Ab Initio Theory
From Molecules to Materials

July 29-31, 2025 Peking University

Workshop Handbook

Organizer

Institute of Theoretical and Computational Chemistry,
College of Chemistry and Molecular Engineering, Peking University

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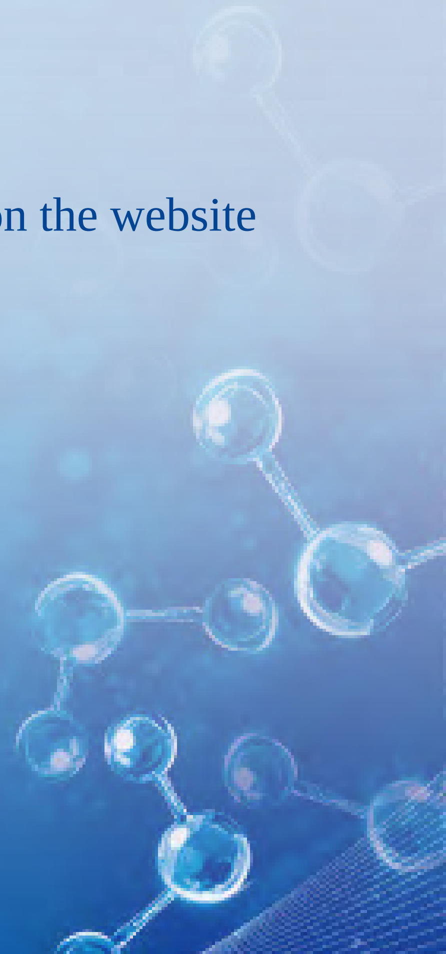

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Program

July 29th

Time	Speaker	Title	Chair
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17:00-17:30	Shichao Sun	Direct Probe of Conical Intersection Photochemistry by Time-Resolved X-ray Magnetic Circular Dichroism	
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5	Tai Wang	Spin-flip TDDFT from Zero Excitation Energy Theorem
6	Ye Li	Localized Orbital Scaling Correction to Linear-response Time-dependent Density Functional Approximations
7	Zixuan Wang	Testing exact-factorization-based density functional approximation on a continuous density model
8	Haoyu Qi	On the Validity of Allen-Heine-Cardona Theory in Molecular Systems
9	Zhebin Guan	Multi-Reference Density Matrix Embedding Theory for Local Excitations
10	Yuqi Wang	A diagrammatical multi-reference perturbation theory
11	Bohan Zhang	MRCCPT: beyond N-electron valence state perturbation theory by coupled-cluster type resummation
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14	Shun Li	Single-Reference Methods Based on Complex Orbitals in Electronic Structure Calculations
15	Xun Wu	The Development of Valence Bond Methods and Algorithm
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18	Baihua Wu	Nonadiabatic Field on Quantum Phase Space
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21	Wenjie Dou	Stochastic Resolution of Identity Approach to the Coupled Cluster Theory for the Excited States of Very Large Systems
22	Chongxiao Zhao	Stochastic resolution of identity to CC2 for large systems
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Useful Information

• Registration Desk

28 July, 2025	14:00-20:00
29-31 July, 2025	8:30-12:00, 14:00-17:00

• Name Badges

During the Workshop, please wear your badges at all times. The badge is your entrance ticket to the chemistry department and the workshop hall.

• Lecture Hall

C101 'XiaoLun' Lecture Hall, Building C, College of Chemistry and Molecular Engineering, Peking University

• Dining Hall (Lunch and Banquet)

Heyuan Theme Restaurant (located on the first floor of Building 5, Zhongguanyuan Global Village PKU)

Note: Please show your meal voucher for dining.

• Posters

Basement Level 2, Building C, College of Chemistry and Molecular Engineering, Peking University.

Note 1: The Poster Session will take place from 16:30 to 18:00 on July 29th.
Note 2: Please remove your poster by 19:00 on July 31st.
Note 3: The poster awards will be announced during the closing ceremony on July 31st.

Abstract

Strong Correlation, Symmetry Breaking, and Self-Interaction Correction in Density Functional Theory: Hidden Connections?[a]

John P. Perdew
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Unlike normal correlation, strong correlation arises when more than one electronic configuration gets a heavy weight in the expansion of the many-electron wavefunction, due to degeneracy or near degeneracy of configurations. Breaking the symmetry can break the degeneracy and restore the normal correlation that density functional approximations to the exchange-correlation energy are able to describe. While this happens commonly in solids (where symmetry breaking is observable) and even in molecules, it is unreliable with standard functionals. Can we make it more reliable by making standard functionals more reliable for normal correlation?

Almost all widely used functionals make self-interaction errors, i.e., they are not exact for all one-electron densities. Since one-electron densities are by definition normally correlated, removing the self-interaction error in one- and two-electron regions without losing accuracy in many-electron regions should improve the description of normal correlation. Such self-interaction correction can also promote symmetry breaking. What’s more, the extreme limit of symmetry breaking is the classical limit, in which any self-interaction corrected functional is exact, because the electron density condenses into localized one-electron blobs that interact only with other such blobs, not with themselves. The development of a reliable self-interaction correction to a meta-GGA like SCAN should tell us if symmetry breaking can reliably describe strong correlation.

