Abstracts of Invited and Contributed Talks, Sep. 5

5A1-1I

Structure and spectroscopy of the hydrated electron: Polarizable QM/MM simulations

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A new one-electron model for finite water cluster anions, $(H_2O)_n^-$, and the bulk aqueous electron, e_{aq}^-, has been developed, based upon a reconsideration of the electron–water pseudopotential using *ab initio* quantum chemistry. The new model employs a polarizable force field for water, and both water–water polarization and electron–water polarization interactions are treated in a fully self-consistent manner. Although not fit directly to any observables, the model is quite accurate (as compared to various *ab initio* benchmarks) for small and medium-size $(H_2O)_n^-$ clusters, and also affords reasonable estimates of known experimental observables for e_{aq}^- in bulk water. We consider this to be the first hydrated-electron model that achieves at least semi-quantitative accuracy all the way from $n = 2$ to $n = \infty$. In the bulk, we find that self-consistent treatment of many-body polarization is qualitatively necessary in order to explain the gross features of the optical absorption spectrum of e_{aq}^-. In particular, the new model predicts the existence of polarization-bound, quasi-continuum states that are absent in non-polarizable models. These states are responsible for the "blue tails" that are consistently observed in optical spectra of e_{aq}^-, but which have not previously been seen in simulations. The implications of these results will be discussed, both in terms of our understanding of hydrated electrons and also in terms of future development of QM/MM methodology.

5A1-3C

Effects of intermolecular electron density modulations on the Terahertz spectral intensity of liquid water

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I. Introduction

The vibrational spectra of liquid water have been measured in a wide frequency range, and their band assignments (with regard to the frequency positions) are well known. However, understanding on the whole spectral profiles (especially with regard to the intensities) is rather far from complete, although it is essential for detecting structural and dynamical properties of water and aqueous solutions.

One problem concerning this is the intensity of the far-IR band observed at ~200 cm^{-1} (~6 THz). This band is known to arise from the molecular translation mode, but molecular translations of a neutral molecule do not give rise to IR intensity without intermolecular interactions. It has been pointed out that the IR intensity arising from intramolecular polarizations induced by intermolecular electrostatic (such as dipole-induced dipole) interactions is not sufficiently strong.

In a recent study [1], it has been demonstrated that the IR intensity enhancement of the OH stretching mode upon hydrogen-bond formation is mainly arising from the *intermolecular* electron density modulation (called *intermolecular charge flux*). A similar analysis is carried out here for the molecular translation mode, to show that in this case also the intermolecular charge flux is the main source of the IR intensity.

II. Computational Procedure, Results, and Discussion

The electron density derivatives $\partial\rho^{(\mathrm{el})}(\boldsymbol{r})/\partial X_{\zeta[m]}$, where $X_{\zeta[m]}$ ($\zeta = x, y$, or z) stands for the translation motion of the mth molecule in the x, y, or z direction, were analyzed for the water molecules in the (water)$_{28}$ and (water)$_{30}$ clusters calculated at the B3LYP/ 6-31+G(2df,p) level. The result shows that significant amplitude of intermolecular charge flux is induced between the hydrogen-bonded water molecules by a molecular translation mode, and the amplitude is about 0.4 times of that induced by the OH stretching mode.

The effect of the charge flux is included in the spectral simulations of liquid water based on classical MD by using a formula based on dipole *derivatives* rather than dipole moments themselves. It is shown that, by including four intensity parameters [$\partial\mu_x/\partial X_x = 1.91$ D Å^{-1}, $\partial\mu_y/\partial X_y = -1.76$ D Å^{-1}, and $\partial\mu_y/\partial\Omega_x = -\partial\mu_x/\partial\Omega_y = 1.57$ D (rad^{-1})] per molecule, the presence of the band at ~200 cm^{-1} is well reproduced.

These results mean that the molecular translational and electronic motions are strongly coupled, and this coupling is observable through the ~200 cm^{-1} far-IR band.

