

# **Report on Workshop "Quantum Monte Carlo meets Quantum Chemistry: new approaches for electron correlation"**

Lugano  
June 15, 2010 to June 18, 2010  
Cecan, Psi-K, Democritos, i2cam,  
Ali Alavi, M. Casula and S. Sorella

<http://www.cecama.org/workshop-466.html>

## Scope of Workshop

The aim of this workshop was to bring together two different communities who share a well-defined common interest, namely the ab-initio calculation of electron correlation problems (principally total energies, but touching other properties such as magnetism, excitations, forces etc), using classes of methods alluded to in the title of the workshop. Despite the commonality of interests, these two communities do not regularly meet on the same conference circuit, and as a result, the interactions are not as strong as might be expected, nor indeed the awareness of techniques and methods which have been developed in the past few years. In addition, we believe that ideas taken from both quantum chemistry and quantum Monte Carlo (QMC) have the potential for synthesis into methods which actually exploit advantages of both types of computational algorithms. Therefore, time seemed ripe to organise a meeting on this topic.

In the event, we had an extremely good turnout, both of invited speakers (27) as well as non-supported participants (26), so that the workshop number (56) well-exceeded the initial target (~40) and, after a careful selection, we have managed to limit this number well below the number of applications (71). From both communities, we had many of the foremost experts at this meeting.

## Main Outcomes of key presentations

On the quantum chemistry (and, more generally, wave function-based methods) side, there were impressive talks in the use of wave function and density-matrix methods in treating both strong correlation systems, as well as large (going to bulk-periodic) systems. Kresse outlined new developments in VASP which moved towards more accurate description on correlation based on the random phase approximation (RPA), and coupled-cluster methods, showing applications to a broad range of wave function-based description of solids. Helgaker gave an intriguing talk on the possible use of Lieb's principle for constructing exact (universal) density functions. Mazziotti showed some progress on the use of reduced density-matrix optimisations, applied to some strong correlation problems. Chan presented some new ideas coming from quantum information theory to optimise density matrix renormalization group (DMRG)-type wave functions, Manby presented an impressive calculation on liquid water at ambient conditions, based on a very efficient implementation of the MP2 method. Alavi presented a new approach (dubbed full configuration interaction QMC or FCIQMC) which combines the FCI with QMC methods, and enables exact solutions to be obtained with a minute fraction of the effort employed to carry out exact diagonalization calculations.

On the quantum Monte Carlo side, many interesting applications were presented.

In solids and weakly bounded systems containing few water molecules and Carbon based compounds, Alfe' showed that the standard Diffusion Monte Carlo (DMC) works quite accurately and provides always benchmark results compatible with experiments.

On the other hand, wave functions containing a large number of determinants were used by Umrigar, Stich, Bressanini to describe faithfully static correlations in important chemical compounds, such as azobenzene, boranes, and azaboranes, and simple Carbon atom and Carbon dimer, as well as to compute excitations and structural properties of fluorescent and photosensitive compounds like the Green Fluorescent Protein (Filippi).

Stella has reported an interesting result on the metal insulator transition in the one dimensional Hydrogen-chain, showing the importance of Resonating Valence Bond correlations near the transition point.

Casula, on the other hand, has studied the metal-insulator structural transition in Silicon, showing that the lack of consistent pseudopotentials in Quantum Monte Carlo calculations may explain why the transition pressure, determined by QMC with Hartree-Fock (HF) and density functional theory (DFT) pseudopotentials, differs significantly from the experimental value.

Finally, Moroni and Sorella reported some significant progress in the calculation of forces, which could open the way to accurate and large-scale geometry optimization and molecular dynamics in a correlated framework.

### Report of Selected discussions

One of the issues to be debated is the reason for continuing scepticism on behalf of many practising quantum chemists to use QMC techniques. Some lively discussions took place on this. On the one hand, it is clear that the accuracy issue remains foremost on the quantum chemist's mind – whilst DMC can deliver in terms of absolute energies, it's performance is less satisfactory for relative energies (i.e. energy differences), owing to sometimes unfavourable error cancellation. On the other hand, the FCIQMC method of Alavi may provide the quantum chemists the sort of compromise that they feel comfortable to accept: i.e. sacrificing the continuum real-space methods of most QMC approaches (which however is replaced by a systematically improvable approximation by expanding the basis sets), while maintaining the key concept of DMC, namely to sample the configuration space. It is the belief of one of the organisers that this hybrid approach will prove successful in enticing the quantum chemists into stochastic frame of mind.

On the other hand, quantum chemistry methods have so far appeared to be inadequate to describe qualitatively new phases of matter, missed at the HF level and not well described by post-HF methods. For instance, all chemists present in the discussion admitted that there is no reliable method to describe even simple superconductors within post-HF methods, whereas within QMC it is now possible to describe by means of a simple correlated wave function both Mott insulators and high temperature superconductors, and more generally qualitative new effects that go beyond simple mean field theories.