This is possible evidence for the preceding sentence: In the strongly correlated singlet ground state of the carbon dimer, three semi-local approximations break the singlet spin symmetry, but only the SCAN meta-GGA , the only one that is accurate for normally correlated sp molecules, describes the correct atomization energy and singlet-triplet excitation energy via symmetry breaking[b]

[a] Supported by DOE DE-SC0018331 and NSF DMR-2426275

[b] J.P. Perdew, S.T.U.R. Chowdhury, C. Shahi, A.D. Kaplan, D. Song, and E. Bylaska, Symmetry Breaking with the SCAN Density Functional Describes Strong Correlation in the Singlet Carbon Dimer, J. Phys. Chem. A 127, 384 (2023)

Development in Density Functional Approximations and Theory for Excited States

Weitao Yang

Department of Chemistry, Duke University, Durham, NC, United States

The accuracy of DFT predictions hinges on the quality of density functional approximations (DFAs). Despite advancements, significant delocalization errors persist, leading to underestimating energy gaps in molecules and materials, incorrectly predicting the dissociation limits of chemical bonds, overdelocalizing charge distributions, and misaligning energy levels at interfaces. These errors stem from the violation of exact conditions on fractional charges, which are consequences of quantum mechanical degeneracy manifested in the classical variable of electron density. Our recent development of the localized orbital scaling correction (LOSC) addresses these errors and elevates DFT to a new level of robustness and accuracy. We will present results for molecules and bulk systems.

The orbital energies from our LOSC calculations reveal hidden excited state information from ground calculations, guiding us to the theory for excited states. Parallelly in terms of total energies, since the 1970s, Kohn-Sham functionals have been employed for ΔSCF calculations of excited state energies, achieving accuracy comparable to that for ground state results, despite a lack of theoretical justification. Our recent research has established the theoretical foundation for ΔSCF calculations of excited states, showing that it is necessary to go beyond electron density and use the first-order density matrix of the noninteracting reference system to define the energy functional. The minimum of this functional corresponds to the ground state energy, consistent with ground state DFT, while the stationary solutions yield excited-state energies and electron densities, consistent with ΔSCF calculations. We also established the linear conditions for fractional charges in the excited state theory and introduced the concepts of excited state chemical potentials. This in turn leads to the clear physical meaning of occupied and virtual orbitals energies as excited state chemical potentials.

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Solving the band gap and optical absorption problems of density functional theory

Leeor Kronik

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Density functional theory (DFT) has struggled, often even qualitatively, in the description of electron and optical spectroscopy. Specifically, the band gap of semiconductors and insulators has been thought to be outside the reach of DFT even in principle, and the associated optical absorption spectrum outside the reach of time-dependent DFT with standard approximate functionals. Charge transfer excitations have also presented significant difficulties in both molecular and solid-state systems.

Here, a novel approach to overcoming these difficulties, involving Wannier-localization based optimal tuning of a screened range-separated hybrid functional, is presented. It is shown that quantitative accuracy for a wide range of systems, from molecules to 3d and 2d materials, is achieved without any empiricism. This opens the door to many DFT-based true predictions of electronic and optical properties, to high-throughput calculations, and to a systematic choice of the starting point for many-body perturbation theory calculations.

Is Density Functional Theory the Basis of Density Functional Approximations?

Anthony Scemama
CNRS and Université Paul Sabatier Toulouse III, France and Andreas Savin
CNRS and Sorbonne Univ., Paris, France

The Hohenberg-Kohn theorem provides a simple expression for the ground state energy, and also tells us how to construct the universal density functional F[n] showing up in this expression. However, this latter step is far too expensive, and the theorem does not provide us a simple way to construct feasible approximations. In practice, one partitions F[n] into a part representing a model system, and a remaining part, G[n], easier to simplify. Density functional theory does not prescribe a path for obtaining simplified forms of the different G[n]. In practice, specific forms (known not to be exact) are imposed, and refined using exact conditions, or learning from some data assumed accurate.

We discuss an alternative path producing approximations. However, no density functionals are constructed. It uses some adiabatic connection (that relates it to density functional theory), and universality comes in through the universal properties of the wave function at short distances between electrons. It is not limited to the ground state, and instead of learning, information from the system itself can be used to provide the missing information. This approach is asymptotically exact. It can be compared with short-range density functional approximations for ground states: the results are close. Also, excitation energies, properties can be calculated, and the interplay between the external potential and the interaction between electrons can be analyzed. As a byproduct, basis set errors can be corrected.

Electron correlation theory: Regularization, Locality and Intermolecular Interactions.