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5A1-4C

Theoretical Analysis on the Effect of Intramolecular Hydrogen Bonding on the Overtone Spectra in Simple 1-n Alkanediols

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I. Introduction

For the OH stretching vibration of a hydrogen bonded OH bond, it is well known that the fundamental peak shifts to lower energy, gains intensity and broadens compared to the free OH bond. Several studies have been performed on fundamental spectrums to understand the relationship between the hydrogen bonding strength versus the peak shift, intensity as well as the broadening. However studies for overtones are scarce. Recently, Kjaergaared et al. have reported the OH stretching overtone spectra of three simple 1-n alkanediols: ethylene glycol (EG), propanediol (PD), and butanediol (BD). In these molecules, the most stable conformer consists of an intramolecular hydrogen bond in which one OH donates a hydrogen while the other OH accepts it.[1,2] Interestingly at the v=4 excitation, while the OH peak corresponding the hydrogen bonded donor OH for EG was observed, the one for BD was not. This disappearance was attributed to the difference in intramolecular vibrational energy relaxation, but a clear explanation was not presented.

II. Results and Discussion

In this presentation we present calculated peak positions, intensities and peak widths for the OH stretching vibration of the donor (hydrogen bonded) and acceptor (free) OH in three 1-n alkanediols reported by Kjaergaard et al. We performed vibrational calculations using the potential energy surface and dipole moment function calculated by the B3LYP, MPW1BK91, MP2, and CCSD(T) methods. To understand the energy flow from the vibrationally excited state, we performed B3LYP/6-31+G(d,p) based direct dynamics trajectory calculations to obtain the classical survival probability in the excited OH bonds. It was found that as Kjaergaard et al. had predicted, the OH energy of the donor OH bond decayed at a rate ten times faster in BD than in EG. This difference will result in a peak that is ten times broader for the BD donor OH, thereby making it hard to experimentally observe. Interestingly, it was calculated that the decay rate of the excited acceptor OH bond decreased when increasing the carbon chain. This feature is in contradiction with the basic assumption that the larger the molecule the faster the decay of the vibrationally excited state. Analysis on the energy flow and the intramolecular vibrational energy dynamics in these diol systems will also be presented.

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5A1-5C

Revealing mysteries of the water hexamer

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Water has been known for its untypical behavior for centuries, as the result of that knowledge it has been extensively studied. Scientists still have an incomplete understanding of its properties. The difficulty in obtaining a good description of water structure is caused by the hydrogen bond based structure existing in this liquid. Experiments and theory are rather convincing that the water trimer, tetramer and pentamer have cyclic minimum energy structures. For larger clusters, the structure is expected to be different and the hexamer minimum structure is at the spotlight of the water research.

After numerous experiments and theoretical modeling, the “cage” and “prism” structures of the water hexamer are found to be the lowest energy minimum configurations. But there is still no definitive answer which of the two is the global minimum. The reason for this uncertainty are very small energy differences between the structures and, hence, a very high accuracy is required for modeling. Several effects has to be accounted for, including high-level electronic correlation, many-body effects, monomer flexibilities, and zero-point energies.

We present extensive theoretical results for water hexamer clusters. The accurate energies were obtained with many-body expansion, i.e., by calculating various many-body components separately. With such an approach, very significant computational savings can be achieved that allow for applying higher level of theory than the standard supermolecular approach. We have also developed a model for calculating other effects present in the hexamer structures. These two approaches enable us to provide an answer to the water hexamer global minimum mystery.

5A1-6C

On the Development of A First-Principle Based Multi-model Method to Study Aqueous Systems: from Clusters, Interfaces to Condensed Phases

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Water is an important substance for life and many of its intriguing properties (magic number water clusters, low temperature amorphous phases and high-pressure phases of ice) are related to the flexibility of hydrogen bonding (H-bonding) to form various structural features. One of the common themes for the above-mentioned subjects is the rough energy landscape of aqueous systems that hinder a straightforward way for a structural determination from first-principle methods. Our recent effort in developing a first-principle based multi-model methods[1] is to integrate the efficiency of empirical models and the accuracy of first-principle methods to study various aqueous systems ranging from large-sized water clusters (n ~ 100), water interfaces, to various condensed phases (low temperature amorphous phases and proton ordering process). For clusters, we can benchmark the commonly used DFT methods against other high-level quantum chemistry methods and in condensed phases, we also seek for comparisons with quantum Monte Carlo methods. In this talk, we will discuss some of the successes and failures[2] we have encounter and how we utilize the information learnt to move toward a consistent picture in simulating aqueous systems.

