(Time-Dependent) Density Functional Theory

SimBioMa workshop held at FU Berlin, 19–31 July 2009

Summary

The workshop has brought together physicists from the field of density functional theory (DFT) with applied mathematicians who develop efficient numerical algorithms for quantum problems.

Recent advances in the direction of time-dependent DFT (e.g., for optimal control problems) have been deeply discussed; this included open systems and non-adiabatic problems as well as numerical approaches employing heterogeneous multiscale methods or efficient rational approximation techniques for electronic structure calculation.

List of speakers

1. Kieron Burke (UC Irvine, USA)
2. Carlos Garcia-Cervera (UC Santa Barbara, USA)
3. Eberhard Gross (FU Berlin, Germany)
4. Jianfeng Lu (Princeton, USA)
5. Angel Rubio (U País Vasco, Spain)
6. Ivano Tavernelli (EPF Lausanne, Switzerland)
7. Rodolphe Vuilleumier (U Paris 6, France)

List of participants

1. Ali Abedi (FU Berlin, Germany)
2. Tim Baldsiefen (FU Berlin, Germany)
3. Attila Cangi (UC Irvine, USA)
4. Alberto Castro (FU Berlin, Germany)
5. Giovanni Ciccotti (U Roma "La Sapienza", Italy)
6. Florian Eich (FU Berlin, Germany)
7. Andrea Floris (FU Berlin, Germany)

8. Tomaso Frigato (FU Berlin, Germany)
9. Henning Glawe (FU Berlin, Germany)
10. Carsten Hartmann (FU Berlin, Germany)
11. Elham Khosravi (FU Berlin, Germany)
12. Andreas Linscheid (FU Berlin, Germany)
13. César Proetto (FU Berlin, Germany)
14. Zheng-Wang Qu (HU Berlin, Germany)
15. Antonio Sanna (FU Berlin, Germany)
16. Burkhard Schmidt (FU Berlin, Germany)
17. Reinhold Schneider (TU Berlin, Germany)
18. Angelica Zacarias (FU Berlin, Germany)
19. Hui Zhu (FU Berlin, Germany)

Discussion

About 25 years ago Runge and Gross laid the groundwork for the formulation of time-dependent density functional theory (TDDFT). Until then, traditional DFT dealt with ground-state properties of atoms, molecules and solids whereas its time-dependent pendant also allowed for *ab-initio* calculations of excited-state properties of molecules.

In a series of lectures, Eberhard Gross (FU Berlin) and Kieron Burke (UC Irvine) outlined the development of DFT as it was devised by Hohenberg, Kohn and Sham until today. Due to the recent advances in experimental control techniques such as femtosecond and attosecond lasers or pulse shaping devices, optimal control problems and highly excited systems have received increasing attention in the last years as both speakers pointed out. As for optimal control problems, the Hamilton-Jacobi-Bellman (HJB) equations to be solved are nonlinearly coupled initial-value partial differential equations that must be solved iteratively; one such instance are the HJB equations originating from the time-dependent KS model that were discussed by Angel Rubio (U País Vasco) and Ivano Tavernelli (EPF Lausanne) from an algorithmic point of view.

Another hotly debated issue that was taken up by many speakers (e.g., Burke, Tavernelli, Vuilleumier) were consistent quantum-classical models that can capture non-adiabatic effects. Quantum-classical models that go beyond the Born-Oppenheimer approximation are of particular interest in the DFT community, for linear response TDDFT that is currently the most popular single-determinant method for modelling excited states of medium and large molecules does not take into account non-adiabatic effects. Rodolphe Vuilleumier (Paris 6)

reported on the applicability of the adiabatic approximation in electrochemistry and compared Born-Oppenheimer with Car-Parrinello based schemes.

A variety of talks was concerned with the numerical aspects of the iterative (i.e., self-consistent) solution of the nonlinear DFT equations where the topics ranged from approximation schemes (Burke) to convergence issues (Lu) or the choice of good basis functions (Vuilleumier). In his contribution, Carlos García-Cervera (UC Santa Barbara) assessed the possibility of numerical algorithms for electronic structure calculation in solids that scale sub-linearly in the total number of atoms. The answer was given in the affirmative where the sub-linearity requires that the the inherent multiscale structure of the particular problem is taken into account. Targeting in the same direction, Jianfeng Lu (Princeton) showed how a systematic coarse-graining using a heterogeneous multiscale method can give rise to a continuum approximation of the KS model that, in turn, can be discretized efficiently by current numerical methods for solving partial differential equations. Fast multipole methods based on rational approximations of the Fermi operator and many-body perturbation approaches for electronic structure calculation were presented by Lu and Rubio.