Martin Head-Gordon
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Rayleigh-Schrodinger perturbation theory, and its ab initio application to many-electron systems via Moller-Plesset (MP) perturbation theory, is not regular order by order, and therefore can exhibit erratic behavior for systems with small HOMO-LUMO gaps. In the first part of this talk, I will discuss a new approach to regularize MP2 theory against divergence in the small gap limit, based on modifying Brillouin-Wigner perturbation theory to be size-consistent as well as regular at second order to define BW-s2. We will also consider the extension to include single excitations.

My second topic is revisiting the design of local correlation methods at the doubles level, for MP2 and BW-s2, as well as higher level methods. The main challenge for local correlation is to achieve full control over errors such that a user only needs to select a single numerical drop tolerance. To achieve this goal, we have designed a new “single threshold” approach to local correlation, that also avoids use of projected AOs and PNOs to span the virtual space, by instead employing a localized orthogonal virtual basis. Accuracy and performance will be assessed via a range of example calculations.

If time permits, I will then discuss the development of an energy decomposition analysis (EDA) scheme based on MP2 and BW-s2. The objective of this theory is to separate intermolecular interactions into four separate and well-defined terms, corresponding to those successfully used at the SCF level. First is a frozen term, corresponding to permanent electrostatics, Pauli repulsions, and dispersion. Second is a term that captures electrical polarization. Third is a term that captures dispersion interactions. The last contribution corresponds to dative or charge-transfer interactions. Some results for large intermolecular interactions will be presented.

Multistate Density Functional Theory

Jiali Gao[1,2], Yangyi Lu[2]

1. Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

2. Institute of Systems and Physical Biology, Shenzhen Bay Laboratory, Shenzhen, China

In this talk, I will introduce multistate density functional theory (MSDFT) of electronic systems. In MSDFT, by introducing the matrix density $\boldsymbol{DD}(rr)$ as the fundamental variable of the Hilbert subspace spanned by the N-lowest eigenstates, we establish a one-to-one correspondence between $\boldsymbol{DD}(rr)$ and the Hamiltonian matrix associated with these N states – in other words, a matrix density functional $\mathscr{H}[\boldsymbol{DD}(rr)]$. Moreover, for any given trial matrix density of rank N, $\boldsymbol{DD}'(rr)$, we have the variation principle of MSDFT $tttt\{HH[\boldsymbol{DD}'(rr))]\} \geq tttt\{HH[\boldsymbol{DD}(rr)]\}$, where the equal sign holds true when $\boldsymbol{DD}'(rr) = \boldsymbol{DD}(rr)$. It turns out that any N-matrix density $\boldsymbol{DD}(rr)$ can be exactly represented by no more than NN_2 Slater determinants, where $\boldsymbol{DD}$ is the number of states of interest, which gives rise to the concept of minimal active space (MAS) – an upper bound of computational scaling with respect to the number of states. Consequently, MSDFT has the desired balance of computational efficiency and accuracy for excited state calculations just as that of a single determinant for the ground state in Kohn-Sham DFT. I will present the exact relationship between KS-DFT and multistate density functional theory (MSDFT), and applications to excited-state energy-transfer processes and energy decomposition analysis of molecular complexes in excited states.

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Doubly hybrid functionals: From molecules to extended materials

Xin Xu[1]

[1] Fudan University, Shanghai, 20048, China

Density functional theory (DFT) is now the most popular computational method in materials science. As the new generation functionals, doubly hybrid approximations (DHAs) have been shown to improve over conventional functionals with unprecedented accuracy in describing various kinds of chemical interactions and properties for finite molecules [1-3]. Recently, we have realized the periodic implementations of DHAs and demonstrated that the accuracy of DHAs achieved for finite molecules can be transferred to extended materials [4-9]. We anticipate that this new advancement will boost the predictive power for accurate descriptions of molecular crystals, as well as those of molecule-surface interactions in heterogeneous catalysis.

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Density Functional Approximations Guided by Exact Constraints

Chen Li

The present-day commonly used density functional approximations (DFAs) suffer from various systematic errors, and they can all be attributed to the violation of some exact constraints. In the first part of my talk, I will focus on two important constraints: (i) the Perdew-Parr-Levy-Balduz (PPLB) linearity condition for fractionally charged systems; and (ii) proper energy behavior in the semi-classical limit ħ→0. Guided by the first constraint, we have developed the localized orbital scaling correction (LOSC) functional that restores the PPLB condition through specially designed localized orbitals, called orbitalets. The LOSC functional can largely improve molecular dissociation problems, HOMO-LUMO gaps and photoemission spectra. Our recent development of combining LOSC with linear response TDDFT has greatly improved excitation energies, particularly for Rydberg and charge-transfer excitations. The second constraint is highly relevant to strongly correlated systems. Through a model atomic calculation, we show that the exact total energy as ħ→0 saturates to a finite value, whereas the mainstream DFAs have qualitatively wrong divergent behavior of . By introducing an effective ħ for valence electrons, we estimate that the ħeff for such systems can be as small as 0.2. Thus, this exact constraint might inspire novel functional approximations for describing strong correlation. In the second part of my talk, I will discuss our recently developed method for solving Schrödinger equations, which allows us to obtain the exact analytic structure of wave functions for one and two-body problems, and can be further generalized to many-body problems. The analytic expression of the ground state wave function is ultimately cast into an exact factorized form including a pre-exponential power factor, an exponential decaying term and a modulator, a mildly-varying and bounded function that can be easily approximated. This novel analytic structure serves as a new starting point for developing approximations that go beyond the single electron picture.

