Frontiers in Density Functional Theory and Beyond – Advances and Challenges

May 30 - June 1, 2019
Kavli Institute for Theoretical Sciences at
University of Chinese Academy of Sciences
Beijing, China

Coordinators

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Roberto Car	Princeton University
Shixuan Du	Institute of Physics
Wenhui Duan	Tsinghua University
Xingao Gong	Fudan University
Steven Louie	University of California, Berkeley
Patrick Rinke	Aalto University

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Arrival

Workshop Dates: May 30 to Jun. 1, 2019

Workshop Venue: Rm. S106, UCAS Teaching Building

Address: UCAS Teaching Building, No. 3 Zhong-Guan-Cun Nan-Yi-Tiao Road, Haidian District, Beijing

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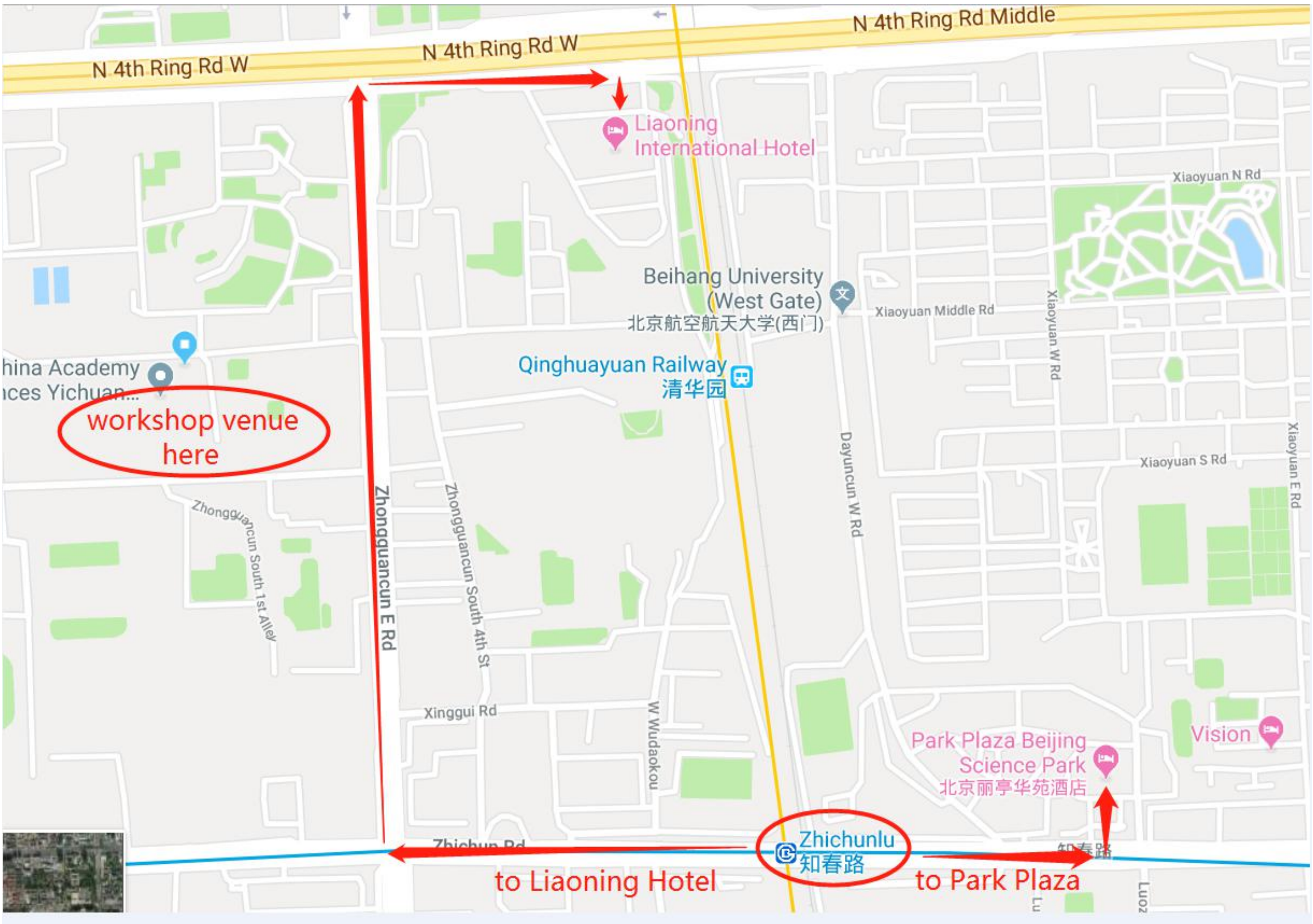

