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Quantum Monte Carlo Methods

Abstracts

PHYS 160 [642328]: Fermion Monte Carlo calculations of the electronic structure of first row dimers

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The now-standard Diffusion Monte Carlo with an approximate fixed node gives a good account of the electronic structure of many systems. There are, however, systems for which the fixed-node error is appreciable. We have generalized the method proposed by Kalos and Pederiva (1) to apply to molecules and have carried out a series of calculations of some first-row dimers. At present the method is rather inefficient, but the results are in agreement with experiment.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

References: (1) M.H. Kalos and F. Pederiva, Phys. Rev. Lett. 85, 3547 (2000)

PHYS 161 [642770]: Analysis of wavefunctions by Monte Carlo methods

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The interpretation of wavefunctions in terms of chemical concepts is a central topic in quantum chemistry. An enormous amount of work has been done within Hartree-Fock and density functional methods, whereas the analysis of correlated wavefunctions has been considered only marginal. We present a computationally simple approach which provides insight into the nature of chemical bonding between individual pairs of atoms. Our approach is based on well established relations between the bond order and charge fluctuations with respect to atomic domains. In a first step atomic domains are obtained from Hartree-Fock or Kohn-Sham densities, using Bader's definition of atoms in molecules. These domains are applied in a second step in quantum Monte Carlo calculations to determine bond orders for pairs of atoms. We illustrate this concept for C-O and C-S bonds in different molecular environments.

PHYS 162 [642012]: Trial wave function construction and the nodes of trial and exact wave functions in quantum Monte Carlo

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Although quantum Monte Carlo is, in principle, an exact method for solving the Schrödinger equation, fermion systems still pose a challenge, due to the sign problem. The fixed-node approach is a widely used approximation; however there are no systematic ways to increase the quality of the trial wave function nodes, reducing the fixed-node bias. Very little is known about the nodal structure of wave functions. A detailed knowledge of the properties of these hypersurfaces would be of great benefit to quantum simulations. Trial wave functions could then be systematically improved within the fixed-node approximation. Here we review what is known about nodes, and study exact and trial nodes of simple systems. Based on these studies, we formulate some conjectures and apply them to build multideterminant wave functions for more complicated systems. Preliminary calculations on Li₂ molecule recovered 99.8% of the correlation energy, with a five-determinant wave function.

PHYS 163 [644587]: Direct calculation of excited state energies by spectral evolution Monte Carlo

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We present recent advances in methodology and applications of a general quantum Monte Carlo scheme to evaluate excited state energies, namely the projection operator imaginary time spectral evolution (POITSE) method. The POITSE approach can provide exact excited state energies independent of nodal approximations. The method is based on diffusion Monte Carlo evaluation of an imaginary time correlation function, whose time dependence contains information on the excited state energies of interest. This information is extracted using a Bayesian inference procedure, the maximum entropy method. We discuss algorithmic details of the approach, and demonstrate its utility and generality with examples taken from van der Waals clusters involving molecules and helium.

PHYS 164 [642486]: Automated histogram filtering approach to optimize wave functions for use in Monte Carlo simulations

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Accurately optimized parameter values for wave functions are necessary for the development and success of quantum Monte Carlo methods. To achieve this objective we previously presented the technique of histogram filtering that optimizes parameters in various explicitly-correlated wave functions as well as the molecular geometry. This optimization was performed manually. In this paper we describe how to computer automate the filtering, incorporating new features designed to make the optimization more robust. We identify and optimize various algorithmic parameters which must be specified for its implementation. As a test case we reproduce our previous results for an eleven-parameter hydrogen molecule wave function, with the expected many-fold increase in efficiency afforded by automation. Our results suggest a reproducible and reliable approach to the exhaustive optimization of sophisticated, explicitly-correlated wave functions, those containing hundreds of variational parameters.

PHYS 165 [644542]: Optimization of quantum Monte Carlo trial wave functions by energy minimization
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We present a quantum Monte Carlo approach for the optimization of correlated many-body trial wave functions by minimization of the expectation value of the system Hamiltonian. This energy minimization approach removes systematic fluctuations in the local energy which are directly correlated with variations in the wave function parameters. The approach is amazingly robust, allowing for the simultaneous optimization of thousands of variational parameters in a few steps. It has been applied successfully to the study of delicate electron correlation properties of periodic solids, providing valuable information on the functional form of optimal correlated wave functions.