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Chen Li is an assistant professor at the College of Chemistry and Molecular Engineering, Peking University. He received his bachelor's degree in chemistry and math from Peking University in 2011. After that, he pursued his PhD study in density functional theory at Duke University under the supervision of Prof. Weitao Yang, and obtained his Ph. D. degree in 2016. In 2017, he joined the Max Planck Institute of Microstructure Physics in Germany as a postdoc research scientist and worked with Prof. Hardy Gross on the topic of time dependent density functional theory beyond Born-Oppenheimer approximation. In 2019, he followed Prof. Gross and moved to the Fritz Haber Center for Molecular Dynamics at Hebrew University of Jerusalem in Israel. In September 2020, He finished his postdoc and joined the chemistry department of Peking University as an assistant professor. Prof. Li is engaged in developing novel electronic structure theory methods, including density functional approximations, and wave function theory based on recently developed technique for solving Schrödinger equations. He is also interested in developing time dependent density functional theory beyond the Born-Oppenheimer approximation for capturing nonadiabatic effects.

TDDFT, the OISTR effect, and the challenge of decoherence

E.K.U. Gross
Fritz Haber Center for Molecular Dynamics, The Hebrew University of Jerusalem, Israel

A prominent goal of present-day condensed-matter physics is the design of electronic devices with ever faster switching times. As an example, the optically induced spin transfer between magnetic sublattices, the so-called OISTR effect, will be presented. This effect allows the switching of magnetic textures on the scale of a femto-second or less. It was first predicted with real-time TDDFT and later confirmed in several experiments. To create from this effect a real-world device, one has to face the problem of decoherence, i.e. the phenomenon that quantum systems tend to lose their "quantumness" due to interactions with other degrees of freedom. Decoherence is responsible for preventing genuine quantum computing at useful scales to this day. For electrons, the principal source of decoherence is the non-adiabatic interaction with nuclear degrees of freedom, i.e. with an "environment" that cannot be removed. In fact, the paradigm of electronic-structure theory where electrons move in the static Coulomb potential of clamped nuclei, while useful in the ground state, is an idealization hardly ever satisfied in dynamical processes when devices are operated or manipulated. Non-adiabaticity, i.e. effects of the coupled motion of electrons and nuclei beyond the Born-Oppenheimer approximation are found everywhere. In this lecture, the exact factorization will be presented as a universal approach to understand and, ultimately, control non-adiabatic effects, in particular decoherence, from an ab-initio perspective.

Stochastic Unraveling of Open Quantum Systems for Non-Interacting Electrons

Roi Baer
Fritz Haber Research Center of Molecular Dynamics.
Institute of Chemistry, The Hebrew University of Jerusalem, 9190401 Israel.

We present recent advancements in stochastic methods for simulating open quantum systems of non-interacting electrons, with the aim of applications in time-dependent density functional theory (TDDFT). The Lindblad master equation, central to modeling such systems, is computationally intensive due to bath-induced electron-electron correlations and the vast number of possible Lindblad operators. I will introduce our stochastic unraveling techniques, including stochastically bundled dissipators and weak second-order quantum state diffusion, which convert the deterministic master equation into efficient stochastic wave function trajectories. These approaches are then combined with auxiliary field Monte Carlo to account for electron correlation. The methods preserve complete positivity, ensuring physically valid evolution, while significantly reducing computational costs. Results on model systems demonstrate the accuracy and scalability of the approaches.

Block-correlated Coupled Cluster Methods for Ground-state and Excited states of Strongly Correlated Systems

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We present recent advances in electronic structure methods for strongly correlated systems using a generalized valence bond (GVB) reference wave function. The proposed block-correlated coupled cluster method (GVB-BCCC) 1,2 serves as a practical multi-reference coupled cluster approach for systems requiring large active spaces, in which conventional multi-reference methods are not available. By incorporating up to three- or four-block correlations, GVB-BCCC achieves near-exact agreement with density matrix renormalization group (DMRG) results for both triplet and singlet ground states.3,4 The unitary BCCC ansatz based on the GVB state (GVB-UBCCC) was proposed for simulating strongly correlate systems on quantum computers.5 Our results demonstrate that GVB-UBCCC2 (with up to two-block correlation) can provide more accurate ground-state energies than the unitary coupled cluster singles and doubles in most cases. To address excited states, we developed an equation-of-motion extension (EOM-GVB-BCCC), which includes up to three-block correlations.6,7 Benchmark calculations on strongly correlated systems demonstrate that EOM-GVB-BCCC3 accurately reproduces singlet-triplet energy gaps, being close to the DMRG results. These results highlight GVB-BCCC and EOM-GVB-BCCC as robust, scalable tools for studying ground and excited states in strongly correlated systems with large active spaces.

