more accurate electronic-structure methods. The embedding must account for all effects that cannot be described by the explicitly described region alone and it must be possible to describe the effect of an applied bias on the electronic structure.

We achieve this with a single-particle Green's function embedding approach, where the embedding is modelled by two parameters only: an energy shift and a level broadening for each orbital of the boundary atoms. Since the density matrix of the embedded system is calculated via integration of this Green's function, the molecule can be charged by tuning the upper integration limit. The embedding model is therefore grand-canonical with respect to the electrons and allows us to model the applied bias in an electrocatalytic reaction.

We study this model on a quasi-infinite one-dimensional system: a hydrogen-atom ring.

In silico studies of electrocatalytic reactions further require a solvent model that can describe the electrolyte solution. We recently implemented a non-linear Poisson–Boltzmann implicit solvation model and optimized the parameters of this model by fitting to experimental data in the form of Sechenov coefficients.

We outline how a combination of these approaches allow us to study electrocatalytic reactions in silico.

Gaussian process regression for double incremental potential energy surface construction

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Abstract

The Potential Energy Surface (PES) provides a detailed information about vibrational motion of molecules. However, quantum chemical PES calculations have a very unfavorable scaling with respect to the system size. This is due to i) a scaling of single point electronic structure calculations and ii) an increasing dimensionality of PES leading to a growing number of single points to be computed.

The previously developed Double Incremental Expansion (DIE) scheme¹ exploits ideas of restricting mode-mode couplings and fragmentation of the molecule into subsystems and, thus, addresses the both

scaling problems. Its integration with the Adaptive Density-Guided Approach (ADGA)² enabled an automatic construction of grids and ensured that the smallest possible number of grid points is used,

while maintaining a highly accurate description of a $\ensuremath{\mathsf{PES}^3}$.

In our ongoing work, we combine this theoretical framework with Gaussian Process Regression (GPR) to further reduce the computational cost of the PES construction. To that end, a very flexible GPR setup has been implemented including new and non-standard kernels based on field-theoretical methods. This

methodology will soon be publicly available in the MidasCpp program⁴ enabling black-box calculations of PESs for much larger molecular systems than accessible to date.

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Investigation of the electronic interaction energy of a lytic polysaccharide monooxygenase and oligosaccharide with novel fragmentation methods

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Abstract

The calculation of electronic interaction energies in biomolecular systems is an important ingredient to understand and predict ligand binding energies. The ligand binding process is usually crucial for an enzyme to function properly. This is evident from the binding of polysaccharide substrate to the metalloenzyme lytic polysaccharide monooxygenase (LPMO). The LPMO catalytically cleaves and depolymerizes polysaccharides, making them potential drivers for sustainable biofuel production. However, due to the LPMOs' large system size, pure *ab-initio* calculations are computationally far too demanding. Fragmentation methods offer an efficient way to achieve quantum chemical descriptions of such large systems with acceptable computational effort.

Herein we present a fragmentation method that enables a first quantum chemical calculation of the electronic interaction energy of the LPMO with an oligosaccharide as substrate. The fragmentation scheme is set up in a recently developed novel framework [1] that allows the inclusion of the metal complex center in a fragmentation scheme explicitly designed for proteins.

We were able to obtain the electronic interaction energy with different quantum chemical methods such as density-functional theory calculations with a quadruple- ζ basis set and perturbation theory calculations with a triple- ζ basis set, showing qualitatively coinciding results. Furthermore, the amino acid-based fragmentation calculation allows for the identification of important individual enzyme sections to the electronic interaction. This analysis can provide further insight into the substrate binding process and potentially help design new, improved LPMOs for biofuel production.

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Wavepacket dynamics in a harmonic potential disturbed by disorder: Entropy, uncertainty and vibrational dynamics

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Abstract

We investigated the wave packet dynamics in an harmonic oscillator which is perturbed by a disorder potential. This perturbation causes the dispersion of an initially Gaussian wave packet which is reflected in the coordinate-space and the momentum-space Shannon entropies. Regarding the sum of the latter two quantities, one arrives at an entropy which is related to the coordinate-momentum uncertainty. Whereas in the harmonic case, this entropy is strictly periodic and

coordinate-momentum uncertainty. Whereas in the harmonic case, this entropy is strictly periodic and can be evaluated analytically, this behavior is lost if disorder is added. There, at selected times, the quantum mechanical probability density resembles that of a classical oscillator distribution function, and the entropy assumes larger values. However, at later times, quantum mechanical revivals occur, and the seen effects are reversed so that a localized wave packet is built, and the entropy decreases close to its initial value.

CO on NaCl(100) : A Quantum Mechanical Description of "O-down" isomers

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Abstract



Recently, inverted ("O-down") CO adsorbates on NaCl(100) were observed experimentally after infrared vibrational excitation of the CO adsorbates. (Lau et al.,Science, 2020,367, 175-178). We characterize these species using periodic density functional theory and a quantum mechanical description of vibrations. We determine stationary points and minimum energy paths for CO inversion, for low (1/8 and 1/4 monolayers (ML)) and high (1 ML) coverages. Transition state theory is applied to estimate thermal rates for "C-down" to "O-down" isomerization and the reverse process. For the 1/4 ML p(1×1) structure, two-dimensional and three-dimensional potential energy surfaces and corresponding anharmonic vibrational eigenstates are obtained from the time-independent nuclear Schrödinger equation. We find (i) rather coverage-independent CO inversion energies (of about 0.08 eV or 8 kJ/mol per CO)and corresponding classical activation energies for "C-down" to "O-down" isomerization rates at 22 K which are vanishingly small for the "C-down" to "O-down" isomerization but non-negligible for the back reaction; (iii) several "accidentally degenerate" pairs of eigenstates well below the barrier, each pair describing "C-down" and "O-down" localized states.

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Theoretical description of oxygen redox chemistry in alkali/oxygen battery materials

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Abstract

The discussion of alkali/oxygen battery chemistry is of utmost importance in the search for an efficient energy storage technology[1]. The motivation for this study is to provide a quantum chemical modeling approach for alkali/oxygen battery reactions through model systems at different length scales and complementary levels of theoretical description to formulate a comprehensive and rich mechanistic picture. First, the individual electronic states of molecular model systems with a few atoms are accurately described in the framework of wave function-based post Hartree-Fock methods such as CASSCF/CASPT2 [2],[3]. Second, theoretical investigations using density functional theory calculations allow the description of extended periodic model systems with metallic surfaces.[3]

The mechanistic picture presented of a barrier-free reaction of oxygen with the metallic surface is consistent with the results obtained for the molecular peroxide model systems. The intercalation of oxygen into the metal surface, as well as small-scale models of surface elements, can then be understood as purely thermodynamic involving the preservation of the O-O bond and two successive electron transfer steps. The energetic order and mechanistic equivalence of the reactions on different length scales is demonstrated.

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Applying ΔMachine Learning to Improve the GFN-Force Field

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Abstract

The GFN force-field (GFN-FF) is a generic, partially polarizable force-field for the entire periodic table up to radon ($Z \le 86$). It features high robustness, sophisticated potential energy terms and is capable of calculating good R_e structures and reasonably accurate interaction energies. Moreover, due to its speed

it is also being used in current research for extensive meta-dynamics simulations (CREST code). However, for applications in the important context of conformer search, GFN-FF lacks the required accuracy to resolve complex conformer ensembles.

To overcome this shortcoming, we propose a Δ Machine-Learning (ML) approach, which infers forces and energies on DFT-level from input FF-level data.

For this purpose, using datasets, such the P-CONF1.6M, which contains a huge number of tripeptide conformers, the ground state energy and nuclear gradient difference between GFN-FF and DFT is learned. For the DFT-calculations state-of-the-art functionals and solvation models are applied, e.g.,

 r^2 SCAN-3c and COSMO-RS. By supervised training the DFT-level gradient and energy is approximated with a neural network on the basis of the 3D-structure and GFN-FF data (including ALPB continum solvation).

So far this ansatz shows promising preliminary results on small peptides (up to 50 atoms), improving the overall accuracy compared the bare GFN-FF prediction. However, it is too early to give a conclusive evaluation, as final ML-architecture and choice of descriptors are still up for debate. A further open question is if Δ ML should be applied to gas phase and solvation free energies seperately or if solution properties should be taken as reference.

Observing and controlling the coupled nuclear and electron dynamics in the nucleobase uracil

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Abstract

Studying photo-induced processes, like the interaction of a molecule with an ultrashort laser pulse, or the coupling at a conical intersection (CoIn), the interplay between electron dynamics and nuclear motion becomes relevant. The nuclear dynamics usually leads to a fast decoherence of the induced coherent electron dynamics. In some systems also a reappearance of the coherent electron dynamics can be observed. We studied this situation for the nucleobase uracil, which exhibits an ultrafast relaxation mechanism mediated by CoIn's. Applying our ansatz for the coupled description of the nuclear and electron dynamics in molecular systems (NEMoI) the excitation by a laser pulse and the nonadiabatic relaxation were explicitly simulated and the coherent electron dynamics monitored.

The insights into the electron and nuclear dynamics given by quantum mechanical simulations create the possibility to modify or control the dynamics. Due to their extraordinary properties Coln's enable optical control possibilities in the few femtosecond regime. We focused on a control scheme relying on the carrier envelope phase (CEP) of a few-cycle IR pulse. Before the wave packet reaches the Coln the laser interaction creates an electronic superposition. The imprinted phase information can be modified by the CEP in order to influence the population transfer through the Coln. This control scheme was applied to the nucleobase uracil, which exhibits multiple crossings of the wave packet over its Coln seam.

EVB-QMDFF - a Versatile Molecular Dynamics Program Package Based on Black-Box Potential Energy Surfaces

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Abstract

Parametric calculations of chemical reaction rate constants either impose some intrinsic approximations or are complicated to handle, whereas full-dimensional dynamical calculations lead to heavy calculational overhead and need analytically parameterized potential energy surfaces.

In order to overcome these problems, the EVB-QMDFF method combining two quantum mechanically derived force fields (QMDFFs) with empirical valence bond (EVB) was developed, which can generate potential energy surfaces for elementary reactions. The newly developed TREQ method constitutes a further improvement which was shown to be able to calculate high-quality rate constants with RPMD in a black-box fashion, using only optimized reaction paths as input.