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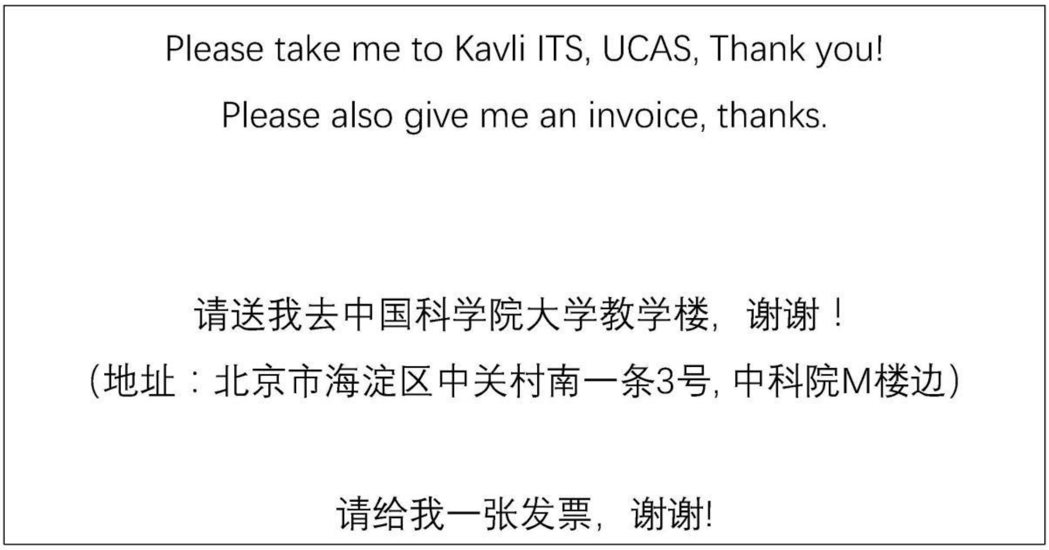

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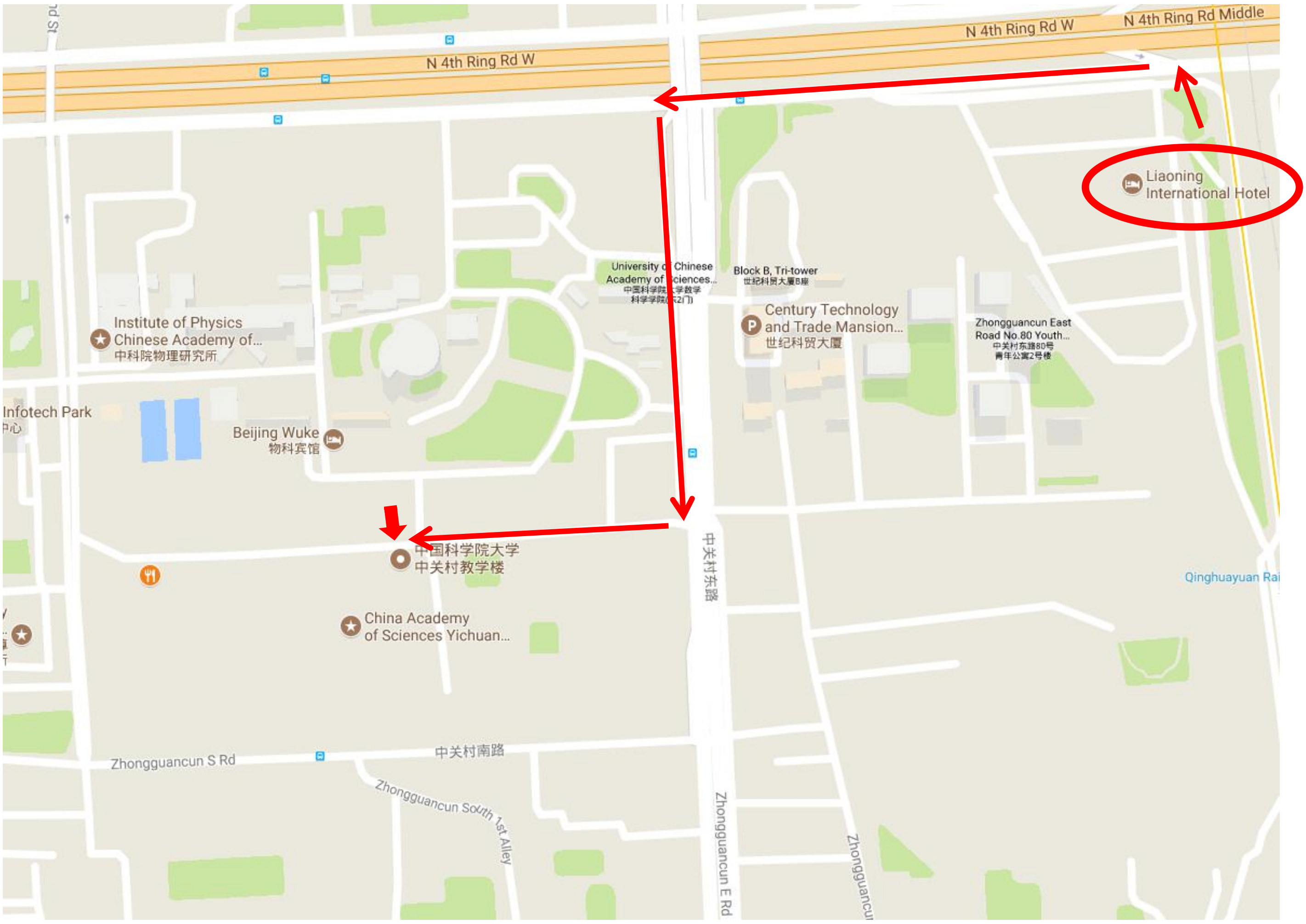

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Workshop Registration

For speakers and pre-registered participants: Please collect your name card at the registration desk, located in the workshop venue. We provide lunch on May 30, 31 and June 1, and you need to demonstrate your workshop name card to enter the dining room

For non-registered participants: you may attend the workshop as an audience, but we cannot provide meals during the workshop.

