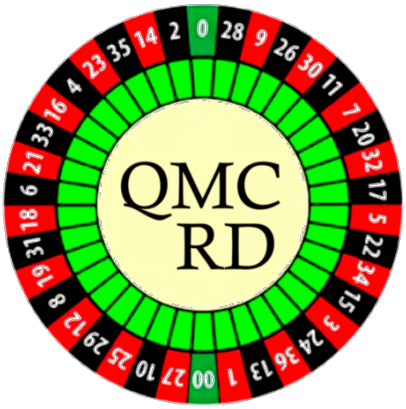
Recent developments in quantum Monte Carlo



October 21, 2021 - October 22, 2021
Rome, Italy

David Ceperley
University of Illinois at Urbana-Champaign, United States

Gaetano Senatore
Università degli Studi di Trieste, Italy

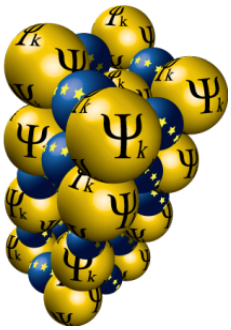
Giovanni Bachelet
Sapienza Università di Roma, Italy

Lilia Boeri
Sapienza Università di Roma, Italy

Fabio Affinito
CINECA, Italy

Irene Iacuitto
CNR, Italy

With the support of:



Psi-k

Sapienza Università di Roma

Enrico Fermi Research Center

Centre Européen de Calcul Atomique et Moléculaire

1. Description

With advances in algorithms and growing computing power, quantum Monte Carlo (QMC) methods have become a powerful tool for the description of a variety of quantum fluids and a viable alternative for high-accuracy calculations of the electronic structure of many atoms, molecules and solids. They are, however, at a less mature stage than today's ready-for-use quantum-chemistry or density-functional packages: while the production of results on a variety of quantum many-body systems has been going on for at least three decades, a significant effort is still devoted to research and development of methods and algorithms, including real-time dynamics, super-accurate optimization strategies for trial wavefunctions and molecular structures, inputs for the density functional theory of van der Waals forces, and eventually neural networks which at least for small molecular systems seem to improve the accuracy of variational quantum Monte Carlo to the point where it outperforms other ab-initio quantum chemistry methods.

Organized by his mentors and former students currently active in the field of computational physics, the workshop is also meant as a celebration of the 60th birthday of Saverio Moroni, a sound condensed-matter theorist who has given key contributions to quantum Monte Carlo methods, their application to a wealth of quantum fluids and chemical systems, and their dissemination in Europe.

It will take place at the Enrico Fermi Research Center, located in via Panisperna 89A, 00184 Rome, the famous building where Enrico Fermi and his group, ”the boys from via Panisperna”, gave crucial contributions to modern physics.

Key References

*[1] J. Kolorenč, L. Mitaš, Rep. Prog. Phys., **74**, 026502 (2011)*
*[2] C. Autieri, P. Barone, J. Sławińska, S. Picozzi, Phys. Rev. Materials, **3**, (2019)*
[3] R. Martin, L. Reining, D. Ceperley, Interacting Electrons, 2016
[4] F. Becca, S. Sorella, Quantum Monte Carlo Approaches for Correlated Systems, 2017
*[5] G. Carleo, L. Cevolani, L. Sanchez-Palencia, M. Holzmann, Phys. Rev. X, **7**, (2017)*
*[6] R. Assaraf, S. Moroni, C. Filippi, J. Chem. Theory Comput., **13**, 5273-5281 (2017)*
[7] David Pfau, James S. Spencer, Alexander G. de G. Matthews, W. M. C. Foulkes, https://arxiv.org/abs/1909.02487v2

2. Program

Day 1 - Thursday October 21st 2021

- 08:30 to 09:30 - Registration
- 09:30 to 09:45 - Welcome & introduction (Bachelet)

New methods and algorithms (chair: Ceperley) 09:45 to 12:00

- 09:45 to 10:00 - Introduction, Ceperley
- 10:00 to 11:00 - Carleo, Foulkes
- 11:00 to 11:30 - Coffee break
- 11:30 to 13:00 - Sorella, Baroni, Guidoni
- 13:00 to 14:30 - Lunch
- 14:30 to 16:00 - Filippi, Mitaš, Umrigar
- 16:00 to 16:30 - Coffee break

Quantum fluids, part 1 (chair: Senatore) 16:30 to 18:00

- 16:30 to 17:00 - Introduction, Senatore
- 17:00 to 18:00 - Boninsegni, Holzmann
- 18:00 to 19:00 - Poster session
- 21:00 to 00:00 - Social dinner