PHYS 190 [644260]: Benchmark quantum Monte Carlo calculations

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While quantum Monte Carlo (QMC) methods have been successfully applied to a wide range of molecular systems, it is imperative that the accuracy of the QMC approaches be measured against well-defined benchmarks. In this work, I present results for atomization energies calculated by fixed-node diffusion Monte Carlo for the 55 molecules in the original (G1) "Pople Set". The root mean square deviation is roughly 2.5 kcal/mol with a maximum deviation from experiment of 14 kcal/mol. These results support claims that QMC provides near "chemical" accuracy, although in several cases (i.e., SO₂, P₂, NO) the deviation from experiment is rather large. For these cases with the largest deviations from experiment, a detailed investigation of possible sources of error has been carried out and will be discussed and compared.

PHYS 191 [642248]: Linear scaling calculations of the local energy in QMC

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The calculation of the local energy is the main contribution to the overall scaling of the diffusion quantum Monte Carlo method. It will be discussed how linear scaling for the calculation of the local energy can be achieved with techniques similar to those used in other ab initio methods. The emphasis is on all-electron calculations for molecules. The accuracy of the local scaling calculations will be demonstrated with benchmark calculations. Applications of the method will be presented.

PHYS 192 [644742]: Application of quantum Monte Carlo to molecular systems

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Recent applications of diffusion Monte Carlo to molecular systems will be described. Computational details that are important for these applications will be emphasized. Topics to be discussed include the singlet-triplet separation in ethylene, hydrogen atom abstraction by chlorine from methanol, and electronic excitation of porphyrin. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The calculations were carried out at the National Energy Research Supercomputer Center (NERSC).

PHYS 193 [639417]: Zero-variance zero-bias principle for observables in QMC: Application to forces
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A simple and stable method for computing accurate expectation values of observable with VMC or DMC algorithms is presented. The basic idea consists in replacing the usual bare estimator associated with the observable by an improved estimator. Using this estimator more accurate averages are obtained: Not only the statistical fluctuations are reduced but also the systematic error (bias) associated with the approximate VMC or DMC probability densities. It is shown that improved estimators obey a so-called Zero-Variance Zero-Bias (ZVZB) property. Using this property the improved estimators can be optimized and the resulting accuracy on expectation values can be very good. As an important example, we present the application of our formalism to the computation of forces. Calculations for some simple diatomic molecules and for more complex systems are presented.

PHYS 194 [642544]: Computing atomic forces in quantum Monte Carlo calculations

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The quantum Monte Carlo (QMC) method is a promising approach for evaluating the electronic structure of chemical systems. Total energies computed with QMC are currently competitive with the best ab initio calculations, and QMC offers much more favorable scaling with system size. As a result, significant methodological research is currently focused on making QMC a powerful and practical tool for investigations of chemical systems. In this talk, I will discuss our new approach for computing atomic forces in QMC calculations. The Hellmann-Feynman theorem (HFT) requires complete wavefunction optimization, and this is seldom feasible within QMC. Therefore, the HFT expression alone yields inaccurate forces. We stochastically compute the total derivative of the energy expectation value, improving accuracy significantly. We will describe the method and exhibit results for small molecular systems, focusing on the feasibility of this approach for the study of molecular reactions involved in combustion chemistry.

PHYS 216 [644926]: Number of excited states of small helium clusters

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A panel discussion at a conference at Schloss Ringberg, Germany, in 1997 identified as an important, unsolved problem in cluster physics the computation of energies of bound states of small 4-He clusters. From this perspective, I shall discuss progress in the computation, as a function of the de Boer parameter, of ground and excited state energies of bosonic van der Waals clusters by means of a correlation function Monte Carlo approach using optimized trial wavefunctions.