The conclusion was that some of the ideas of QMC should be exported in quantum chemistry methods, while it is beneficial for certain QMC applications, like those aiming at studying excited states, to have as initial guess a multi-reference wave function, generated by state-of-the-art quantum chemistry approaches, like the complete active space (CAS) method.

The basic objective of the workshop was to invite leaders from two disciplines to be exposed to each other's methods and ideas, and to interact and debate on the pros and cons of the methods. Of course it will take some time before actual ideas are implemented into new methods and codes. However, we feel that a very useful interaction took place, with healthy and lively debates.

We believe the basic theme of the workshop is far from exhausted, and worthy of another workshop in three or four years time, where some of the above methods have had more time to develop.

### Programme:

Day 1 - June, 15th 2010

Session I

\* 09:00 to 09:10 - Welcome

\* 09:10 to 10:00 - Martin Head-Gordon

Introduction to quantum chemistry methods

\* 10:00 to 10:50 - David Ceperley

#### An Introduction to Quantum Monte Carlo

\* 10:50 to 11:10 - Coffee Break

\* 11:10 to 11:40 - Martin Head-Gordon

(Relatively) simple wave functions for describing strong electron correlations in molecules

\* 11:40 to 12:30 - Michel Caffarel

Multi-Jastrow trial wavefunction for quantum Monte Carlo

\* 12:30 to 14:00 - Lunch Break

#### Session II

\* 14:00 to 14:30 - Discussion

\* 14:30 to 15:20 - William Matthew Colwyn Foulkes

Finite-size errors in continuum quantum Monte Carlo calculations

\* 15:20 to 16:10 - Ivan Stich

Electronic structure of lowest singlet states of azobenzene

\* 16:10 to 17:00 - Dario Alfe

Recent quantum Monte Carlo calculations of weakly bound systems

\* 17:00 to 17:20 - Coffee Break

\* 17:20 to 17:40 - Dario Bressanini

QMC calculations on Boranes and Azaboranes

\* 17:40 to 18:10 - Lorenzo Stella

Metal-insulator transition of one-dimension Hydrogen chains: a Variational Monte Carlo study

\* 18:10 to 18:30 - Discussion

\* 19:30 to 22:00 - Dinner

#### Day 2 - June, 16th 2010

#### Session III

\* 08:50 to 09:40 - Fred Manby

Systematically improvable electronic structure calculations for solids and liquids

\* 09:40 to 10:30 - Michele Casula

Diamond to betatin transition in Silicon: a playground for pseudopotentials.

\* 10:30 to 10:50 - Coffee Break

\* 10:50 to 11:40 - Beate Paulus

The method of increments - a wavefunction-based correlation methods for solids and surfaces

\* 11:40 to 12:30 - Lorenzo Maschio

Local-correlation methods for the study of non conducting crystalline systems : the CRYSCOR program

\* 12:30 to 14:00 - Lunch Break

#### Session IV

\* 14:00 to 14:30 - Discussion

- \* 14:30 to 15:20 - Georg Kresse  
Quantum chemistry methods for solids and surfaces: RPA and CCSD
- \* 15:20 to 16:10 - Saverio Moroni  
Fixed-node calculation of force constants
- \* 16:10 to 16:30 - Coffee Break
- \* 16:30 to 17:20 - Cyrus Umrigar  
Natural Orbital and Gauss-Slater Basis for Molecules
- \* 17:20 to 18:00 - Discussion

Day 3 - June, 17th 2010

Session V

- \* 08:50 to 09:40 - Lubos Mitas  
Many-body nodal structures of ground and excited states, pairing effects and release node methods
- \* 09:40 to 10:30 - Ali Alavi  
QMC in discrete spaces : a way to overcome the sign problem ?
- \* 10:30 to 10:50 - Coffee Break
- \* 10:50 to 11:40 - David Mazziotti  
Two-electron Reduced-Density-Matrix mechanics : theory and applications
- \* 11:40 to 12:30 - Trygve Helgaker  
The rigorous calculation of the universal density functional by the Lieb variation principle
- \* 12:30 to 14:00 - Lunch Break

Session VI

- \* 14:00 to 14:30 - Discussion
- \* 14:30 to 15:20 - Krzysztof Szalewicz  
Calculations of interaction energies with micro to femtohartree accuracies
- \* 15:20 to 15:40 - Coffee Break
- \* 15:40 to 16:30 - Garnet Chan  
New wavefunctions in quantum chemistry
- \* 16:30 to 17:20 - Claudia Filippi  
Excitations in photosensitive biomolecules from quantum Monte Carlo

Session VII

- \* 17:20 to 18:30 - Poster Session

Day 4 - June, 18th 2010

Session VIII

- \* 08:50 to 09:40 - Laura Gagliardi  
Recent developments in multiconfigurational quantum chemical methods and their application to water oxidation

\* 09:40 to 10:30 - Shiwei Zhang

Auxiliary-field quantum Monte Carlo for quantum chemistry : recent progress and open issues

