

Ab-initio Simulation methods beyond Density Functional Theory

Carlo Pierleoni

Physics Department, University of L'Aquila, Italy

1 Organization

Organizers

Name: Carlo Pierleoni
Affiliation: Physics Department, University of L'Aquila, Italy
Phone: +39-0862433056
Fax: +39-0862433033
EMail: carlo.pierleoni@aquila.infn.it

Name: Lubos Mitas
Affiliation: Department of Physics, North Carolina State University
Phone: + 919 515 0406
Fax: + 919 515 6538
EMail: lmitas@unity.ncsu.edu

Schedule

We propose a 3 days workshop to be held in late June or late September 2005.

Budget

The regular budget for CECAM activities of 7,000 euros for a 3-day workshop should cover large part of the expenses.

We are planning to apply to the PsiK-ESF network for additional resources. Moreover, expenses for some USA participants will be covered by the NSF-sponsored Materials Computation Center (MCC) (<http://www.mcc.uiuc.edu/travel/>).

Format

The workshop will gather about 20-25 participants. Most of them will be invited to give a talk. Each talk will be planned for a time slot of one hour, of which 40 minutes of presentation and 20 minutes for discussion. We plan to have 4 talks in the morning and 3-4 talks in the afternoon for a total number of about 20 talks. Depending on the variety of expertises that we will be able to gather, we will possibly reduce the number of talks

and organize, during one afternoon, an informal discussion sessions for brainstorming of new ideas and opportunities.

2 Proposal

Scientific background

Ab-initio simulation methods have become widely used research tools in condensed matter physics, materials research, quantum and molecular chemistry. It was twenty years ago when the Car-Parrinello method was introduced and it has led to a small revolution: it enabled to efficiently couple the Molecular Dynamics of classical nuclei with the Density Functional Theory (DFT) electronic structure calculations. This was a significant breakthrough which opened a way to the use of simulation methods for realistic systems with accuracy well beyond the limits of effective force fields. Over the last two decades, even the current limits of DFT have become a barrier to study a number of important physical and chemical phenomena. It is well-known that DFT is less reliable in predicting excited state properties such as optical gap and spectra. DFT shows serious deficiencies in describing van der Waals interactions, non equilibrium geometries such as reaction barriers, systems with transition metals and/or cluster isomers with competing bonding patterns [1,2]. As a consequence, current ab-initio predictions of metalization transition at high pressures, or even prediction of phase transitions are often only qualitative (hydrogen is an extreme case but even in silicon the diamond/ β -tin transition pressure and the melting temperature are seriously underestimated[3]).

More accurate many-body methods exist such as Quantum Monte Carlo (QMC) and correlated quantum chemical methods, but also diagrammatic methods such as GW+BSE. Over the last decade, the developments in QMC has addressed the questions of accurate use of pseudopotentials for treating heavy atoms[2,4] and there are a number of new developments for efficient calculations of nuclear forces [5,6,7,8,9]. Also very recently new ideas in Auxiliary Field QMC have been proposed as a promising alternative for complex materials[10]. New developments in quantum chemical calculations for dynamics on multiple energy surfaces have been tested on molecular systems[11]. Furthermore, methods for efficient sampling and/or evolving of both ionic and electronic degrees of freedom simultaneously have been tested and applied for the first time in the last three years.

Recently an efficient method which couples Metropolis Monte Carlo for the nuclei at finite temperature (either classical or quantum) with QMC for ground state electrons has been developed [12,13]. Although it has been applied only to the most favorable case so far, namely high pressure metallic hydrogen, further progress is being actively pursued. The study revealed surprisingly large LDA bias in predicting the structure of liquid metallic hydrogen and in locating the melting line. New developments for many-body wave functions such as analytic backflow[14], pairing-BCS wave functions[15] and pfaffian wave functions not only improve the description of correlation effects but also point towards perspectives for studies of yet unexplored low-temperature phenomena. Another exciting development has been achieved in coupling the QMC method with the DFT driven molecular dynamics so that one can get the QMC accuracy "on-the-fly" to estimate

dynamical ground and excited state properties at finite temperatures [16]. Already the first results look very promising, i.e, method enabled to calculate vaporization heat of water with unprecedented accuracy correcting thus about 40% of the DFT error. In addition, first attempts to simulate the dynamics of the ions completely within the QMC framework (i.e., using QMC for both energies and forces) have been carried out and currently are being further advanced [17].

Motivation and objectives

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

- efficiency of MC vs MD in the many-body framework: energy differences vs forces
- QMC/MD with noisy forces/Langevin dynamics
- energy difference methods in auxiliary fields QMC
- large-scale wave function optimizations, "on-the-fly" optimizations
- quantum chemical methods vs QMC for cluster, nanostructures and confined systems
- new types many-body wave functions, efficient description of correlation for dynamical simulations

The main goals of the workshop will be to:

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

We believe that the workshop can contribute very significantly to stimulate further progress of this emerging and promising new field of simulations of condensed and molecular systems in the many-body framework.

3 Tentative list of participants

- * Markus Holzmann, CNRS-LPTL, Paris VI, France
- * Michel Caffarel, CNRS-LPC Paris VI, France
- * Claudia Filippi, Lorentz Center, Leiden, Netherlands
- * Michael Rohlfing, International University Bremen, Germany
- * Martin Fuchs, Fritz Haber Institute, Berlin, Germany
- + Dominik Marx, Ruhr-Universität, Bochum, Germany
- + Massimo Mella, Cardiff School of Chemistry, UK
- + Dario Alfè, University College of London, London, UK
- * Sandro Sorella, SISSA, Trieste, Italy
- * Saverio Moroni, INFN-Roma1, Italy
- * Carlo Pierleoni, University of L'Aquila, Italy
- * David M. Ceperley, University of Illinois at Urbana-Champaign, USA
- * Shiwei Zhang, College of William and Mary, Williamsburg, USA
- * Todd Martinez, University of Illinois at Urbana-Champaign, USA
- * Lucas Wagner, North Carolina State University, USA
- + Jeffrey Grossman, LLNL, Livermore, USA
- + Simone Chiesa, University of Illinois at Urbana-Champaign, USA
- + Kevin Schmidt, Arizona State University, Tempe, USA
- * Lubos Mitas, North Carolina State University, USA

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