PHYS 217 [639824]: A "shake'n'see" DMC approach to the study of structure and stability of small protonated water clusters

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The study of small protonated water clusters $(\text{H}_2\text{O})_n\text{H}^+$ ($n=1-6$) has been carried out employing the OSS3 potential energy surface developed by Ojamae, Singer, and Shavitt [J. Chem. Phys. **109**, 5547 (1998)]. To correct the total and binding energy for the vibrational motion, the zero point energy of the clusters has been calculated by means of the harmonic approximation and by the diffusion Monte Carlo method. Comparing these results at 0 K, it appears that the anharmonicity accounts for a decrease of 1.5-5.5 mhartree (0.9-3.5 Kcal/mol) in the total and binding energy of the protonated clusters. Interestingly, we found all the cyclic isomers to show instability during the diffusion Monte Carlo simulations, and to convert into tree-like or linear isomers having sometimes a slightly higher equilibrium potential energy. The proton binding energy to a water cluster is also decreased by roughly 12 mhartree (7.5 Kcal/mol) by including the zero point energy.

PHYS 218 [643388]: HF and HCl dimers in small helium clusters: Vibration-tunneling dynamics in a quantum environment

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Results of diffusion Monte Carlo (DMC) calculations of the interchange tunneling splittings of $(\text{HF})_2$ and $(\text{HCl})_2$ in small helium clusters are presented. $(\text{HCl})_2$ is much floppier than $(\text{HF})_2$; the ground-state tunneling splitting of the free dimer is twenty times that of free $(\text{HF})_2$. For $(\text{HF})_2$, the tunneling splitting decreases rapidly with the binding of the first four He atoms, and much more slowly with the addition of more He atoms. The decrease of tunneling splitting due to just four He atoms accounts for 74% of the reduction in tunneling measured recently for $(\text{HF})_2$ in nanodroplets of over 2000 He atoms. The first four He atoms are exceptionally effective in quenching the tunneling by virtue of residing in the equatorial ring encircling the transition state of the tunneling pathway. DMC calculations are in progress to characterize the vibration-tunneling dynamics of $(\text{HCl})_2$ microsolvated by helium clusters of increasing size.

PHYS 219 [638703]: Towards a universal potential for water

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This talk details the first quantum simulations of water clusters and simulations of liquid water using a polarizable potential energy surface fit to water dimer spectroscopic data. The determinations of the VRT(ASP-W)II and III potential energy surfaces are presented, the result of fitting the ASP-W ab initio potential to spectroscopic data, using state of the art Discrete Variable Representation techniques. Next, we determine the vibrational ground-states of larger water clusters using VRT(ASP-W)II and III in Diffusion quantum Monte Carlo (DMC) simulations. The results from VRT(ASP-W)II and III are compared to those from the ab initio ASP-W potential as well as several bulk potentials. VRT(ASP-W)III is shown to be the most accurate model for the vibrational ground-states of larger water clusters to date. The importance of many-body induction and three-body dispersion are discussed, and simulation results of liquid water are presented.

PHYS 220 [641959]: Quantum Monte Carlo descriptions of molecular interactions relevant to biopolymers
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In biopolymers such as proteins, nucleic acids and their complexes, electron correlations often play an important role. Examples include the van der Waals interactions between stacking bases, the hydrogen bonding between base pairs, and the interfacial interactions between nucleotides and peptides. Quantum Monte Carlo approaches are then applied to the descriptions of these interactions as appropriate tools to account for the electron correlations and also the nuclear quantum effects primarily associated with hydrogen atoms. Discussions will be given of the usefulness of the quantum Monte Carlo methods, including an attempt to cope with large-scale calculations for huge molecules with the aid of a "fragment" approximation which has recently been found to be very efficient for the descriptions of the electronic properties of biopolymers.

PHYS 221 [644352]: CH₃OH - H₂O and CH₃CH₂OH - H₂O complexes: A quantum Monte Carlo study of solvation effects

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Results of a diffusion Monte Carlo study with constraint dynamics of the hydrogen bonded methanol - water and the ethanol - water dimer are presented. The effect of the internal rotation of both the methyl and hydroxyl groups on the relative stability of the water - donor and alcohol - donor isomers has been found to be critical. In addition, the OH red shift of the alcohol - donor isomers has been computed within an adiabatic approximation. The accuracy of this model was tested by calculating the frequency shift of the DF fundamental in the HF - DF dimer, for which accurate results are available from fully coupled quantum 6D calculations.

