HL 61: Joint Focussed Session: Theory and Computation of Electronic Structure: New Frontiers IV

Time: Wednesday 15:00–17:00   Location: TRE Phy

Topical Talk   HL 61.1   Wed 15:00   TRE Phy
Progress in diffusion quantum Monte Carlo calculations —
•RICHARD NEEDS — Cavendish Laboratory, J J Thomson Avenue, Cambridge CB3 0HE, UK

My group has developed the CASINO code [1] for performing variational and diffusion quantum Monte Carlo calculations. Fixed-node diffusion quantum Monte Carlo is the most accurate method known for calculating the energies of large many-particle quantum systems. The key ingredient is an accurate trial many-body wave function which controls the statistical efficiency and accuracy of the calculations. Accurate wave functions can be obtained by building correlation effects on top of mean field descriptions such as density functional theory or Hartree-Fock theory. About 80% of the correlation energy can typically be included by multiplying the mean-field determinant by a Jastrow factor which is small when electrons are close together and tends to unity at large separations. Such wave functions provide an excellent description of electron correlation in closed shell molecules but are often not much better than density functionals for small open shell systems. The wave functions of open shell systems can, however, be greatly improved by introducing more determinants, pairing functions, and backflow transformations, and extremely good results can be obtained. The calculations are expensive but the polynomial scaling with system size allows calculations for 1000 or more particles. The discussion of the methodology will be illustrated by recent applications to atoms, molecules and extended systems.

[1] http://www.tcm.phy.cam.ac.uk/~mdt26/casino2.html

HL 61.2   Wed 15:30   TRE Phy
N^3 **implementation for molecules and clusters of Hedin's GW scheme** — •DIETRICH FOERSTER[1], PETER KOVAL[2], and DANIEL SANCHEZ-PORTAL[2] — [1]CPMOH, University of Bordeaux 1, Cours de la Liberation 351, Talence, France — [2]Centro de Fisica de Materiales, Paseo Manuel Lardizabal, 5, Donostia-San Sebastian, Spain

In the context of organic semiconductors it is useful to be able to predict key properties of their molecular constituents, such as their lumo and homo levels.

To make such predictions possible, we developed a new implementation of Hedin's GW approach for one-electron Green's function that scales like N^3 rather than N^4 with the number of atoms (see also the contribution by Peter Koval).

We achieved an N^3 scaling by using a local basis in the space of dominant orbital products.

This local basis has already been applied in a TDDFT code and it is also suitable in the Bethe Salpeter approach. To accelerate calculations in these frameworks for large molecules, we reanalyze the product basis and reduce its dimension.

HL 61.3   Wed 15:45   TRE Phy
Applications of a dominant product basis in many-body perturbation theory — •PETER KOVAL[1], DIETRICH FOERSTER[2], and DANIEL SANCHEZ-PORTAL[1] — [1]Centro de Fisica de Materiales, Paseo Manuel Lardizabal, 5, Donostia-San Sebastian, Spain — [2]CPMOH, Universite Bordeaux 1, Cours de la Liberation 351, Talence, France

The knowledge of excitation properties of molecules is crucial in developing organic semiconductor devices. Many-body perturbation theory is one of the most promising theories for characterization of excitations in electronic systems. In particular, Hedin's GW approximation for one-electron Green's function is capable of calculating lumo and homo of molecules with $O(N^3)$ computational complexity like TDDFT (see the contribution of Dietrich Foerster).

In this work, we implement the Hedin's G_0W_0 approximation on top of DFT calculations performed with SIESTA [1] code. We apply a dominant product technique [2] to span the space of orbital products and to reduce the dimensionality of dielectric matrix.

We discuss several results for ionization potentials and electron affinities of large molecules, revealing strengths and limitations of our implementation.

[1] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, D. Sánchez-Portal, J. Phys. **C 14**, 2745 (2002).
[2] P. Koval, D. Foerster, and O. Coulaud, J. Chem. Theory Comput. **6**, 2654 (2010); and references therein.

HL 61.4   Wed 16:00   TRE Phy
Using Finite Element method to tackle the Hartree-Fock equations — •AMÉLIE FAU and DENIS AUBRY — MSSMat laboratory, Ecole Centrale Paris

It is well know that the Schrödinger equation cannot be solved exactly, except maybe for very simple cases, as it represents a many-body interaction problem. However, it is possible to derive approximations of the Schrödinger equation from variational principles. The Hartree-Fock equations are then generally solved thanks to a set of basis functions, e.g. Gaussians, Slater-type orbitals or plane waves.

