CFCAM Discussion Meeting

The orbital free alternative

Institut Henri Poincaré
May 30 and 31, 2011

energie atomique • energies alternatives

Monday, May 30th

09:30 - 09:40 *Welcome*

09:40 - 10:00 Jean Clérouin

10:00 - 10:30 Lee Collins

10:30 - 11:00 *Coffee break*

11:00 - 11:45 Sam Trickey

12:00 - 14:00 *Lunch break*

14:00 - 14:45 Jim Dufty

14:45 - 15:30 Luc Kazandjian

15:30 - 15:45 *Coffee break*

15:45 - 17:00 Discussions

Meeting dinner at *Le Petit Prince de Paris*

Tuesday, May 31st

09:45 - 10:30 Ann Mattson

10:30 - 10:45 *Coffee break*

10:45 - 11:30 Tomasz Wesolowski

11:30 - 12:00 Flavien Lambert

12:00 - 14:00 *Lunch break*

14:00 - 16:00 Discussion towards a new CECAM proposal

Jean Clérouin

CEA DAM DIF

Orbital free methods for dense plasmas: a short story

In this introductory talk, I will review the historical motivations that lead to the concept of orbital free molecular dynamics (OFMD) for the simulation of dense plasmas. We will emphazize the limitations of the traditional orbital based quantum molecular dynamics method (QMD) in terms of temperature and density when applied to warm dense matter. These difficulties are overcome in the orbital free molecular dynamics approach, based on the Thomas-Fermi theory. The transition between QMD and OFMD with increasing density is discussed. A possible scheme combining the advantages of both approaches will be proposed.

Lee A. Collins

Theoretical Division, Los Alamos National Laboratory

We present calculations of static and dynamical properties for several systems over an extensive range of densities and temperatures using an orbital-free molecular dynamics formulation. Comparisons at low temperatures are made with the Kohn-Sham Density Functional program VASP and at higher temperatures and densities with various limiting models such as the one-component plasma and Landau formulas.

Samuel B. Trickey

Quantum Theory Project, Dept. of Physics and Dept. of Chemistry, University of Florida, Gainesville

Orbital-free DFT is immensely appealing both for intellectual purity and for the potential for making materials, cluster, and biomolecular simulations much faster. The challenge of OF-DFT commonly is said to be to find a sufficiently accurate approximation for the Kohn-Sham kinetic energy functional T_s. But Perdew's exchange-correlation functional Jacob's ladder raises a concomitant challenge: higher-rung E_{xc} functionals use the KS orbitals explicitly. OF-DFT progress therefore requires pursuit of improved orbital-independent approximations for both T_s and E_{xc}. Consistent treatment of finite temperature T adds requirements both for temperature dependence of those functionals as well as for the non-interacting (KS) entropy. There are few T-dependent functionals in the literature, yet the temperature range of interest in, *e.g.* warm dense matter, is immense, to $\mathcal{T} \approx 10$ eV or higher.
In this diverse context, I shall discuss three aspects of functional development:

- Recent work on constraint-based single-point T_s approximations ($\mathcal{T} = 0$) of the modified-conjoint GGA type (``mcGGA'') and beyond. Beyond-mcGGA functionals are required to remove nuclear-site singularities in the so-called Pauli term. That raises the issue of how to select fruitful combinations of higher-order derivatives and how to constrain those combinations. In passing, this topic also raises the issue of numerical solution of the OF-DFT Euler equation;
- Recent improvements in the GGA-type E_{xc} functionals by tightening and refining the enforcement of important, relevant constraints, giving the VMT and VT{84} functionals. VT{84}, in combination with PBE E_c, gives heats of molecular formation with $\approx 50\%$ smaller mean

absolute deviation than PBE-PBE with relatively little harm to geometries, while also giving NMR ^{13}C chemical shifts of quality better than those from PW91;
- Unpublished comparison calculations on the existing T-dependent approximate functionals, on ground-state functionals used at finite T (a common practice in present studies of warm dense matter), and on finite-temperature Hartree-Fock.

I acknowledge, with thanks, the contributions of Jim Dufty, Frank Harris, Valentin Karasiev, and Travis Sjostrom to the KE and finite $\mathcal{T}$ work and of Alberto Vela, Jorge Martín del Campo, José Luis Gázquez, and Victor Medel to the E_{xc} work.
Supported in part by U.S. Dept. of Energy Grant DE-SC 000213 .