To make these methods available to the public, a new open-source molecular dynamics program package named EVB-QMDFF was built. It is able to calculate rate constants of high quality without the requirement to be an expert on the field.

Based on the initial objective of calculating reaction rate constants, a broader range of applications was implemented as well, making EVB-QMDFF a stand-alone RPMD program package that is able to perform several kinds of calculations such as: TS and IRC optimizations, NVE, NVT and NpT molecular dynamics of large solvent systems described by merged QMDFFs of several single molecules, free energy samplings with different collective variables and molecular force simulations of bond ruptures.

Investigation and Evaluation of Homogeneous Transition Metal Catalysed Reaction Mechanisms: Transition Structure Guesses and Energy Decomposition Based on PNO-LCCSD(T)-F12

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Abstract

To get a sufficiently accurate guess for a transition structure (TS) the woelfling program¹ as implemented in TURBOMOLE was modified. The woelfing program optimises a reaction path (RP) between two intermediate structures to approximate the minimum energy path (MEP) with a finite number of images (\rightarrow structures). When the RP contains a lot of structural rearrangement it can be the case that no image ends up being sufficiently close to the desired TS. A new approach to shorten the RP and thereby naturally increasing the likelihood of the images ending up close to the TS is presented. With this new approach it is possible to get a more accurate guess in a more efficient manner compared to the straight forward usage of the woelfling program with many images.

In order to validate the barrier heigths calculated by means of DFT, PNO-LCCSD(T)-F12² single point calculations were performed. The HF, pair and triple correlation energy contributions were evaluated and attributed to predefined regions of the reaction system. The change in energy between two neighboring structures was analysed respectively. This data could be used to evaluate the role of specific interaction types and ligands. Also it seems possible to use the results from the energy decomposition to devise a scheme to treat the regions independently in regards of higher order correlation contributions.





Efficient trust-region augmented Hessian SCF methods for open-shell molecules

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Abstract

Open-shell single or multi-configurational (MC) self-consistent field (SCF) calculations often show convergence issues when using standard solvers that exploit only information from the electronic gradient. For those (MC)SCF calculations trust-region second-order methods that also make use of the electronic Hessian should be used that show robust and guaranteed convergence towards true energy minima. An efficient trust-region augmented Hessian (TRAH) method [1] was implemented in the ORCA quantum chemistry package for restricted and unrestricted Hartree-Fock and Kohn-Sham DFT as well as the complete active space SCF methods. The most time-consuming step, i.e., transformations of the Hessian with trial vectors, is implemented in an integral-direct fashion such that (MC)SCF calculations on molecules with hundreds of atoms become standard calculations. Efficient preconditioning of the micro iterations is discussed in this contribution. A full second-order TRAH implementation for state-averaged CASSCF is also presented.

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Lithium Diffusion in Crystalline Li_xSi_y from *Ab Initio* Molecular Dynamics Simulations

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Abstract

The Li_XSi_Y class of compounds exhibits a broad variety of crystal structures depending on the exact stoichiometry, with surprising differences in lithium diffusivity. We perform a systematic series of *ab initio* molecular dynamics simulations in order to characterize the mobility of lithium atoms, both from a local and from a long-range perspective. Our study shows the crucial importance of including interstitial sites in description of diffusion. Since the diffusive behavior of lithium in these compounds can be attributed to recurring diffusion paths, we identify pathways in our simulation trajectories and further investigate them by means of nudged elastic band calculations to obtain energy profiles. We show the connection between diffusion mechanisms and migration energy barriers and especially highlight the relevance of point defects for low migration energies. Furthermore, we study the influence of the motion of lithium and silicon atoms that are adjacent to diffusing lithium atoms along their paths and draw special attention to the importance of this motion for energetic stabilization of self-interstitial lithium atoms.

On Cavity Transition States and Resonant Reactant-Localization - Insights into Cavity-Altered Chemical Reactivity from a Time-Independent and a Time-Dependent Perspective.

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Abstract

The microscopic mechanism behind cavity-altered chemical reactivity under vibrational strong coupling^[1] has received some interest in recent years, however, is still an open problem from a theoretical perspective^[2]. In this contribution, we discuss some new insights for vibrational polaritons formed in a cavity-altered thermal isomerization reaction model for the ammonia

inversion under vibrational (ultra)strong coupling conditions^[3]. From a time-independent perspective, we characterize the cavity transition state and minimum energy path of the cavity potential energy surface (cPES) for different light-matter interaction regimes. Further, we obtain fully quantum mechanical thermal reaction rates calculated from cumulative reaction probabilities based on an absorbing boundary Green's function approach. We find quantum-light-induced topological changes at the transition state, which lead to a significant reduction of reaction and tunneling rates. From a time-dependent perspective, we identify a dynamical localization of the reactant wave packet along the reaction coordinate, which emerges as the cavity mode is tuned resonant to the reactant mode. We find, that this resonant reactant-localization results from a strong excitation of the system perpendicular to the cavity reaction path. Further, the nature of the resonance condition is studied as function of the interaction regime and related to the cPES topology of the inversion model.

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Fine tuning of Förster Resonance Energy Transfer between chromophores confined in lipid membranes: a computational approach.

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Abstract

The efficiency of the Förster Resonance Energy Transfer (FRET) is governed by the distance and arrangement of energy donor and acceptor.[1] We performed a computational investigation of the FRET in an artificial bio-inspired system to explore the possibilities of controlling this process between chromophores embedded into membranes. The system comprises an N-substituted perylene diimide (C4-PDI-C4) as donor and an alkylated ruthenium tris-bipyridyl derivative (Ru(bpy)₂bpyC9) as acceptor embedded into opposite lipid membrane leaflets (Figure 1). Time dependent evolution of the chromophores was explored by means of classical molecular dynamic simulations in combination with umbrella sampling methods. Furthermore, using density functional theory calculations, we computed optical properties such as absorption and emission spectra as well as the magnitude and orientation of the transition dipole moments with special attention to the sampling of the conformational space.

The membrane confines both position and relative arrangement of the chromophores. Since the FRET is highly dependent on distance and directionality of the transition dipole moments,[1] the embedding in the membrane not only controls the rate of energy transfer, but also the participating electronic states. Distinct arrangements of the perylene diimide donor lead to a population of specific excited states of the ruthenium-based acceptor due to the alignment of the transition dipole moments. Thus, our study shows how the control of the insertion modes into the membrane opens the possibility for direct tuning of the FRET efficiency.

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Figure 1: C4-PDI-C4 as energy donor and Ru(bpy)₂bpyC9 as acceptor embedded into a membrane. Transition dipole moments depicted as two-headed arrows.

Phase Stability Simulation of Copper Chalcogenide Nanoparticles from First Principles

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Abstract

Transition Metal chalcogenides (TMS) and especially copper/sulfide based chalcogenide nanoparticles have shown a broad range of possible applications, including sensing, catalysis, cancer-treatment, plasmonics and photovoltaics. Due to the promising nature of $Cu_{2-x}S$ nanocrystialline polymorphes it might be a promising candidate for replacing toxic Cd based quantum dots. Copper sulfide as a chemical compound shows a big variety of non-stochiometric and mixed phases in which covelite (CuS) and digenite (Cu_{1.8}S) are among the five known phases stable under ambient conditions

The thermodynamic properties of covellite and digenite bulk and surface structures were studied within the scalar relativistic zero point corrected DFT framework, providing a finite temperature description of the bulk and surface free Energy within the frozen phonon approachs. The study includes the calculation of formation and reaction energy of the bulk polymorphes as well as the calculation of the formation of idealized particles predicting the synthetically outcome of the nanoparticle formation in size and structure under a broad range of temperatures.

This model can be extended to a high throughput analysis of available data bases, which allows the evaluation of the chosen model with data provided by experiments and might lead to the prediction of yet unknown compounds.

Excited states of a flavin chromophore in crystal and MOF environments

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Abstract

Flavins are luminescent chromophores that play an important role in biological photoreception. [1] Their luminescence properties strongly depend on their environment. 10-methyl-isoalloxazine (MIA) shows only weak fluorescence in the crystalline state, while it turns into a potent fluorescence emitter when embedded into various metal organic frameworks (MOFs). In this study, we investigate the fluorescence emission of MIA in its crystal structure and in MIL53-Al with plane-wave methods [2] and with combined quantum mechanics/molecular mechanics (QM/MM) strategies. [3] Our calculations show that the mechanism of fluorescence quenching involves multiple π -interacting MIA molecules. The MOF can restore MIA fluorescence to its intensity in aqueous solution [4] with only little influence on absorption and emission wavelengths, thus providing a solid environment for technical applications.

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Accelerating spectroscopy with Machine Learning

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Abstract

Machine Learning has significant potential in helping accelerate theoretical chemistry calculations and elevate our understanding of chemistry to the next level. While ML has been successfully applied to the prediction of ground-state properties of molecules[<u>1</u>], the field of excited-state research has proven to be more challenging.

We benchmark several graph neural networks, which have previously not been used to predict spectra [2][3], in their ability to predict excitation spectra of the organic molecules of the QM9 dataset. Our results show how an ML algorithm set up and trained in a matter of few hours can generate highly accurate spectra. Further, we demonstrate how the prediction of spectra is affected by different molecular features such as molecular weight and functional groups across the dataset. As well as generating quick spectra, we believe that ML can be used to discover new structure-property relationships and help improve our understanding of chemistry. Our initial results show that interpretability techniques such as graph attribution [4] can help improve our understanding of how machines 'learn' to predict spectra.