\* 10:30 to 10:50 - Coffee Break

\* 10:50 to 11:40 - Peter Knowles

The variational coupled cluster method and approximate pair functionals

\* 11:40 to 12:30 - Discussion

\* 12:30 to 14:00 - Lunch Break

#### Session IX

\* 14:00 to 14:50 - Jeongnim Kim

QMC, harnessing computing powers of today and beyond

\* 14:50 to 15:10 - Leonardo Guidoni

Structure and harmonic frequencies of the water molecule by Quantum Monte Carlo

\* 15:10 to 16:00 - Sandro Sorella

Algorithmic differentiation and the calculation of forces by quantum Monte Carlo methods

\* 16:00 to 16:10 - Closing word

#### Abstracts of presented papers

##### ***Introduction to quantum chemistry methods*** ***Martin Head-Gordon***

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##### ***An Introduction to Quantum Monte Carlo*** ***David Ceperley***

###### Abstract

The various types of quantum Monte Carlo (QMC) are introduced including Variational, Diffusion, Reptation, Path Integral and Auxiliary Field, as well as lattice techniques, with an emphasis on the strengths and weakness of each approach.

Several examples of recent work, including phase transitions in Silicon and Hydrogen and discussed. Some of the overall problems and research directions of QMC algorithms will be

enumerated. Finally, we will have a discussion of the role of QMC as computation advances to the petascale and exascale capability.

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##### ***(Relatively) simple wave functions for describing strong electron correlations in molecules*** ***Martin Head-Gordon***

###### Abstract

Full configuration interaction within a space of valence active orbitals consisting of one per valence electron is a model for strong correlations that can get the "right answer for the right reason" because any spin-coupling of the valence electrons (or any number of broken bonds in other words) can be described exactly in the space.

This is one variant of CASSCF. However, its cost is exponential in the number of valence electrons, so that a hard limit of roughly 16 electrons applies today, and for realistic medium or large molecules, the "right answer" as defined by CASSCF is not available to us, and we are forced to make sometimes drastic truncations of the active space.

Therefore approximations to CASSCF are imperative. I shall discuss a hierarchy of coupled cluster approximations to CASSCF that truncates the cluster expansion not only by rank as is traditional, but also in a balanced way by spatial locality, such that exactness is achieved for a given number of pairs of electrons, while strict extensivity is retained, at minimum cost [1,2]. I shall discuss results for the 1 pair model (perfect pairing), 2 pair model (perfect quadruples) and 3 pair model (perfect hexuples). These methods are subsets of valence optimized orbital CCD, CCDTQ and CCDTQPH respectively, that retain only linear, quadratic and cubic numbers of amplitudes. The PQ and PH equations are computer generated and implemented by a new algorithm that automatically includes sparsity arising from pair locality to yield reduced scaling. A variety of benchmark calculations on the convergence of the PP, PQ, PH hierarchy will be presented.

Finally, corrections to these models for dynamic correlation will also be described [4]. These corrections are based on coupled cluster equations where up to two external virtual indexes substitute for the active virtual indexes in the reference PX models.

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### ***Multi-Jastrow trial wavefunction for quantum Monte Carlo*** ***Michel Caffarel***

University Paul Sabatier

#### **Abstract**

A new type of electronic trial wavefunction suitable for quantum Monte Carlo calculations of molecular systems is presented. In contrast with the standard Jastrow-Slater form built with a unique global Jastrow term, it is proposed to introduce individual Jastrow factors attached to molecular orbitals. Such a form is expected to be more physical since it allows to describe differently the local electronic correlations associated with various molecular environments (1s-core orbitals, 3d-magnetic orbitals, localized two-center sigma-orbitals, delocalized pi-orbitals, atomic lone pairs, etc.). In contrast with the standard form, introducing different Jastrow terms allows to change the nodal structure of the wavefunction, a point which is important in the context of building better nodes for more accurate Fixed-Node Diffusion Monte Carlo (FN-DMC) calculations.

Some illustrative applications for several atoms and molecules are presented.

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- [3] J.A. Parkhill and M. Head-Gordon, Mol. Phys. 108, 513 (2010).
- [4] J.A. Parkhill and M. Head-Gordon, J. Chem. Phys. (submitted).

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### ***Finite-size errors in continuum quantum Monte Carlo calculations*** ***William Matthew Colwyn Foulkes***

Imperial College London

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## ***Electronic structure of lowest singlet states of azobenzene***

**Ivan Stich**

University of Bratislava

### **Abstract**

A combination of QMC and quantum chemistry (CAS-SCF) techniques are used to obtain energies at selected points on the potential energy surfaces of a large and technologically important photoswitchable molecule, azobenzene, along the torsion pathway (CNNC dihedral angle), in the ground and first excited singlet states. We study the excitation energies of both cis- and trans-conformers, and energy of the transition state located at 90°. Chemical accuracy is obtained by a systematic control of nodal surface convergence using a novel development of analysis of nodal surface structure. The nodal analysis allows to improve the nodes in a systematic, controlled and computationally feasible way. Our results not only outperform all the available quantum chemistry results such as CAS-SCF, CAS-PT2 [1-3], and DFT results with proper spin symmetry (ROKS) [4], but the accuracy is sufficient to identify potential inaccuracies in some of the experimental results [5], i.e., the results have predictive quality. The CAS-SCF/QMC combination of methods ideally balancing the relative strengths of both methods enhanced by the access to the properties of the nodal surfaces along with the control over their convergence opens an avenue for boosting the reach of chemical accuracy electronic structure calculations by an order of magnitude or more.

