Ab-Initio Simulation methods beyond Density Functional Theory

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1 Workshop Details

1.1 Details

Timing
Number of days : 0
Start : 2005-09-23
end : 2005-09-25

Location of the activity
CECAM
46 allé e d'Italie
69007 Lyon
France

1.2 Description

The current efficiency of highly accurate QMC methods and also path integrals MC methods is reaching such a levl that dynamical and thermodynamical calculations of real systems within correlated wave functions/density matrices are becoming feasible and scientifically very attractive. We feel that this meeting could be a very stimulating event for realizing these research opportunities and will expose the frontiers of current developments to the CECAM participants. The aim of the present workshop is to get together a relatively small number of experts (aound 20-25) from the communities which include QMC method developers, with a few experts from quantum chemistry community and possibly from GW community, who have carried out several important methodological developments in recent years. Since there is a number of fundamental scientific questions and technical challenges to address, we are convinced that the time is ripe to exchange the ideas, share the experience and stimulate further developments of this new generation methods. The key issue to be addressed can be summarized as follows:

- Efficiency of MC vs MD in the many-body framework: energy differences vs forces
- QMC/MD with noisy forces/Langevin dynamics
- Large-scale wave function optimizations, ”on the fly” optimizations
- Quantum chemical methods vs QMC for cluster, nanostructures and confined systems
- New types many-body wave functions, eficient description of correlation for dynamical simulations

The main goal of the workshop will be to

- Enable exchange of ideas and developments over the last few years
- Define promising lines of research for future developments in this field
- Envision opportunities for applications of these developments to important problems in physics and chemistry

2 Requested Support

CECAM

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Psi-k

COST - MolSimu

3 Participant List

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4 Presentation List

Coupled Electron-Ion Monte Carlo Study of Hydrogen Fluid

Kris Delaney

University of Illinois at Urbana-Champaign, United States

Abstract

We present details of the Coupled Electron-Ion Monte Carlo method (CEIMC) [1,2] applied to the problem of the equation of state of pure hydrogen. The aim is to develop a method that can predict state information outside the range of temperatures and pressures that are accessible with other well-established methods, such as PIMC ($T\rangle 5000K$) or ground-state quantum Monte Carlo methods (T=0K).

The CEIMC approach couples a finite-temperature Monte Carlo simulation of atomic nuclei (classical or quantum path integrals) to a zero-temperature quantum Monte Carlo simulation of the electronic subsystem. This segregation is a good approximation at low temperatures, for which thermal excitation of electrons is negligible.

The nuclear configuration space is sampled using Boltzmann statistics. Configurational energy differences are computed within the Born-Oppenheimer (BO) approximation with variational Monte Carlo or reptation quantum Monte Carlo. Both methods supply unbiased but noisy estimates of BO energy differences, requiring a modified Metropolis algorithm to sample nuclear configurations.

Using a guiding electronic wavefunction generated through a fast band-structure calculation, we study the so-called plasma phase transition, the conditions under which a fluid of pure molecular hydrogen dissociates.

References

[1] D. Ceperley, M. Dewing and C. Pierleoni, in ”Bridging Time Scales: Molecular Simulations for the Next Decade”, eds. P. Nielaba, M. Mareschal and G. Ciccotti, Springer-Verlag, pgs. 473-500 (2002).

[2] C. Pierleoni, D. M. Ceperley and M. Holzmann, Phys. Rev. Lett. 93, 146402 (2004)

Linear scaling electronic structure calculations and accurate statistical mechanics sampling with noisy forces

Krajewski Florian

ETH Zurich, Switzerland

Abstract

Statistical sampling of the ionic Boltzman distribution can be based either on empirical force fields or on electronic structure calculations. In the latter case the use of linear scaling algorithms is imperative in order to simulate large systems. We modify a previous stochastic linearly scaling electronic structure algorithm [F. R. Krajewski and M. Parrinello, Phys. Rev. B textbf71, 233105 (2005)] in a manner that is suitable for obtaining statistical mechanics averages over ionic configurations. We show that the noise inherent in our stochastic evaluation of the interatomic forces can be corrected. We demonstrate the accuracy of our method by performing simulations based on the Langevin equation on a tight binding model for Si in the semiconducting and in the liquid metallic phase. Our approach can be adapted to other stochastic schemes for evaluating interatomic forces such as quantum Monte Carlo.