A Joint Venture of Theoretical Methods to Compute Accurate Hyperfine Coupling Constants of Nitroxide Spin Probes in Aqueous Solution

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Abstract

The isotropic hyperfine coupling constant (HFCC) is an important observable within EPR spectroscopy. With the aim to push forward the cutting-edge of first principles-based calculations of HFCCs of spin probes in aqueous solution, we have employed rigorous statistical mechanics combined with correlated electronic structure techniques to accurately compute the HFCCs of a pH sensitive nitroxide probe (HMI). Solvation effects are described either by fully atomistic simulation, liquid-state integral theory, and implicit solvation approaches by means of ab initio molecular dynamics (AIMD), embedded cluster reference interaction site model (EC-RISM) theory, and polarizable continuum embedding (using CPCM), respectively. The HFCCs are computed using open-shell domain based local pair natural orbital coupled cluster theory (DLPNO-CCSD) as well as from hybrid density functional theory (using revPBE0-D3 as in AIMD) for an ensemble of explicitly solvated configurations sampled from AIMD. Re-solvating the same ensemble of "vertically desolvated" instantaneous spin probe configurations by EC-RISM embedding and subsequent computation of the HFCCs is shown to provide significantly better results compared to using CPCM embedding since only the former solvation model captures the inherent heterogeneity of the local solvation structure close to the spin probe. The HFCC thermal averages of HMI in water as obtained from the different computational methods are gauged against X-band continuous wave EPR measurements at ambient conditions.

Density Functional Embedding Scheme for Molecules and Periodic systems coupled with Wave Function Methods and Real Time-Time Dependent Density Functional Theory

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Abstract

An implementation of density functional embedding theory, within the frozen density embedding formalism [1], for molecules and periodic systems in the TURBOMOLE program package [2] using Gaussian basis functions is presented. The subsystem of interest may be described by density functional theory (DFT) or wave function theory (WFT) methods, while the environment density is determined using DFT. Employing an embedding potential based either on non-additive kinetic energy density functional or a level-shift projection operator [3], DFT-in-DFT or WFT-in-DFT is performed. While the embedding potential may be updated during the embedding procedure for DFT-in-DFT calculations, the WFT-in-DFT utilize a fixed embedding potential. The Coulomb contribution to the Kohn-Sham matrices of the subsystems as well as to the embedding potential is efficiently calculated using a combination of density fitting and continuous fast multipole methods [4].

Furthermore, the embedding scheme is coupled with a recent and highly efficient real time-time dependent DFT implementation [5] that allows for the study of the non-linear optical response of the embedded subsystem.

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Quantum-mechanical study of photochemical processes in Direct Laser Writing (DLW)

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Abstract

3D Direct Laser Wiring (DLW) technique based on two-photon Polymerization (TPP), initiated by the light of specific wavelength, is a powerful and versatile approach that allows for the fabrication of 3D complex functional materials on micro and nanoscale. New insights into further optimization of DLW by even better photoresists can be achieved through the study of properties and operation mechanisms of photoinitiators towards faster 3D printing. The Goal of my research is to increase sensitivity and solubility of photoinitiators via increase of their absorption characteristics. However, since there is a scarce knowledge about photophysical properties of different photoresists used in DLW, in my presentation I will focus on the explanation of photochemical processes upon multiphoton absorption and on hypothetical radical formation mechanisms. With the use of density functional theory (DFT) and time-dependent DFT I will investigate different photoinitiators, e.g.: 7-diethylamino-3-thenoylcoumarin (DETC), Irgacure 369 and Irgacure 651 that belong to different Norrish types PIs and are characterized by different mechanisms of radical generation with specific rates. I will therefore explain the fragmentation reactions of Norrish type I PIs by the cleavage of a C-C bond and I will demonstrate interplay of different photoactive processes (internal conversion, intersystem crossing, fluorescence, phosphorescence, absorption cross-sections of two-photon absorption) on the radical generation of Norrish type II PIs. Finally, I will compare the set of performed TD-DFT calculations to BSE/GW light absorption calculations and explain pros and cons of the use of both QM approaches for studying photoinitiators.

Theoretical evaluation of Vibrationally Promoted Electronic Resonance (VIPER) spectroscopy using two-photon excitation

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Abstract

In recent years, combined electronic-vibrational nonlinear spectroscopies have gained increased attention. In this context, the versatile Vibrationally Promoted Electronic Resonance (VIPER) experiment [1,2] allows electronic excitation with the selectivity of infrared (IR) spectroscopy and has been employed, e.g., to induce a selective cleavage of photolabile protecting groups (PPGs) [3]. Furthermore the introduction of two-photon (2P) excitation is desirable since it provides an intrinsic 3D resolution, a lower noise level, an increased penetration depth and minimized photodamage. This makes 2P excitation highly attractive for biological systems, among a wide range of possible applications [4]. In this work, we present theoretical simulations together with experimental results for 2P-VIPER measurements of the laser dye coumarin 6. Coumarin-based PPGs are widely used due to their favourable experimental properties [5]. In our theoretical investigation, vibrationally resolved electronic spectra including vibrational pre-excitation are computed using a development version of the FCclasses program [6], which is based on the efficient evaluation of Franck-Condon overlap integrals. Franck-Condon as well as Herzberg-Teller contributions are considered, which are compared with previously computed one-photon VIPER results [2]. Additionally, the role of interference terms in the total spectrum is evaluated in detail.



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Deciphering the Mechanism of Cobalt-Valine Catalyzed O-Arylation Reaction: A DFT study

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Abstract

O-arylation reactions represent a synthetically important class of reactions that are widely employed for the preparation of diaryl ethers. Cobalt catalyzed cross-coupling reactions are gaining importance owing to the low cost, mild reaction conditions, and high chemo selectivity. In the present work, a detailed computational investigation into the mechanism of the Co(II) catalyzed C-O cross-coupling of phenols with aryl iodides, is carried out for the first -time, using Density Functional Theory employing B3LYP-D3 functional augmented with CPCM solvation model using acetonitrile as the solvent. The Co and I atoms are described using (LANL2DZ) for the inner electrons and its associated double- ζ basis set for the outer electrons. The C, H, N, O, and Cl atoms were described by a 6-31+G(d) basis set. L-valine is the ancillary ligand used in this study. The active catalyst species is tetrahedral, L-valine ligated cobalt (II) phenoxide complex. The investigated O-arylation reaction proceeds through a σ – bond metathesis mechanism involving the concerted breaking of the Csp^2 – I bond and the formation of the Csp^2 – O bond proceeding through a four-centered transition state. Frontier Molecular Orbital (FMO) analysis was performed to investigate the effect of functional groups at the *para* position of the substrates. The substitution by electron-withdrawing groups (EWG) considerably decreases the energy of FMO's involved. Hence, the presence of EWG on aryl iodides tends to favor the reaction by reducing the LUMO energy while for the phenolic substrates, it tends to decrease the energy of the HOMO leading to an increased HOMO-LUMO gap.

Core-Level X-Ray Spectroscopies With Relativistic Hamiltonians: The Uranyl Ion Case

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Abstract

Actinides are broadly used in several fields of science and technology, among other as catalysts in chemical processes [1]. To characterize their behavior one often employs spectroscopic techniques, and among existing methods X-ray spectroscopy is particularly promising in the context of actinides given its great sensitivity and selectivity. With the introduction of advanced X-ray spectroscopy techniques and light sources in recent years, it has recently become possible to investigate different core states of uranium-containing complexes.

Analyzing such spectra requires theoretical models capable of describing the electronic structure of actinide species in the ground and excited states. This, in turn requires the use of approaches describing both electron correlation and relativistic effects.

In this work we showcase the use of the Core-Valence-Separated Equation-of-Motion Coupled-Cluster Singles and Doubles (CVS-EOM-CCSD) framework recently implemented in the DIRAC code [2,3] to investigate the core excited and ionized states of the uranyl ion (UO_2^{2+}) in the gas phase and at the crystalline environment of the dicesium uranyl tetrachloride (Cs₂UO₂Cl₄). For the latter, we combine the CVS-EOM-CCSD method with the Frozen Density Embedding (FDE) method [4].

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Current-induced chemical reaction dynamics in single-molecule junctions

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Abstract

Acquiring a comprehensive understanding of chemical reactions at molecule-metal interfaces is of decisive importance for designing functionalities of molecular electronic devices and for electrochemical catalysis. Based on the flux correlation function formalism, we present a mixed real and imaginary-time hierarchical equation of motion approach, which provides a numerically exact and unified description of equilibrium and non-equilibrium as well as slow and fast reaction dynamics at molecule-metal interfaces. The method is applied to a generic vibronic model which comprises a single electronic level and a reaction mode coupled to multiple fermionic leads. As a specific example, we investigate intramolecular proton transfer in a molecular junction over a broad range of parameters, ranging from off-resonant to resonant (i.e., low to high bias voltage) as well as nonadiabatic to adiabatic (i.e., weak to strong molecule-lead coupling) transport regimes. The obtained results reveal the influence of strong molecule-lead coupling on reaction dynamics.

Optimized Auxiliary Basis Sets for Long-Range Exchange Contributions using Cholesky Decomposition

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Abstract

The smooth separation of the Coulomb-operator using the error-function¹ has proven to be an important method to generate accurate properties using TDDFT. As a result, it is highly interesting to optimize the evaluation of long-range exchange contributions, as they are one of the computationally most demanding steps in the procedure. To accelerate this step it is possible to use the resolution of the identity (RI) formalism in combination with the RI-C basis sets. Taking into account which type of integrals are used to optimize these auxiliary basis sets and which type of integral they should represent it shows that they contain many contributions that are not needed and generate additional computational cost. In this contribution we present a way to generate optimized auxiliary basis sets to fit

long-range exchange contributions using the atomic Cholesky decomposition (aCD) technique.² These basis sets can be generated on-the-fly with minimal overhead for each element defined in a given basis set using a given range-separation factor. In addition we applied the method of natural auxiliary functions (NAFs)³ to the RI and to the aCD approach and compare the reduction in auxiliary basis set sizes and the resulting savings in computational cost.

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Reliable energetics of manganese spin crossover complexes with ab initio approaches

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Abstract

Abstract

Manganese SCO complexes form a small but ever expanding family of compounds with thermally accessible states of different electronic configuration and total spin.^[1] Accurate prediction of spin-state energetics is essential for the theoretical description of these systems. Even though considerable progress has been achieved in both density functional theory (DFT) and wavefunction theory methods, there is not yet a general-purpose protocol for the prediction of SCO properties of transition metal complexes.^[2]

In this work,^[3] we present a detailed study of spin-state energetics of a diverse set of Mn spin crossover complexes using the DLPNO-CCSD(T) method.^[4] We propose a robust and efficient computational protocol based on a combined and balanced mix of extrapolation to the complete basis set and infinite

pair natural orbital (PNO) space limits. The results are subsequently used to evaluate multireference wavefunction-based (CASSCF/NEVPT2) and DFT approaches, highlighting their inability to provide a balanced description of spin-state energetics for these complexes. The DLPNO-CCSD(T) protocol proposed in this study can serve as a generally applicable reference-quality quantum chemical method for studying spin crossover systems.