For any inquiries please contact Mr. Peiming Yan (Page 3) for help

Internet Connection

It is highly recommended if you do have a eduroam account, which is covered in the workshop venue and no need for identity check or pre-registration, which is usually accessed by using your institutional email address and email password.

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Conference Program

May 30, Thursday | Room S106

	[Session 1] Chair: S. T. Pantelides (Vanderbilt Univ.)	
09:00-09:40	**Steven G. Louie** (UCBC)	Many-electron correlations in multiple-particle excitations and nonlinear optical processes in materials
09:40-10:20	**Myrta Gruening** (QUB)	Nonlinear optics from first-principles real-time approaches
10:20-10:50	*Coffee Break*	
	[Session 2] Chair: S. G. Louie (UCSB)	
10:50-11:30	**Weitao Yang** (Duke Univ.)	Analysis and elimination of the delocalization and static/strong correlation error in density functional approximations
11:30-12:10	**Patrick Rinke** (Aalto Univ.)	GW and beyond: Core excitations, strong correlation and artificial intelligence
12:10-14:00	*Lunch & Break*	
	[Session 3] Chair: S. X. Du (IOP, CAS)	
14:00-14:40	**Xinguo Ren** (USTC)	Periodic GW and RPA methods within a numeric atomic-centered basis set framework
14:40-15:20	**James R. Chelikowsky** (Univ. of Texas)	Real-space numerical grid methods for electronic structure calculations—the future
15:20-15:50	*Coffee Break*	
	[Session 4] Chair: X. G. Zhang (Univ. of Florida)	
15:50-16:30	**Jerry Bernholc** (NCSU)	Towards Exascale electronic structure and quantum transport calculations
16:30-17:10	**Karsten W. Jacobsen** (TUD)	Computational screening of light absorbing materials

May 31, Friday | Room S106

08:45-09:00	**Fuchun Zhang** (Kavli ITS, UCAS)	
	[Session 1] Chair: W. Yang	
09:00-09:40	**Xiao Zheng** (USTC)	Improving density functional calculations for molecular electron affinities
09:40-10:20	**Sokrates T. Pantelides** (Vanderbilt Univ.)	Formation energies of charged defects - resolution of long-standing difficulties
10:20-10:50	*Coffee Break*	
	[Session 2] Chair: M. Gruening	
10:50-11:30	**Xin-Zheng Li** (Peking Univ.)	On the quantum nature of the nuclei and its influence
11:30-12:10	**Igor Ying Zhang** (Fudan Univ.)	Simultaneous attenuation of both self-interaction and error and nondynamic correlation error in density functional theory: A spin-pair distinctive adiabatic-connection approximation
12:10-14:00	*Lunch & Break*	
	[Session 3] Chair: Y. Y. Zhang (UCAS)	
14:00-14:40	**Xiaoguang Zhang** (Univ. of Florida)	Multi-phonon processes in solids from first-principles
14:40-15:20	**Wenjian Liu** (Peking Univ.)	Recent advances in TD-DFT
15:20-16:00	**Jan Herman** (Freie Universität)	Unifying density-functional and interatomic approaches to van der Waals interactions
15:00-15:50	[Poster Session]	

Jun. 1, Saturday | Room S101

	[Session 1] Chair: W. Duan (Tsinghua Univ.)	
09:00-09:40	**Xin Xu** (Fudan Univ.)	The XYG_3 type of doubly hybrid density functionals: From molecular systems to extended solids
09:40-10:20	**Martin Head-Gordon** (UCBC)	Progress and problems in the design of density functionals
10:20-10:50	*Coffee Break*	
	[Session 2] Chair: P. Rinke	
10:50-11:30	**Andreas Görling** (Univ. of Erlangen-Nuremburg)	Opening up new areas for density-functional theory by orbital-dependent exchange-correlation functionals
11:30-12:10	**Julien Toulouse** (Sorbonne Univ.)	Multideterminant density-functional theory for strong correlation

Abstracts

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Many-electron correlations in multiple-particle excitations and nonlinear optical processes in materials

Steven G. Louie

Physics Department, University of California at Berkeley, and Lawrence Berkeley National Lab, Berkeley, California 94720 U.S.A.

Excited-state phenomena in a material typically give rise to its defining attributes and determine its usefulness. These phenomena are particularly important in processes of energy conversion, transport and storage. However, *ab initio* methods for them - especially for correlated multiple-particle (3- or 4-particle) excitations, nonlinear optical processes, and ultra-fast electron dynamics including relevant electron-electron interactions - have been under explored and hence limiting their studies for real materials. In this talk, we report recent progress on the *ab initio* theory and computation of such excited-state phenomena based on the interacting Green's functions approach to many-body perturbation theory. We present: 1) our new formalism and computational method for 3- and 4-particle Green's functions with applications to trions, biexcitons, and singlet fission; and 2) our development of a time-dependent GW approach for time-dependent processes and nonlinear optics, which has led to the discovery of giant exciton effects in shift currents in two-dimensional semiconducting materials.