A Test of Reliability and Efficiency of Qmc Forces

Lucas Wagner
North Carolina State University, United States

Abstract

Ab initio molecular dynamics using Density Functional theory has been very successful in the past decade; however, there are still some situations where the commonly used functionals are inaccurate. Intermolecular forces and transition metal oxides, especially, are well-known examples of such inacurracies. Quantum Monte Carlo, with its many-body treatment of electron correlation, is expected to correct a major part of these deficiencies and with its scaling similar to DFT, large simulations are possible. A major stumbling block has been the calculation of forces that are both correct and efficient within QMC. Over the past years, there have been several attempts to obtain such forces, and for small(few-atom) systems, but no systematic comparison of their efficiency, accuracy, and scaling. We show data on a set of representative systems, comparing some of the proposed approaches [1-3]. All these approaches are done within reptation Monte Carlo algorithm, which allows for unbiased estimators even for systems containing transition metals.

References

[1] Chiesa, Ceperly, Zhang. PRL 94 036404
[2] Filippi and Umrigar. PRB 61 R16291
[3] Pierleoni and Ceperley. ChemPhysChem 6 1

Lattice Regularized Diffusion Monte Carlo Simulations of iron dimer

Michele Casula
SISSA / ISAS, Italy

Abstract

The transition metal compounds play a crucial role in various fields, ranging from biomolecular reactions to magnetic solid state properties. On the other hand, they are extremely challenging due to the strong dynamic correlation present in the unfilled d-shell, which makes the predictions of the density functional theory completely unreliable and requires the use of more accurate post-Hartree-Fock methods, limited however to small systems. The Lattice Regularized Diffusion Monte Carlo (LRDMC) method, recently introduced [M. Casula, C. Filippi, and S. Sorella, Phys. Rev. Lett. 95, 100201 (2005)], seems to be an effective alternative, since it can provide very accurate results with a favorable size scaling. One of the main advantages of this framework is the possibility to include non-local potentials in a consistent variational scheme, substantially improving both the accuracy and the computational stability upon previous non-variational diffusion Monte Carlo approaches. Here, we apply the LRDMC framework to the iron dimer. Despite its simplicity, its neutral and anionic ground states are controversial, and we try to clarify their symmetry by comparing our LRDMC results with experimental data. We use a fully optimized Jastrow geminal wave function and we carry out LRDMC simulations to study the bond length, the binding energy and the zero point motion of the lowest energy states.

The Surface Energy of the Electron Gas

Matthew Foulkes
Imperial College London, United Kingdom

Abstract

A few years ago, in a paper in Phys. Rev. B, Yan, Perdew and co-workers wrote: ”For the surface energy of jellium at alkali-metal densities, the local-density approximation (LDA) and more advanced density-functional methods disagree strongly with the wave-function-based Fermi hypernetted-chain and diffusion Monte Carlo methods.” More recently, Sottile and Ballone extrapolated the results of their DMC simulations of jellium spheres to obtain a surface energy in agreement with density-functional theory but not with earlier DMC simulations of flat surfaces. This talk describes our investigation of the causes of these disagreements and explains why QMC calculations of surface energies are so difficult. We discuss the treatment of finite-size errors; report some unexpected problems faced during the construction and optimisation of trial wavefunctions; and explain the importance of aiding error cancellation by comparing like with like. Many of these issues are generic and will be encountered more and more often as the use of QMC methods spreads. Reassuringly, if somewhat disappointingly, our final results (variational MC only so far) agree with density-functional theory and with the DMC results of Sottile and Ballone.

Kink-based path integral studies of atoms and molecules

Randall Hall
Louisiana State University, United States

Abstract

A kink-based path integral approach has been developed for use in simulating molecular systems at finite temperatures. The goal of the approach is to alleviate the infamous “sign” problem that occurs in fermionic path integral calculations as well as offering a simulation technique that can simultaneously treat electronic and geometric degrees of freedom. The method uses Gaussian basis functions and results MP2-level accuracy in initial calculations on small molecules. Developments in the method to treat relatively weak interactions such as hydrogen bonding are the subject of current work. The method will be described and results from test calculations will be presented.