To avoid to impose a general form to the approximate wave function, we use localized trial functions. We consider here the Finite Element Method as a new approach to solve these Hartree-Fock equations. We shall present the main properties of our computations with the different advantages and drawbacks involved by this strategy. We will present numerical results about different electronic systems: such as atoms or molecules (LiH, BeH2).

HL 61.5   Wed 16:15   TRE Phy
Finite-basis correction applied to the optimized effective potential within the FLAPW method — •CHRISTOPH FRIEDRICH, MARKUS BETZINGER, and STEFAN BLÜGEL — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

The optimized-effective-potential (OEP) method is a special technique to construct local exchange-correlation (xc) potentials from general orbital-dependent xc energy functionals. Recently, we showed that particular care must be taken to construct local potentials within the all-electron full-potential augmented-plane-wave (FLAPW) approach. In fact, we found that the LAPW basis had to be converged to an accuracy that was far beyond that in calculations using conventional functionals, leading to a very high computational cost. This could be traced back to the convergence behavior of the density response function: only a highly converged basis lends the density enough flexibility to react adequately to changes of the potential. In this work we derive a numerical correction for the response function, which vanishes in the limit of an infinite, complete basis. It is constructed in the atomic spheres from the response of the basis functions themselves to changes of the potential. We show that such a finite-basis correction reduces the computational demand of OEP calculations considerably: the local potential converges at much smaller basis sets than before and its construction becomes numerically stable. We also discuss a similar correction scheme for GW calculations.

HL 61.6   Wed 16:30   TRE Phy
A conventional, massively parallel eigensolver for electronic structure theory[1] — •V. BLUM[1], M. SCHEFFLER[1], R. JOHANNI[2], H. LEDERER[2], TH. AUCKENTHALER[3], TH. HUCKLE[3], H.-J. BUNGARTZ[3], L. KRÄMER[4], P. WILLEMS[4], B. LANG[4], and V. HAVU[5] — [1]Fritz Haber Institute, Berlin — [2]RZ Garching — [3]TU München — [4]BU Wuppertal — [5]Aalto University, Helsinki

We demonstrate a robust large-scale, massively parallel conventional eigensolver for first-principles theory of molecules and materials. Despite much research into $O(N)$ methods, standard approaches (Kohn-Sham or Hartree-Fock theory and excited-state formalisms) must still rely on conventional but robust $O(N^3)$ solvers for many system classes, most notably metals. In particular, our eigensolver overcomes parallel scalability limitations where standard implementations of certain steps (reduction to tridiagonal form, solution of reduced tridiagonal eigenproblem) can be a serious bottleneck already for a few hundred CPUs. We demonstrate scalable implementations of these and all other steps of the full generalized eigenvalue problem. Our largest example is a production run with 1046 Pt (heavy-metal) atoms [1] with converged all-electron accuracy in the numeric atom-centered orbital code FHI-aims,[2] but the implementation is generic and should easily be portable to other codes. [1] P. Havu *et al.*, Phys. Rev. B **82**, 161418 (2010). [2] V. Blum *et al.*, Comp. Phys. Comm. **180**, 2175 (2009). [1] ELPA research consortium, funded by German Ministry of Research and Education (BMBF). http://elpa.rzg.mpg.de

HL 61.7   Wed 16:45   TRE Phy

Accurate and efficient density-functional calculations for the electronic entropy — •Rudolf Zeller — Institute for Advanced Simulation, Forschungszentrum Jülich, D-52425 Jülich

The calculation of the electronic entropy S(T) as function of temperature is a numerically demanding problem for metallic systems because S(T) depends logarithmically on the Fermi-Dirac distribution which varies rapidly near the Fermi level. Therefore, very accurate Brillouin zone samplings are usually needed.

I will present a technique based on complex energy contour integration and show how significant reduction of the number of sampling points can be achieved and how the problem of undetermined phases of complex valued logarithms can be avoided. The technique exploits the analytical properties of the Green function of the single-particle Kohn-Sham equation and has been implemented within the full-potential Korringa-Kohn-Rostoker method, where the use of Lloyd's formula guarantees fast convergence with respect to the angular momentum cutoff.

As a by-product I obtain a broadening scheme for total energy calculations with error elimination up to the sixth power of T. I will also explain particular advantages of Fermi-Dirac broadening (besides its direct physical significance) compared to other broadening schemes.