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Multiscale Simulation of the Reaction Centre Excitation in Photosystem II

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Abstract

Photosystem II is a multi-subunit pigment-protein complex that utilizes sunlight to trigger chargeseparation and catalyse water oxidation. The charge separation cascade is initiated in the reaction centre (RC), which is composed of six pigments (four Chlorophyll a and two Pheophytin a) arranged symmetrically along the D1 and D2 core poly-peptides. Biological evolution favoured productive electron transfer only along the D1 side with the precise nature of the initial excitation event(s) remaining under debate. In this work, ¹⁻² we employ multiscale quantum mechanics/molecular mechanics (QM/MM) coupled with high-level computations (full time-dependent density functional theory with rangeseparated functionals benchmarked against coupled cluster theory) to investigate the excited state profile of the RC. Our results describe for the first time at a fundamental electronic structure level precisely how differential protein electrostatics create the observed excitation asymmetry within the RC. By simultaneous quantum chemical treatment of multimeric pigment assemblies, we identify the critical pairs of RC pigments associated with low-lying charge-transfer states and we eventually propose a novel model to describe excitation of Photosystem II reaction centre based on two parallel charge-separation pathways, Among others, our new model explains the triggering of charge separation by direct absorption of far-red photons (700-800 nm), i.e. beyond the known "red-limit" (680 nm) of oxygenic photosynthesis.

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On the influence of molecular embedding on excited-state dynamics of an azodicarboxamide-based molecular switch

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Abstract

Molecular switches, which can be triggered by light to switch between two or more well-defined states differing in their chemical or physical properties, enable to spatially and temporally control by light of molecular processes. For the development of smart functional materials these photo-responsive molecular species are fundamental. A detailed insight into their light-induced motion and in particular the excited-state dynamics is fundamental for their molecular embedding and thus for their application.

Here, we present a hybrid quantum mechanics (CASPT2 and TDDFT)/molecular mechanics (QM/MM) study to elucidate the photodynamics of a novel molecular switch based on a light-triggerable azodicarboxamide unit. Due to its volume-conserving dynamics, this novel switching unit is a promising candidate for implementation in highly dense environments such as polymers.

We report a detailed picture of the molecular motion at the atomic level based on a relevant number of excited-state trajectories. We show that the azodicarboxamide-based molecular switch undergoes both a forward and backward pedalo-type motion upon excitation. Trans-cis photoisomerization on the other hand, which is well-known to occur for other azo-based chromophores, is shown to be a negligible pathway. Moreover, we investigate by atomistic simulations the influence of molecular embedding by comparing the excited-state dynamics in the gas-phase with the photo-induced motion in solvation. We show an impact on the conical intersections involved in the light-induced motion depending on the molecular embedding. By elucidating the volume-conserving pedalo-type motion, we provide a rational basis for the implementation of azodicarboxamide switchting units in functional materials.

Towards reliable doubly excited states with DFT/MRCI

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Abstract

Doubly excited states play an important role in many chemical, physical and biological processes such as singlet fission in photovoltaic devices [1] or photoisomerization in rhodopsins. [2] Experimentally these states are difficult to investigate because they are not easily observed in one-photon experiments. Theoretical approaches such as the often-used TD-DFT method cannot model double excitations while higher-level methods like CC3, CCSDT or CASPT2 are often only available for small molecules due to their computational cost. [3] The combined density functional theory and multireference configuration interaction (DFT/MRCI) [4,5] is a semiempirical approach initially developed by Grimme and Waletzke and further improved in our group. It is proven to be very accurate and useful to efficiently calculate singly excited states and their properties. We encountered, however, critical double excitation cases where DFT/MRCI vastly underestimates vertical excitation energies. Particularly affected are states in compounds like formaldehyde, nitromethane or dithiosuccinimide with significant Coulomb and exchange interactions that are caused by non-bonding orbitals. We present recent developments improving these cases.

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First-Principle Investigation of Fluorination Reactions in the Simons Process Mediated by Late Transition Metals

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Abstract

The main pathway towards fluorinated compounds is electrochemical fluorination (ECF), of which the Simons process is industrially the most important one. Its mechanism is not well understood and especially theoretical investigations are scarce.

The mechanism is believed to proceed via formation of Ni_XF_V films on the nickel anode. Simplest models

of such films are surfaces of NiF2 and NiF3, which were reported by our group.^{1,2} Among those we have

identified surfaces with high-valent Ni(IV) and $[F_2]^-$ moieties readily available to mediate fluorination reactions. We want to model fluorination of CO and CH₄. To start, we have investigated the adsorption of CO and CH₄ on the twice oxidised (001) surface of NiF₂, which we will present here. All the calculations were done by means of periodic DFT, with the PBE functional and added dispersion correction.

Furthermore, we are also investigating a possible replacement of the nickel anode with copper. We have started by investigation of the CuF_2 bulk structure, from which we have prepared models of its low Miller index surfaces, with the same computational set-up. With this we hope to gain more insight into why Ni works so well as an anode material and other late transition metals do not. Here we will present the results on structural and electronic properties of CuF_2 and stability of its various low Miller index surfaces.

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Development of a Force Field for Cellulose in Aqueous 1-Ethyl-3methylimidazolium Acetate

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Abstract

Cellulose is one of the most important bio-polymers and has a broad range of applications. Because of its poor solubility in most solvents, only a small percentage of cellulose can be further processed. Ionic liquids such as 1-ethyl-3-methylimidazolium acetate ([EMIm][OAc]) can dissolve cellulose,[1] but the reason for the solubility is still not fully understood. With the help of molecular dynamics (MD) simulations, it is possible to observe the solvation process on a molecular level. This can be realized by force field MD simulations instead of time consuming *ab initio* MD simulations (AIMD). Therefore, we developed the novel force field *BILFF* (**B***io-Polymers in lonic Liquids Force Field*) for [EMIm][OAc] with water [2] to reproduce radial, spatial, and combined distribution functions, hydrogen bond lifetimes, diffusion coefficients, and several other quantities from reference AIMD simulations. The force field is validated by comparison to experimental data such as density, bulk modulus and thermal expansion coefficients at different temperatures. The development of BILFF enables further considerations of interactions, concentration-related effects and the behavior of the system under external influences.



Figure 1: Radial distribution function of a hydrogen bond in [EMIm][OAc] calculated from AIMD (black) and force field MD with our new force field (red).

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A method for efficient calculation of nonlinear spectroscopic response for systems with relaxation

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Abstract

Time-resolved spectroscopy is a powerful tool for studying excited-state dynamics in various objects. A multitude of different experimental configurations allows to evaluate various dynamical characteristics of a system and produces a number of experimental methods including pump-probe spectroscopy, four-wave mixing techniques, and others. Interpretation of results of non-linear spectroscopic experiments is not straightforward and has to be performed via theoretical modeling. Most approaches to calculation of non-linear signal intensities use an interaction picture ansatz combined with the perturbation approach with respect to electric field intensity and a number of subsequent simplifications which rely on certain assumptions regarding the system parameters.

In this work an alternative approach to calculation of the nonlinear spectroscopic signal is presented. For a system with a constant relaxation tensor, an ansatz based on the tensor eigenvalues allows to derive a closed-form expression for the signal intensity in a system with any relation between the pulse duration, optical period and characteristic times of the system. This allows to avoid using the commonly used approximations such as the snapshot, slow envelope or rotating wave approximations. For two frequently used spectroscopic methods, namely pump-probe and three-pulse photon echo spectroscopy, the resulting closed-form expressions for the signal are provided explicitly with rotational averaging. Sample calculations of non-linear spectroscopic response in a natural light-harvesting complex are provided as an illustration.

Atomistic insight into the intermolecular interaction of solvated molecular motors and their collective structural properties in Metal-Organic Frameworks

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Abstract

Photo-responsive molecular motors enable to influence phenomena at the atomic scale with high precision as a response to light. To transfer their unique properties into designated functionality, their molecular embedding and implementation within functional materials are important to amplify their motions and to promote collective and cooperative behavior. Despite advances in the development of such photo-responsive functional materials, a thorough understanding of the governing molecular interactions is still limited. However, this is crucial for predictions and to rationally design such assembled machineries.

Here, we report an ab-initio parametrized and validated force fields, which accurately and efficiently describe structural and dynamic properties of molecular motors. These force fields are developed by employing a genetic algorithm-based protocol and further utilized to perform two atomistic studies.

On the one hand the intermolecular interaction of molecular motor with their solvation environment was investigated by conducting Molecular Dynamic simulations. The change on both the location of the primary interaction sites and the orientation of the solvent molecules was revealed by analyzing the solvation shells as a function of the motor state. On the other hand, atomistic simulations enabled us to decipher the interplay of molecular motors embedded in Metal-organic frameworks (MOFs). Our studies give an insight into the collective structural behavior and elucidate the impact of motor-motor interactions on the local and global properties of the motor-functionalized MOF.

Our results provide atomic insights into the potential to tune molecular processes by molecular motor, which is fundamental for the development of responsive functional materials.

The Class of Molecular Compounds H_n NOPS (n = 0, 2, 4)

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Abstract

The six elements oxygen, carbon, hydrogen, nitrogen, phosphorus and sulfur are the most abundant essential non-metals in the human body [1]. In space, some hundred different molecules have been detected that are made up of the same elements [2,3]. If carbon is excluded, the remaining five elements still form many molecular compounds, some of which are well known from planet Earth and from space, e.g. ammonia (NH₃), water (H₂O), phosphane (PH₃) and hydrogen sulfide (H₂S).