[1] Constraint-based Single-point Approximate Kinetic Energy Functionals, V. V. Karasiev *et al*, Phys. Rev. B **80** 245120 (2009)
[2] Conditions on the Kohn-Sham Kinetic Energy and Associated Density, S. B. Trickey *et al*, Int. J. Quantum Chem. **109**, 2943-52 (2009)
[3] Tightened Lieb-Oxford Bound for Systems of Fixed Particle Number, M. M. Odashima *et al*, J. Chem. Theory Comput. **5**, 798-807 (2009)
[4] Variable Lieb-Oxford Bound Satisfaction in a Generalized Gradient Exchange-Correlation Functional, A. Vela *et al*, J. Chem. Phys. **130** 244103 (2009)
[5] The VT{84} Exchange Functional, A. Vela *et al*, unpublished.

James W. Dufty

Department of Physics, University of Florida

Properties of the Finite Temperature Non-interacting Density Functionals

Accurate representations of the free energy, internal energy, and entropy for non-interacting particles in an external potential are central to the formulation of orbital free density functional theory. Expressions for these properties are recalled from the equilibrium statistical mechanics of non-uniform systems, both as functionals of the density and of the one particle density matrix. Scaling laws and bounds (upper and lower) are noted. A one particle density matrix corresponding to the finite temperature Thomas-Fermi approximation is identified and discussed. An exact mapping of the desired functionals onto the corresponding Thomas-Fermi forms is defined and evaluated approximately for weak coupling. The result is a non-local Thomas-Fermi approximation including linear response.

Research supported under US DOE Grant DE-SC0002139

Luc Kazandjian

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Application of orbital-free molecular dynamics to equation of state, viscosity and self-diffusion coefficient

Equation of state, viscosity, and self-diffusion coefficient are computed through orbital-free molecular dynamics in the isokinetic ensemble. For the equation of state, two free-energy functionals are considered, one with a gradient correction and one without, and a mixing rule valid with both functionals is proposed. Viscosity is obtained without resorting to extrapolation of the stress autocorrelation function or of its integral over time, and the statistical error is carefully evaluated. Results of self-diffusion coefficients are also shown.

Ann E. Mattsson

Multiscale Computational Materials Methods, Sandia National Laboratory
The subsystem functional scheme and orbital free functionals

An alternative to the conventional scheme for developing functionals within Density Functional Theory (DFT), based on fulfilling constraints, is the recently proposed subsystem functional approach [1]. This approach has been successfully [2] applied in the construction of the orbital free Armiento-Mattsson 2005 (AM05) [3] exchange-correlation functional. I will discuss the fundaments of the subsystem functional framework and discuss the advantages of using this approach also for temperature dependent, orbital free, kinetic energy functionals.

[1] The subsystem functional scheme: The Armiento-Mattsson 2005 (AM05) functional and beyond, A. E. Mattsson and R. Armiento, Int. J. Quantum Chem. **110**, 2274 (2010)
[2] The AM05 density functional applied to solids, A. E. Mattsson *et al*, J. Chem. Phys. **128**, 084714 (2008)
[3] Functional designed to include surface effects in self-consistent density functional theory, R. Armiento and A. E. Mattsson, Phys. Rev. B **72**, 085108 (2005)
[4] Implementing and testing the AM05 spin density functional, A. E. Mattsson and R. Armiento, Phys. Rev. B **79**, 155101 (2009)

Tomasz Wesolowski

Department of Physical Chemistry, University of Geneva
Multi-scale simulations methods based on Frozen-Density Embedding Theory

Frozen-Density Embedding Theory (FDET) was formulated originally for embedding a Kohn-Sham system in an environment characterized exclusively by its charge density [1,2] and extended further for embedding other systems: interacting wavefunction [3] and one-particle density matrix [4]. According to FDET, the partial minimization of the total energy with respect to the variation localized in the embedded system can be achieved using an additional potential (orbital-free embedding potential), which is uniquely determined by the charge densities into which the total charge density is partitioned. Due to the absence of any quantum-chemical descriptors of the environment, FDET provides an exact formal framework for multi-scale methods involving both quantum-chemical and classical levels. We will

- overview the formal framework of FDET emphasizing the links with orbital-free DFT;
- provide illustrative examples of simulations based on FDET and aiming at modelling environment effects on electronic structure of species in condensed phase.