References

[1] RW Hall, *An Adaptive, Kink-Based Approach to Path Integral Calculations*, J. Chem. Phys. **116** 1-7 (2002)

[2] RW Hall, *Kink-Based Path Integral Calculations of Atoms He-Ne*, Chem. Phys. Lett. **362** 549-553 (2002)

[3] RW Hall, *Simulation of electronic and geometric degrees of freedom using akink-based path integral formulation: application to molecularsystems*, J. Chem. Phys. **122** 164112-1-164112-8 (2005)

Ab Initio Molecular Dynamics Beyond the Born-Oppenheimer Approximation

Todd Martinez
UIUC, United States

Abstract

The ab initio multiple spawning (AIMS) method has been developed for fist principles molecular dynamics including quantum effects such as tunneling and population transfer between electronic states (breakdown of the Born-Oppenheimer approximation). We discuss recent developments and benchmarks in the multiple spawning dynamics method which underlies AIMS. We show that accurate results can be obtained in models with hundreds of dimensions, even when the underlying electronic basis is not the “natural” adiabatic representation. We provide an overview of recent applications ranging from photoinduced cisň-trans isomerization to excited state intramolecular proton transfer (ESIPT) and photodynamics of DNA bases. The role of simultaneous degeneracies of three electronic states in ESIPT is discussed. Extensions of AIMS to condensed phase systems have been pursued using a combination of reparameterized multireference semiempirical (RPMRSE) methods and hybrid quantum mechanical/molecular mechanical (QM/MM) representations of potential energy surfaces. We show that the RPMRSE methods can approach the accuracy of multi-reference perturbation theories such as CASPT2 with limited reparameterization effort. Several representative examples of nonadiabatic dynamics in solution and protein environments using this “nearly” AIMS method are presented and the influence of the solvent/protein environment on excited state reactivity is assessed.

Coupled Electron-Ion Monte Carlo Simulations of Dense Hydrogen

David Ceperley
University of illinois at Urbana Champain, United States

Abstract

Quantum Monte Carlo (QMC) methods are the most accurate and general methods for computing total electronic energies, however, they have been limited to temperatures greater than 5000K, or to zero temperature. In recent years, we and others have been working on methods that utilize the Born Oppenheimer approximation to allow simulations coupling the correlated quantum systems and a system of ions. Such an algorithm could allow the sort of progress which occurred when Car and Parrinello coupled local density functional theory with molecular dynamics of ions.

Using quantum Monte Carlo, one estimates the Born-Oppenheimer energy change which is then used in a Metropolis simulation of the ionic degrees of freedom. We modify the usual Metropolis acceptance probability to eliminate the bias caused by noise in this energy difference, allowing more noisy estimates of the energy difference and reducing the sampling time of the electronic degrees of freedom. We have implemented a method for estimating the energy change with correlated sampling technique so that the variance of the difference is smaller than of each energy individually using either variational MC or reptation MC. We have performed simulations of liquid H2 and liquid metallic H down to temperatures as low as 300K. We discuss some possible advantages of the CEIMC method relative to Car-Parrinello simulations concerning how the quantum effects of the ionic degrees of freedom can be included and how the boundary conditions on the phase of the wavefunction can be integrated over.

Towards more accurate variational wavefunctions for strongly correlated systems

Sandro Sorella
SISSA, Italy

Abstract

I will briefly discuss recent progress in describing electron correlation by means of variational wave functions, that can be simulated by the statistical method-the Variational Quantum Monte Carlo- (VMC), in an affordable computational time. I will discuss recent successful applications of so called antysimmetried geminal functions (AGP), to transition metal oxides and Hydrogen under strong pressure. These applications have been made possible thanks also to a recent advance in the energy optimization techniques. that allows to deal with many variational parameters within the VMC. Within this scheme a large part of the correlation energy can be taken into account by appropriate 2-body and 3-body Jastrow factors. I will also discuss that, based on an analogy with the Hubbard model, these type of geminal wave functions should be suitable of further improvements not only by introducing triplet correlations in the geminal (by the so called Pfaffian introduced recently, K. Schmidt, L. Mitas) but especially by adding to these wave functions the so called backflaw correlations, introduced by Feynmann long time ago for the Helium.

Noncovalent interactions: diffusion Monte Carlo study of biomolecular model systems

Martin Fuchs
Fritz-Haber-Institut der MPG, Germany

Abstract

Density-functional theory (DFT) calculations are a powerful tool for studying biomolecules. Hydrogen bonding is a key aspect in such systems where, moreover, also Van der Waals dispersion forces may play an important role. For these ”non-covalent” interactions the accuracy of standard functionals like generalized gradient approximations (GGA) can be rather uncertain. Benchmarking DFT is thus essential. Accurate total energies of molecules or solids can be obtained by diffusion Monte Carlo (DMC) calculations. DMC remains computationally feasible even in larger systems where conventional correlated methods like coupled cluster will become impractical. While already applied with success to chemically bonded systems, little is known about how DMC performs for non-covalent bonds.