### **Key References**

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## ***Recent quantum Monte Carlo calculations of weakly bound systems***

**Dario Alfe**

University College London

### **Abstract**

Weak interactions between molecules and surfaces are of great scientific and technological interest. For example, understanding water interactions with carbon based surfaces is at the base of the study of many phenomena like lubrication, ice nucleation and water formation in the interstellar medium (ISM). Oxide surfaces are also naturally hydrated, and these interactions are important for corrosion, weathering of rocks and circulation of pollutant into the environment. The interaction between atomic and molecular hydrogen with carbon based surfaces is also important to understand, in order to explain the formation of molecular hydrogen in the ISM and also to study the feasibility of storing hydrogen for mobile application. Despite the great importance, theoretical and experimental techniques meet a challenge for these weakly interacting systems. On the theory side, standard quantum mechanics methods like density functional theory with current exchange-correlation functionals are simply not accurate enough, while highly accurate quantum chemistry (QC) methods can only be used on clusters, making it difficult to extrapolate the results to extended systems. Here I will present some recent diffusion Monte Carlo (DMC) results on the interactions between water and hydrogen with various acenes, and also on fully periodic graphene. I will also present a number of recent benchmarks of DMC on the water monomer and the water dimer, as well DMC calculations on crystals like MgH<sub>2</sub> and LiH. Comparison with experiments or QC results show that DMC is very accurate on these systems.

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**QMC calculations on Boranes and Azaboranes**  
**Dario Bressanini**

Universita' dell'Insubria

Abstract

Electronic energies of BH<sub>3</sub>, B<sub>2</sub>H<sub>6</sub>, BH<sub>3</sub>CO, CO, NH<sub>3</sub>, BH<sub>3</sub>NH<sub>3</sub>, BH<sub>4</sub><sup>+</sup>, CH<sub>3</sub><sup>+</sup>, CH<sub>4</sub>, BH<sub>2</sub><sup>+</sup>, and BH<sub>3</sub>CH<sub>3</sub><sup>+</sup> have been calculated by diffusion Monte Carlo simulations. The values were corrected for zero point energies by quartic force fields at MP2/aug-cc-pVTZ level. More than 95% of the correlation energy is usually recovered, so energy differences rely very little on cancellation error. For dissociation energies and protonation energies an overall good agreement with experimental data and best theoretical values is found. Borane dimerization energy  $D_e = -43.5(2)$  kcal/mol is slightly less than the most recent W4 estimate  $D_e = -44.43$  kcal/mol {Karton, 2007 #47}. Azaborane dissociation energy  $D_e = 31.6(2)$  kcal/mol is in agreement with a previous CCSD(T)/CBS value  $-31.64$  kcal/mol {Dixon, 2005 #91}. Thermochemical data can be safely predicted by FN-DMC calculations.

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**Metal-insulator transition of one-dimension Hydrogen chains: a Variational Monte Carlo study**  
**Lorenzo Stella**

Nano-Bio Spectroscopy Group and ETSF Scientific Development Centre

Abstract

Metal-Insulator Transitions (MIT) due to long-range electron-electron correlations cannot be modelled by Density Functional Theory (DFT) in any local or semi-local approximation, while many-body techniques, e.g., Dynamical Mean-Field Theory (DMFT) and Quantum Monte Carlo (QMC), have been mostly applied to semiempirical models. In this work, we present an extensive ab-initio Variational Monte Carlo (VMC) study of Hydrogen chains, which provide a prototypical example of one-dimensional MIT. To this end, we have monitored the dependency of the complex polarisability on the chain geometry by changing both the interatomic distances and the chain dimerisation. Our VMC findings give valuable analytic insights on the many-body wavefunction of the chains that can be used to model the long-range electron-electron correlations which drive the MIT. Quality of the results has been benchmarked against accurate Diffusion Monte Carlo (DMC) calculations. Finally, we discuss the possibility of developing novel DFT functionals which include the long-range electron-electron correlations responsible for the MIT of one-dimensional Hydrogen chains, and address the implications for more realistic three-dimensional systems.

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**Systematically improvable electronic structure calculations for solids and liquids**  
**Fred Manby**

University of Bristol

Abstract

For gas-phase molecules the availability of systematically improvable electronic structure theory has been of decisive importance in chemistry. Extending this success to condensed-phase systems is challenging owing to the increased numbers of particles and, in the case of liquids, the need for extensive sampling. In this talk I will provide an update of our work on using molecular electronic structure theory for crystalline solids and for liquid water.