Day 2 - Friday October 22nd 2021

Quantum fluids, part 2 (chair: Senatore) 10:00 to 13:00

- 10:00 to 11:00 - Fantoni, Gori-Giorgi
- 11:00 to 11:30 - Coffee break
- 11:30 to 13:00 - Vitali, Pierleoni, Casula
- 13:00 to 14:30 - Lunch

Solid state physics (chair: Boeri) 14:30 to 18:00

- 14:30 to 15:00 - Introduction, Boeri
- 15:00 to 16:00 - Grosso, Attaccalite
- 16:00 to 16:30 - Coffee break
- 16:30 to 17:30 - De Palo, Varsano

Round Table / Conclusions (Organizers + Moroni) 17:30 to 18:30

3. Abstracts (alphabetic first author)

Optical excitations in layered materials: the case of hexagonal boron nitride

Claudio Attaccalite
CNRS Aix-Marseille Université, France

Hexagonal boron nitride is a large band gap material with an atomic structure similar to graphite. In recent years it has attracted a lot of attention as a possible substrate for 2D materials, and for its optical properties. In this talk I will present a series of new experimental results and the corresponding theoretical interpretation. In particular I will discuss the role of bound excitons on the optical properties and their coupling with phonon modes [1,2].

*[1] L. Artús, M. Feneberg, C. Attaccalite, J. Edgar, J. Li, R. Goldhahn, R. Cuscó, Adv. Photo. Res., **2**, 2000101 (2021)*
*[2] A. Segura, R. Cuscó, C. Attaccalite, T. Taniguchi, K. Watanabe, L. Artús, J. Phys. Chem. C, **125**, 12880-12885 (2021)*

Stochastic perturbation theory: a prequel to Reptation quantum Monte Carlo

Stefano Baroni
International School for Advanced Studies (SISSA), Trieste, Italy

The (never ending?) search for exotic phases of helium on graphite

Massimo Boninsegni
University of Alberta, Canada

In the course of almost three decades, my collaboration with Saverio has taken us through a number of different physical systems, which we have investigated using various QMC methodologies, some of which were developed ad hoc. One of the subjects that has kept us busy is the study of the phase diagram of helium on graphite, a relatively "old" system, which still elicits much interest, also generating a great deal of controversy.

In this talk, I shall offer an overview of our research activity on helium on graphite, highlighting the most important results, with special emphasis on the methodological aspects.

Neural-network quantum states in continuous space

Giuseppe Carleo
EPFL, Switzerland

In this talk I will discuss recent advances in the numerical simulation of many-body quantum systems using variational representations of many-body quantum states based on artificial neural networks [1]. First, I will overview the progress in the description of ground states of lattice models, highlighting strategies that have proven successful to improve existing state of the art variational results. I will then discuss challenges concerning the extensions of neural-network quantum states to study quantum systems with continuous degrees of freedom. In this context, I will show how a suitable symmetry-extended neural quantum states based on "deep sets" [2] can be successfully applied to study Helium 4.

*[1] G. Carleo, M. Troyer, Science, **355**, 602-606 (2017)*
[2] G. Carleo, G.M. Pescia, in preparation

Phase diagram of high-pressure hydrogen including nuclear quantum effects

Michele Casula
Sorbonne University, France

We compute the phase diagram of hydrogen and deuterium at low temperatures and high pressures (P > 300GPa) correctly accounting for accurate electronic correlations by quantum Monte Carlo, and for nuclear quantum effects and anharmonicity by the self-consistent harmonic approximation. We predict that phase III transits into the molecular metallic phase VI at 420(40) GPa, then to the atomic phase at pressures larger than 550 GPa. The transition pressures increase by 15 GPa and 80 GPa, respectively, if hydrogen is replaced with deuterium. Our results strongly support the claim of a phase transition occurring at 420 GPa into a metallic non-superconducting phase. However, for the atomic superconducting phase our data suggest much larger transition pressures than those predicted so far.

Long-range order in electron-hole bilayer with valley degeneracy

Stefania De Palo
CNR - IOM, Italy

Using quantum Monte Carlo simulations we have determined the zero temperature phase diagram of a symmetric electron-hole bilayer with twofold valley degeneracy, as function of the interlayer distance and in-layer density. From the investigation of the pair correlation functions together with the two-body density matrix to assess the long-range order, we find that the effect of the valley degeneracy is to favour quadriexcitons at small distance and of the four-component plasma at large distance, while it only slightly affects the value of the excitonic condensate fraction.