Here we apply DMC to biomolecular model systems that showcase the performance of present-day DFT [1]: formamide-water, tautomerizing via proton transfer; formamide chains, displaying cooperative strengthening of hydrogen bonds; (methyl-) formamide dimers, where GGAs may miss dispersion interactions dependent on the hydrogen bond geometry. For all these systems our DMC hydrogen bond strengths agree well with post-Hartree-Fock data. In addition we calculate adenine-thymine, a DNA base pair where hydrogen bonding and stacking interactions compete. GGAs and hybrid functionals are adequate for the hydrogen bonded conformers, but fail to bind the stacked pair. Second order perturbation theory (MP2) markedly overestimates the stacking energy compared to coupled cluster [CCSD(T)]. Our DMC results confirm those from CCSD(T) studies [2].

Work done with Claudia Filippi (Instituut Lorentz, Univ. Leiden, The Netherlands), Joel Ireta, and Matthias Scheffler (Fritz-Haber-Institut der MPG, Berlin, Germany).

References

[1] J. Ireta, J. Neugebauer, and M. Scheffler, J. Chem. Phys. A 108, 5692 (2004).

[2] P. Jurecka and P. Hobza, J. Am. Chem. Soc. 125, 15608 (2003).

Recent developments and applications of quantum Monte Carlo techniques

Dario Alfe
University College London, United Kingdom

Abstract

I will discuss some recent development of ’linear scaling’ quantum Monte Carlo (QMC) techniques based on non-orthogonal localised orbitals. I will then present some recent application of QMC, with results obtained for the structural properties, Schottky formation energy, and surface energy of the (001) surface in MgO. The results are in good agreement with the available experimental data.

Structure of fermion nodes and pfaffian wavefunctions with singlet and triplet pairs

Lubos Mitas
Department of Physics, North Carolina State University, United States

Abstract

I will talk about our effort to understand nodes of fermionic wavefunctions, in particular, about the structure of nodes and number of nodal cells for ground and excited state wavefunctions. We have also explored some of the possibilities offered by the functional forms which go beyond the Slater determinants such as singlet pairing determinats and also combination of singlet and triplet pairs in the form of a pfaffian. We find improvements in the nodal structure and consistently more systematic results for the amount of recovered correlation energy in atoms and small molecules.

The Fermion Monte Carlo: a method to alleviate the Sign Problem

Roland Assaraf
CNRS, France

Abstract

We present the results of mathematical study on the Fermion Monte Carlo algorithm, a stochastic method introduced by M. H. Kalos and coworkers to handle Fermionic systems. The role of the different ingredients of the method is discussed. It is shown that the Fermion Monte Carlo algorithm alleviates the unstability of Quantum Monte Carlo simulations by performing a mapping to a problem with a reduced fermion-bose gap. However a full stability is in general not achieved. The full stability observed when a third ingredient is included [M. H. Kalos and F. Pederiva, Phys. Rev. Lett. **85** , 3547 (2000)], namely using non symmetric guiding functions, is the counterpart of a slowly converging population control error.

References

[1] R. Assaraf, M. Caffarel and A. Khelif, The Fermion Monte Carlo revisited.

[2] M. H. Kalos and Francesco Pederiva, Phys. Rev. Lett. **85** 3547 (2000).

[3] Z. Liu, S. Zhang and M. H. Kalos, Phys. Rev. E, **50** 3220 (1994).

[4] D.M. Arnow, M. H. Kalos, M. A. Lee and K. .Schmidt, J. Chem. Phys. **77** 5562 (1982).

Hartree-Fock Revisited

Bernard Bernu
CNRS, France

Abstract

One-body solutions are often needed as input of various sophisticated methods. Hartree-Fock framework is (supposed to be) well understood. But the solutions of Hartree-Fock equations converge with difficulty. We discuss the convergence problems of this equation and present a new scheme which allow us to find rapidly solutions at all densities for the homogeneous electron gas in two dimensions. The method does not need any assumption about the symmetries of the ground states.

Some combinatorial ideas for path resummations, and their application to Fermion QMC

Ali Alavi
Cambridge, United Kingdom

Abstract

By re-summing the path integral formula for the partition function, we devise a method for fermion QMC based on sampling ”graphs”. The sign-problem for smapling graphs is greatly improved. We show how the method works for a dissociating N$_2$ molecule.