[1] Q. C. Nguyen, Y-S Ong, and J-L Kuo, "*A multi-scale approach to study thermal behavior of protonated water clusters*", J. Chem. Theory and Comp. **5**, 2629 (2009)
[2] X. F. Fan, D. Bing, J. Zhang, Z. X. Shen, and J-L Kuo, "*Predicting the hydrogen bond ordered structures of ice Ih, II, III, VI and ice VII: DFT methods with localized based set*", Comp. Mater. Sci. 49, S170 (2010)

5A2-1I

Nucleation and growth of calcium carbonate: how non-classical is it?

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The interface between calcium carbonate and water is one of the most fascinating "hard-soft" interfaces, being of significance to mineralogy and biomineralization processes. $CaCO_3$ is known to form an amorphous precursor (ACC) that can subsequently evolve to produce crystalline polymorphs. To add to the complexity, the ACC precursor is not a single well-defined material as it can vary in water content and have polyamorphic characteristics [1]. Furthermore, it has been demonstrated that stable pre-nucleation species also exist [2], but their relationship to ACC remains unknown.

In this presentation we will explore the use of computer simulation methods to try to unravel the complexities of the nucleation and growth processes for calcium carbonate. Central to this is the development of a force field that is accurately calibrated against experimental free energies [3] since failure to do so can result in qualitative errors for interfacial properties. Based on this we have explored the stability of ACC versus crystalline nanoparticles while accounting for the variable water content in the amorphous structure [4]. In the light of this, and new experimental results, we propose a model to explain the non-classical aspects of the nucleation mechanisms of calcium carbonate, the origins for which can be traced back to the interfacial properties.

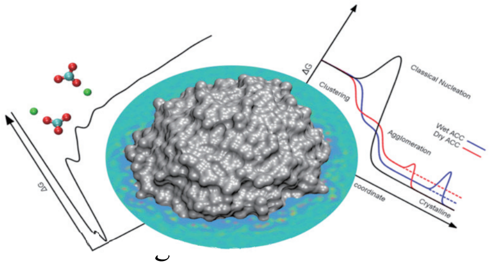

Figure 1: Montage showing from left to right, the free energy of ion pairing, the hydration of ACC and the consequences for nucleation and growth.

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[2] D. Gebauer *et al.*, *Science*, **322**, 1819 (2008)
[3] P. Raiteri *et al.*, *J. Phys. Chem. C*, **114**, 5997 (2010)
[4] P. Raiteri and J.D. Gale, *J. Am. Chem. Soc.*, **132**, 17623 (2010)

5A2-3C

Novel ZIFs material as molecular separator studied by computer-aided modeling approaches

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Zeolite imidazolate frameworks (ZIFs), a new class of porous crystalline material, have recently been gained the attention of the scientists from various fields. Besides the unique properties such as high thermal and chemical stabilities, one most benefit is that the large variety of ZIFs can be achieved by virtue of flexibility with the various linker and the metal types. As a result, during 5 years, over 90 new ZIFs structures [1,2] have been reported and in which they were found to be the potential materials in gas adsorption and separation applications. However, the information on atomic level in terms of gas binding sites, adsorption and diffusion mechanisms describing the basic properties of adsorbate/adsorbent system are still unclear. This becomes the main goal of this work aimed to better understanding of the above mentioned properties using computer modeling approaches. Such kind of computer aided structural design is commonly used to seek for the future promising materials in gas adsorption and separation processes.

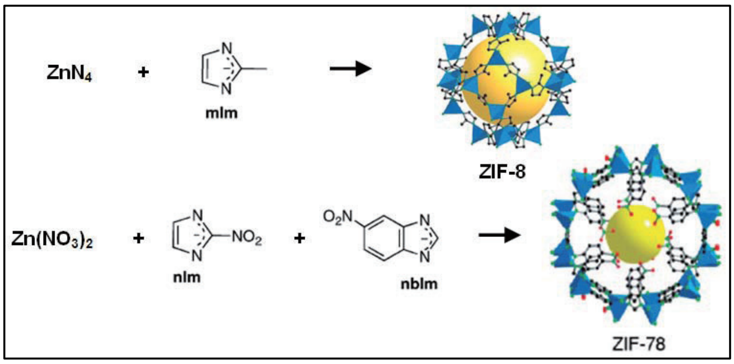

Figure 1. Schematic of building units in ZIF-8 and ZIF-78.