A quantum Monte Carlo method for nuclear matter

Stefano Fantoni
Fondazione Internazionale Trieste, Italy

I will first briefly discuss of my work done in collaboration with Saverio Moroni and the wonderful time I had the privilege to spend with him. Then I will present few results obtained for the equation of state of neutron and nuclear matter by using a quantum Monte Carlo method (the so called Auxiliar Fields Diffusion MonteCarlo,) originally developed for Hamiltonians which include tensor and other spin interactions such as those that are commonly encountered in nuclear structure calculations. The main ingredients are a Hubbard-Stratonovich transformation to uncouple the spin degrees of freedom along with a fixed node approximation to maintain stability. Comparison with other modern Many-Body methods for Nuclear Physics, such as Green Function Monte Carlo and Fermi Hyper Netted Chain are also provided. Particularly interesting are the studies made to analyze three-body nuclear interaction models, such as the Argonne-Urbana model or those derived from chiral effective field theory.

Variational principles and excited states in quantum Monte Carlo

Claudia Filippi
University of Twente, Netherlands

We will illustrate here the performance of quantum Monte Carlo methods for the computation of excited-state properties of prototypical photo-sensitive molecules. We will also discuss the use of different variational principles in quantum Monte Carlo to target the states involved in the excitation.

Approximating many-electron wave functions using deep neural networks

Matthew Foulkes[1], David Pfau[2], James Spencer[2], Alex Matthews[2]
[1]Imperial College London, United Kingdom
[2]DeepMind Ltd, United Kingdom

Given access to accurate solutions of the many-electron Schrödinger equation, most of condensed matter physics, chemistry and materials physics could be derived from first principles. Exact wave functions of systems with more than a few electrons are out of reach because they are NP-hard to compute in general, but approximations can be found using polynomially scaling algorithms. The key challenge for many of these algorithms is the choice of an approximate parameterized wave function, which must trade accuracy for efficiency. Neural networks have shown impressive power as practical function approximators and promise as a way of representing wave functions for spin systems, but electronic wave functions have to obey Fermi-Dirac statistics. This talk introduces a deep learning architecture, the Fermionic neural network, which is capable of approximating many-electron wavefunctions and greatly outperforms conventional approximations. The use of FermiNet wave functions boosts the accuracy of the simple and appealing variational quantum Monte Carlo method until it rivals the very best conventional quantum chemical approaches.

Noncovalent interactions from models for the Møller−Plesset adiabatic connection

Paola Gori-Giorgi[1], Tim Daas[1], Stefan Vuckovic[2], Fabio Della Sala[3], Eduardo Fabiano[3]
[1]Vrije University Amsterdam, Netherlands
[2]UCI Irvine, United States
[3]CNR-IMM Lecce, Italy

The adiabatic connection (AC) that has as weak-interaction expansion the Møller-Plesset (MP) perturbation series has been recently shown to have a large coupling-strength expansion in terms of functionals of the Hartree-Fock density with a clear physical meaning [1,2]. Based on these findings, in this work [3] we explore a new class of functionals that approximate directly the MP AC by interpolating between MP2 and the large-coupling strength limit, which is size consistent for fragments with a non-degenerate ground state [4]. These functionals have the same cost as double hybrids and greatly reduce the large MP2 errors for typical pi-stacking complexes (e.g., benzene-pyridine dimers), without using dispersion corrections. Furthermore, they are also competitive with state-of-the-art dispersion enhanced functionals and can even significantly outperform them for a variety of datasets, such as CT7, DI6 and L7. In this work the strong coupling limit has been approximated with some empiricism, while work to achieve a full non-empirical description is in progress. To this end, energies of a modified electron liquid would be a useful ingredient that could be obtained from QMC.

*[1] M. Seidl, S. Giarrusso, S. Vuckovic, E. Fabiano, P. Gori-Giorgi, J. Chem. Phys., **149**, 241101 (2018)*
*[2] T. Daas, J. Grossi, S. Vuckovic, Z. Musslimani, D. Kooi, M. Seidl, K. Giesbertz, P. Gori-Giorgi, J. Chem. Phys., **153**, 214112 (2020)*
*[3] T. Daas, E. Fabiano, F. Della Sala, P. Gori-Giorgi, S. Vuckovic, J. Phys. Chem. Lett., **12**, 4867-4875 (2021)*
*[4] S. Vuckovic, P. Gori-Giorgi, F. Della Sala, E. Fabiano, J. Phys. Chem. Lett., **9**, 3137-3142 (2018)*

The young Saverio: the years in Pisa

Giuseppe Grosso
Università di Pisa, Italy

This talk is in honor of Saverio Moroni on the occasion of his 60th birthday. I outline his first years of research activity in the group of Solid State Physics in Pisa, his results on the iterative recursion and renormalization methods, and other related methods, for the electronic structure of solids. Even if the mathematical research in this field goes back to the middle of nineteen century, only after almost one hundred years its formal apparatus has been exploited for the evaluation of Green's functions, local density of states, bound and resonant states, etc. in quantum mechanical problems of periodic or aperiodic materials. Among them, Saverio played an important role in the electronic structure of quantum wells, lattices, superlattices, surfaces and electron-phonon coupling.