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**Diamond to betatin transition in Silicon: a playground for pseudopotentials.**  
**Michele Casula**

Ecole Polytechnique, Palaiseau

## Abstract

I will discuss the diamond to betatin transition in Silicon under pressure, from the perspective of an effective pseudized Hamiltonian. I will show how the quality of the pseudopotentials affects the transition pressure. I will present some quantum Monte Carlo calculations done with different type of pseudopotentials in order to analyze what is the best strategy to combine pseudization and quantum Monte Carlo.

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### ***The method of increments - a wavefunction-based correlation methods for solids and surfaces*** **Beate Paulus**

Institute of Chemistry and Biochemistry, Free University of Berlin

## Abstract

Electronic structure calculations e.g. for the hexagonal close-packed (hcp) structures of magnesium, zinc and cadmium revealed problems of present-day density functionals (DFT) to correctly describe the crystal structures and the cohesive properties of zinc and cadmium [1]. The application of the method of increments [2] for the correlation energy in solids based on any size-extensive correlation method like coupled cluster to metals such as magnesium [3], zinc, and cadmium [4] considerably improved our understanding of binding in these metals compared to the DFT approach.

We have now extended our studies into different directions, e.g. to the other group 2 metals, to metallic ytterbium or to open shell metals like lithium. In Beryllium we found significant covalent contributions to the binding of metallic beryllium [5], for the group 1 and 11 metals we are developing an embedding relying on dimers [6].

In the second part of the talk the method of increments is extended to adsorption processes on surfaces.

The standard density functional methods have their difficulties with describing dispersion forces, especially the long-range van der Waals interactions. Here we want to present as application the adsorption of CO, N<sub>2</sub> O, NO and gold atoms on two different surfaces of the CeO<sub>2</sub> [7] as an example for ionic surfaces and of H<sub>2</sub> S and H<sub>2</sub> O on graphene as example for a purely van der Waals bound system [8]. First results combining the two extensions of the method of increments will be shown for a magnesium surface.

Support of this work by the German Research Foundation (DFG), Priority Programmes SPP 1145 and SPP 1178, is gratefully acknowledged.

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**Local-correlation methods for the study of non conducting crystalline systems : the CRYSCOR program**  
**Lorenzo Maschio**

University of Torino

Abstract

The CRYSCOR project[1,2] is aimed at exploiting the availability of high-quality Hartree-Fock solutions for non-conducting crystalline systems, based on atomic-orbital Gaussian-type-function representation, as provided by the CRYSTAL code[3] in order to extend to periodic systems local correlation  $O(n)$  techniques as proposed by Pulay, Werner and co-workers[4]. After several years of development, the CRYSCOR program has been recently released in its first public version, CRYSCOR09 (see [www.cryscor.unito.it](http://www.cryscor.unito.it)).

The objective is to provide a public code, characterized by high flexibility, generality and ease of use, for estimating the electron correlation contribution to a number of crystalline properties, first of all ground state energy. For the time being, the code can efficiently provide the solution of periodic local-MP2 equations for nonconducting systems periodic in three dimensions (bulk crystals), two dimensions (surfaces), one dimension (polymers) or, as a limiting case, zero dimensions (molecules). A fundamental role is played by the use of approximate evaluation of four-index composite electron-repulsion integrals, which represent the bottleneck of all MP2 methods. Thanks to the recent adaptation and implementation of the fast local Density-Fitting techniques to Periodic systems[5], the average time needed for obtaining the MP2 energy is comparable to that of the corresponding Hartree Fock calculation.

In this talk features and capabilities of the code will be shown, and an overview on systems we have studied at the LMP2 level will be presented, together with the most recent results. These include evaluation of cohesive energies of molecular crystals[6,7] and rare gas crystals, adsorption energies of molecules on surfaces and simulation of Compton profiles[8].

Parallelization of the code is also in progress, which will allow to further extend its applicability to the study of larger unit cells and basis sets. The main strategies and algorithms adopted for the parallelization will be presented in some detail, with preliminary benchmarks.

Key References

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**Quantum chemistry methods for solids and surfaces: RPA and CCSD**  
**Georg Kresse**

University of Vienna

Abstract

For extended systems, density functional theory currently possesses the optimal balance between computational efficiency and accuracy. Thus its wide spread acceptance and application in quantum chemistry, materials science, and computational catalysis is in no way astonishing.

Despite this success, challenging problems remain: even for simple chemical reactions involving small molecules reaction energies are wrong by up to one eV, some semiconductors are predicted to be metals, many oxides, in particular, correlated oxides are not well described, equilibrium volumes and elastic constants are generally wrong by several percent, and, finally, van der Waals like forces are not accounted for. There is now emerging evidence that an improved description will require the evaluation of non-local exchange and a compatible correlation functional constructed by many electron techniques or many electron perturbation theory.