Using the DFT calculations together with MD simulations, the adsorption sites of the three gases, *i.e.*, H_2, CO_2 and CH_4 were investigated in which the imidazolate (IM) linker group was found to be the favorable adsorption site of the three gases. Moreover, the dynamic properties such as the adsorption isotherm and self-diffusivities (D_S) were calculated. Consequently, the membrane selectivity was calculated and compared to that obtained experimentally [2]. The obtained D_S of H_2 in ZIF-8 is in the order of 10^{-8} m^2 s^{-1} while those of the CO_2 and CH_4 are 10^{-10} and 10^{-11}, respectively. This indicates the selectivity of ZIF-8 in separation process. In addition, the calculated data for the ZIF-78 also indicate its ability as a promising candidate in separation of CO_2 in gas mixture.

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5B1-1I

Quantum dynamics of photoprocesses in extended molecular systems: coherence and correlations at the nanoscale

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The photophysics of extended systems like conjugated polymers or molecular aggregates is characterized on the one hand by the properties of the molecular building blocks and on the other hand by the delocalized nature of the electronic excitations, i.e., the formation of excitonic states. The dynamical phenomena induced by photoexcitation therefore involve an interplay of site-site interactions entailing excitation energy transfer (EET) and charge transfer (CT), and on-site vibronic coupling and trapping effects. Due to the prominent role of electron-phonon coupling, often accompanied by coherent dynamical effects on ultrafast time scales, an explicit quantum dynamical treatment is generally required. Our approach combines parametrized Hamiltonians, based on semiempirical and *ab initio* calculations, with accurate quantum dynamics simulations using the multiconfiguration time-dependent Hartree (MCTDH) method [1]. In addition, we employ transformation techniques [2,3] by which a relevant set of effective modes are constructed that allow for a hierarchical description of non-adiabatic dynamics in high-dimensional systems. Against this background, the talk will focus on coherent excitation transfer driven by torsional dynamics in poly-phenylene-vinylene (PPV) type systems [4], and on ultrafast exciton dissociation at polymer heterojunctions in fluorene-based TFB:F8BT blends [3] as well as at oligothiophene-fullerene junctions [5]. Particular consideration is given to the role of excitonic coherence *vs.* static and dynamic conformational disorder.

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5B1-3I

Quantum dynamical treatment of systems with many degrees of freedom using time-dependent multiconfiguration methods

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The accurate theoretical treatment and simulation of quantum dynamical processes in many-body systems is a central issue in chemical and condensed matter physics. In this talk, the multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) method [1] is discussed as an example of an approach that allows an accurate description of quantum dynamics in systems with many degrees of freedom. The ML-MCTDH method is a variational basis-set approach, which uses a multiconfiguration expansion of the wavefunction employing a multilayer representation and time-dependent basis functions. It extends the original MCTDH method [2] to significantly larger and more complex systems. Employing the second quantization representation of Fock space, the ML-MCTDH method has recently been extended to allow the treatment of indistinguishable particles [3,4]. The performance of the ML-MCTDH method is illustrated by several application to models of charge and energy transport in molecular systems in the condensed phase [4,5,6,7].

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5B1-5C

Quantum Dynamics Simulation in Balanced Resolution Representation in Time-Space

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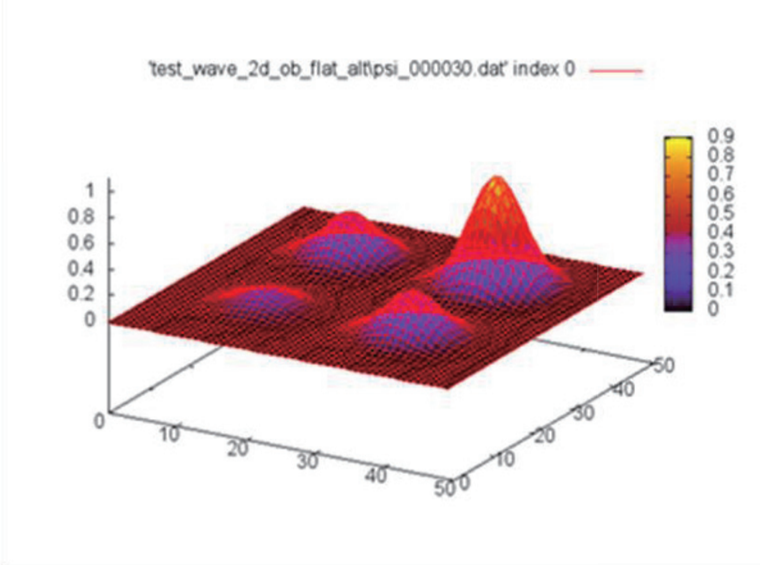
I. Abstract