Quantum computing for correlated systems

Leonardo Guidoni
University of L'Aquila, Italy

Solving the electronic structure of correlated lattice models and molecular systems will probably be one of the firsts problems in which quantum computers might show advantage over classical computers [1,2]. In the near future, the near-term gate-model quantum computers (as implemented by IBM, Google, Microsoft, Rigetti, IonQ and other companies) will still have limitations due to reduced number of qubits, high level of noise or short coherence time. New theoretical techniques and algorithms to tackle the electronic structure must be designed by theoretical and computational physicists and chemists to take advantage of such imperfect devices. The present contribution will review in an introductive manner the basic concepts of quantum computation and the main algorithms that are currently used on currently available quantum computers to solve prototypical examples of electronic structure problems. To alleviate the hardware limitations, we have recently proposed a non-unitary version of the Variational Quantum Eigensolver algorithm that can be used to effectively improve the variational space of wavefunction ansatzes. [3-4] Using the proposed strategies it is possible to recover a large amount of electron correlation energy using shallow-depth quantum circuits. A further improvement has been achieved by optimizing the Hamiltonian itself with respect a circuit (wavefunction) ansatz of a given topology, exploiting the invariance of the molecular Hamiltonian by orbital rotations.

*[1] S. McArdle, S. Endo, A. Aspuru-Guzik, S. Benjamin, X. Yuan, Rev. Mod. Phys., **92**, 015003 (2020)*
*[2] A. Kandala, A. Mezzacapo, K. Temme, M. Takita, M. Brink, J. Chow, J. Gambetta, Nature, **549**, 242-246 (2017)*
[3] F. Benfenati, L. Guidoni, G. Mazzola, P. Barkoutsos, P. Ollitrault, I. Tavernelli, Extended wavefunctions for the Variational Quantum Eigensolver, 2019
*[4] F. Benfenati, G. Mazzola, C. Capecci, P. Barkoutsos, P. Ollitrault, I. Tavernelli, L. Guidoni, J. Chem. Theory Comput., **17**, 3946-3954 (2021)*

Quantum fluids: from helium to electrons

Markus Holzmann
CNRS, France

From the very beginning of quantum Monte Carlo simulations, continuous efforts have been devoted to improve ground-state calculations of liquid helium and of the electron gas. Despite the very different character of the microscopic interactions in these two systems, methodological improvements obtained with helium turned out to similarly affect the electron gas calculations; and vice versa. In this talk I will review some of such joint developments, and may speculate on some future ones.

Quantum Monte Carlo and spins: systems with spin-orbit interactions

Luboš Mitaš
North Carolina State University, United States

Most electronic-structure quantum Monte Carlo (QMC) calculations are routinely carried out using a static, collinear setting for electron/particle spins. Recently, we expanded the fixed-phase QMC with spins as quantum variables in order to treat spin-orbit or other spin-dependent Hamiltonians within two-component spinor formalism (see e.g. [1] and references therein). The approach also enables us to apply the fixed-phase method to nominally fixed-node (real) trial functions which become complexified, with several advantages in diffusion Monte Carlo calculations. The results thus obtained and further aspects of this approach will be discussed.

*[1] C. Melton, L. Mitaš, Phys. Rev. E, **96**, 043305 (2017)*

Energy gap closure and metal-insulator transition in solid and fluid hydrogen with pressure