In this talk, the simplest many electron approach, the random-phase approximation (RPA) to the correlation energy[1] is discussed. Results for lattice constants, bulk moduli, and atomisation energies of prototypical solids[3,4] are presented. Setting out from the observation that the RPA generally improves upon available density functionals, we apply the method to more challenging problems, such as surface energies, adsorption energies of small molecules on surfaces, and van der Waals bonded systems. The results suggest that energies from exact exchange and RPA are generally better than for the available density functionals, accounting equally well for van der Waals bonding, ionic, covalent, and metallic bonding. A slight tendency towards underbinding is observed, making accurate predictions (chemical accuracy) not yet possible.

Furthermore, results of MP2 calculations are presented for prototypical insulators and semiconductors and compared to the RPA results [5]. For MP2 a tendency for under-correlation and over-correlation is found for large gap and small gap systems, respectively. This is obviously a result of the neglect of higher order diagrams, which are accounted for in coupled cluster methods. First results of CCSD calculations for extended solids are presented.

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[5] M. Marsman, A. Gruneis, J. Paier and G. Kresse, J. Chem. Phys 130, 184103 (2009).

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***Fixed-node calculation of force constants***  
***Saverio Moroni***

DEMOCRITOS Trieste

Abstract

We describe a method to compute derivatives of the fixed-node energy in a consistent way, i.e. with no other bias than the fixed-node approximation. It features (i) a path-integral Metropolis method instead of a branching random walk, (ii) a short-time approximation to the propagator which is better behaved near the nodes than the usual drift-diffusion Green's function, and (iii) an extension of the so-called space-warp transformation to deal with the displacement of the nodes. As an illustrative result we calculate the harmonic frequency of Li<sub>2</sub>.

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***Natural Orbital and Gauss-Slater Basis for Molecules***  
***Cyrus Umrigar***

Cornell University

Abstract

A simple yet general method for constructing basis sets for molecular electronic structure calculations is presented. These basis sets consist of atomic natural orbitals from a multi-configurational self-consistent field calculation supplemented with primitive functions, chosen such that the asymptotics are appropriate for the potential of the system. Primitives are optimized for the homonuclear diatomic molecule to produce a balanced basis set. Two general features that facilitate this basis construction are demonstrated.

First, weak coupling exists between the optimal exponents of primitives with different angular momenta. Second, for a given form of the basis, the optimal primitive exponents for a chosen system depend weakly on the particular level of theory employed for optimization (though for different forms of bases, different levels of theory can give different energy orderings). The explicit case considered here is a basis set appropriate for the Burkatzki-Filippi-Dolg pseudopotentials.

Since these pseudopotentials are finite at nuclei, the recently proposed Gauss-Slater functions are the appropriate primitives. Double-zeta and triple-zeta bases are developed for elements hydrogen through argon. These new bases offer significant gains over the corresponding Burkatzki-Filippi-Dolg bases at various levels of theory.

Finally, the importance of including primitives with F angular momentum is investigated.

F primitives are found to be important for traditional quantum chemistry methods but not for diffusion Monte Carlo calculations. This basis works well for ground states but requires augmentation for certain excited states.

#### Key References

F. R. Petruzielo, Julien Toulouse, C. J. Umrigar, <http://arxiv.org/abs/1005.3318>

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### ***Many-body nodal structures of ground and excited states, pairing effects and release node methods*** ***Lubos Mitas***

North Carolina State University

#### Abstract

I will talk about recent progress in quantum Monte Carlo (QMC) methods. In particular, the focus will be on new insights in understanding the nodal structures of ground and excited state wavefunctions, beyond the fixed-node approximation studies in electronic and ultracold unitary gas systems and on treatment of spins in QMC calculations.

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### ***QMC in discrete spaces : a way to overcome the sign problem ?*** ***Ali Alavi***

University of Cambridge

#### Abstract

We have recently [1,2] developed a QMC algorithm for sampling Slater determinant (SD) space which we demonstrate to be exact, i.e. it can converge onto the full configuration-interaction energy of the system in the specified one-electron basis. There are two key attributes to the algorithm which make it efficient: the first is walker annihilation, and the second is a "survival of the fittest" criterion, which enable the space of Slater determinants to be sign-coherently sampled with relatively few walkers. We will show examples of this algorithm in action: atoms (and cations and anions) and first row dimers such as C2 and F2 in substantial basis sets, and transition metal dimers such as Cr2. In these cases, the size of the SD space vastly exceeds the number of walkers need to converge the energy. Extensions of the algorithm to more flexible forms of the wavefunction, and the calculation of other

properties (such as forces) will also be briefly mentioned.