Quantum dynamics can be simulated using classical fluid formulation. First, we present a classical fluid dynamics formulation of Schrödinger equation on Multiwavelet Wavelet (MW) spectral space. While the MW formalism is powerful in very accurate evaluation of near equilibrium properties such as electric polarizability, it reveals a serious problem of instability in solving Time-dependent equations. We find that the instability can be removed using elaborated techniques introducing Cayley algorithm for time progression operator [1] or other types of wavelet basis functions such as Mayer wavelet [2]. However, we need to introduce a balanced resolution representation in time domain as well as space domain for simper solution of the problem. We present a very simple solution of time-dependent Schrödinger equation in such balanced representation on even grid time-space using local unitary transformation considering internal co-ordinate freedoms.



Solution of 2Dimensional Time Dependent Schrödinger equation

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5B1-6C

Semiclassical molecular dynamics including spin-orbit coupling and electric fields

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I. Introduction

Research in the area of chemical reaction control and analysis is attaining progressively shorter timescales. We have reached the femto- and attosecond regime, where traditional approaches to manipulate larger and larger systems are reaching their limits. New techniques are necessary to study the interaction of electrons and nuclei with strong laser fields in multiple molecular states including also relativistic effects.

II. The SHARC method

We have developed an ab initio molecular dynamics (MD) code including arbitrary coupling as a general tool for studying excited-state processes. Up to now, spin-orbit couplings are not included in standard ab initio MD packages and the description of laser interactions in MD is in its infancy. In our new method, termed SHARC (surface-hopping-in-the-adiabatic-representation-including-arbitrary-couplings), we treat all couplings on the same footing and incorporate them into the system's Hamiltonian via a unitary transformation [1]. In this adiabatic representation, transitions are treated by a variation of the surface hopping technique.

III. Numerical applications

In order to test the method, IBr is taken as a model system, where spin-orbit coupling plays an important role for the dissociation dynamics. Additionally, the influence of laser control via the non-resonant dynamic Stark effect is investigated [2]. As MD allows for the handling of many atoms, the photo-induced dynamics including the interplay between triplet and singlet states of large molecular systems will be accessible. Further applications of the SHARC method to complex systems include the relaxation of DNA nucleobases via triplet states after photoexcitation.

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5B2-1I

Electronic Structure and First Principles Dynamics on Graphical Processing Units

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Massively parallel processors that can perform more than a hundred arithmetic operations per clock cycle, such as graphical processing units (GPU), have recently become mainstream in the era of petascale computing. However, in addition to the remarkable performance, these architectures posses certain limitations, such as imbalanced performance of single and double arithmetic operations and high sensitivity to various strategies for code optimization. We discuss how precision can be effectively controlled in ground state (HF, DFT) and excited state (CIS, TD-DFT) molecular dynamics by splitting the entire calculation into single precision and double precision parts, providing double precision quality results almost at the speed of purely single precision arithmetic. Using our newly developed TeraChem program, we discuss results from *ab initio* molecular dynamics calculations of solvated proteins with up to 1000 atoms. We show that charge transfer effects are not negligible and comment on the implications for simulations using empirical force fields. If time permits, we also present results for excited states of photoactive proteins using CIS and TDDFT methods, where the entire protein is modeled with *ab initio* quantum chemistry.

5C1-1I

The MP2-F12 method in the Turbomole program package

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I. Introduction

The implementation of the explicitly correlated second-order Møller-Plesset perturbation theory (MP2-F12) method [1,2] in the Turbomole program package [2,3] is presented and discussed. A brief introduction to explicitly correlated coupled-cluster methods, as implemented in Turbomole, is also given [4].

II. MP2-F12 theory

Turbomole's MP2-F12 implementation makes use of density fitting, which greatly reduces the prefactor for integral evaluation. Methods are available for the treatment of ground states of open- and closed-shell atoms and molecules, using unrestricted as well as restricted (open-shell) Hartree–Fock reference determinants [5]. The implementation has been parallelized.

III. Performance assessment

The performance of the Turbomole implementation is assessed by performing calculations on the molecule ethylenedioxytetrafulvalene, on a cluster model for the adsorption of methanol on the zeolite H-ZSM-5, and on the (antirheumatic) drugs leflunomide, prednisone, and methotrexate.