Carlo Pierleoni
University of L'Aquila, Italy

We study the gap closure with pressure in molecular crystalline [1] and in the fluid hydrogen [2] by Quantum Monte Carlo methods. Nuclear quantum and thermal effects are considered from first principles with Coupled Electron Ion Monte Carlo [3,4,5]. The fundamental electronic gap is obtained from grand-canonical Quantum Monte Carlo methods [6] properly extended to quantum and thermal nuclei [1,7] and properly extrapolated to the thermodynamic limit [6]. In the crystal, nuclear zero point effects cause a large reduction in the gap (~ 2eV), reducing the gap closing pressure from 530GPa for ideal crystals to 360GPa for quantum crystals. Since the direct gap remains open until ~450GPa, the emerging scenario is that upon increasing pressure in phase III (C2/c-24 crystal symmetry) the fundamental (indirect) gap closes and the system enters into a semimetal phase in which the density of states at the Fermi level increases with pressure up to ~450GPa when the direct gap closes. Our work partially supports the interpretation of recent experiments in high pressure hydrogen [8,9]. In the low temperature fluid phase, below the critical point of the liquid-liquid phase transition line, the gap closes at the transition confirming that molecular dissociation and metallization occur simultaneously. Above the critical temperature, molecular dissociation sets in while the gap is still open. When the gap closes, the decay of the off- diagonal reduced density matrix shows that the liquid enters a gapless, but localized, phase: there is a crossover between the insulating and the metallic liquids. Compared to different density functional theory (DFT) functionals, our QMC calculations provide larger values for the fundamental gap and the electronic density of states close to the band edges, indicating that optical properties from DFT, observed to agree with experiments [10], potentially benefit from error cancellations.

*[1] V. Gorelov, M. Holzmann, D. Ceperley, C. Pierleoni, Phys. Rev. Lett., **124**, 116401 (2020)*
*[2] V. Gorelov, D. Ceperley, M. Holzmann, C. Pierleoni, Phys. Rev. B, **102**, 195133 (2020)*
[3] Computer Simulations in Condensed Matter Systems: From Materials to Chemical Biology Volume 1, (Springer Berlin Heidelberg, Berlin, Heidelberg, 2006)
*[4] C. Pierleoni, M. Morales, G. Rillo, M. Holzmann, D. Ceperley, Proc. Natl. Acad. Sci. USA., **113**, 4953-4957 (2016)*
*[5] G. Rillo, M. Morales, D. Ceperley, C. Pierleoni, The Journal of Chemical Physics, **148**, 102314 (2018)*
*[6] Y. Yang, V. Gorelov, C. Pierleoni, D. Ceperley, M. Holzmann, Phys. Rev. B, **101**, 085115 (2020)*
*[7] V. Gorelov, D. Ceperley, M. Holzmann, C. Pierleoni, J. Chem. Phys., **153**, 234117 (2020)*
*[8] M. Eremets, A. Drozdov, P. Kong, H. Wang, Nat. Phys., **15**, 1246-1249 (2019)*
*[9] P. Loubeyre, F. Occelli, P. Dumas, Nature, **577**, 631-635 (2020)*
*[10] G. Rillo, M. Morales, D. Ceperley, C. Pierleoni, Proc. Natl. Acad. Sci. USA., **116**, 9770-9774 (2019)*

The phase diagram of the Hubbard model by variational auxiliary-field QMC

Sandro Sorella
SISSA, Italy

A systematically improvable variational wave function [1] is proposed for the numerical solution of strongly correlated systems. This is achieved by combining the stochastic optimization technique, well established in standard variational Monte Carlo, with the accuracy of the auxiliary-field quantum Monte Carlo method, based on the Hubbard-Stratonovich transformation. Within this approach, the phase diagram of the 2D Hubbard model can be understood in details, thanks to the simplicity and clarity of the standard variational Monte Carlo approach, while maintaining state-of-the-art accuracy in energy and correlation functions. By decreasing doping, stripes are found to be stable only after the phase-separation instability. A possible d-wave superconducting phase is therefore restricted to the large doping region ~20%.

[1] S. Sorella, The phase diagram of the Hubbard model by Variational Auxiliary Field quantum Monte Carlo (https://arxiv.org/abs/2101.07045)

Green's functions for cross-node and fixed-node diffusion Monte Carlo

Cyrus Umrigar
Cornell University, United States

I will talk about two ideas that I have not yet tested on real systems, though they were developed and tested on toy systems a long time ago. First, release-node diffusion Monte Carlo (RN-DMC) is usually done with a drift-diffusion-reweighting Green's function with a Bosonic guiding wavefunction. An alternative may be to do "cross-node" DMC using an antisymmetrized pair-product Green's function with the usual Fermionic trial wavefunction as the guiding function. Most of the talk will be about using position-dependent drift and diffusion to get a better Green's function and therefore smaller time-step errors in fixed-node DMC.