Properties of Dense Helium at Giant Planet Interiors

Burkhard Militzer
Carnegie Institution of Washington, United States

Abstract

The properties of hydrogen-helium mixtures at high pressure are crucial to address important questions about the interior of giant planets e.g. whether Jupiter has a rocky core and whether it was formed by core accretion. Understanding dense, fluid hydrogen and helium is also of interest for the characterization of the more than 100 extrasolar giant planets that have be detected in recent years by radio velocity measurements. Using first principles simulations, we study the properties of hydrogen-helium mixtures as a function of pressure, temperature and composition[1]. In this presentation, we focus on the equation of state calculation [2,3] of pure helium and the comparison with shock wave experiments. Shock wave measurements are the only laboratory technique available today to directly probe the conditions present in the interior of giant planets. Our calculations demonstrate that the shock properties of helium differ sub-

stantially from those of hydrogen. We make suggestions for new shock experiments of helium in order to validate the hydrogen experiments and to understand processes giant planet interiors. Our calculations will also become relevant for the interpretation of the gravitational moments that will be measured by the Jupiter orbiter mission Juno to be launched under NASA's New Frontiers program.

References

[1] B. Militzer, "Hydrogen-Helium Mixtures at High Pressure", J. Low Temp. Phys., in press (2004), cond-mat/0411458.

[2] B. Militzer, D. M. Ceperley, "Path Integral Monte Carlo Calculation of the Deuterium Hugoniot",Phys. Rev. Lett. 85 (2000) 1890.

[3] S. A. Bonev, B. Militzer, G. Galli, "Dense liquid deuterium: Ab initio simulation of states obtained in gas gun shock wave experiments", Phys. Rev. B 69 (2004) 014101.

Quantum Monte Carlo method using Gaussian basis sets

Shiwei Zhang
College of William and Mary, United States

Abstract

We discuss some recent developments in an auxiliary-field Monte Carlo method for quantum chemistry type of calculations, using Gaussian basis sets. The method is based on the phaseless Slater determinant random walk approach that we have been working on in the past few years. It takes the form of an ensemble of independent-particle calculations in auxiliary fields. Each random walker is an independent-particle wave function, i.e., a Slater determinant. The random walkers evolve as auxiliary fields are sampled, and a many-body wave function is obtained as a stochastic superposition of independent-particle solutions. The random walks are constrained in Slater determinant space by a phaseless approximation to deal with the phase problem. Generalizing our previous formalism with a plane-wave basis and pseudopotentials, we cast the method in an arbitrary single-particle basis. All-electron calculations are performed on small molecules, using Gaussian basis sets, to test the method and study its characteristics.

Quantum Monte-Carlo examines the accuracy of density functionals and anisotropy effects for the diamond to beta-tin transition in silicon

Richard Hennig
Ohio State University, United States

Abstract

Under pressure silicon displays a at least twelve crystallographic phases with a steady increase of coordination number and a transition from insulating to metallic. Density functional calculations support the experimental sequence, however, the transition pressures depend strongly on the specific density functional approximations. We use diffusion Monte-Carlo calculations for silicon phases to test the accuracy of current density-functional approximations based on the local density (LDA), the density gradient (PW91, PBE), and the kinetic energy density (TPSS [1]), as well as a screened hybrid functional (HSE [2]).

The accuracy of different pseudopotentials in quantum Monte-Carlo calculations is tested for the Si dimer molecule. Hartree-Fock pseudopotentials correctly predict the experimental bond length and binding energy while LDA and GGA pseudopotentials provide bond lengths 0.02 to 0.04 A too short and show errors in the binding energy of about 50 meV.
For crystalline Si in the diamond structure Diffusion Monte Carlo predicts the correct cohesive energy, lattice constant, and bulk modulus. The pressure for the transition to metallic beta-tin is larger in diffusion Monte-Carlo than in experiments. Previous diffusion Monte-Carlo calculations gave 16.5(5) GPa [3]. Our value of 14(1) GPa is closer to the experiments ranging from 10 to 13 GPa. Diffusion Monte Carlo and density functional calculations show that the diamond to beta-tin transformation is sensitive to anisotropic stresses; an anisotropy of about 1 GPa lowers the prediction to agree with experiments. Diffusion Monte Carlo for high-pressure Si phases shows that the functionals LDA, PW91, PBE, and TPSS underestimate their energies relative to the diamond ground state. The screened hybrid functional HSE improves the description of the covalent bonds in Silicon and provides energies in close agreement with diffusion Monte-Carlo.

References

[1] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria. ”Climbing the density-functional ladder: Nonempirical metageneralized gradient approximation designed for molecules and solids.” Phys. Rev. Lett. 91, 146401 (2003)

[2] J. Heyd, G. E. Scuseria, and M. Ernzerhof. ”Hybrid functionals based on a screened Coulomb potential.” J. Chem. Phys. 118, 8207 (2003).