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Adaptive Control of Numerical Error in All-Electron Simulation of Periodic Solids

Edward Valeev

To address the shortcomings of mainstream numerical representations used for electronic structure simulations – namely, the unsystematic convergence and poor conditioning of atomic orbitals (AOs), and the lack of dynamic range for explicit simulation of core electrons with plane waves (PW) – we are exploring how to use the multiwavelet numerical representations for high-precision simulation of electronic structure of correlated electrons. We recently introduced first multiconfiguration self-consistent field approach applicable to general molecules with multiwavelet representation of orbitals. Here we report the extension of such multiwavelet numerical technology to infinite solids treated under Born-van-Karman (BvK) periodic boundary conditions. For robust convergence to the thermodynamic limit of one-body methods with exact exchange (Hartree-Fock, generalized Kohn-Sham) and many-body methods it is essential to use the Poisson kernel smoothly restricted to the Wigner-Seitz supercell. Efficient evaluation of the resulting matrix elements is possible with relatively minor modifications of the standard nonperiodic formalism. Initial applications to mean-field simulation of paradigmatic solids in up to 3 dimensions will illustrate the potential of the multiwavelet representation for all-electron simulation of solids.

Fast Density Functional Quadrature Using the Inclusion-Exclusion Principle

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For more than 30 years, Becke's quadrature scheme [l] has been the method of choice for integrating density functionals over molecular electron densities. It constructs a molecular grid by superimposing atom-based grids and then using a Hirshfeld stockholder scheme [2] to correct the quadrature weights so that double-counting effects are removed. It is implemented in many of the most popular quantum chemistry software packages, including Q-Chem.

In this lecture, I will describe a different approach in which we first partition the density using a Hirshfeld scheme but then use the Inclusion-Exclusion principle [3] to expand the density functional energy as

$E = E_1 + E_2 + E_3 + \ldots$

where

E_1 is a sum of atomic energies F_i and is roughly 97% of E

Each F_i is a 1-centre integral that can be computed efficiently using local spherical polar coordinates.

E_2 is a sum of diatomic energies F_{ij} and is roughly 3% of E

Each F_{ij} is a 2-centre integral that can be computed efficiently using local spheroidal coordinates.

E_3 is a sum of triatomic energies F_{ijk} and is roughly 0.1% of E

Each F_{ijk} is a 3-centre integral that can often be approximated by a simple quadrature.

and so on.

I will report results using a variety of molecules and argue that this approach is both computationally and conceptually useful.

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Ab initio Computational Methods of Valence Bond Theory

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Valence bond (VB) theory, as one of modern chemical bonding theories, offers intuitive insights into various chemical problems. However, ab initio VB theory has long faced challenges in computational efficiency and accuracy. This talk will first introduce the fundamental of valence bond theory, including basic concepts and methods of ab initio VB theory, and then some recent advances in algorithms and methods of ab initio VB theory will be presented. By implementing the low-rank algorithms, such as the resolution of the identity (RI) and the chain of spheres for exchange (COSX), the computational cost of valence bond self-consistent field (VBSCF) method is significantly reduced, and thereby enhancing its efficiency. Furthermore, I will present post-VBSCF methods, including second-order valence bond perturbation theory (VBPT2) and density functional valence bond (DFVB). These methods incorporate dynamic correlation into VB calculations, and substantially improving accuracy of ab initio VB methods.

Advancing Functional Theories for Strongly Correlated Systems.

Neil Qiang Su

Kohn-Sham density functional theory (KS-DFT) and reduced density matrix functional theory (RDMFT) represent two formally exact functional theories toward the many-electron problem. However, the slow progress in systematically eliminating intrinsic errors in commonly used approximate functionals limits the applicability of functional-based description to strongly correlated systems. In practice, approximate functionals in KS-DFT are better suited for capturing dynamic correlation, whereas those in RDMFT are more effective for strong correlation. Therefore, developing a new theoretical framework that bridges these two functional theories, together with effective strategies to combine their respective functional approximations, can open new avenues for enhancing the predictive power of functional-based methods. This talk will present some of our group's efforts along this direction.

New DFT approaches beyond the zero-sum game: importance of the exact-exchange energy density