Nonlinear optics from first-principles real-time approaches

Myrta Gruening

Queen's University of Belfast

In the past decades, many-body approaches based on the GW approximation and the Bethe-Salpeter equation have become the state-of-the-art for calculating optical absorption in solids and nanostructures. In this talk, I'll first present a real-time approach derived from the non-equilibrium Green's function, that allows to extend the GW+BSE approach beyond the linear regime.[1,2] Using this approach, I'll address the importance of many-body effects and in particular of excitonic effects for nonlinear optical properties.[3] For example, I'll look at the case of single-layer monochalcogenide whose strong Second Harmonic Generation cannot be reproduced within the independent-particle approximation.[4]

In the second part of the talk, I'll then discuss the possibility of a real-time approach based on time-dependent density-functional theory, that can describe excitonic effects.[5]

[1] *Real-time approach to the optical properties of solids and nanostructures: Time-dependent Bethe-Salpeter equation*
Attaccalite, C., Gruning, M. & Marini, A., (2011) Physical Review B 84, 24, 245110

[2] *Nonlinear optics from an ab initio approach by means of the dynamical Berry phase: Application to second- and third-harmonic generation in semiconductors*
Attaccalite, C. & Grüning, M., (2013) Physical Review B 88, 235113

[3] *Second harmonic generation in h-BN and MoS_2 monolayers: Role of electron-hole interaction*
Grüning, M. & Attaccalite, C., (2014) Physical Review B 89,081102

[4] *How strong is the Second Harmonic Generation in single-layer monochalcogenides? A response from first-principles real-time simulations*
Claudio Attaccalite, Maurizia Palummo, Elena Cannuccia, Myrta Grüning

[5] *Dielectrics in a time-dependent electric field: a real-time approach based on density-polarization functional theory*
Grüning, M., Sangalli, D. & Attaccalite, C., (2016) Physical Review B 94, 035149

Analysis and elimination of the delocalization and static/strong correlation error in density functional approximations

Weitao Yang

Department of Chemistry and Department of Physics, Duke University, USA Key Laboratory of Theoretical Chemistry of Environment School of Chemistry and Environment, South China Normal University

The perspectives of fractional charges and fractional spins provide a clear analysis of the errors of commonly used density functional approximations (DFAs). These errors, the delocalization and static correlation error, of popular DFAs lead to diversified problems in present-day density functional theory calculations. For achieving a universal elimination of these two errors, we develop a localized orbital scaling correction (LOSC) framework: it accurately characterizes the distributions of global and local fractional electrons and spins, and is thus capable of correcting system energy, energy derivative and electron density in a self-consistent and size-consistent manner. Our approach introduces the explicit derivative discontinuity and largely restores the flat-plane behavior of electronic energy at fractional charges and fractional spins. The LOSC–DFAs lead to systematically improved results, including the dissociation of ionic species, single bonds, multiple bonds without breaking the space or spin symmetry, the band gaps of molecules and polymer chains, the energy and density changes upon electron addition and removal, and photoemission spectra.

We further carried the comparison of experimental quasiparticle energies for many finite systems with calculations from the GW Green function and the localized orbitals scaling correction (LOSC). Extensive results with over 40 systems clearly show that LOSC orbital energies achieve slightly better accuracy than the GW calculations with little dependence on the semilocal DFA, supporting the use of LOSC DFA orbital energies to predict quasiparticle energies. This also leads to the QE-DFT (quasiparticle energies from DFT) approach: the calculations of excitation energies of the N-electron systems from the ground state DFA calculations of the (N - 1)-electron systems. Results show good performance with accuracy similar to TDDFT and the delta SCF approach for valence excitations with commonly used DFAs with or without LOSC. For charge transfer and Rydberg states, good accuracy was obtained only with the use of LOSC DFA. The QE-DFT method has been further developed to describe excited-state potential energy surfaces (PESs), conical intersections, and the analytical gradients of excited-state PESs.

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1. J. Cohen, P. Mori-Sanchez, and W. Yang. Insights into current limitations of density functional theory. Science, 321:792, 2008. 2. P. Mori-Sánchez, A. J. Cohen, and W. Yang, “Localization and Delocalization Errors in Density Functional Theory and Implications for Band-Gap Prediction,” Physical Review Letters, 100: 146401, 2008. 3. P. Mori-Sanchez, A. J. Cohen, and W. Yang. Discontinuous Nature of the Exchange-Correlation Functional in Strongly Correlated Systems, Physical Review Letters, 102:066403, 2009. 4. J. Cohen, P. Mori-Sanchez, and W. Yang. Challenges for Density Functional Theory. Chem. Rev.

112:289, 2012 5. C. Li, X. Zheng, N. Q. Su, and W. Yang, “Localized orbital scaling correction for systematic elimination of delocalization error in density functional approximations,” National Science Review, 5: 203–215, 2018. 6. N. Q. Su, C. Li, and W. Yang, “Describing strong correlation with fractional-spin correction in density functional theory,” Proceedings of the National Academy of Sciences, 115:9678–9683, 2018. 7. Y. Mei, C. Li, N. Q. Su, and W. Yang, “Approximating Quasiparticle and Excitation Energies from Ground State Generalized Kohn-Sham Calculations,” arXiv:1810.09906 2018; J. Phys. Chem. A, 123(3), 666– 673, 2019 8. Y. Mei and W. Yang, “Excited-State Potential Energy Surfaces, Conical Intersections, and Analytical Gradients from Ground-State Density Functional Theory,” J. Phys. Chem. Lett., 10, 2538–2545, 2019.