[3] D. Alfe, M. J. Gillan, M. D. Towler, and R. J. Needs. ”Diamond and $beta$-tin structures of Si studied with quantum Monte Carlo calculations.” Phys. Rev. B 70, 214102 (2004).

Trial Wavefunctions for He3

Markus Holzmann
LPTL, Jussieu, Paris, France

Abstract

Fixed node Quantum Monte Carlo calculations for liquid He3 at zero temperature provide an important benchmark for the progress of microscopic calculations for quantum liquids. Despite many years of research the calculated equation of state and the magnetic susceptibility is still in disagreement with experimental results [1]. We will present results on more complicated trial wavefunctions to improve the nodal error which help to reduce some of the discrepancies.

References

[1] F.H. Zong, D.M. Ceperley, S. Moroni, and S. Fantoni,
Mol. Phys. 101, 1705 (2003).

Energy and variance optimization of many-body wave functions

Cyrus Umrigar
Cornell University, United States

Abstract

We present a simple, robust and efficient method for varying the parameters in a many-body

wave function, both for continuum and lattice problems, to optimize the expectation value of the energy$ˆ 1$. The method is compared to what is currently the most popular method for optimizing many-body wave functions, namely minimization of the variance of the local energy$ˆ 2$. The variance minimization method is far more efficient than it straightforward energy minimization because for a sufficiently flexible variational wave function, it is possible to lower the energy on the finite set of Monte Carlo (MC) configurations on which the optimization is performed, while in fact raising the true expectation value of the energy. On the other hand, if the variance of the local energy is minimized, each term in the sum over MC configurations is bounded from below by zero and the problem is far less severe$ˆ 2$. Our new energy optimization method gets around this problem by adding terms to the straightforward expression for the Hessian that are zero when the integrals are performed exactly, % Hessian of the energy that have zero expectation value, but that cancel much of the statistical fluctuations for a finite Monte Carlo sample. With the additional terms, the Hessian is written as a sum of covariances resulting in much reduced fluctuations. In case the wave function parameters are linear in the exponent, part of the Hessian can be written as a tri-covariance, as also pointed out by Sorella$ˆ 3$, making it apparent that further cancellations of fluctuations occur. The optimization of Jastrow parameters converges in two Monte Carlo steps if a sufficiently large sample is used, but, it is more computationally efficient to first do 2 or 3 iterations with small samples followed by a single large-sample iteration. The estimated gain in efficiency increases with system size, ranging from 3 orders of magnitude for small molecules to 5 orders of magnitude for the larger molecules we used as test cases.

We discuss the different problems (and their solution) that affect optimization of the Jastrow parameters vs. the optimization of the determinantal parameters – for the Jastrow, the eigenvalues of the Hessian typically span 11 orders of magnitude; for the determinantal parameters, terms in the expectation values may diverge.

References

1) C. J. Umrigar and Claudia Filippi, Phys. Rev. Lett., 94, 150201-1 (2005).
2) C. J. Umrigar, K.G. Wilson and J. W. Wilkins, Phys. Rev. Lett., 60, 1719 (1988).
3) S. Sorella, Phys. Rev. B 71, 241103 (2005).

Excited states from Many-Body Perturbation Theory: Spectra and Total Energies

Michael Rohlfing
International University Bremen, Germany

Abstract

We discuss many-body perturbation theory for excited electronic states (electrons, holes, and pair states) [1]. This is realized within the GW approximation for the electronic self-energy operator and the corresponding electron-hole interaction kernel. The latter is required to solve the Bethe-Salpeter equation (BSE) for electron-hole pair states. The method yields highly accurate band-structure energies, ionization energies, electron affinities, and electron-hole excitation energies, and allows to evaluate optical spectra. In addition to the spectra, the GW+BSE approach allows to investigate the total energy of excited electronic states. This enables the discussion of excited-state geometry relaxation, spectral broadening, Stokes shifts, and excited-state dynamics. As examples, results for exciton self-trapping in the polymer PPP [2] and atom expulsion from alkali halide surfaces will be discussed.

References

[1] M. Rohlfing and S. G. Louie, Phys. Rev. B 62, 4927 (2000).

[2] E. Artacho, M. Rohlfing, M. Cote, P.D. Haynes, R.J. Needs, and C. Molteni, Phys. Rev. Lett. 93, 116401 (2004).

A method for computing forces in diffusion Monte Carlo

Shiwei Zhang
College of William and Mary, United States

Abstract

Computation of ionic forces using quantum Monte Carlo methods has long been a challenge. We introduce a simple procedure, based on known properties of physical electronic densities, to make the variance of the Hellmann-Feynman estimator finite. We obtain very accurate geometries for the molecules H2, LiH, CH4, NH3, H2O and HF, with a Slater-Jastrow trial wave function. Harmonic frequencies for diatomics are also in good agreement with experiment. An antithetical sampling method will also be discussed for additional reduction of the variance.