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This lecture reports on our recent progress in developing density functionals that provide notable escape from the usual zero-sum game between trying to minimize self-interaction/delocalization and static-correlation errors, which is so central for the further development of improved density functional approximations. Our approaches are based on use of the exact-exchange (EXX) energy density, and we start from local hybrid (LH) functionals.[1] The position-dependent EXX admixture of LHs is shown to provide the flexibility required to fulfil the different requirements in different regions of coordinate space, e.g., in the core, valence and asymptotic regions, or in different parts of a composite system. Strong-correlation-corrected LHs (scLHs) and in particular their range-separated variants (scRSLHs)[2] allow substantial improvements on spin-restricted bond dissociation and on other properties related to static correlation, such as spin-symmetry breaking in open-shell transition-metal complexes. The best scRSLHs like LH23tdE[3] or LH25tdE[4] nevertheless provide at the same time excellent frontier-orbitals for IPs, EAs or gaps, and accurate CT excitation energies in TDDFT. Further developments regarding the use of neural networks to machine-learn the local mixing function (LMF) in LHs will be described. The first LH with such an n-LMF (LH24n) achieved a WTMAD-2 value for the large GMTKN55 molecular test suite of only 3.10 kcal/mol but was still without sc-correction terms.[5] The latter point has been tackled for the very recent LH25nP functional, which has an n-LMF optimized in the presence of an sc-factor and not only gives the so-far lowest WTMAD-2 value of a rung 4 functional (2.47 kcal/mol) but also simulates static correlation aspects well. I will also mention the first local double hybrid functionals based on an n-LMF,[6] as well as the first doubly local double hybrids based on PT2 correlation-energy densities. All functionals are or will be available for fast and routine molecular calculations within the Turbomole code, but we hope for a more widespread use in different codes, and also for extended systems.

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Recent developments in Transcorrelated methods

Ali Alavi

Transcorrelated methods are a class of explicitly correlated methodology in which correlation functions are used to non-unitarily similarity-transform the Schrodinger hamiltonian into another many-body hamiltonian with both desirable and, unfortunately, undesirable characteristics. Among desirable characteristics are the removal of Coulomb singularities, and generally speaking, reduction in the strength of interactions, leading to smoother and more compact wavefunction expansions. On the negative side, the TC hamiltonian is non-hermitian, causing headaches for optimisation of the wavefunctions, and also contains three-body interactions. Both problems create bottlenecks in efficient implementation of TC methods. We outline our work in removing these bottlenecks, namely how to optimise correlation functions for TC methods, how to efficiently handle the three-body interactions, and recently, we have shown that use of pseudopotentials greatly helps the TC method, by removing problematic core electrons. The resulting methodology shows great promise in scaling up to large systems, allowing calculations with unprecedented accuracy using high-level quantum chemistry methods (such as CCSD(T), FCIQMC, DMRG etc) which are basis-set converged, applied to solid-state systems.

Entanglement-Minimized Orbitals (EMOs) for Classical and Quantum Computing

Zhendong Li

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Quantum entanglement makes efficiently describing the electronic structure of molecules challenging on classical computers. In this talk, I will introduce a randomized orbital optimization algorithm to find entanglement-minimized orbitals (EMOs) using low bond dimension matrix product states. On one hand, this method allows us to identify genuine challenging systems with strong multiconfigurational characters and often lead to approximate ground states with lower energies at the same computational cost. On the other hand, the resulting EMOs can be used in quantum computation, which can significantly boost the success probability of quantum phase estimation and alleviate computational resources in variational quantum computation.

Molecular dynamics, machine learning, and the water phase diagram

Roberto Car

After recalling the basic principles of molecular dynamics simulation, I will discuss how machine learning and neural network representations boost ab-initio molecular dynamics, opening the way to studies that were unthinkable just a decade ago. As an example, the water phase diagram over a vast range of pressures and temperatures could be predicted semi-quantitatively from first-principles density functional theory. Finally, I will present recent work based on Feynman path integral simulations to study the effects of quantum nuclei on the melting properties of water using different functional approximations and the MB-pol model.

Hybrid: quantum + neural network approach for molecular wavefunction and HEOM + MPS for CISS

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(1)We introduce a hybrid framework to describe molecular wavefunction using a combination of an efficient quantum circuit and a neural network. Numerical benchmarking on molecular systems shows that our hybrid quantum-neural wavefunction approach achieves near-chemical accuracy, comparable to advanced quantum and classical techniques. Taking the isomerization reaction of cyclobutadiene as an example, which has been considered as a challenging issue with multireference feature or strong correlation effect, our approach is validated on a superconducting quantum computer with high accuracy and significant resilience to noise.

(2)We develop a hierarchical equation of motion (HEOM□+ matrix product state (MPS) approach to handle electron-phonon coupled model considering both local and non-local effects coupled with spin-orbit coupling for a circularly stacked molecular aggregate. We evaluate the electron mobility for spin up and spin down through our HEOM/MPS approach in order to understand the chiral induced spin selectivity.

Unified Implementations of Relativistic Hamiltonians and Wavefunctions

Wenjian Liu

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In this lecture, I will introduce a unified implementation of relativistic Hamiltonians based solely on physical arguments [1] as well as a unified implementation of relativistic wavefunctions via programming techniques [2,3]. The latter was made possible by first introducing a diagrammatical representation of four- or two-component relativistic Hamiltonians that is topologically the same as that used in the unitary group approach for evaluating the basic coupling coefficients between spin-free configuration state functions, and then by making full use of the metaprogramming furnished by C++. Once the module for the relativistic Hamiltonian matrix is made ready, no other modifications of the existing templates used for nonrelativistic wavefunction methods are necessary. In particular, there is no need to distinguish complex and real algebra.

