

Density Functional Theory: Fundamentals and Applications in Condensed Matter Physics

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1 Overview of the Field

A complete quantum mechanical description of a solid requires the solution of the many-body Schrödinger equation [8]. The numerical approximation of this equation, however, is impractical: using a straightforward numerical discretization, the number of degrees of freedom grows exponentially with the number of electrons, and therefore only systems with very few atoms can be considered. In [18], Hohenberg and Kohn proved that there exists a universal functional of the electronic density $F[u]$ such that the ground state energy associated to an external potential v can be obtained by minimizing the energy

$$E[u] = F[u] + \int v(\mathbf{x})u(\mathbf{x}) d\mathbf{x}. \quad (1)$$

Further refinements of the theory were presented by Levy [21] and Lieb [23].

In (1), however, the shape of functional $F[u]$ is unknown, and must be approximated. There are two main approaches for its approximation, which have given origin to what are known as Orbital-Free Density-Functional Theory (OFDFT), and Kohn-Sham Density-Functional Theory (KSDFT).

In OFDFT, the functional F is replaced by an explicit functional of u . The simplest such approximation is the Thomas-Fermi functional [32, 13], and by now several such approximations have been proposed [34, 35, 37, 36, 39]. To achieve good physical accuracy, however, complicated, nonlocal kinetic energy functionals must be used. An example of such functionals is the Wang-Teter functional. Although in principle it captures linear response effects, the kinetic energy is unbounded below, rendering it useless for practical use [2]. Density dependent kernels have been developed, and although they do not seem to suffer from this difficulty, they are not well understood, their numerical implementation becomes cumbersome, and there does not seem to be a systematic way of improving their accuracy.

In a different direction, Kohn and Sham introduced an approximation scheme by decomposing the energy functional $F[u]$ as [20]

$$E[u] = \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \psi_i|^2 d\mathbf{x} + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{u(\mathbf{x})u(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d\mathbf{x} d\mathbf{y}, + F_{\text{XC}}[u] + \int_{\mathbb{R}^3} v(\mathbf{x})u(\mathbf{x}) d\mathbf{x}, \quad (2)$$

with $u = \sum_j |\psi_j|^2$, and $\{\psi_j\}$ and orthonormal family of functions in $L^2(\mathbb{R}^3)$. The first term is the kinetic energy of N non-interacting electrons, and the other contributions to the energy in (2) are Hartree,

exchange-correlation, and external potential energies, respectively. The idea of approximating the total energy using non-interacting electrons goes back to the Hartree-Fock method [31]. A fundamental difference is that whereas the Hartree-Fock energy is only an approximation to the true energy, the Kohn-Sham functional is exact. The exchange and correlation energy, however, is not known explicitly, and must be approximated.

There are by now a number of extensions of the Hohenberg-Kohn theorem and the Kohn-Sham approximation scheme to other situations of practical interest, such as Time-Dependent DFT [30], and Current-Dependent DFT [33]. Although all these approaches are in principle exact, it is precisely the quality of the approximation to the exchange-correlation energy that determines the quality of the overall scheme. Among the simplest approximations are the Local Density Approximation (LDA), and the Generalized-Gradient Approximation (GGA), in which the exchange-correlation term is approximated by a functional of the density alone, or the density and its gradient, respectively. Although some of these approximations have proved to be successful in practice, there is currently no real understanding of the actual accuracy of the different models. Furthermore, from a mathematical standpoint, there are not many results even in the simple cases of the LDA and GGA. For the LDA, the existence of solutions is known; however, in the GGA case, the existence is known only for $N = 1$ [3].

From the numerical point of view, the Kohn-Sham equations also present some challenges. The complexity of the self-consistent iteration introduced by Kohn and Sham scales as $O(N^3)$, which is impractical for the study of large systems. In the past twenty years, a number of new methodologies have appeared in the literature, which attempt to exploit the locality of the problem in order to reduce the computational complexity. Locality, in quantum mechanics, refers to the property that a small disturbance in a molecule only has a local effect in the electron density, a phenomenon coined by W. Kohn as *nearsightedness* [19]. Examples of these attempts are the Divide and Conquer methods [38, 1], Orbital Minimization [29], Density Matrix Minimization [22, 17], the Fermi Operator Expansion [16], and, more recently, the Localized Subspace Iteration [15]. There have also been several advances in the design of numerical algorithms for metallic systems [27, 28].