Evidence of ideal excitonic insulator in MoS_2 under pressure

Daniele Varsano
CNR, Italy

Spontaneous condensation of excitons is a long-sought phenomenon analogous to the condensation of Cooper pairs in a superconductor. It is expected to occur in a semiconductor at thermodynamic equilibrium if the binding energy of the excitons—electron (e) and hole (h) pairs interacting by Coulomb force—overcomes the band gap, giving rise to a new phase: the "excitonic insulator" (EI). Transition metal dichalcogenides are excellent candidates for the EI realization because of reduced Coulomb screening, and indeed a structural phase transition was observed in few-layer systems. However, previous work could not disentangle to which extent the origin of the transition was in the formation of bound excitons or in the softening of a phonon. Here we focus on bulk MoS_2 and demonstrate theoretically that at high pressure it is prone to the condensation of genuine excitons of finite momentum, whereas the phonon dispersion remains regular. Starting from first-principles many-body perturbation theory, we also predict that the self-consistent electronic charge density of the EI sustains an out-of-plane permanent electric dipole moment with an antiferroelectric texture in the layer plane: At the onset of the EI phase, those optical phonons that share the exciton momentum provide a unique Raman fingerprint for the EI formation. Finally, we identify such fingerprint in a Raman feature that was previously observed experimentally, thus providing direct spectroscopic confirmation of an ideal excitonic insulator phase in bulk MoS_2 above 30 GPa.

Ground and excited states of fermi superfluids from QMC calculations

Ettore Vitali
California State University, United States

I will present recent methodological progress in the big challenge of computing ground state and excited states properties of Fermi superfluids from first principles. Results for spectral functions and spin and density dynamical structure factors will be presented for dilute attractive Fermi gases and for fermions moving on optical lattices. Exact results for the pairing gap of a two-dimensional Fermi gas will be discussed, and calculations of the dispersion of the Nambu-Goldstone mode and possibly the Higgs mode for optical lattice systems will be presented. In addition, the property of spin-polarized optical lattice systems will be discussed, in connection with the stability of the exotic Fulde-Ferrell-Larkin-Ovchinnikov superfluid phase.

4. Posters (alphabetic first author)

Trex: targeting real chemical accuracy at exascale

Fabio Affinito
CINECA, Italy

In order to compete in the demanding rush in high-precision quantum chemical simulation methods, the TREX Center of Excellence (CoE) federates European scientists, High Performance Computing (HPC) stakeholders, and SMEs to develop and apply high-performance software solutions for quantum mechanical simulations at the exascale. The final goal of the project is to develop a set of flagship Quantum Monte Carlo codes, able to exploit the capabilities of the recent exascale computers at its highest.
To achieve this goal, TREX's main focus will be the development of a user-friendly and open-source software suite in the domain of stochastic quantum chemistry simulations, which integrates TREX community codes within an interoperable, high-performance platform. This will permit to greatly enhance the tools available to the scientific community for the design of new materials and the understanding of the fundamental properties of matter. In parallel, TREX will work on show-cases to leverage this methodology for commercial applications as well as develop and implement software components and services that make it easier for commercial operators and user communities to use HPC resources for these applications.

Electronic properties and binding energies of electron-positron systems with quantum Monte Carlo

Jorge Alfonso Charry Martínez, Matteo Barborini, Dmitry Fedorov, Alexandre Tkatchenko
University of Luxembourg, Luxembourg

The positron, besides all its intriguing fundamental properties as the antimatter counterpart to the electron, may form metastable bound states with atomic/molecular systems before its annihilation [1]. One possible mechanism behind the formation of bound positron-electron states is the polarization of the electronic cloud towards the positron. Furthermore, the positron can take away an electron forming a positronium (Ps) atom, which then can interact non-covalently with regular matter [2]. If on one hand the study of these interactions is already challenging due to the complexity in reproducing the electron-positron correlation effects, even more challenging is the evaluation of their electric response properties such as polarizabilities [3]. Here we propose a simple yet accurate wave function built from positronium geminal orbitals, integrated and optimized via quantum Monte-Carlo (QMC) methods. We apply this approach to study the electronic properties and the binding energies of electron-positron systems, starting from Ps, Ps^-, Ps_2, PsH, and the recently proposed positronic bonding molecule $e^+H^-{}_2$ formed between the otherwise repelling hydride anions [4]. We compare our results when possible with accurate Full-Configuration-Interaction calculations based on molecular orbitals.