The class of molecular compounds mentioned in the title contains 42 members (phosphorus considered as trivalent, sulfur as divalent), of which 13 occur as pairs of stereoisomers. None of these compounds seems to be known from experiment, only one compound in the set (HS-P(OH)-NH2) plays a role as the parent compound for insecticides [4]. We report on results of a theoretical study on all 55 compounds [5]. Their molecular structures were fully optimized at the explicitly correlated coupled cluster level of theory (CCSD(T)-F12) and subsequently characterized via normal mode analysis [6]. Results of interest include typical as well as untypical bond lengths and the energetic sequence of the molecules in this set.

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r²SCAN-D4: Dispersion corrected meta-generalized gradient approximation for general chemical applications

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Abstract

We combine a regularized variant of the strongly constrained and appropriately normed semilocal density functional [] with the latest generation semi-classical London dispersion correction. The resulting density functional approximation r²SCAN-D4 has the speed of generalized gradient approximations while approaching the accuracy of hybrid functionals for general chemical applications.

We demonstrate its numerical robustness in real-life settings and benchmark molecular geometries, general main group and organo-metallic thermochemistry, as well as non-covalent interactions in supramolecular complexes and molecular crystals. Main group and transition metal bond lengths have errors of just 0.8%, which is competitive with hybrid functionals for main group molecules and outperforms them for transition metal complexes. The weighted mean absolute deviation (WTMAD2) on the large GMTKN55 database of chemical properties is exceptionally small at 7.5 kcal/mol. This also holds for metal organic reactions with an MAD of 3.3 kcal/mol. The versatile applicability to organic and metal-organic systems transfers to condensed systems, where lattice energies of molecular crystals are within chemical accuracy (errors <1 kcal/mol).

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Real time time-dependent density functional theory: A versatile tool for the simulation of spectroscopic experiments

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Abstract

Real time time-dependent density functional theory (RT-TDDFT) has become a standard tool for the simulation of the response of molecules with respect to electro-magnetic perturbations. In this contribution its application to various sorts of spectroscopic simulations is presented in a unified frame work. Results for UV-VIS absorption, electric circular dichroism as well as extensions to vibrational spectroscopy, in particular (resonance) Raman and (resonance) Raman optical activity spectra, are shown and challenges in practical simulations, such as gauge dependence and pseudo-potentials, are discussed.

Insights on the helical induction of dynamic helical cis-transoid poly((4carboxyphenyl)acetylene) by chiral amines using Density Functional Theory

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Abstract

Helical conformation plays an important role in biological functions, such as recognition, catalysis and structural support of superstructures. Synthetic helical polymers often have an associated inversion barrier and obtaining structural information of dynamic helical polymers requires advanced experimental techniques. Yashima et.al. showed that chiral amines can induce one-handed helical structure in stereoregular cis-transoid poly((4-carboxyphenyl)acetylene) (poly-1), showing intense bands of circular dichroism (CD) [1-3]. Helical models were created based on poly-1. Scan calculations over the dihedral backbone using density functional theory (DFT) on dimer of poly-1 backbone were performed to understand the helicity. From these results, Clockwise twist with value of 145 degrees (CW), and Counterclockwise twist with value of -145 degrees (CCW) for backbone dihedral were obtained. Dissociation energies were calculated using DFT in 4 monomer polymer-amine complexes using CW and CCW sense. The results obtained reveal a clear affinity trend showing that R and S amine conformations have a major affinity for CW and CCW, respectively. Bader charge analysis reveals important electronic local effects at the contact points between amines and polymer which gives an explanation for the affinity results.

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Robust Δ SCF calculations with direct energy functional minimization methods for molecules and materials using the mixed Gaussian and plane waves approach

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Abstract

The direct energy functional minimization method using the orbital transformation (OT) scheme in the program package CP2K has been explored for Δ SCF calculations with fractional occupations. This allows to exploit the Δ SCF method for various kind of molecules and periodic systems. Vertical excitation energies of molecular heteroaromatic systems and condensed phase systems, such as solvated ethylene and solvated uracil obeying periodic boundary conditions, are reported using the Δ SCF method. We also tested the robustness of for fractional-occupation OT for a Re-phosphate molecule attached to the surface of anatase (TiO₂). Additionally, we have implemented a recently proposed State-Targeted Energy Projection (STEP) algorithm (Carter-Fenk et al. JCTC, 2020, **16**, 8, 5067–5082) for diagonalization based SCF in CP2K. It is found that the OT scheme for fractional-occupation Δ SCF provides a smooth and robust SCF convergence for all investigated excitation energies and (non-)periodic systems.



Study of CO adsorption on silicon(100) surface with a combined approach of periodic slab calculations and wavefunction-in-DFT embedding

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Abstract

Traditionally, the simulation of photochemical reactions in adsorbate-semiconductor systems is possible by using periodic slab calculations or cluster models, that are typically embedded in a combination of effective core potentials and a point charge field. Furthermore, it is required to use multi configuration/multi reference methods, for example CASSCF, to model electronically excited states. However, the application of these methods is currently limited to embedded cluster models. Nevertheless, this approach shows some non negligible disadvantages: Due to high computational effort, only small clusters can be explored, so that it is only feasible to model low surface coverages. Additionally, the cluster size is often too small to obtain molecular orbitals that are band kind.

We address these drawbacks by applying a new wavefunction/DFT-in-DFT embedding scheme, which has been only used rarely for modeling adsorbate-semiconductor systems.

Periodic slab calculations serve as a basis for constructing large cluster systems, which allow the application of various wavefunction/DFT-in-DFT embeddings. The focus is on the application of CASSCF/NEVPT2 as a wavefunction method in the embedding scheme to compute electronically excited states. Furthermore, the description of the environment with a DFT method allows to model different surface coverages, which is a crucial step towards modeling real systems.

We present the asymmetric/symmetric CO adsorption on the silicon(100) surface as a model system. Our results show that different surface states play a significant role for the nontrivial adsorption, that are unknown yet.

A computational study of azulene and naphthalene on Si(001)

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Abstract

In material science, the Si(001) surface is highly investigated surfaces and is ideal for organic functionalization for its high reactivity caused by the buckled-dimer reconstruction.^[1] Nonalternant aromatics (like azulene) are intresting for surfarce functionalization due to its unusually properties.^[2] But up to now, no studies investigate azulene on Si(001).

We investigate the adsorption structure, adsorption dymanics and bonding character of azulene on Si(001) and alternating-aromatic isomer naphthalene. For that we are using a combination of density functional theory, ab initio molecular dymanics, reaction path sampling and energy decomposition analysis for extended systems.

Both azulene and naphthalene are chemisorbed on Si(001) and form four covalent C-Si bonds, whereby the interaction is stronger for azulene. The pEDA results confirm this and show a surface-to-molecule. The bonds can describe as donor-acceptor and as electron share bonding nearly equivalently. AIMD and NEB show direct absorption path for azulene. The path for naphthalene is pseudo directly with only one ring bonded precursor. Naphthalene probably has a narrow adsorption funnel, because it was very difficult for naphthalene to find the chemisorbed structures by optimization and AIMD.



Figure 1: Adsorption path for azulene (a) and naphthalene (b) from vacuum to Si(001).

Acknowledgements

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Ionization Energies and Redox Potentials of Hydrated Transition Metal Ions: Evaluation of Domain-Based Local Pair Natural Orbital Coupled Cluster Approaches

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Abstract

Hydrated transition metal ions are among the simplest prototypical systems that can be used to model properties in complex chemical environments. They have been employed for evaluating various quantum chemical methods for spin state energetics and redox properties. Yet, these seemingly simple systems continue to present challenges for computational chemistry. In this work, we explore the applicability of the domain-based pair natural orbital implementation of coupled cluster theory (DLPNO-CC) to the calculation of ionization energies and redox potentials for hydrated ions of the first transition row (3d) metals in selected oxidation states. In terms of defining the model, we address the question of balancing the construction of a minimally hydrated guantum cluster, combined with a continuum model. In terms of methodology, we explore the convergence of the coupled cluster expansion focusing particularly on the role of perturbative triples excitations, and additionally examine convergence with respect to the PNO space. Our recent implementation of the conductor-like polarizable continuum model (CPCM) for the DLPNO approach is employed to determine self-consistent redox potentials at the coupled cluster level. Our results establish conditions for convergence of the DLPNO-CCSD(T) energetics and stress the necessity of explicit consideration of the second solvation sphere even with CPCM. Finally, various multilevel/multilayer approaches are explored that combine a higher-level description of the first with a lower-level description of the second solvation sphere. Thus, we establish optimal methodological choices for employing DLPNO-based coupled cluster theory along with the CPCM implementation in complex explicitly solvated open-shell systems.

Benchmarking under uncertainty - Towards the prediction of polar organic reactivity

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Abstract

To understand chemical reactions and their mechanisms, insight into the reactivity of the involved species is crucial. The quantification of reactivity, its prediction and the rationale behind its trends. One

of the most significant works in this respect is that of Herbert Mayr and co-workers,^[1] who have proposed a simple relationship linking the decadic logarithm of the rate constant (log k) to three reactivity parameters. The group has also collected a vast amount of kinetic data from which such

parameters have been obtained for a limited chemical space. In this work, ^[2] we have reviewed said parameters as well as calculated probability distributions. With uncertainty propagation these can be used to obtain uncertainty estimates for log k. With these log k values and their associated uncertainties we can evaluate the accuracy of *ab initio* predictions for activation barriers over an extended chemical space. We dub this practice as benchmarking under uncertainty, whereby reactions which have so far not been measured can also be included. In order to illustrate this concept, the reactions of six nucleophiles with six electrophiles typical for Mayr's database of reactivity parameters have been used. Our results highlight the main components of the free energy which limit the accuracy of activation barrier computations.

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Automated exploration of reaction networks in chemical vapor deposition by density functional theory

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Abstract

Properties and quality of materials grown by chemical vapor deposition crucially depend on the reactivity of the employed precursor molecules. Gas phase studies exploring the decomposition of for example triethylgallane and tert-butylphosphine (TBP) already resulted in reaction networks spanning more than 60 elementary reactions. However, a proper model for the whole CVD process (Figure 1) must include the substrate surface. This additional level of complexity promotes the development of automated procedures.