5 Program

Day 1: Sept. 23 2005

Session : 1
09:00 to 09:45 : Presentation
Coupled Electron-Ion Monte Carlo Simulations of Dense Hydrogen
David Ceperley

09:45 to 10:30 : Presentation
A Test of Reliability and Efficiency of Qmc Forces
Lucas Wagner

10:30 to 11:00 : Coffee Break

11:00 to 11:45 : Presentation
Kink-based path integral studies of atoms and molecules
Randall Hall

11:45 to 12:30 : Presentation
Some combinatorial ideas for path resummations, and their application to Fermion QMC
Ali Alavi

Session : 2
16:30 to 17:15 : Presentation
Linear scaling electronic structure calculations and accurate statistical mechanics sampling with noisy forces
Krajewski Florian

17:15 to 17:45 : Presentation
Quantum Monte Carlo method using Gaussian basis sets
Shiwei Zhang

15:15 to 16:00 : Presentation
Properties of Dense Helium at Giant Planet Interiors
Burkhard Militzer

16:00 to 16:30 : Coffee Break

14:30 to 15:15 : Presentation
Coupled Electron-Ion Monte Carlo Study of Hydrogen Fluid
Kris Delaney

17:45 to 18:15 : Presentation
A method for computing forces in diffusion Monte Carlo

CECAM workshop Program

Shiwei Zhang

Day 2: Sept. 24 2005

Session : 3
09:45 to 10:30 : Presentation
Ab Initio Molecular Dynamics Beyond the Born-Oppenheimer Approximation
Todd Martinez

09:00 to 09:45 : Presentation
Lattice Regularized Diffusion Monte Carlo Simulations of iron dimer
Michele Casula

10:30 to 11:00 : Coffee Break

11:00 to 11:45 : Presentation
Towards more accurate variational wavefunctions for strongly correlated systems
Sandro Sorella

11:45 to 12:30 : Presentation
Hartree-Fock Revisited
Bernard Bernu

Session : 4
14:30 to 15:15 : Presentation
Trial Wavefunctions for He3
Markus Holzmann

15:15 to 16:00 : Presentation
Energy and variance optimization of many-body wave functions
Cyrus Umrigar

16:00 to 16:30 : Coffee Break

16:30 to 17:15 : Presentation
Structure of fermion nodes and pfaffian wavefunctions with singlet and triplet pairs
Lubos Mitas

17:15 to 18:00 : Presentation
Recent developments and applications of quantum Monte Carlo techniques
Dario Alfe

Day 3: Sept. 25 2005

Session : 5
09:00 to 09:45 : Presentation
The Fermion Monte Carlo: a method to alleviate the Sign Problem
Roland Assaraf

09:45 to 10:30 : Presentation
The Surface Energy of the Electron Gas
Matthew Foulkes

10:30 to 10:45 : Coffee Break

10:45 to 11:30 : Presentation
Noncovalent interactions: diffusion Monte Carlo study of biomolecular model systems
Martin Fuchs

11:30 to 12:15 : Presentation
Excited states from Many-Body Perturbation Theory: Spectra and Total Energies
Michael Rohlfing

12:15 to 13:00 : Presentation
Quantum Monte-Carlo examines the accuracy of density functionals and anisotropy effects for the diamond to beta-tin transition in silicon
Richard Hennig