PHYS 454 [642190]: Linear scaling quantum Monte Carlo: Applications to semiconductor nanomaterials
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A method for performing QMC calculations where the computational time required to evaluate the local energy of a configuration of electron coordinates scales linearly with the number of electrons will be presented. Truncated, maximally localized Wannier functions are chosen to represent the single particle orbitals in the Slater determinant part of the many-body wavefunction. This choice of orbitals yields increasingly sparse Slater determinants as the system size is increased yielding a near linear scaling of the computational time.

The application of these QMC techniques to the evaluation of a variety of optical properties of semiconductor quantum dots will be presented. We present a comparison of the size dependence of optical absorption gaps predicted by QMC, density functional and semi-empirical techniques. We also present predictions of the energy difference between optical absorption and emission in quantum dots.

PHYS 455 [643555]: Electronic structure of systems with transition metals by quantum Monte Carlo
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Recently, we have carried electronic structure calculations for several types of systems which contain transition metal (TM) atoms. This includes TMO molecules, TM@Si₁₂ clusters, perovskite transition metal solids, and biomolecules. We focus on calculations of excited states such as low-spin/high-spin splittings especially for near-degenerate states, optical excitations and electronic gaps in solids. For this purpose we use a combination of methods and developments which include optimizing mean-field approaches for generating one-particle orbitals, configuration interaction for analysis and building trial wave functions and correlated sampling in variational and diffusion Monte Carlo calculations. This enables us to shed new light on electronic structure challenges in these systems such as identification of ground states and stability of TM@Si₁₂ systems ahead of experiment and prediction of band gaps of solid materials for which experimental results are contradictory or inconclusive.

PHYS 456 [644868]: Diffusion Monte Carlo studies of excitation energies in solids and quantum dots

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It is well known that commonly used density functionals tend to greatly underestimate the band gaps of solids. In contrast diffusion Monte Carlo yields band gaps and band widths that are in reasonable agreement with experiment and tend to overestimate these by about 10 - 20%. We discuss the likely reason for this overestimate.

Quantum dots containing one to several tens of electrons are analogous to atoms with tunable properties, exhibiting shell structure and obeying Hund's first rule. They are both of considerable technological interest and of theoretical interest because it is possible to go from a weak correlation to a strong correlation regime by tuning the relative strength of the external potential to the electron-electron potential. We find that the Hartree-Fock approximation is a poor approximation for dots and that the local spin density approximation is significantly better but nevertheless inadequate for predicting the correct ordering and values of the ground and excited state energies.

PHYS 457 [644036]: Diffusion quantum Monte Carlo studies of Wigner crystals

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We report diffusion quantum Monte Carlo (DMC) calculations for Wigner crystals in two and three dimensions. Very accurate calculations are required to obtain reliable values of the fluid/crystal transition densities. The orbitals within the Slater-Jastrow guiding wave functions are optimized within DMC, and finite size errors, time-step errors and population control errors are analyzed. In three dimensions we compare our crystal data with the recent fluid DMC data of Zong, Lin, and Ceperley, and find a transition density of $r_s \sim 106$. We compare our DMC data with Hartree-Fock results, which allows us to understand the effects of correlation on Wigner crystals.

PHYS 458 [641293]: QMC computations for homogeneous and inhomogeneous jellium systems

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Jellium systems provide a suitable playground to check the predictions of many-body theories by QMC computations. I present Fixed-Node Diffusion MC results for homogeneous and inhomogeneous systems. In the case of homogeneous systems, the focus is on the paramagnetic to ferromagnetic transition, on the Wigner crystallization, and on glassy low density phases. I present new results, and I discuss the comparison with previous computations. In the case of inhomogeneous systems, I present results for isolated and for interacting jellium spheres. In the case of isolated spheres, total energy, electron and spin density have been computed for a wide range of sizes and background densities. The QMC results are compared to the predictions of recent approximations for the exchange and correlation energy proposed by J. P. Perdew and co-workers. Interacting jellium spheres provide benchmark results for non-local correlations in valence electron systems.