Our MPI parallelized approach consists of three main steps: In a first step, the adsorption minima for the precursor of interest are calculated. This is achieved in a brute force manner by running a set of structural optimizations in which the molecule is systematically placed above the surface. In a second step all decomposition products are created: A distance criterium is used to identify bonded atoms in the precursor. By breaking and rearranging bonds, all decomposition products are formed. In a third step, reaction paths connecting individual structures are automatically selected and calculated. The reaction path optimization is done by a tailored and improved implementation of the nudged elastic band (NEB) method. Here, internal coordinates are exploited for the initial path interpolation. In addition, the NEB is carried out in a serial manner to prevent force evaluations for already converged regions of the reaction path. We applied our approach to model systems like GaH₃ and PH₃ on GaP(001) and to TBP on GaP(001).



Figure 1: Schematic overview of the elemental steps in the chemical vapor deposition.

Approximate versus Exact Embedding for Chiroptical Properties

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Abstract

We present a new implementation of linear-response properties from frozen-density embedding timedependent density-functional theory (FDE-TDDFT) in the subsystem program Serenity [1,2]. In particular, we investigate chiroptical properties such as optical-rotation parameters in the context of an *exact* variant of FDE-TDDFT which leverages projection-based embedding to reproduce supermolecular Kohn-Sham TDDFT reference results. We provide a detailed analysis of the approximations typically introduced in applications of FDE-TDDFT, namely (i) using non-additive kinetic-energy functionals instead of projection techniques, (ii) restricting the basis, for example by employing monomer instead of supermolecular basis sets, and (iii) neglecting inter-subsystem response couplings. Lastly, we apply this methodology to reinvestigate microsolvated (*P*)-dimethylallene, a system which was previously studied in an application of FDE for optical-rotation calculations [3]. We discuss the observed discrepancies between the subsystem and supermolecular calculations and demonstrate that the missing ingredient leading to these errors can be traced down to missing response couplings rather than an intrinsic weakness of FDE.



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The activation efficiency of mechanophores can be modulated by adjacent polymer composition

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Abstract

Mechanophores are small molecular subunits embedded in a polymer that respond to external forces via changes in their geometries (e.g. bond rupture), which is the working principle of many mechanochemical transformations. However, the activation of mechanophores competes with unspecific scission of the polymer chain. Hence, a better control over the force required to activate mechanophores is highly desirable, which necessitates an understanding of force transduction from the polymer to the mechanophore at the molecular level.

In this contribution, it is shown that the linker between the mechanophore and the polymer backbone determines the force required to activate the mechanophore. Using quantum chemical methods, it is demonstrated that the activation force of three mechanophores (Dewar benzene, benzocyclobutene and gem-dichlorocyclopropane) can be adjusted over a range of 300% by modifying the chemical composition of the linker. The results are discussed in terms of changes in electron density, strain distribution and structural parameters during the rupture process. Using these findings it is straightforward to either significantly enhance or reduce the activation rate of mechanophores in stress-responsive materials, depending on the desired use case. The methodology is applied to switch a one-step "gating" of a mechanochemical transformation to a two-step process.

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Insights into Reaction Kinetics in Confined Space: Real Time Observation of Water Formation under a Silica Cover

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Abstract

Using the combined powers of experiment and theory, we were able to explain the origin of a travelling reaction front, observed in real time with low energy electron microscopy. Combined insights from experiment, DFT simulations and kinetic modelling were able to show that the velocity with which the water-formation-reaction occurs on a ruthenium surface, confined by the presence of a 2D silica sheet, is controlled by diffusion mechanisms and not by the widely accepted transition state effect.

First-Shell Solvation and Counterion Effects in Homogeneous Reactions: a Reduced 9,10-Diboraanthracene-Catalyzed Hydroboration as a Case Study

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Abstract

The fast developing field of main group chemistry brings forth more and more molecules and compounds rivaling transition metals with respect to their catalytic activity. Whereas the reaction mechanisms of the latter are well understood for the most part, in the case of highly reactive main group element compounds the determination of the catalytic cycle can be challenging. Experimental data can hint at the course of the reaction, but unstable key intermediates oftentimes remain elusive.

In this work, we use density functional theory expanded by thermochemistry corrections to establish a method for environment modelling for thermodynamic calculations. It allowed us to investigate the hydroboration reaction via a reduced diboraanthracene derivative as a case study. Free energy calculations revealed, both implicit and explicit solvent is necessary to reproduce experimental data and to get a full picture of the energetic profile for this reaction, which was observed to be dependent on the counterions of the catalyst.

Finding new design principles of OLED emitters through theoretical investigations of Zn(II) carbene complexes

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Abstract

The interest in new OLED emitters has strongly increased in recent years. The field of theoretical chemistry can be an important factor in the search for new emitters, which can harvest singlet and triplet excitons. Therefore, especially complexes which show phosphorescence or thermally activated delayed fluorescence (TADF) are in demand. In order to obtain efficient TADF, fast (reverse) intersystem crossing ((r)ISC) and therefore a small S₁-T₁ energy gap and high spin-orbit coupling (SOC) are crucial. For Cu(I)-carbene complexes we found S₁ and T₁ states of ligand-to-ligand charge-transfer (LLCT) character with small metal-to-ligand charge-transfer (MLCT) contributions to be favorable for TADF whereas ligand-centered $\pi\pi^*$ states have to be avoided.[1]

In this work we present quantum chemical investigations of Zn(II) carbene complexes which have a d10 configuration as well. In search of new design criteria for TADF emitters, we chose carbene ligands with different s-donor and p-acceptor strengths and investigated their influence on the photophysical properties. In contrast to the Cu(I) complexes, no MLCT contributions to the excitations of the Zn(II) complexes can be expected. Instead, we found an increase of the SOC for complexes in which sulfur contributes to the electronic excitations. Thus, especially the Zn(II) complexes with a dithiophenol donor and a strong π -acceptor carbene ligand seem to be interesting as potential TADF emitters.

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Proton transfer in o-Nitrophenol: contrasting dynamics after core-ionization, valence ionization and electron excitation

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Abstract

Excited state transfers of proton and hydrogen or coupled-electron proton transfer belong among the fastest chemical reactions involving non-adiabatic transitions. In this work, we present our investigation of non-adiabatic dynamics of proton or hydrogen transfer in o-Nitrophenol, where the intramolecular proton transfer takes place from the hydroxyl group to the nitro group. We contrast this process in various energy ranges: the process can be initiated by core-ionization of the 1s electron of the oxygen atom, valence ionization of electrons in the HOMO-n state, and electron excitation into the strongly absorbing S_2 state. The potential energy surfaces were explored with multi-reference ab initio methods

and molecular dynamics simulations in corresponding states, which were performed in timescales relevant to the type of excitation. We have applied the Landau-Zener surface hopping scheme to account for the non-adiabatic transitions. For the core-ionized state, we observed fast proton transfer to be completed in around 15 fs. For the excited S_2 state, the transfer is again ultrafast, with a lifetime of

60 fs. The proton transfer upon the valence ionization represents only a minor channel as the least bound electrons are located on the aromatic ring. We discuss the possible experimental relevance of the present system for studies of nuclear dynamics coupled with electronic decay.

Learning Conductance - Machine Learning Approaches for Molecular Electronics

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Abstract

Experimental studies of the charge transport through molecules rely mostly on scanning-tunneling or mechanically-controlled break-junctions experiments¹. In the latter, a molecular junction is formed and broken repeatedly while measuring the charge transport, resulting in many conductance traces for different conformations, elongations, and possibly different number of molecules in the junction².

This experimental situation is a challenge for theoretical studies. On the one hand, the structural evolution of the junction has to be modeled (which can be tackled using molecular dynamics), on the

other hand, transport calculations have to be performed for a multitude of geometries³. This poses limits on the cost of the quantum chemical approach to calculate the transport properties.

Using machine learning techniques such as Gaussian process regression and active-learning approaches, we aim to overcome these limitations in order to harness the power of more expensive quantum chemical calculations or ways to model charge transport. Additionally, we explore properties of the structural evolution of the simulated break-junctions and their relationship to the charge transport properties.



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Design of Metal-Organic Frameworks for Flue Gas Capture

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Abstract

Sulphur dioxide is a main component of flue gas, a consequence of thermal combustion in many industrial processes. Although modern desulfurization procedures significantly reduce the amount of this toxic and polluting agent, ca. 40-450 ppm SO₂ remain in the filtered and cooled flue gas. Removal of this residual is a challenging task. The material must not only adsorb SO₂ at very low partial pressures and temperatures, it also has to withstand the aggressive mixture of SO₂, H₂O and other compounds. Metal-organic frameworks are a rapid developing class of new materials that can be specifically tailored for this function. They consist of a metal center and an organic linker, forming regular networks with defined pores or channels, where molecules can be adsorbed. In this study, we investigate together with experimentalists the SO₂ adsorption properties of MIL-53 [1], DMOF [2] and other compounds with a combination of DFT-plane-wave and Monte-Carlo simulations. We show that computational modelling can be used as an efficient tool to design pore size, low pressure adsorption and MOF-stability.

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Anharmonic CCSD(T) Vibrational Frequencies for a Set of Molecular Dimers

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Abstract

Accurate vibrational frequencies are crucial for the modeling of vibrational spectra and the calculation of Gibbs/Helmholtz free energies. The anharmonic nature of individual normal modes as well as the coupling between modes can be captured by second-order vibrational perturbation theory (VPT2) [1,2]. While this approach is mostly used to describe rigid or semi-rigid isolated molecules, Howard et al. [3] have for instance shown that VPT2 calculations utilizing CCSD(T) yield also very good results for the water dimer and the HF dimer.

Herein, we explore the quality of VPT2 calculations for intermolecular interactions utilizing a diverse set of small molecular dimers, which are held together by dispersion interactions alone or also by intermolecular hydrogen bonds. To accurately capture all intermolecular interactions, CCSD(T) was utilized throughout. Our VPT2 results are compared with available experimental data or high-level calculations of potential-energy surfaces. One problematic issue are large-amplitude motions [2] (e.g., inter-/intramolecular rotations), which can in a first approximation be decoupled from the other modes and described by a one-dimensional model system. Furthermore, we also discuss the accuracy of a simpler approach utilizing Morse oscillators. Later on, this CCSD(T) dataset can be used as reference data to benchmark the quality of density-functional approximations for intermolecular vibrations.