Advances in the numerical computations of DFT have made it possible to study materials with ab-initio simulations, in which the underlying physical model is quantum mechanics.

2 Objectives of the Workshop

Since its inception, DFT has been a very popular tool in the physics and chemistry community. In the mathematics community, however, there has not been that much work done, except in a few exceptional cases [2, 1, 3, 6, 7, 24, 25, 26, 12]. One of the main purposes of the workshop was to raise awareness on this important topic by bringing together an interdisciplinary group of experts in the field to discuss the latest developments in the modeling, theory, and simulations of quantum mechanical systems, in the context of density functional theory.

The main topics discussed were:

1. Fundamental aspects of DFT: Approximation of the exchange-correlation and kinetic energy functionals.
2. Extensions of DFT: Time-dependent, spin-orbit coupling, CDFT.
3. Materials modeling: defects.
4. Numerical DFT: linear and sublinear scaling methods.

3 Recent Developments and Open Problems

From a mathematical viewpoint, much has been learned about the existing models in the past few years. For example, questions of existence of solutions, that had been open for a long time, have been answered [3]; and there has been special interest in the derivation of coarse-grained models from quantum mechanical theories [14, 4, 9, 11, 10, 5].

Numerically, a significant amount of effort has been put to the development of linear scaling techniques and acceleration of the self-consistent iteration. However, a rigorous theory is still lacking.

There have been considerable efforts in an attempt to increase the chemical accuracy of current models, and development of effective theories for complex systems, such as ferromagnetic materials, and topological insulators.

Despite these recent developments, there are still some important open problems. For example, a rigorous derivation of effective models for the treatment of defects in solids in the context of Kohn-Sham DFT or other theories that go beyond DFT, both in the ground state and in dynamics, is still missing. Much has been done in the context of crystalline solids with localized defects, but more needs to be done to understand disordered systems, such as heavily doped and organic semiconductors. Deeper understanding of spin-orbit interactions, as well as relativistic effects, will be necessary for the study of new materials such as ferromagnetic materials, topological insulators. Transport properties are fundamental for the study of electronic systems, however, a rigorous first principles approach is still lacking. This will be of enormous importance for the study of nano-optical devices, and solar cells, for example.

At the more fundamental level, a deeper understanding of the connection between the many-body Schrödinger equation and reduced theories such as Kohn-Sham or orbital-free DFT is of importance for the systematic development of accurate exchange-correlation functionals with improved chemical accuracy.

4 Presentation Highlights

A number of researchers from different scientific areas, some of them not experts in the topics discussed, was invited to the workshop. As a result we had a mixed audience with variable degrees of knowledge on the topics covered in the workshop. We planned four tutorial talks on different topics: Introduction to Quantum Chemistry (Gero Friesecke), Electronic Transport (Roberto Car), Density Functional Theory (Kieron Burke and John Perdew), and Analysis and Algorithms for the Kohn-Sham model (Weinan E and Jianfeng Lu). The tutorials started with an introduction to the topic, and ended with the state-of-the-art and open problems.

The first talk in the workshop was a tutorial on Quantum Chemistry by Prof. Gero Friesecke. The basic many-body Schrödinger equation was introduced, and a number of approximations and reduced models were discussed, with an emphasis on wave-function methods such as Hartree-Fock, the Configuration Interaction method, and the Coupled-Cluster method. Examples were given to describe the accuracy and efficiency of each approach, and for each one its limitations were discussed, which paved the way for a number of open challenges in the field.

The second tutorial was presented by Prof. Kieron Burke (Prof. John Perdew, originally scheduled to deliver the tutorial, was unable to attend the meeting). The main topic was ground-state density functional theory, and a number of topics were discussed. The Kohn-Hohenberg density functional is unknown, and therefore for practical applications it must be approximated. This approximation is not trivial, and some of the currently available functionals, as well as the challenges of developing new improved functionals, were discussed in this tutorial. Some of the difficulties arise from the lack of understanding of the connection between the density-functional and the many-body problem, and part of the tutorial was dedicated to a semiclassical approximation, which could elucidate this connection. Dr. Pina Romaniello discussed this connection from the point of view of many-body perturbation theory in her talk. An alternative approach based on approximating exchange-correlation *potentials* rather than exchange-correlation *energy functionals* was discussed by Dr. Viktor Staroverov.