Results and future directions

The meeting has made clear that there is a great need for efficient numerical algorithms in the field of DFT, and it has demonstrated that applied mathematics provides a variety of tools to put the self-consistent DFT approach as it is prevalently employed in physics and chemistry on a (more) rational basis. This clearly helps to devise appropriate numerical schemes, but it also may extend the range of possible applications of (TD)DFT.

Conversely there are plenty of recent promising developments in TDDFT such as consistent quantum-classical models that go beyond the adiabatic approximation that attracted the attention of the mathematicians.

All participants of the workshop have agreed that both mathematicians and physicists or chemists do largely benefit from this first contact and, surely, other initiatives will follow.

Scientific program

Monday, 07/20/09

9–13 *Eberhard Gross (FU Berlin)*
Overview: Hohenberg-Kohn (HK) and Kohn-Sham (KS) theorems / spin DFT and similar generalizations of HKS

15–19 *Eberhard Gross (FU Berlin)*
Time-dependent DFT lectures (TDDFT): Runge-Gross theorem and TDKS / general response theory / TDDFT response equations

Tuesday, 07/21/09

9–13 *Kieron Burke (UC Irvine)*
Local density approximation / exact conditions / generalized gradients / adiabatic connection + hybrids

15–19 *Kieron Burke (UC Irvine)*
Understanding approximate exchange-correlation functionals from the perspective of semi-classics

Wednesday, 07/22/09

9–13 *Rodolphe Vuilleumier (Paris 6)*
Basis-sets: wavefunction and density / pseudo-potentials

15–19 *Rodolphe Vuilleumier (Paris 6)*
Optimization: self-consistency, orthonormalization, preconditioning, diagonalization, density mixing, and constraints

Thursday, 07/23/09

9–13 *Carlos García-Cervera (UC Santa Barbara)*
Linear scaling methods for DFT / sublinear scaling methods for DFT computations of solids

15–19 *Rodolphe Vuilleumier (Paris 6)*
Born-Oppenheimer MD, extrapolation, orbital localization and order(N) methods, electrochemistry

Friday, 07/24/09

9–13 *Carlos García-Cervera (UC Santa Barbara)*
Multiscale modeling using sparse representations

15–19 *Jianfeng Lu (Princeton)*
Continuum limit of Kohn-Sham DFT models: connection between physical models on different levels

Monday, 07/27/09

9–13 *Eberhard Gross (FU Berlin)*
TDDFT calculation of optical excitation spectra

15–19 *Ivano Tavernelli (EPF Lausanne)*
Casida formulation of the TDDFT / Linear response Sternheimer formulation of TDDFT

Tuesday, 07/28/09

9–13 *Eberhard Gross (FU Berlin)*
Fully time-dependent problems: Strong lasers, time-dependent quantum transport, optimal control

15–19 *Kieron Burke (UC Irvine)*
DFT for open quantum systems / high excitations and scattering in TDDFT

Wednesday, 07/29/09

9–13 *Angel Rubio (U País Vasco)*
Exchange-correlation kernel from many body theory

15–19 *Jianfeng Lu (Princeton)*
New developments of rational approximation of Fermi-Dirac function: fast algorithms for extracting diagonal of the inverse matrix with application to electronic structure calculation

Thursday, 07/30/09

9–13 *Kieron Burke (UC Irvine)*
Beyond the adiabatic approximation

15–19 *Ivano Tavernelli (EPF Lausanne)*
Non-adiabatic effects in TDDFT / methods for the solution of the time-dependent KS equations

Friday, 07/31/09

9–13 *Angel Rubio (U País Vasco)*
Algorithms for time propagation: propagating TDKS equation

15–19 *Jianfeng Lu (Princeton)*
Convergence of self-consistent iteration