*[1] G. Gribakin, J. Young, C. Surko, Rev. Mod. Phys., **82**, 2557-2607 (2010)*
*[2] M. Bromley, J. Mitroy, J. Phys.: Conf. Ser., **199**, 012011 (2010)*
*[3] Z. Yan, J. Phys. B: At. Mol. Opt. Phys., **35**, L345-L349 (2002)*
*[4] J. Charry, M. Varella, A. Reyes, Angew. Chem. Int. Ed., **57**, 8859-8864 (2018)*

Towards a systematic embedding of electrons and quantum harmonic oscillators

Matej Ditte, Matteo Barborini, Alexandre Tkatchenko
University of Luxembourg, Luxembourg

Computational embedding strategies, based on the partitioning of the system of interest in different sub-spaces each treated with a different level of theory and thus of accuracy, are essential tools to describe many important phenomena in nature, which are often beyond the computational capabilities of accurate uniform quantum approaches [1]. Although such methods lead to a significant reduction of the total computation cost, this comes at the price of having to approximate the interactions within and between the sub-systems [1]. Here we propose a new approach for embedding a molecular system in a bath of charged quantum harmonic oscillators, constructed to mimic the long-range response of the real environment [2]. This embedding approach leads to a single many-body Hamiltonian of electrons and distinguishable particles, i.e. drudons [3], describing the entire system with a significant reduction of degrees of freedom. To construct the system's ground state we propose a variational ansatz that is integrated and optimized through quantum Monte Carlo methods [4]. Due to the reduction of degrees of freedom, this approach opens new possibilities in describing quantum effects of large environments on an electronic sub-system.

[1] L. Chung, W. Sameera, R. Ramozzi, A. Page, M. Hatanaka, G. Petrova, T. Harris, X. Li, Z. Ke, F. Liu, H. Li, L. Ding, K. Morokuma, Chem. Rev., ***115****, 5678-5796 (2015)*
[2] J. Hermann, R. DiStasio, A. Tkatchenko, Chem. Rev., ***117****, 4714-4758 (2017)*
[3] A. Jones, A. Thompson, J. Crain, M. Müser, G. Martyna, Phys. Rev. B, ***79****, 144119 (2009)*
[4] B. Austin, D. Zubarev, W. Lester, Chem. Rev., ***112****, 263-288 (2011)*

Electronic band gaps from quantum Monte Carlo methods

Vitaly Gorelov
Ecole Polytechnique, France

We develop a method for calculating the fundamental electronic gap of semiconductors and insulators using grand canonical quantum Monte Carlo simulations. We discuss the origin of the bias introduced by supercell calculations of finite size and show how to correct the leading and subleading finite-size errors either based on observables accessible in the finite-sized simulations or from density-functional theory calculations. Our procedure is applied to carbon, silicon, and molecular hydrogen crystals, and compared to experiment for carbon and silicon. In molecular hydrogen, we also consider renormalization of the electronic gap due to nuclear quantum and thermal effects from the first principles with Coupled Electron Ion Monte Carlo. Our work partially supports the interpretation of recent experiments in high pressure hydrogen.

Benchmark of DFT functionals for lithium adsorbed on graphite using quantum Monte Carlo

Michele Ruggeri[1], Carlo Pierleoni[2], Kyle Reeves[3], Mathieu Salanne[3]
[1]CNRS, Maison de la Simulation, France
[2]Università dell'Aquila, Italy
[3]Sorbonne Université, France

An accurate description of the interaction between lithium and graphite is critical to understand the behavior and properties of Li-ion batteries. Density Functional Theory (DFT) is typically the method of choice when studying the properties of lithium - graphite interfaces, due to the balance between its computational cost and its accuracy. DFT results however depend on the choice of the exchange-correlation functional used in the computations, choice that is system-dependent and empirical. To identify the best functional to describe lithium in the proximity of a graphite surface we used Quantum Monte Carlo (QMC) simulations to benchmark several DFT functionals in the study of the adsorption of a Li atom on a graphite substrate. Adsorption curves were determined for different geometries of the system, both using fixed node Diffusion Monte Carlo and DFT, employing several commonly used functionals. We found that the BLYP-D2 functional provides the most accurate description of the adsorption. Additionally, we show a comparison of electronic densities obtained via QMC and DFT for a Li atom close to graphite.