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Influence of Chiral Initiators on the Secondary Structure of Aib-Peptides in Electronic CD Spectra

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Abstract

Electronic circular dichroism (ECD) spectra are often used for structural analysis, especially for polymers. They show the deviations in absorption for excitations with differently circular polarized light. For an effect to occur a chiral property is needed, which for the achiral Aib-peptide is the secondary structure. Multiple time-dependant (td) DFT methods were used to calculate the ECD spectra of different initiator-Aib molecules in several secondary structures. The importance of various parameters in the td-DFT calculations was tested. An influence of the initiator's chirality, as well as the peptide's secondary structure was found.

Calculation of the excitation spectra of tetraphenyldibenzoperiflanthene (DBP) in vacuum and on hexagonal boron nitride (h-BN).

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Abstract

In this work, the excitation spectrum of tetraphenyldibenzoperiflanthene (DBP) in vacuum was calculated and the results were compared with experimental data. Hexagonal boron nitride is used to decouple organic molecules like DBP from metal surfaces. To investigate the influence of h-BN on such an organic molecule, the geometry of DBP on h-BN was optimized using a periodic calculation. For this purpose, benzene on h-BN was used as a model system to evaluate different methods and levels of theory.

DFT Study on the Phase transformation mechanism in silica bilayer films.

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Abstract

Silica, in its crystalline and glassy forms, is of immense technological importance, with applications ranging from integrated circuits to supports for heterogeneous catalysis. A detailed understanding of the silica structure and its crystal-vitreous phase transformation is therefore of utmost importance. Experimental studies have reported the observation of the transformation of a 5-7-5-7 to a 6-6-6-6 Si-O-Si ring system in a crystalline bilayer silica [1]. In addition, apparent activation energies for a crystalline to vitreous transformation were obtained in UHV and O₂ atmosphere for a silica bilayer supported on Ru(0001) system [2]. In this work, DFT calculations were performed to investigate the formation mechanism of Stone-Wales type defect starting from a perfectly hexagonal silica bilayer structure. The process found shows a complex formation mechanism, in which the two layers exhibit decoupled behavior in terms of chemical bond rearrangements [3]. Charge density analysis is used to rationalize the influence of the metal support and to investigate the effect of interfacial O/Ru(0001) on the energetics of the transformation. [1] P. Y. Huang, S. Kurasch, J. S. Alden, A. Shekhawat, A. A. Alemi, P. L. McEuen, J. P. Sethna, U. Kaiser, D. A. Muller, Science 342, 224 (2013). [2] H. W. Klemm, PhD Thesis, TU Berlin (2018). [3] H. W. Klemm, M. J. Prieto, F. Xiong, G. B. Hassine, M. Heyde, D. Menzel, M. Sierka, T. Schmidt, H. J. Freund, Angew. Chem. Int. Ed. 59, 10587 (2020).

Time-Resolved X-ray Absorption Spectroscopy of Pyrazine at the Nitrogen Kedge: On the Validity of the Lorentzian Limit

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Abstract

Ultrafast X-ray absorption spectroscopy offers a valuable tool for studying electronic and structural configurations of molecular systems. Due to the complex nature of the underlying processes when probing structural dynamics on the femtosecond timescale detailed theoretical studies are required to unravel the high information content and to link the spectroscopic observables with the underlying structure and dynamics. For this purpose a time-dependent theoretical framework is needed that is able to describe non-adiabatic phenomena. While effects of nuclear motion on valence-excited states are generally included when simulating transient X-ray absorption spectroscopy, the dynamics on coreexcited states is often neglected substantiated by the very short core-hole lifetime. In this work, we calculate time-resolved X-ray absorption spectra of pyrazine at the nitrogen K-edge including any motional effect coming from both, valence- and core-excited state dynamics. We investigate the influence of the core-hole lifetime on the resulting spectra and demonstrate the consequences of the short-time approximation. While the photoinduced dynamical processes are well monitored when neglecting nuclear dynamics after X-ray probe excitation, the transient X-ray absoprtion spectra lack vibronical structure. We further demonstate the impact of an explicit description of the external electric field and show that when the pump excitation pulses are long compared to the nuclear dynamics, blurring effects occur making the probe response effectively time-independent.

Charge-Transfer States in Solution: A Protocol for Predicting Singlet-Triplet Gaps of TADF Emitters within Chemical Accuracy by Mean-Field Calculations

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Abstract



The adiabatic energy gap between the lowest singlet and triplet excited states ΔE_{ST} is a fundamental property for organic electronics, e.g., for thermally-activated delayed-fluorescence (TADF) emitters. However, since the photophysics of many electroluminescent materials involve charge-transfer (CT) states, the poor performance of time-dependent density functional theory (TD-DFT) for CT states and a lack of accurate excited-state solvation models, severely limit the accuracy and reliability of computational predictions.

We present an alternative way to calculate ΔE_{ST} using a state-specific (spin-restricted) open-shell Kohn-Sham (UKS/ROKS) self-consistent field (SCF) approach as implemented in the Q-Chem program, which naturally includes excited-state orbital-relaxation effects and consistently accounts for dielectric stabilization by the molecular environment through a polarizable-continuum model. Tests on a representative benchmark set of 27 TADF emitters with reliable experimental ΔE_{ST} data revealed an extraordinary performance with a mean absolute deviation of only 0.022 eV – less than half of chemical accuracy (0.05 eV) and few deviations >0.05 eV, also for electronically challenging cases. Due to the compact split-valence basis set, the protocol is routinely applicable to large molecules (>150 atoms) and achieves a robust convergence to the lowest excited state in almost all cases.

Photoelectron Differential Cross Sections - Comparison of Approximate Methods

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Abstract

Energy and angle resolved photoelectron spectra of molecules give direct information on the wave function of the emitting molecule. More specifically, following a number of approximations, a connection to the emitting orbital can be made. We show the ranges of validities on these approximations and visualize the changes in photoelectron cross sections for different typical approximations to the calculation.

The continuum wave function for the photoelectron was approximated for all calculations as a plane wave. Additionally, we constrain ourselves to one-photon transitions using Fermi's golden rule. For the bound state, the applicability of the orbital approximation as a special case of the Dyson orbital approximation to describe the transition is of particular interest. Additional approximations are typically made to the interaction operator, which is often taken to be just the electric dipole operator. We show the influence of going beyond the electric dipole approximation, to the full single-photon vector potential. Lastly, different initial and final bound states can lead to the same emitting orbital. We show exemplarily the resulting changes in differential cross section for a selection of single-determinant wave functions.

Neural Network Potentials for Vibrational Frequencies of Molecular Systems

<u>Dilshana Shanavas Rasheeda</u>, Petr Melichar, Jörg Behler University of Göttingen, Göttingen, Germany

Abstract

The study of vibrational frequencies of molecular systems is an active field of research. Benchmarking vibrational frequencies with theoretical approaches is a challenging work. The quality of computed vibrational frequencies depends on electronic structure methods and also the treatment of anharmonicity.

The molecular systems involved here are the formic acid monomer and dimer, respectively. The aim is to see how accurate High Dimensional Neural Network Potential (HDNNP) can be for these systems starting from simple systems like the isolated monomer and dimer up to complexes with several N2 molecules. It also aims to see how well HDNNP can describe the trends in fundamental frequencies of these molecular systems. The project attempts to reach that accuracy of high level wavefunction based methods using a HDNNP. The construction of a high accuracy PES which describes vibrations well can greatly increase time efficiency for describing dynamical processes.

Excited State Properties of Molecular Ions in a Broken-Symmetry Maximum Overlap Self-Consistent-Field Approach

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Abstract

A theoretical prediction of molecular properties of excited states typically requires an explicit treatment of electronic densities of each state, especially for processes that do not involve the corresponding ground state, and often the calculation of potential energy hypersurfaces or energy derivatives with respect to displacements of the nuclei. Molecular ions can complicate these calculations due to spatially compact wavefunctions and (avoided) crossings of potential energy curves.

To compute a suitable description of excited states, one usually relies on time-dependent (TD) density functional theory (DFT), time dependent Hartree-Fock (HF) or CI/CC methods. In this contribution, excited states of small molecular (highly) charged ions containing heavy elements are investigated. Therefore, relativistic effects become an important factor. Computationally, a two-component zeroth order regular approximation (ZORA) complex generalized HF (cGHF) and complex generalized Kohn-Sham (cGKS) DFT in combination with the maximum overlap approach was used in order to obtain the excited states. Within ZORA, various properties of the individual states can be obtained efficiently.

"A DFT study on tetracoordinated homo/heteroleptic copper (I) complexes with photoredox properties"

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Abstract

In recent years, visible-light photoredox catalysis has become a practical tool for driving energyintensive chemical reactions. The introduction of transition metal photoredox catalysts (TMPRCs) is considered as an effective tool to achieve this goal. Traditional octahedral complexes of ruthenium and iridium dominate the field of photoredox catalysis, due to their exceptional photoelectrochemical properties. Nevertheless, both Ru and Ir are in short supply and too expensive to support sustainable technologies.

To meet this challenge, luminescent Cu(I) complexes are considered as one of the most plausible candidates to replace the traditional Ru and Ir photoredox catalysts in the near future. One of the

important characteristics of the Cu(I) complexes is that they have a suitable d^{10} electronic configuration

in the ground state which prevents the population of non-emissive ³MC states, which is very common in the second and third rows of transition metals and increases the lifetime in the excited state ³MLCT, thus allowing effective redox transformations. In the ground state they present a pseudo-tetrahedral geometry, after photoexcitation an electron is promoted generating an excited state, in which the metal

undergoes an oxidation to Cu(II) with electronic configuration d⁹. A charge transfer MLCT (from metal to ligand) occurs, where the distortion of the metal center adopting a pseudo-square planar geometry takes place influencing the non-radiative deactivation pathways. This structural reorganization results in the reduction of the excited species lifetime and quantum yield together with the bimolecular quenching of the excited state. The research is performed employing both conceptual and computational approaches through DFT.
Novel Application of Game Theory to Machine Learning Unlocks New Potentials

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Abstract

In addition to mechanistic QSAR models, models based on statistical learning have seen a surge in popularity in the field of predictive chemistry. The latter, referred to as "machine learning", have been of particular interest in areas where traditional methods are either insufficient or computationally prohibitive. Predictive chemistry by means of such models has always been considered to be a "black box": despite excellent predictive power, the models themselves are opaque to mathematical or theoretical scrutiny. [1]

Here, we present the implementation of a novel framework that promises to resolve this issue. First, a state-of-the-art XGBoost model is used to derive a traditional "black box" prediction. Next, the Shapley Additive Explanations (SHAP) method applies linear optimization methods from game theory to predict, on a case-wise basis, the log-likelihood effect of each predictor/input variable with respect to the original prediction. This produces a case-wise effect matrix that is additive with respect to the original prediction [2]. This method is applied to a predictive chemistry task, whereby structure-based chemical representations are used to predict biotoxicity. The benchmark ClinTox dataset, which includes 1491 labelled compounds, is used [3].