#### Key References

- [1] GH Booth, AJW Thom, A Alavi, J Chem Phys, 131, 054106, (2009)  
[2] D Cleland, GH Booth, A Alavi, J Chem Phys, 132, 0411103, (2010)
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#### ***Two-electron Reduced-Density-Matrix mechanics : theory and applications*** **David Mazziotti**

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637, USA

#### Abstract

In 1959 Charles Coulson popularized the challenge of computing the ground-state energy as a functional of the two-electron reduced density matrix (2-RDM) without the many-electron wavefunction. Recently, theoretical and computational advances have led to two classes of 2-RDM methods [1]: (i) the variational calculation of the 2-RDM subject to approximate N-representability conditions and (ii) the non-variational calculation of the 2-RDM from the anti-Hermitian contracted Schrödinger equation. I will develop the background for the 2-RDM methods, discuss recent theoretical and computational advances, and present some applications, including the detection of poly-radical correlation in polyaromatic acene chains, the treatment of protonated acetylene and malonaldehyde beyond the Born-Oppenheimer approximation, and the computation of energy barriers in the electrocyclic conversion of bicyclobutane to gauche-1,3-butadiene.

#### Key References

- 1] Two-electron Reduced-Density-Matrix Mechanics with Application to Many-electron Atoms and Molecules, edited by D. A. Mazziotti, Advances in Chemical Physics Vol. 134 (Wiley, New York, 2007).
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#### ***The rigorous calculation of the universal density functional by the Lieb variation principle*** **Trygve Helgaker**

Centre for Theoretical and Computational Chemistry Department of Chemistry University of Oslo.

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#### ***Calculations of interaction energies with micro to femtohartree accuracies*** **Krzysztof Szalewicz**

University of Delaware

#### Abstract

Most of current large-scale calculations of interaction energies for dimers containing a few atoms reach accuracy somewhat better than 1 milliH whereas such energies are of the order of a few milliH. Calculations of such accuracy are sufficient for determining characteristic points on potential energy surfaces, predicting rovibrational spectra of dimers, and for simulations of condensed phase. For some systems, in particular for dimers of rare gas atoms, much more accurate potentials are needed. It has been possible to reach microH accuracy for the argon dimer and nanoH accuracy for the helium dimer. This work required applying explicitly correlated Gaussian-type geminal (GTGT) basis sets, extrapolation techniques, and high levels of electron excitations, up to the quadruple ones. The GTG basis sets are able to reach femtoH accuracies for the interaction of two hydrogen atoms. The helium dimer results are consistent with the most recently published quantum Monte Carlo values, but have smaller error bars. For this system, the most accurate interaction energy to date, with only 0.6 nanoH uncertainty, was obtained using four-electron explicitly correlated Gaussian basis sets. At this level of accuracy, relevant for creating new metrology standards, one has to include several effects above the

Born-Oppenheimer level: the adiabatic, relativistic, and quantum electrodynamics effects.

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***New wavefunctions in quantum chemistry***  
**Garnet Chan**

Cornell University, Ithaca

Abstract

I will discuss a few recent developments. These will include (i) the use of the density matrix renormalization group in quantum chemistry, and (ii) a pedagogical overview of developments in tensor networks.

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***Excitations in photosensitive biomolecules from quantum Monte Carlo***  
**Claudia Filippi**

Faculty of Science and Technology, University of Twente

Abstract

Despite significant progress in electronic structure methods, the computation of the excitation energies of even relatively small organic molecules remains a demanding task. I will here illustrate the performance of quantum Monte Carlo on several prototypical photoactive molecules and compare to other first-principle methods considered promising for the computation of excited potential energy surfaces (e.g. multi-configuration perturbation theory and coupled cluster). I will then focus on the calculations of the excitations of Green Fluorescent Protein (GFP), one of the main workhorses of molecular biology. I will show how different theoretical approaches yield a large spread in excitation energies for the GFP chromophore in the gas phase and discuss the difficulties in reconciling theory and experiments when modeling a realistic protein-chromophore complex.

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***Recent developments in multiconfigurational quantum chemical methods and their application to water oxidation***  
**Laura Gagliardi**

University of Minnesota

Abstract

Chemical systems with a multiconfigurational electronic structure represent a major challenge for modern quantum chemistry. The CASSCF/CASPT2 approach [1] is one of the most elegant ways to treat non-dynamical electron correlation; however, it is severely limited by the size of the active space, which may include at most 15-16 electrons in 15-16 active orbitals.

We have extended this method to the restricted active space RASSCF/RASPT2 regime [2], which permits to address significantly larger active spaces, including up to 30 electrons in 30 orbitals, by considering more limited sets of excitations.

We are now working on a further extension, the Split-CAS method, which allows the selection of the important configurations, by still using large active spaces.[3]

In this lecture I will describe the main features of the Split-CAS method. I will also present results of the RASPT2 method applied to organic systems and a Ru-based catalyst employed for water oxidation.

Key References

[1] B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, Chem. Phys. 48, 157 (1980); B. O. Roos, in Advances in Chemical Physics: Ab Initio Methods in Quantum Chemistry-II, Wiley, Chichester, England, (1987), Chap. 69, p. 399.