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Chirality-Driven Magnetization Emerges from Relativistic Four-Current Dynamics

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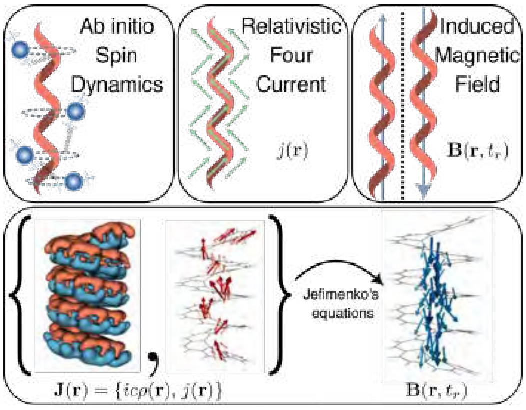
Chirality-Driven Magnetization Emerges from Relativistic Four-Current Dynamics

Xiaosong Li, University of Washington, Seattle, WA 98195



Chirality-induced spin selectivity (CISS) is a striking quantum phenomenon in which electron transport through chiral molecules leads to spin polarization, even in the absence of magnetic fields or magnetic components. Although observed in systems such as DNA, helicenes, proteins, and polymers, the fundamental physical origin of CISS remains unresolved. Here, we introduce a time-dependent relativistic four-current framework, in which charge and current densities evolve according to the time-dependent variational principle. Real-time relativistic four-current simulations enable direct analysis of helical currents and induced magnetization dynamics. Applied to helicenes---axially chiral molecules lacking stereocenters---our simulations reveal curvature-induced helical electron currents that generate spontaneous magnetic fields aligned along the molecular axis. These fields are handedness-dependent and reach magnitudes of 10-1 Tesla per single helicene strand. Our results suggest that CISS may arise from intrinsic, relativistic curvature-induced helical currents and the associated magnetic fields within chiral molecules. This four-current mechanism offers a self-contained explanation for spin selectivity, independent of interfacial effects or strong spin-orbit coupling. Furthermore, our results lead to several testable hypotheses that can be explored in experiments.

Insights into the Chemistry of Aqueous Oxide Interfaces from Machine Learning Molecular Dynamics

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Aqueous solution-oxide interfaces have a critical role in many environmental, biological, and energyrelevant processes. As the molecular scale properties of these interfaces are still challenging to probe experimentally, many studies have relied on theoretical simulations to complement the experimental observations and obtain an atomistic understanding. While first principles simulations provide the best accuracy, they are limited to rather small system sizes and time scales due to their high computational cost. In recent years, machine learning potentials capable to reproduce the accuracy of first-principles methods have emerged as a promising approach to circumvent these limitations. In this talk, I shall discuss recent applications of deep neural network based molecular dynamics simulations to

understand the structure and properties of aqueous solution-metal oxide interfaces. Focusing on the interfaces of TiO_2, a prototypical metal oxide well known for its numerous applications in photocatalysis

and electrochemistry, specific topics will include a characterization of the Electrical Double Layer at the TiO_2-electrolyte interface under different pH conditions and external electric fields [1], and the effects of various organic compounds, such as formic acid and methanol, on the structure and chemistry of water at the interface [2].

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New developments in density-matrix based quantum embedding theory

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Electronic structure theory for strongly correlated systems (SCSs) is regarded as one of the greatest challenges in molecular quantum chemistry and condensed matter theory. There are continuous efforts in developing various quantum embedding techniques to treat complex SCSs accurately and efficiently. Density-matrix embedding theory (DMET), formulated based on the Schmidt decomposition of Slater determinants, provides a systematic framework to combine low- and high-level quantum chemistry methods to treat strongly correlated systems. In this talk, I will present our recent efforts of further developing DMET-based quantum embedding approaches and their applications to strongly correlated single-impurity systems like 3d/4f single-ion magnets (SIMs) and lanthanide luminescent systems [1-4].

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Driven similarity renormalization group with a large active space

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The driven similarity renormalization group (DSRG) based on a density matrix renormalization group (DMRG) reference provides a promising route for molecules involving many strongly correlated electrons. In this work,1 we present a new implementation of the DMRG-DSRG method, where the explicit build of high-order reduced density matrices is avoided by forming matrix-product-state compressed intermediates. This algorithm facilitates the application of DSRG second- and third-order perturbation theories to dodecacene with an active space of 50 electrons in 50 orbitals. This active space appears the largest employed to date within the framework of internally contracted multireference formalism. The DMRG-DSRG approach is applied to several challenging systems, including the singlet-triplet gaps of oligoacenes ranging from naphthalene to dodecacene, the vertical excitation energies of zeaxanthin, and the ground-state potential energy curve of chromium dimer.