The following tutorial was presented by Dr. Jianfeng Lu (jointly with Prof. Weinan E, who could not attend the workshop), and focused on some of the mathematical and numerical challenges in the analysis of the Kohn-Sham model. On a more fundamental level, Yan Alexander Wang discussed the differentiability properties of the Kohn-Hohenberg functional in his talk.

The last tutorial was dedicated to the topic of Electronic Transport, and was presented by Prof. Roberto Car. One of the main challenges in the study of electron transport in a quantum system is the issue of collisions. In this tutorial Prof. Car introduced some of the approaches developed for the study of transport, such as the Quantum Boltzmann equation, and after pointing out some of the difficulties, described the development of a Quantum Master Equation. Some of the challenges and open problems were discussed as well. Open systems and the issue of dissipation in a quantum system were also discussed by Prof. Matthias Ernzerhof in his talk.

One important challenge that is still open in the study of quantum systems is the issue of strong correla-

tions, which explains entanglement in quantum systems, and appears in systems with strong magnetic effects and in heavy atoms. Current reduced theories such as DFT are unable to capture this effect. A constrained mean-field approach was presented by Prof. Gustavo Scuseria.

Virginie Ehrlacher discussed the important issue of charge screening for crystals with a defect in the context of Thomas-Fermi-von Weiszäcker (TFW) DFT. A variational model, rigorously derived as the thermodynamic limit of a sequence of finite systems, was presented to model local defects and it was shown that local defects are always neutral. As a result TFW DFT cannot be used to study charged defects.

Prof. Emil Prodan gave a lecture on Topological Insulators, a relatively new class of materials displaying robust physical properties as a result of strong spin-orbit interactions. This is a fairly new area within condensed-matter physics, and where collaboration between mathematics and physics can prove to be fundamental for new discoveries.

Prof. Gang Lu presented a first principles approach for the study of electronic properties in bulk heterojunction solar cells, another area of research that has received much attention recently, and where a multidisciplinary approach could be fundamental.

A study of the properties of large atoms, and its ionization energies, was presented by Kieron Burke. Relativistic corrections for large atoms were discussed by Prof. Jan Phillip Solovej.

A number of talks were dedicated to numerical issues in DFT. The main difficulties in the numerical developments of efficient methodologies for DFT are 1) how to discretize the problem effectively in a way that local effects are captured near the atomic locations while using a reduced number of degrees of freedom, and 2) how to accelerate convergence of the self-consistent iteration. For the former, several ideas were presented, such as the use of enriched basis by John Pask; adaptive mesh refinements by Aihui Zhou, with error estimators discussed by Reinhold Schneider; and the systematic construction of basis functions by solving small local problems in the context of Discontinuous Galerkin FEM by Lin Lin. A detailed analysis of the convergence of spectral approximations was presented by Yvon Maday. With regards to the convergence of the self-consistent iteration, Yakun Chen presented a new idea based on a shooting method that produces a robust and efficient algorithm.

5 List of Abstracts

5.1 Tutorials

Kieron Burke, Department of Chemistry and Department of Physics, University of California, Irvine. *TDDFT - past, present, and future*.

Roberto Car, Department of Chemistry and Program in Applied and Computational Mathematics, Princeton University. *Tutorial on Electronic Transport*.

Gero Friesecke, TU Munich, Germany. *Some mathematical challenges in quantum chemistry*: I was asked by the organisers not to assume prior expertise in quantum chemistry and density functional theory. So I will start with

- the basic models (many-body Schroedinger equation, with or without nuclear motion), and
- the basic questions (quantities one would like to predict, such as absorption spectra, binding energies, potential energy surfaces for the nuclei and their subsequent use for geometry optimization or MD, and the associated accuracy requirements).

I will then try to give an informal overview over the main approaches that have been developed to reduce the basic equations into computationally feasible electronic structure models: wave function methods including HF, CI, CC, Monte Carlo; reduced density matrix methods; and – very briefly in order not to conflict with the other tutorials – DFT. This will then naturally lead into some of the main challenges.