GW and beyond: core excitations, strong correlation and artificial intelligence

Patrick Rinke∗

Aalto University Department of Applied Physics, 00076 Aalto, Finland email:
patrick.rinke@aalto.fi

The GW approximation to many-body perturbation theory (MBPT) has been incredibly successful in theoretical spectroscopy. Yet, challenges abound and new frontiers await. In this presentation, I will introduce our first exploration of perturbative GW (G0W0) for core excitations [1]. We have implemented the real-frequency contour deformation technique into the all-electron numerical atomic orbital code FHI-aims [2]. The real-frequency treatment proves to be necessary to treat core excitations accurately. The computed core level binding energies deviate by generally less than 0.5 eV from experiment (on an absolute scale) outperforming the popular density-functional theory based Delta Self-Consistent Field (ΔSCF) method. To tackle strongly correlated systems, we have developed a new quantum embedding theory [3]. It captures strong (static) correlation in a subspace by configuration interaction (CI) theory and high-energy dynamic correlation with MBPT in the GW and Bethe-Salpeter equation (BSE) approximation. For the challenging multi-reference problems of H2 and N2 dissociation, we obtain good agreement with benchmark results. Our theory treats ground and excited states on equal footing, and we compute vertical excitation energies of N2 and free-base porphyrin in excellent agreement with high level quantum chemistry methods. Despite the successes of theoretical spectroscopy, calculations and experiments are costly and time consuming. For this reason, we recently enhanced theoretical spectroscopy with artificial intelligence (AI). Once trained, the AI can make predictions of spectra instantly and at no further cost. I will present artificial neural networks that can learn excitation spectra of molecules with an accuracy of 97% [4].

∗This work was performed in collaboration with D. Golze, M. Dvorak, A. Stuke, K. Ghosh, L. Himanen, M. Todorovi´c, and A. Vehtari

[1] D. Golze, J. Wilhelm, M. van Setten, and P. Rinke, Chem. Theory Comput. 14, 4856 (2018) [2] X. Ren, P. Rinke et al., New J. Phys. 14, 053020 (2012) [3] M. Dvorak and P. Rinke, Phys. Rev. B 99, 115134 (2019) [4] K. Ghosh, A. Stuke, M. Todorovi´c, P. B. Jørgensen, M. N. Schmidt, A. Vehtari, and P. Rinke, Adv. Sci. 1801367 (2019)

Periodic GW and RPA methods within a numeric atomic-centered basis set framework

Xinguo Ren

CAS Key Laboratory of Quantum Information, Unversity of Science and Technology of China

We have implemented the periodic G^0W^0 method for quasiparticle energy calculations and the random-phase approximation (RPA) for ground-state total energy calculations within the all-electron, numerical atomic orbital (NAO) basis-set framework. A straightforward implementation of such correlated methods within the NAO framework is extremely expensive in terms of both the memory demand and CPU times. Here we employed a localized variant of the resolution of identity (RI) approximation, enabling a significant reduction of the computational cost to evaluate and store the two-electron Coulomb repulsion integrals. We demonstrate that the error due to localized RI approximation is controllable and can be made negligibly small by enhancing the set of auxiliary basis functions (ABFs) used to expand the products of two single-particle NAOs. An efficient algorithm, suitable for the NAO framework, has been developed to deal with the Coulomb singularity in the Brillouin zone sampling. We performed systematic convergence tests and identified a set of computational parameters (basis sets, enhanced ABFs, and k-point grid), with which reliable G^0W^0 and RPA results can be obtained. Our implementation is carried out within the all-electron, NAO-based software package -- FHI-aims. Benchmark results for 3-dimensional insulators/semiconductors as well as 2-dimensional materials will be presented.

Real-space numerical grid methods for electronic structure calculations—The future

James R. Chelikowsky

Center for Computational Materials, Oden Institute of Computational Engineering and Sciences, Departments of Physics and Chemical Engineering, University of Texas at Austin, Austin, Texas 78712 USA

Two physical ingredients, pseudopotentials and density functional theory, are widely used and accepted in electronic structure computations for a wide variety of materials applications. If we wish to address large, complex systems, the implementation of these ingredients on high performance computational platforms is vital. Real space grid methods offer a compelling vehicle for such computations. These methods are mathematically robust, very accurate and well suited for modern, massively parallel computing resources]. I will illustrate the utility of these methods as implemented in the PARSEC code. Key algorithms in this code include subspace filtering based on Chebyshev polynomials, spectrum splicing for added level of parallelism, Cholesky QR algorithms to improve the performance of orthogonalization, and a 2D partition of the wave functions for efficient matrix-vector operations. Applications will be illustrated for nanostructures containing tens of thousands of atoms.