[1] Y. Yang, V. Gorelov, C. Pierleoni, D. Ceperley, M. Holzmann, Phys. Rev. B, ***101****, 085115 (2020)*

Modelling materials and large molecular complexes using quantum Monte Carlo

Andrea Zen
University College London, United Kingdom

Computer simulations are becoming useful in providing insight in the physical and chemical processes taking places in nature. Simulations yield molecular level understanding, which is often complementary information to the understanding provided by experimental investigations. Yet, they are only useful when they can accurately model the physical system. High accuracy is often only obtained by resorting to first principles, and by modelling the quantum mechanics features of the system of interest at the atomic level. Thriving nanotechnologies and exciting experiments pose big challenges to computational approaches. On the one hand, the systems to be simulated are large and computationally expensive, and their physical and thermal properties require sampling of a large phase space (using molecular dynamics or other techniques). On the other hand, the high accuracy required to evaluate inter-atomic interactions often means using very accurate and expensive approaches to solve the Schrodinger equation. We discuss here some recent developments in diffusion quantum Monte Carlo (QMC), which is one of the most accurate approaches available to assess the ground state electronic states and their properties in molecular systems, solids and surfaces. QMC simulations are computationally expensive and often demands the employment of high-performance computers. However, recent developments have drastically reduced the overall cost of QMC, especially in the evaluation of interaction energies.
QMC methods can be used to benchmark cheaper but less accurate approaches (such as density functional theory, or empirical force fields) promoting their further developments. The combination of this hierarchy of methods, often coupled with machine learning techniques, provides high accuracy for systems whose size would preclude a full quantum mechanics approach.

5. Participant list

Organizers

Affinito, Fabio
CINECA, Italy
Bachelet, Giovanni
Sapienza Università di Roma, Italy
Boeri, Lilia
Sapienza Universita" di Roma, Italy
Ceperley, David
University of Illinois at Urbana-Champaign, United States
Iacuitto, Irene
CNR, Italy
Senatore, Gaetano
Università degli Studi di Trieste, Italy

Amato, Flavio - Accenture, Italy
Attaccalite, Claudio - CNRS Aix-Marseille Université, France
Azadi, Sam - Imperial College London, United Kingdom
Bandi, Bharathi - IIT Bombay, India
Barborini, Matteo - University of Luxembourg, Luxembourg
Baroni, Stefano - International School for Advanced Studies (SISSA), Trieste, Italy
Beneduce, Camilla - Università degli Studi di Roma "La Sapienza", Italy
Bishnoi, Bhupesh - AIST, Japan
Boninsegni, Massimo - University of Alberta, Canada
Carleo, Giuseppe - EPFL, Switzerland
Casula, Michele - Sorbonne University, France
Cazzato, Paolo - Università "La Sapienza", Italy
Chanana, Anuja - JNCASR, India
Charry Martínez, Jorge Alfonso - University of Luxembourg, Luxembourg
Cucciari, Alessio - Sapienza - University of Rome, Italy
De Palo, Stefania - CNR - IOM, Italy
De Santis, Gianluca - Sapienza University of Rome, Italy
Di Cataldo, Simone - Sapienza University of Rome, Italy
Ditte, Matej - University of Luxembourg, Luxembourg
Ethirajan, Sudheesh Kumar - Carnegie Mellon University, United States
Fantoni, Stefano - Fondazione Internazionale Trieste, Italy
Filippi, Claudia - University of Twente, Netherlands
Foulkes, Matthew - Imperial College London, United Kingdom
Giannessi, Federico - Unversity of "La Sapienza", Italy
Gorelov, Vitaly - Ecole Polytechnique, France
Gori-Giorgi, Paola - Vrije University Amsterdam, Netherlands
Grosso, Giuseppe - Università di Pisa, Italy
Guidoni, Leonardo - University of L'Aquila, Italy
Holzmann, Markus - CNRS, France
Huber, Timothy - Northern Illinois University, United States
Jurado, David - Albert-Ludwig-Universitaet Freiburg, Germany
Kühne, Thomas - University of Paderborn, Germany
Marchetti, Emiliano - CNR, Italy
Messina, Manlio - AT&T, Czech Republic
Mitaš, Luboš - North Carolina State University, United States

Nakano, Kosuke - SISSA, Italy
Pierleoni, Carlo - University of L'Aquila, Italy
Pietronero, Luciano - Enrico Fermi Research Center, Italy
Prajwal, Kumar A - IIT Bombay, India
Rella, Claudia - University of Geneva, Switzerland
Rescigno, Maria - Sapienza Universita' di Roma, Italy
Resta, Raffaele - CNR, Italy
Rostami, Habib - Stockholm University, Sweden
Ruggeri, Michele - CNRS, Maison de La Simulation, France
Senese, Riccardo - University of Oxford, United Kingdom
Simonetti, Maria Grazia - La Sapienza University, Italy
Sorella, Sandro - SISSA, Italy
Staffieri, Gregorio - Sapienza Università di Roma, Italy
Umrigar, Cyrus - Cornell University, United States
Varsano, Daniele - CNR, Italy
Vitali, Ettore - California State University, United States
Vulpiani, Angelo - University Sapienza, Italy
Zen, Andrea - University College London, United Kingdom