In addition to state-of-the-art predictive power, we demonstrate the degree to which the explanatory, "effect matrix", can be used to diagnostically assess the chemical mechanisms implied by the model. This effort provides for improved synergies between theory and data-science and greatly enhances the chemists toolkit.

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Deriving a robust atomistic model of light-harvesting antennae in biological Chlorosomes

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Abstract

The chlorosomes of green sulfur bacteria are a uniquely efficient example of natural light-harvesting systems, containing tubular or lamellar antennae aggregates that accommodate densely packed bacteriochlorophyll (BChI) *c*, *d*, *e* molecules. While several other biological light-harvesting antennae systems have been characterized in great detail by X-ray diffraction, this has not been successful for chlorosomes. A detailed atomistic model of the antennae aggregates is desirable, as it delivers crucial information for understanding their functionality. So far all work has been based on hypothetic molecular models that have been derived from *in-silico* modeling.^[1] However, potential

energy surfaces of aggregates bear high complexity, allowing also formation of kinetically trapped

configurations.^[2] Spectroscopy experiments can deliver indirect information about structural features in molecular aggregates, but for systems bearing high architectural complexity, the recorded signals are not straightforwardly interpretable. In recent work, we have developed a *rigid-function optimization* technique, that enables a direct translation of the spectral information obtained from polarization-resolved fluorescence spectroscopy experiments into structural packing arrangements based on accurate quantum chemical calculations, making use of the fact that the collective transition dipole moment can be interpreted as a result of the addition of the individual monomer transition dipole

moments, modulated by their quantum mechanical amplitudes.^[3] Our simulations gave rise to an unprecedented packing motif that is fundamentally different from those considered so far for the natural systems. In our ongoing work, we advance these technique in order to derive a new atomistic picture for structure and function of antenna aggregates in biological Chlorosomes.

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Surprisingly high adsorption affinities of poly(heptazine imide) salts for helium and water induced by charge separation

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Abstract

The potassium salt of poly heptazine imide (K-PHI) is a promising photocatalyst for various chemical reactions. The structural constellation of the material leads to a charge separation between the 2D

anionic PHI framework and the intercalated K^+ cations. This results in an interesting adsorption environment for polar as well as for otherwise non-adsorbing, non-polar gas molecules. Here, structures and adsorption energies of different molecules are studied by DFT structure optimizations. The energy decomposition analysis based on absolutely localized molecular orbitals (ALMO-EDA) demonstrates that charge transfer and polarization are significant for the remarkably high adsorption energies of helium (-4.6 kJ/mol) and water (-95 kJ/mol) on this system. Exchanging the potassium with bigger cations such

as Cs⁺ potentially even further increases the adsorption affinity.

Structure prediction calculations of carbon nitride polymorphs with CN₂ stoichiometry

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Abstract

Carbon nitrides exhibit versatile properties interesting for sustainable energy applications, such as water splitting, visible-light sensitivity and catalytic activity, while being chemical robust and available at low cost.

With our work we aim to find new, thermodynamic- and kinetically stable Polymorphs with $x-CN_2$ stoichiometry, hoping for the high nitrogen content to enhance the photocatalytic performance compared to graphitic carbon nitride (g-C₃N₄).

The minima-hopping method, based on density-functional tight-binding (DFTB), was used initially to sample the potential energy landscape of CN₂. The obtained structures were further equilibrated and evaluated with DFT-PBE and sorted according to their total energy.

Spin-crossover iron complexes in excited electronic states: a challenge for theory

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Abstract

Transition metal complexes nowadays play an essential role as photosensitizers, photoemitters, and dyes. Iron compounds and especially iron spin-crossover complexes represent a convenient alternative to extensively studied noble metal complexes. However, before going to real applications, a profound mechanistic studies of excited states structure and photoinduced dynamics as well as of the influence of ligands' chemical derivation on excited state ordering should be performed. To this end, high-level theoretical studies are required in combination with ultrafast spectroscopic studies.

In this work, we analyze the capabilities and caveats of optimally-tuned long-range corrected density functional theory for modeling the ground and excited-state properties of a series of iron(II) spincrossover complexes. The choice of the main theoretical approach in the current study is motivated by an objective to accurately describe long-range metal-to-ligand charge-transfer (MLCT) states, which are crucial for creating long-living excited states involved in further photocatalytic reactions. However, for reliable prediction of excited-states dynamics in this class of systems, a balanced description of MCLT and metal-centered (MC) is warrant. The ordering and character of singlet and triplet excited states are shown to be very sensitive to the applied computational scheme as compared to the reference CASPT2 calculations. The elaborated computational protocol was used to assign absorption spectra, electrochemical measurements, including experiments with extended ligand systems, as well as the analysis of peculiarities of potential energy surfaces in excited electronic states.

Disordered protein NMR chemical shifts from fragment-based quantum chemical calculations

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Abstract

Prediction of chemical shifts facilitates the construction of structural ensembles that best represent the experimentally measured NMR data of intrinsically disordered proteins (IDPs). Structural characterization of IDPs thus requires both NMR experiment and computational techniques. Fast semi-empirical prediction tools proved extremely useful but their functionality is limited to proteins with standard residues only. Extension to proteins with post-translationally modified amino acids such as phosphorylated residues is hardly possible.

Quantum chemical (QM) calculations are an appealing alternative to the semi-empirical predictions. However, the high flexibility of IDPs requires the QM calculations to be combined with molecular dynamics (MD) simulations.The multiscale computational approach inevitably accumulates errors from the various modelling levels involved. We combine classical MD simulation and density functional (DFT) methods along with fragmentation techniques to tackle the large system size. In oarticular, our fragmentation is based on the adjustable density matrix assembler.

In our poster contribution, we will demonstrate the effects of statistical averaging, structural ensemble size as well as the effects of a basis set. Our results prove that good to great quantitative agreement with experiment is achieved for all nuclei provided that the systematic error is balanced by the choice of a suitable NMR standard. We show limitations of the combined computational approach and analyze errors that affect the accuracy of the computational scheme.

Photoelectron cross sections without Fermi's Golden Rule

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Abstract

Molecular photoelectron spectra are commonly obtained theoretically in Fermi's Golden Rule framework, where the continuum wave function is often approximated by the slowly converging partial wave expansion.

On the poster, we present an alternative approach to address the photoionization cross section. Therein, the photoelectron wave function is represented as an

outgoing wave with the Dyson orbital as a source. With this, one arrives at the intuitive interpretation of photoionization and avoids employing long expansion series since the continuum solution is unique. While we expect this methodology to be particularly beneficial in the case of

complexly shaped and delocalized Dyson orbitals, we present here results on atomic and molecular systems to demonstrate its properties.

Accurate Thermochemistry and Structures from Second Order PerturbationTheory: The OO-REMP Hybrid Perturbation Theory

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Abstract

We present an open shell generalization and an orbital optimized variant of the REMP hybrid perturbation theory that reproduces non-multireference atomization

energies with a mean absolute deviation of 1 kcalmol⁻¹[1]. The underlying

REMP approach emerges as a constrained mixture of the unperturbed Hamiltonians $H^{(0)}$ of the Møller-Plesset perturbation theory (MP) and the "Retaining the Excitation Degree Perturbation Theory" (RE) as

 $H^{(0)}_{REMP} = (1 - A) H^{(0)}_{RE} + A H^{(0)}_{MP}$

REMP builds on complementary errors in the parent methods and results in a systematic internal error compensation leading to an improvement upon both parent methods.

Analogous to OO-MP2 and OO-CEPA(0), an orbital-optimized variant termed OO-REMP was implemented and benchmarked. Orbital optimization is achieved by minimizing the second order energy functional

 $E^{(2)}_{REMP}$ w.r.t. amplitudes and orbital coefficients of the single-determinantal reference wavefunction.

OO-REMP systematically outperforms the parent methods OO-MP2 and OO-RE as well as REMP based on canonical orbitals. For both closed and open shell thermochemistry

benchmark sets, mean absolute deviations below 1 kcalmol⁻¹ are achieved. Equilibrium bond lengths for closed- and open shell molecules are predicted with mean absolute errors of about 0.3 pm. In general, the performance of OO-REMP is near to that of CCSD(T)

while having a more favorable formal computational scaling. It will be shown

that regardless of the considered property, a REMP mixing parameter of $A \approx 0.25$ represents a reliable and robust choice.

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Deciphering beryllium and boron chemistry through multireference and valence bond calculations

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Abstract

The past few years have witnessed significant advances in low-valent, main-group chemistry. Indeed, by the use of appropriate Lewis base ligands, such as N-heterocyclic carbenes (NHCs) and cyclic (alkyl) (amino) carbenes (CAACs), highly reactive molecules featuring s- and p-block elements with completely new structural motifs and bonding schemes can be stabilized and experimentally prepared. Given their peculiar electronic structures, single reference methods are often not suitable for properly describing these systems computationally. In this work, we apply multireference and modern valence bond methods to investigate the ground and excited state properties of low-valent beryllium- and boron-based molecules, biradicals, and biradicaloids. Particular attention is given to base-stabilized borylenes and bisboranes, boron-doped polycyclic aromatic backbones, molecules featuring boron-boron multiple bonds, and the neutral and dianionic CAAC-stabilized beryllole ring.