Towards Exascale Electronic Structure and Quantum Transport Calculations

Jerry Bernholc

Department of Physics, North Carolina State University, NC 27695-8202, USA

The development of robust, adaptive software and algorithms that can fully exploit exascale capabilities and future computing architectures is critical to designing advanced materials and devices with targeted properties. We have developed an open-source code that discretizes the DFT equations on real-space grids that are distributed over the nodes of a massively parallel system via domain decomposition. Multigrid techniques are used to dramatically accelerate convergence while only requiring nearest neighbor communications. The real-space multigrid (RMG) code scales from desktops and clusters to supercomputers consisting of ~200k cores and 20k GPUs, including the Cray XE-XK systems and the new IBM-NVIDIA pre-exascale Summit. Multilevel parallelization with MPI, threads and/or Cuda programming enables adaptation to future exascale supercomputers. RMG is distributed via www.rmgdft.org, with over 3,400 downloads do date. Advanced functionalities are provided through interfaces to other codes and code modules. We will describe the non-equilibrium Green's function module based on variationally-optimized localized orbitals, by which quantum transport properties can be studied for devices containing tens of thousands of atoms with full DFT accuracy. For a system with ten thousand atoms, our initial implementation scales linearly from 100 to 1000 nodes on Summit, already gaining ~4x speed-up from GPUs over CPU-only calculations. Several applications will be described, including a nanocircuit that could potentially enable electrical sequencing of DNA, and a novel experimentally realizable graphene-nanoribbon-based negative differential resistance device that has been grown with atomic precision by our experimental collaborators.

In collaboration with E. L. Briggs, W. Lu, Z. Xiao, Y. Li and M. Hodak.

Computational screening of light absorbing materials

Karsten W. Jacobsen

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The world needs energy from sustainable sources like the sun, wind, and water. Harvesting light from the sun and turning it into electricity or fuels in an efficient way are scientific and engineering materials challenges. Modern silicon solar cells have reached close to maximal performance, and further increase of efficiency will require development of tandem devices, where several semiconductors are combined to increase the light absorption. In recent years, we have focused on identification of new large-band-gap semiconductors with a band gap around 2 eV, which can be combined with silicon in tandem devices. We have employed computational screening with focus on material stability, light absorption, carrier mobility, and defect properties. The screening studies have resulted in the identification of a number of candidate materials including a ternary sulfide, which was successfully synthesized and found to possess promising properties.

Future computational screening studies can be expected to benefit from machine learning for more efficient searching in materials space and for fast calculation of material properties. A particular challenge is the prediction of properties of new materials, where the atomic positions are not accurately known. I shall show that a materials description using symmetry-labeled Voronoi quotient graphs in combination with message passing neural networks is a promising approach to address this challenge.

Improving density functional calculations for molecular electron affinities

DaDi Zhang[1], Xiaolong Yang[1], Xiao Zheng[1*], Weitao Yang[2*]

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Electron affinity (EA) is the energy released when an additional electron is attached to an atom or a molecule. EA is a fundamental thermochemical property, and it is closely pertinent to other properties such as electronegativity and hardness. However, accurate prediction of EA is difficult with density functional theory methods. The large error of the calculated EAs originates mainly from the intrinsic delocalization error associated with the approximate exchange-correlation functional. We employ a non-empirical global scaling correction approach [1-5], which explicitly imposes the rigorous Perdew-Parr-Levy-Balduz condition [6] to the approximate functional, and achieve a substantially improved accuracy for the calculated EAs. In our approach, the EA is given by the scaling corrected Kohn-Sham LUMO energy of the neutral molecule, without the need to carry out self-consistent-field calculation for the anion.

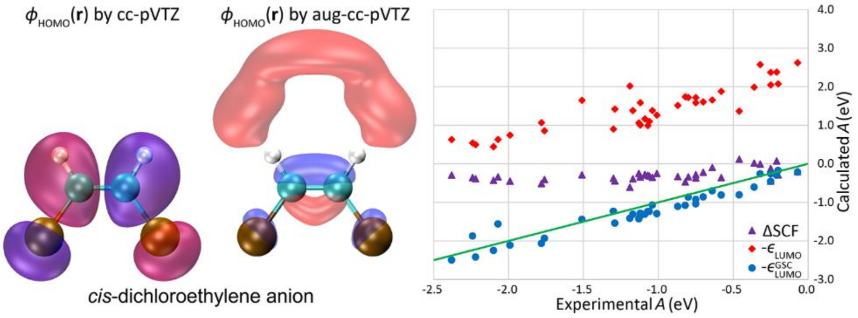

Figure 1. Left: Contour plot of HOMO for a molecular anion. Right: Calculated molecular electron affinities versus experimental values.