Basis sets of varying size (from aug-cc-pVDZ to aug-cc-pV5Z) are used, including correlation-consistent basis sets optimized for explicitly correlated calculations. The largest calculation was performed in a basis set with 3652 basis functions.

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5C1-3I

Local explicitly correlated MP2 theory using pair natural orbitals

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Abstract

Localization in the framework of pair natural orbitals is explored at the explicitly correlated MP2-F12 level of theory. Our results demonstrate that very small virtual active spaces, 20-50 orbitals per significant pair, return more than 98% of the basis set limit correlation energy. The extension of pair natural orbital ideas to the complementary auxiliary basis set for the RI also affords enormous truncation of the auxiliary orbital space without significant loss of accuracy.

Resolving Coulomb operator
A new approach toward faster QM methods

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Two-particle interaction described by Coulomb operators

$$r_{ij}^{-1} \equiv |\boldsymbol{r}_i - \boldsymbol{r}_j|^{-1} \tag{1}$$

is the most difficult part of non-relativistic Schrödinger equation for chemical systems. We replace these troublesome terms by products of one-particle function

$$r_{ij}^{-1} \approx \sum_{k=1}^{K} \phi_k(\boldsymbol{r}_i)\phi_k(\boldsymbol{r}_j) \tag{2}$$

and obtain the reduced-rank Schrödinger equation (RRSE). In analogous to resolution of the identity and Cholesky decomposition, this new approach allows us to expand Coulomb matrix elements into products of auxiliary integrals.

$$(a|r_{12}^{-1}|b) \approx \sum_{k=1}^{K} (a|\phi_k)(\phi_k|b). \tag{3}$$

This opens possibilities to significantly reduce time and memory complexity of many QM methods. We find that ϕ_k proportional to product of a spherical Bessel function and a spherical harmonics is the one well-suited for computational purposes.

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5C1-6C

New three-body correlation expression applied to solid surface Quantum Monte Carlo simulation.

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Abstract

This paper presents a near analytical expression for the two-electron and nucleus three-body correlation terms that are essential, yet so time consuming to optimise in the variational step of Quantum Monte Carlo simulations used to determine free-parameters in the Jastrow factor.

The expression is devised using co-ordinate systems in six-dimensional space, previously used by Fano and Rao.

The quasi-exact expression obtained is applied in a series of solid state simulations of molecules adsorbed at solid surfaces.

The simulations are carried out with the CASINO code due to Needs *et al* running on a Bluegene parallel system on more than 10000 processors.

The Fixed node error in the Diffusion monte carlo step is limited by expanding the trial wave-function in a Coulomb Sturmian basis in co-ordinate space and plane waves in the first Brillouin zone of Fourier transform space.

Keywords: Coulomb Sturmian basis, nodal structure, Fourier Transform, *ab initio* quantum chemistry.

5C2-1I

Strong Correlations from Constrained Mean-Field Approaches

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One of the fundamental challenges in modern quantum chemistry is the efficient incorporation of strong correlations at low computational cost. Localizing the exchange hole and using symmetry broken orbitals in DFT are standard tricks towards achieving this goal. However, this is insufficient and unpleasant from the perspective that it goes hand-in-hand with the introduction of self-interaction error in an uncontrolled manner, one that has proven extremely difficult to overcome. Our work has recently focused on incorporating strong correlations into mean-field approaches via selective symmetry breaking followed by a restoration step. Constrained-pairing mean-field theory (CPMFT) [1] introduces pairings between electrons in an active space and yields a two-particle density matrix (2pdm) ansatz that exclusively describes strong correlations. The model breaks electron number conservation which is correct only on average but expectation values calculated from its effective 2pdm contain no particle number fluctuations. On the other hand, Constrained Unrestricted Hartree-Fock (CUHF) theory [2,3] limits spin symmetry breaking to an active space. Based on it, we have developed a novel approach for obtaining high-spin ROHF wave functions. If the active space is properly chosen, CUHF greatly benefits from a controlled broken-symmetry effect while avoiding the massive spin contamination of traditional UHF. Spin projection operators can be applied to restore symmetry and obtain multireference wave functions with moderate computational cost. Singlet-triplet energy splittings show that our scheme outperforms fully unrestricted methods. This constrained approach can be used in spin density functional theory with similar favorable effects.

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