[1] T. A. Wesolowski and A. Warshel J. Phys. Chem. **97**, 8050 (1993).
[2] T. A. Wesolowski, One-electron Equations for Embedded Electron Density: Challenge for Theory and Practical Payoffs in Multi-Level Modeling of Complex Polyatomic Systems In: Computational Chemistry: Reviews of Current Trends - Vol. 10 World Scientific, 2006, pp. 1-82.
[3] T .A. Wesolowski, Phys. Rev.A. **77**, 012504 (2008)
[4] K. Pernal and T. A. Wesolowski, Int. J. Quantum Chem. **109**, 2520 (2009)

Flavien Lambert

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Testing ICF approximative models by Kohn-Sham and Orbital Free Molecular Dynamics

In this tallk, we present the *ab initio* evaluation of transport coefficients in extreme thermodynamic conditions relevant to Inertial Confinement Fusion. The role of thermal conduction in combustion wave propagation is emphasized as well as the need for a careful determination of microscopic coefficients governing it. Inertial Confinement Fusion offers a new class of problems where the coupling between orbital based and orbital free methods are particularly well adapted.

[1] Ab Initio Determination of Thermal Conductivity of Dense Hydrogen Plasmas, V. Recoules *et al*, Phys. Rev. Lett. **102**, 075002 (2009)

[2] On the transport coefficients of hydrogen in the inertial confinement fusion regime, F. Lambert *et al*, Phys. Plas. **18**, 056306 (2011)

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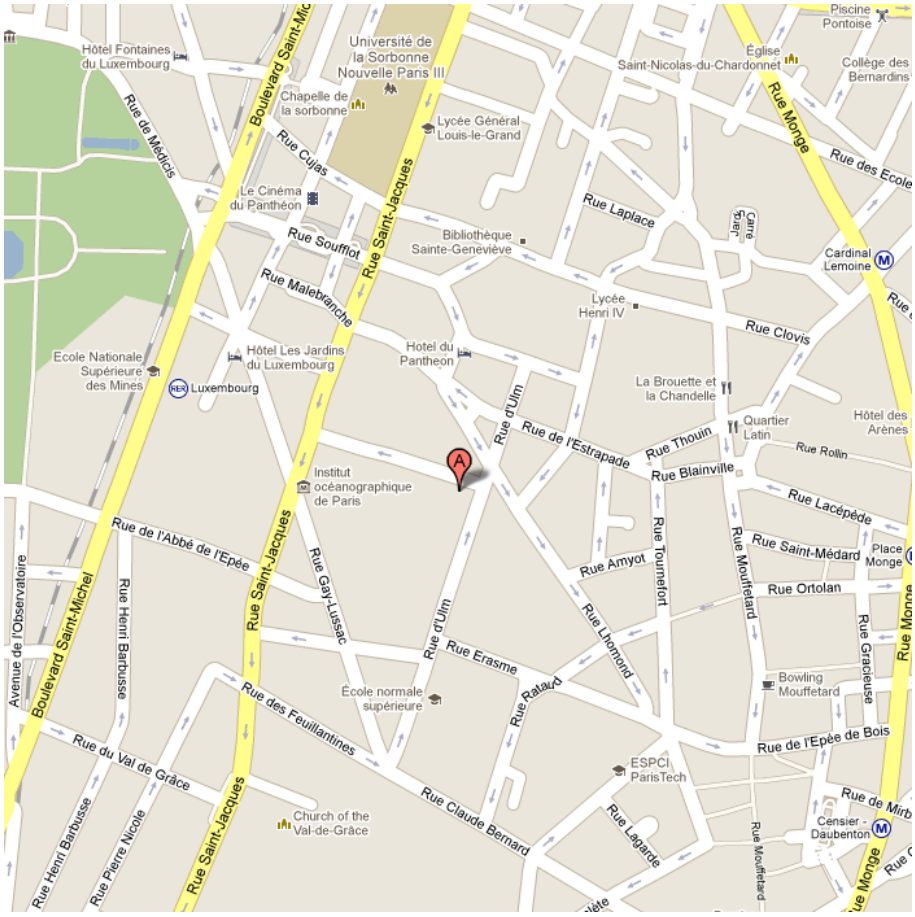

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