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Formation energies of charged defects – resolution of long-standing difficulties

Sokrates T. Pantelides[1]
Blair Tuttle[1,2], Andrew O'Hara[1], Yuning Wu[3], and Xiao-Guang Zhang[3]
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Formation energies of defects in semiconductors is an essential ingredient in the study of a wide range of semiconductor properties. For several decades, they have been calculated using supercells, but, for charged defects, the standard definition leads to a divergence that is removed by setting the average electrostatic potential to zero. Several techniques have been developed to further address inherent difficulties. These difficulties are exacerbated in 2D materials where unphysical electric fields appear in the vacuum regions, requiring new methods to remove them. Here we trace the origin of the divergence to the fact that the definition of charged-defect formation energies violates the principles of statistical mechanics for defects in semiconductors. Moreover, the *ad hoc* elimination of the divergence at each iteration in the self-consistency loop results in a potential and charge density that are not connected by Poisson's equation, i.e., self-consistency is compromised. We then describe a fundamental resolution of the issue that leads to a *new definition of charged-defect formation energies without a divergence or other difficulties*[1]: so-called "charged defects" are not truly charged -- a neutral defect releases a bound electron to the conduction bands or takes up an electron from the valence bands. The crystal is always neutral and for every "charged" defect, there is a neutralizing carrier in some band state (or elsewhere), i.e., the supercell is neutral and thus the entire crystal is neutral in agreement with physical reality. We show that the jellium definition can be derived from the new definition by invoking approximations whose validity cannot be assessed *a priori*, which sets up the new definition as a standard. Calculations for bulk materials reveal that the differences in the two approaches are relatively small, but for 2D materials, in particular BN, the differences can exceed 1 eV. Convergence with supercell size is as fast as for neutral defects.

1. Y.-N. Wu, X. G. Zhang and S. T. Pantelides, "*Fundamental resolution of difficulties in the theory of charged point defects in semiconductors*", *Phys. Rev. Lett.* **119**, 105501 (2017).

On the quantum nature of the nuclei and its influence

Yexin Feng,[1] Ji Chen,[1] Wei Fang,[2] Angelos Michaelides,[2] Enge Wang,[1]
and Xin-Zheng Li,[1]

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Molecules and condensed matters are entities composed by interacting electrons and nuclei. Therefore, an ideal computer simulation needs to address both the electronic and the nuclear systems accurately, as well as their couplings. Compared with the more and more accurate quantum treatments of the interacting electronic systems, theoretical descriptions of the nuclei still largely remain at the classical level. In this talk, we will explain our recent investigations on the quantum nature of hydrogen bonds [1], H tunneling mechanisms [2-4], and optical reflectances [5]. The basic technique we use is *ab initio* path-integral molecular dynamics. To accommodate the requirements associated with some specific problems, it was combine it with different computer simulation methods in each case.

[1] J. Guo, J. T. Lü, Y. X. Feng, J. Chen, J. B. Peng, X. Z. Meng, Z. C. Wang, Z. R. Lin, X. Z. Li, E. G. Wang, Y. Jiang, **Science 352**, 321 (2016)
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Simultaneous attenuation of both self-interaction error and nondynamic correlation error in density functional theory: A spin-pair distinctive adiabatic-connection approximation

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We present a spin-pair distinctive algorithm in the context of adiabatic-connection fluctuation-dissipation (ACFD) theorem[1], which enables to quantify the self-interaction error (SIE) and the nondynamic/strong correlation error (NCE) in the direct random-phase approximation (dRPA)[2]. Using this knowledge, we propose a spin-component scaled dRPA (scsRPA) correlation model with simultaneous attenuation of both the SIE and the NCE. Along with the exact exchange, scsRPA is shown to present a comprehensive improvement over dRPA, as well as the well-established PBE and PBE0 functionals, for bonding energies of pronounced multi-reference characters and transition-metal complexes of strongly correlated systems, while consistently provide an accurate description for reaction energies, reaction barriers, and non-covalent bond interactions of weakly correlated systems.

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Multi-phonon processes in solids from first-principles

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Hot carrier capture by defects in semiconductors and resonant Raman scattering are both shown to be multi-phonon processes. We have constructed a comprehensive computational approach for these processes using the density functional theory. For carrier capture, we distinguish between thermal equilibrium and nonequilibrium conditions. In the thermal-equilibrium case, capture is mediated by a nonadiabatic perturbation Hamiltonian, which is equal to linear electron-phonon coupling to first order. In the nonequilibrium case, the primary capture mechanism is within the Born-Oppenheimer approximation (adiabatic transitions), with coupling to the defect potential inducing Franck-Condon electronic transitions, followed by multi-phonon dissipation of the transition energy, while the nonadiabatic terms are of secondary importance. We report first-principles density-functional-theory calculations of the capture cross section for a carbon defect in GaN. As a second example, we present a first-principles calculation of the resonant Raman spectrum of MoS_2/WS_2 heterostructure. In this case, atomic displacements between the electronic ground state and the excited states due to charge transfer between the two layers lead to finite phonon matrix elements allowing inelastic multi-phonon relaxation to accompany the absorption and emission of photons. For each excited state, the relative Raman intensity, peak width and shape are obtained directly from a sum over all configurations of multiple phonon modes and compared to experiments. Temperature dependence of the Raman peak is calculated, which also agrees well with experiment, and predicted resonance intensity as a function of laser energy is calculated.

Recent advances in TD-DFT

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Abstract In this talk I shall highlight some in-house developments of frequency-domain relativistic TD-DFT[1-9], spin-adapted open-shell TD-DFT[10-16], linear-scaling TD-DFT[17,18] that is based on a very efficient bottom-up localization of occupied and virtual molecular orbitals[17,19,20], nonadiabatic TD-DFT for derivative couplings between excited states[21,22], as well as direct determination of interior roots of TD-DFT for high-lying excited states[23,24]. Strategies for excited states of even larger systems are also to be discussed in the merit of renormalization.