PHYS 482 [643955]: Quantum Monte Carlo study of photoactive molecules

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In order to understand photochemical process in photoactive molecules, it is important to correctly describe the energetics of the primary photoinduced conformational changes in the excited state. While many studies have demonstrated the use and reliability of the diffusion quantum Monte Carlo (QMC) method for the description of ground state properties, relatively little experience exists concerning its application to low-lying excited states. Using QMC, we investigated photochemical reaction paths in prototypical molecules such as ethylene, formalimine and the protonated Schiff base $C_5H_6NH_2$. Our results indicate that the fixed-node approximation can accurately describe the energetics of the excited state along the reaction path if one makes an adequate choice of the trial wave function. We also compare our QMC results to those obtained with traditional quantum chemical and density functional based methods.

PHYS 483 [637162]: Diffusion Monte Carlo approaches for studying the structure of weakly bound complexes

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In this talk, some of our recent work in which DMC approaches are used to investigate the structure and spectroscopy of weakly bound complexes will be presented. While DMC provides a powerful method for gaining information about states of the systems of interest for which there are no nodes or for which the positions of the nodes can be determined by symmetry, extracting information about vibrationally excited states or vibrational states that are delocalized among two or more diabatic potential surfaces is less straight forward. In particular, we will show that DMC can provide an accurate description of the wave functions and energies of the ground and low-lying vibrationally excited states of weakly bound systems through comparisons of DMC and variational results for complexes of neon atoms with OH. In addition recent extensions of these approaches to studies of complexes of opened shell molecules will be presented and the role of the non-zero electron angular momentum on the structure of the cluster will be discussed.

PHYS 484 [644737]: Molecular thermochemistry via path integral Monte Carlo

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Most present-day approaches to molecular thermochemistry rely on a harmonic approximation to molecular vibrations. We present a method (1) for going beyond the harmonic analysis, which uses path integral Monte Carlo to calculate the vibrational and rotational contributions to molecular thermochemistry and properties. Anharmonic effects are found to be as large as 2.5 kcal/mol for the molecules studied. This presents a limit in the accuracy achievable in many present-day thermochemical calculations. We find that our method can calculate molecular heat capacities to within a few percent, even at temperatures of several thousand K.

Our method requires the evaluation of thousands of single-point energies with techniques such as MP2 or coupled cluster theory. The high computational cost is greatly reduced with a novel potential energy caching scheme.

1.) K. R. Glaesemann and L. E. Fried J. Chem. Phys. 118 (4): 1596-1603 (2003).

PHYS 485 [643733]: Simulations of impurity rotational dynamics in quantum cryogenic solids

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High-resolution infrared absorption spectra of solid parahydrogen containing impurities such as N₂, CO, and HCl reveal that these impurities undergo nearly free rotation in single substitutional sites in the H₂ matrix. The spectra provide information about molecular dynamics in highly quantum cryogenic condensed phases, information that complements that obtained from studies of molecular chromophores in helium nanodroplets by virtue of the well-defined crystal structure of the surrounding H₂ matrix. An impurity's rotational motion is hindered by the H₂ solid's crystal field, which is mediated by the highly-correlated large-amplitude zero point motions executed by H₂ molecules surrounding the impurity. Theoretical analysis of the impurity spectra could thus provide insight into the coupling between impurity rotations and the correlated translational motions of nearby H₂ molecules. We present quantum Monte Carlo simulations of diatomic chromophores in solid H₂ matrices, extracting from these simulations information about impurity rotational dynamics in highly quantum cryogenic solids.

PHYS 486 [671199]: Quantum Monte Carlo calculations of electronic structure of large molecules: C₂₀ and C₆₀

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Quantum Monte Carlo (QMC) methods offer high accuracies and favorable N³ scaling for large molecules. But, QMC methods have not been useful in optimization of structures or determination of gradients. Some recent improvements overcome some of the difficulties. These are examined in all-electron calculations of structures and gradients for C₂₀ and C₆₀.

PHYS 487 [636866]: Estimating Bohm's quantum potential via expectation modelling

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We will discuss our recent work involving the development of statistical methods for estimating the multidimensional density associated with a discrete bundle of de Broglie-Bohm trajectories. We show that by constructing the quantum density as a discrete sum of non-equivalent gaussians, we can incorporate the ideas of Bayesian statistical analysis and an expectation maximization procedure to compute an approximate quantum force suitable for driving an ensemble of quantum trajectories. While our focus is on time-dependent dynamics, the method has strong parallels with QMC as we shall discuss in this talk.