6 Organizer's report

6.1 Conclusions.

The workshop has been very successful and resulted in a lively exchange of ideas on new developments in correlated electrons numerical methods with the emphasis on new techniques to develop ab-initio simulation methods based on the QMC solution of the electronic problem. It had gathered together about 25 participants, mainly from the QMC community but the presence of several scientists from the Quantum Chemistry and DFT communities has been very much welcome and fruitful. In general, the presentations have been quite informal and open to discussion during and after the talks. This informal and stimulating exchange of ideas has been one of the most successful aspects of the meeting and highly appreciated by the participants.
Our main conclusion are as follows:
- A number of interesting and promising techniques to perform Ab-Initio Simulation beyond Density Functional Theory have been reported. The Monte Carlo route (CEIMC), in which only electronic energies are required from QMC, is the most developed so far. The method and some results have been presented in two separate talks during the workshop. Interesting progresses and benchmarks on force methods within QMC has been reported for both light and heavy elements. This study has shown that QMC forces for light elements can be computed at a level of accuracy sufficient to be used in a Molecular Dynamics simulation of the nuclei. On the contrary significant challenges are still present for heavier elements such as transition metals. The most recent results suggest that the research is going in the right direction especially using more advanced methods such as Reptation Monte Carlo.
- PIMC methods are also powerful techniques for finite temperature systems. An interesting method based on PIMC in orbitals space has shown to be capable to treat both electronic and nuclear degrees of freedom in small molecules. A related promising method in the space of determinants has been reported. In this method an analytical re summation of diagrams allow to considerably reduce the sign problem. In this respect it is very interesting to follow the future developments of the methods and its performance for large systems. Restricted PIMC for many fermions systems at temperatures above few thousand kelvin are well developed. New interesting results on high pressure helium has been reported in agreement with experimental data and in striking disagreement with ab-initio DFT predictions.
- A recently developed linear scaling method in CPMD has shown ideas on how to use noisy forces in a dynamical simulation of the nuclei. This is exactly the situation to be faced in a QMC based MD simulation. A preliminary account of a first attempt in this direction has been presented for hydrogen with very promising results.
- Another important aspect of QMC method in general is to develop new and more accurate and flexible wavefunctions. Interesting ideas on methods how to include correlations have been suggested. The functional forms which include correlations in an efficient ways such as Bardeen- Cooper-Schrieffer wavefunctions which are capable of capturing the pair correlations more consistently has been tested. Furthermore, ideas based of pfaffian wave functions has been tested out ans show promise for even higher accuracy (pfaffians are generalizations of determinants which enable to include both singlet and triplet pairing effects into a single wave function). Tests with molecular and condensed matter systems have been reported.
- A new QMC method based on lattice discretization has been proposed and tested. Its significant advantage over continuum QMC is that it enables to use the fixed node approximation for nonlocal pseudopotential while keeping the energy upper bound property. Although the cur-

rent methods do handle this problem the cost is significant and the lattice reformulation enables possibly other speed-ups in efficiency.
- A number of talks on the use of QMC for real materials has been presented. Recent successes of QMC but also its limitations for these very complex situations have been highlighted. We believe the situation is still one step away from the possibility to actually explore the nuclear motion in these cases but testing of reaction paths and isomer spaces look very promising.

6.2 Recommendations.

- the CEIMC, applied so far to hydrogen, should be developed toward the direction of studying more complex systems. Important advances would be to explore the use of pseudopotentials to allow considering heavier elements.
- the next idea which is becoming of key importance is the flexibility and efficiency of the wavefunctions for dynamical calculations, bond-breaking and description of several electronic states in parallel. This will be undoubtedly one of the most active and promising areas considering the impact and interest in presented talks in this direction. Efficiency of the wavefunctions has been always at the heart of successful electronic structure methods employed in dynamical framework and it remains such for the future as well. New mathematical developments such as pfaffians and pairing wavefunctions hold a significant promise for the future.
- the dynamical calculations with the noise have also a great promise within quantum Monte Carlo techniques. These methods have inherent stochasticity which enables to merge it with Langevin-type simulations rather naturally and hold a significant potential for the successful development in the future. New ideas to explore the discretization techniques such as lattice formulations are very interesting as well. They enable to formulate the quantum problem in the language and representations which are very close to quantum field theory and therefore open door into experience and ideas which has been developed in this area of research over the past twenty years or so.
- the quantum Monte Carlo/Molecular Dynamics (QMC/MD) is a very recent development which is in its first steps to be established as a viable simulation methods. Some of the algorithmic parts are already developed; some needs more work and development. The method holds a great promise for phenomena where the character of the processes involved simply requires proper description at the quantum level such as proton and electron transfers in biomolecules, excitations in molecular dynamics, or optical properties at finite temperatures
- some work has been presented on transport and quantum dynamics. So far this field has not been much explored by the quantum Monte Carlo methods. We believe that in future this will become much more active area for research. Basically, once the static and classical ion/QMC electrons types of calculations get more established it will be natural to extend the QMC techniques to this direction.

Each of the mentioned topics could become an exciting theme for future CECAM activities such as summer workshops or summer schools for graduate students and postdocs. We hope to propose some of these ideas for a future workshop in a two or three years timeframe. We also want to mention that these are all the *most advanced* directions where the feasibility of new algorithms is being pushed beyond ordinary limits and fundamental barriers such as exponential scaling of several quantum computational problems is being attacked. This is both very challenging and very exciting field of research which has a significant potential for breakthroughs in simulation studies of real materials. We highly recommend and hope that CECAM will keep a visible presence in this unique area of research in the future.