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Unifying density-functional and interatomic approaches to van der Waals interactions

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Van der Waals (vdW) interactions originate from nonlocal correlations in electronic motion, dictate thermodynamic properties of many molecular solids, layered and nanostructured materials, and biological compounds, and govern processes ranging from molecular adsorption to biological self-assembly. Semilocal and hybrid approximations to density functional theory (DFT) neglect this long-range part of the electron correlation, which has motivated the development of a plethora of approaches that recover this missing part, with no method so far being simultaneously sufficiently general, accurate, and efficient. I will review the current state of the art in modelling vdW interactions in the context of DFT, classify the different approaches along the lines of the adiabatic-connection fluctuation–dissipation theorem, and present a model that attempts to cross the boundaries between the different classes. This unified model combines ingredients from nonlocal density-functional approaches and interatomic models, inherits broad applicability of the former and good accuracy of the latter, and as a result enables a consistent treatment of vdW interactions in covalent, ionic, and hybrid metal-organic interfaces by a single method.

The XYG3 type of doubly hybrid density functionals: From molecular systems to extended solids

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Doubly hybrid (DH) functionals have emerged as a new class of density functional approximations (DFAs), which not only have a non-local orbital-dependent component in the exchange part, but also incorporate the information of unoccupied orbitals in the correlation part, being at the top rung of Perdew's view of Jacob's ladder in DFAs. In particular, the XYG3 [1] type of doubly hybrid (xDH) functionals use a low rung functional (e.g. B3LYP) to perform the self-consistent-field calculation to generate orbitals and densities, with which a top rung DH functional is used for final energy evaluation. The xDH functionals have been shown to have remarkable accuracy for molecular systems. This talk presents the results that the xDH functionals are extended from molecular systems to extended solids. This is achieved by combining the xDH functionals with the XO (i.e., eXtended ONIOM [2]) method that allows for the overlapping fragmentation. Here the high level is described with the cluster model at the xDH level, while the low level for the whole system is now described with the periodic boundary condition (PBC) at the PBE level. The method, thus coined as XO-PBC@XYG3 [3], is applied to the cohesive energy predictions for molecular crystals, which shows promise in discriminating the multiple crystal packing motifs that have important implications for pharmaceuticals, organic semiconductors, and many other chemical applications.

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Progress and problems in the design of density functionals

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Density functional theory (DFT) is the most widely used electronic structure theory. Crucial to its future is the problem of designing functionals with improved predictive power. In the first part of my talk, I shall describe a new approach to functional design, “survival of the most transferable”, which my group has developed over the past five years, and show how the resulting functionals offer greatly improved accuracy for chemical energy differences relative to existing functionals of a given class. In the second part of the talk, I will discuss the performance of present-day DFT on additional types of data, such as electrical properties, and bond-stretching that represent challenges to present-day density functionals, including those designed in my group.

Opening up new areas for density-functional theory by orbital-dependent exchange-correlation functionals

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Using Kohn-Sham (KS) orbitals and their eigenvalues as input variables of exchange-correlation functionals in density-functional theory (DFT) leads to obital-dependent functionals which open up new opportunities many of which have not yet been fully explored. Because KS orbitals and eigenvalues are implicit functionals of the ground state electron density the realm of the KS formalism of DFT is not left. The exchange energy and the corresponding local multiplicative exchange potential can be treated exactly with the help of KS orbitals and their eigenvalues. The adiabatic-connection fluctuation-dissipation (ACFD) theorem gives access to correlation energy and potential. Such ACFD methods are much more accurate than conventional DFT methods and, in contrast to the latter, can describe Van der Waals interactions and are able to treat multireference electronic structure systems, i.e., strong correlation [1,2,3,4]. ACFD methods require besides the Hartree kernel the exchange-correlation kernel, the frequency-dependent functional derivative of the exchange-correlation potential. In the simplest case the exchange-correlation kernel is neglected what amounts to the direct random phase approximation, which, however, suffers from unphysical self-interactions leading to correlation energies that are strongly overestimated in magnitude. By additionally taking into account the full frequency-dependent exchange kernel an ACFD approach free of self-interactions is obtained [3]. In a further step the correlation kernel can be considered by a power series approximation (PSA) in terms of quantities obtained from the exact exchange kernel [4]. Here expansions of the frequency dependent density-density response function and the exchange-correlation kernel with respect to the coupling constant along the adiabatic connection are presented and analyzed. This leads to a sequence of equations for the exchange kernel and all orders of the correlation kernel which can be used to devise a hierarchy of ACFD methods towards an exact treatment of the Kohn-Sham correlation energy. The PSA can be motivated and justified from the exact expansions of the response function and the exchange-correlation kernel and their relation. Results form different finite and infinite renormalized PSA ACFD methods for molecules and the homogeneous electron gas are presented.

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Multideterminant density-functional theory for strong correlation

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I will present two recently developed approaches for rigorously combining a multideterminant wave function with a density-functional approximation, with the aim of efficiently describing strongly correlated molecular systems.

1) The combination of a long-range selected configuration-interaction wave function with a shortrange correlation functional of the density and the on-top pair density [1].

2) The combination of a standard wave-function method with a correlation density functional correcting for the incompleteness of the one-electron basis set [2,3].

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