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Nonadiabatic Field: A Conceptually New Approach for Nonadiabatic Transition Dynamics

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Nonadiabatic transition dynamics lies at the core of many electron/hole transfer, photoactivated, and vacuum field-coupled processes. About a century after Ehrenfest proposed “Phasenraum” and the Ehrenfest theorem, we report a conceptually novel trajectory-based nonadiabatic dynamics approach, nonadiabatic field (NaF), based on a generalized exact coordinate–momentum phase space formulation of quantum mechanics, which includes U(F)/U(F-1) constraint phase space for electronic degrees of freedom (DOFs) and infinite phase space for nuclear DOFs. It does not employ the conventional Born–Oppenheimer or Ehrenfest trajectory in the nonadiabatic coupling region. Instead, in NaF the equations of motion of the independent trajectory involve a nonadiabatic nuclear force term in addition to an adiabatic nuclear force term of a single electronic state. A few benchmark tests for gas phase and condensed phase systems indicate that NaF offers a practical tool to capture the correct correlation of electronic and nuclear dynamics for processes where the states remain coupled all the time as well as for the asymptotic region where the coupling of electronic states vanishes. NaF has been integrated in the PSiNad (phase space-integrated non-adiabatic dynamics) simulation package, where both benchmark models and ab initio electronic structure methods can be used to study nonadiabatic transition processes.

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Stochastic Resolution of Identity Approach to the Coupled Cluster Theory for the Excited States of Very Large Systems

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We develop a stochastic variant of the approximate second-order coupled cluster singles and doubles model, termed sRI-CC2. By utilizing a set of stochastic orbitals, we efficiently decouple the critical 4-index electron repulsion integrals via a stochastic resolution of identity (sRI). This method achieves a substantial reduction in computational scaling from $O(N^5)$ to $O(N^3)$, where N represents the system size, allowing for the calculation of excited-state properties in very large systems containing thousands of electrons at the coupled cluster level. We benchmark the sRI-CC2 method to quantify stochastic errors and evaluate its performance across a variety of molecular and extended systems. Our results demonstrate that sRI-CC2 accurately predicts singlet-triplet band gaps for a series of thermally activated delayed fluorescence (TADF) molecules, addressing the significant overestimation (often by nearly eVs) observed in time-dependent density functional theory (TDDFT) calculations. Furthermore, the sRI-CC2 framework can be extended to compute spectra and analytical gradients. These advancements highlight the broad applicability of sRI-CC2 for studying excited-state electronic structures and dynamics.

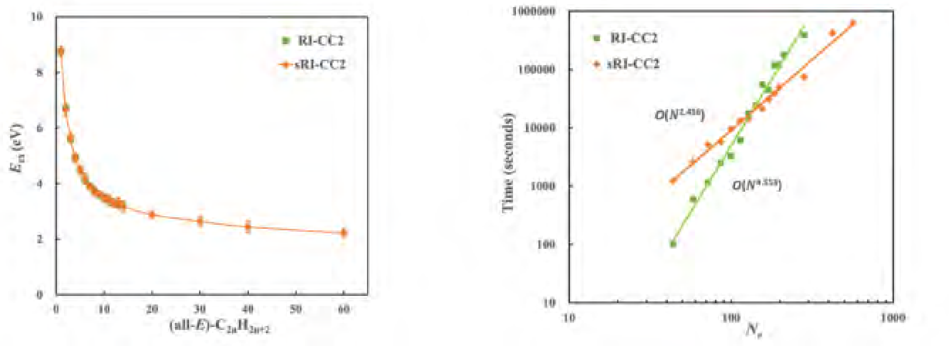

Fig. 1: Excitation energies for a series of alkenes chains. sRI-CC2 reproduces RI-CC2 results for small systems. sRICC2 exhibits an experimental scaling of O(*N*2.5), such that it can calculate systems with thousands of electrons. (J. Chem. Theory Comput. 20, 5188 [2024])

Direct Probe of Conical Intersection Photochemistry by Time-Resolved X-ray Magnetic Circular Dichroism

Shichao Sun*, Bing Gu, Hang Hu, Lixin Lu, Diandong Tang, Vladimir Y. Chernyak
Xiaosong Li*, Shaul Mukamel*

The direct probing of photochemical dynamics by detecting the electronic coherence generated during passage through conical intersections is an intriguing challenge. The weak coherence signal and the difficulty in preparing purely excited wave packets that exclude coherence from other sources make it experimentally challenging. We propose to use time-resolved X-ray magnetic circular dichroism to probe the wave packet dynamics around the conical intersection. The magnetic field amplifies the relative strength of the electronic coherence signal compared to populations through the magnetic field response anisotropy. More importantly, since the excited state relaxation through conical intersections involves a change of parity, the magnetic coupling matches the symmetry of the response function with the electronic coherence, making the coherence signal only sensitive to the conical intersection induced coherence and excludes the pump pulse induced coherence between the ground state and excited state. In this theoretical study, we apply this technique to the photodissociation dynamics of a pyrrole molecule and demonstrate its capability of probing electronic coherence at a conical intersection as well as population transfer. We demonstrate that a magnetic field can be effectively used to extract novel information about electron and nuclear molecular dynamics.