[2] P.-A. Malmqvist, K. Pierloot., A. R. Moughal Shahi, C. J. Cramer and L. Gagliardi The Restricted Active Space followed by second order perturbation theory method: theory and application to the study of CuO<sub>2</sub> and Cu<sub>2</sub>O<sub>2</sub> systems J. Chem. Phys. 128, 204109 (2008)

[3] G. Li Manni, F. Aquilante, and L. Gagliardi in preparation.

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### ***Auxiliary-field quantum Monte Carlo for quantum chemistry : recent progress and open issues*** **Shiwei Zhang**

College of William and Mary

Abstract

I will report on the current status in the development and application of the phaseless auxiliary-field quantum Monte Carlo (AFQMC) approach. This is an orbital-based many-body method applicable with any single-particle basis. With Gaussian basis sets, the method treats the same Hamiltonian as in the corresponding quantum chemistry calculation. It takes the form of parallel streams of random walks, each of which resembling a density-functional theory (DFT) calculation in a fluctuating external potential. An approximate constraint is applied to the random walk paths to control the sign/phase problem. In about 100 molecular and solid systems tested to date, the method has given results at or near chemical accuracy. Both ground- and excited-state calculations have been performed. The method scales as  $M^3$ - $M^4$  with basis size  $M$ . I will discuss the conceptual framework and its connection with other methods, and open issues. Recent progress includes the implementation of a modified Cholesky method for larger basis sets, and the formulation of pairing (or GVB) wavefunctions as constraining wave functions.

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### ***The variational coupled cluster method and approximate pair functionals*** **Peter Knowles**

Cardiff University, UK

Abstract

In this talk, I will present benchmark results for variational coupled-cluster theory, that show that it can provide a more robust methodology than standard projection CC, particularly when electron correlation effects are strong. I will then discuss feasible approximations to VCC, and their relationship to the Coupled Electron Pair Approximation.

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### ***QMC, harnessing computing powers of today and beyond*** **Jeongnim Kim**

NCSA

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### ***Structure and harmonic frequencies of the water molecule by Quantum Monte Carlo*** **Leonardo Guidoni**

University of L'Aquila

Abstract

(1) Department of Physics, La Sapienza University of Rome, Italy.

(2) International School for Advanced Studies (SISSA) and Democritos CNR-IOM, Trieste, Italy.

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The correct description of water-water intermolecular interactions is still a challenge for electronic structure methods. We have shown that Quantum Monte Carlo methods are able to describe correctly both the dipole moment and the binding energy of the water dimer [1]. This quantity, together with the water-water dispersion curve, is crucial for a proper description of the hydrogen bond. We used as variational wave function an AGP (Antisymmetrised Geminal Power) wave function with Jastrow factors, fully optimized through a stochastic reconfiguration procedure [2]. Within this scheme we obtained Variational Monte Carlo (VMC) results which are of the same quality than their corresponding Diffusion Monte Carlo calculations.

In the present contribution we have used the extended AGP molecular orbitals scheme described in reference [3] to study the electronic and structural properties of the water monomer and dimer as well as the vibrational properties of the single water molecule. Full geometry optimization of the monomer and the dimer has been performed using ionic forces calculated at the VMC level using the scheme introduced in reference [4]. Vibrational properties of the water molecule are also calculated by Hessian diagonalization at the geometry optimised structure. The obtained harmonic frequencies and normal modes are in good agreements with experimental data and previously reported quantum chemistry calculations [5].

#### Key References

- [1] F. Sterpone, L. Spanu, L. Ferraro, S. Sorella and L. Guidoni, J. Chem. Theo. Comp., 4, 14281434, (2008).
- [2] S. Sorella, Phys. Rev. B 64, 024512 (2001).
- [3] M. Marchi, S. Azadi, M. Casula, and S. Sorella, J. Chem. Phys, 131, 154116 (2009).
- [4] C. Attaccalite and S. Sorella, Phys. Rev. Lett. 100, 114501 (2008).
- [5] D. Feller, A. Peterson, J. Chem. Phys, 131, 154306 (2009).

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### ***Algorithmic differentiation and the calculation of forces by quantum Monte Carlo methods*** **Sandro Sorella**

International School for Advanced Studies (SISSA), Trieste

#### Abstract

We describe an efficient algorithm to compute forces within quantum Monte Carlo by means of algorithmic differentiation.

This allow us to apply the so called warp algorithm in the differential form[1,2] and compute all 3N force components of a system with N atoms with a computational effort that is comparable with the one for obtaining the total energy.

Few examples on how the method works for an electronic system containing several water molecules will be presented. Within the present technique the possibility to apply quantum Monte Carlo for calculating finite temperature thermodynamic properties of material is becoming feasible in the near future.

#### Key References

- [1] Claudia Filippi and C. J. Umrigar Phys. Rev. B 61, R16291 (2000)
  - [2] R. Assaraf and M. Caffarel J. Chem. Phys. 119, 10536 (2003).
-

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