Jianfeng Lu, Courant Institute of Mathematical Sciences, New York University. *Density Functional Theory: Analysis and Algorithms*: This minicourse will consist of an introduction to density functional theory; overview of analysis results for DFT; macroscopic limit of Kohn-Sham density functional theory; introduction of algorithmic issues of DFT; overview of some recent results on development of algorithms for metallic (and insulator) system.

5.2 Talks

Kieron Burke, Department of Chemistry and Department of Physics, University of California, Irvine. *Non-empirical derivation of density and potential functional approximations*: I will discuss our progress in deriving new approximations for both exchange-correlation and for the non-interacting kinetic energy. A sufficiently accurate kinetic energy functional would make solving the KS equations unnecessary. Semiclassical techniques are applied to yield accurate results as functionals of the potential, rather than of the density. Our most recent calculations reach high accuracy for the ionization energies of atoms.

I will focus on recent work (with Cangi, Lee, Elliott, and Hardy Gross) in which the universal functional of Hohenberg and Kohn is given as a coupling-constant integral over the density as a functional of the potential. Conditions are derived under which potential-functional approximations are variational. Construction via this method and imposition of these conditions are shown to greatly improve the non-interacting kinetic energy needed for orbital-free Kohn-Sham calculations.

Yakun Chen, Department of Chemistry, University of British Columbia, Vancouver, Canada, *Linear-expansion Shooting Technique for Accelerating Self-consistent Field Convergence*: Based on the corrected Hohenberg-Kohn-Sham energy functional (cHKS) [1,2], we present a new method to accelerate self-consistent field (SCF) convergence by utilizing shooting technique. We have developed three different linear-expansion shooting techniques (LIST)–LISTd, LISTs and LISTi, by imposing different conditions. Case studies show that overall the LISTi method is a robust and efficient algorithm for accelerating SCF convergence whereas LISTd and LISTs methods are advantageous in the early stage of SCF convergence. More importantly, the LIST method outperforms Pulays DIIS [3,4] and its recent improvements, including EDIIS [5,6] and ADIIS [7].

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Virginie Ehlacher, CERMICS - Ecole des Ponts ParisTech, France, *Local defects are always neutral in the Thomas-Fermi-von Weizsäcker theory of crystals*: The aim of this article is to propose a mathematical model describing the electronic structure of crystals with local defects in the framework of the Thomas-Fermi-von Weizsäcker (TFW) theory. The approach follows the same lines as that used in E. Cancès, A. Deleurence and M. Lewin, Commun. Math. Phys., 281 (2008), pp.129177 for the reduced Hartree-Fock model, and is based on thermodynamic limit arguments. We prove in particular that it is not possible to model charged defects within the TFW theory of crystals. We finally derive some additional properties of the TFW ground state electronic density of a crystal with a local defect, in the special case when the host crystal is modelled by a homogeneous medium.

Matthias Ernzerhof, Department of Chemistry, University of Montreal. *Density functional theory for open systems: Theory and applications*: We describe a generalization [1] of ground-state DFT that preserves its formal structure, i.e., the basic equations remain unchanged, while the external potential and the electron density become complex valued functions instead of real valued ones. As a consequence, the ground-state energy is also replaced by a complex energy, which is interpreted as a resonance-state energy. Resonance states are metastable and their lifetime is proportional to the inverse of the imaginary part of their energy. A suitable choice of the external complex potential enables one to model systems such as metastable molecules on surfaces and electron transport [2] through molecular electronic devices. We discuss [3] several applications of our theory as well as limitations of existing exchange-correlation energy functionals to represent the complex exchange-correlation energy.

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3. Y. Zhou and M. Ernzerhof, in preparation.

Lin Lin, Program in Applied and Computational Mathematics, Princeton University. *Adaptive local basis for Kohn-Sham density functional theory in Discontinuous Galerkin framework*: Kohn-Sham density functional theory is the most popular electronic structure theory in chemistry and material science. Numerically Kohn-Sham density functional theory gives rise to a matrix eigenvalue problem. The eigenfunctions (also called orbitals) are non-smooth with localized features in real space around atom sites. A proper discretization on a uniform mesh generally requires a large number of plane waves to capture the localized feature, therefore resulting an eigenvalue problem with large matrix dimension. The matrix dimension can be reduced by incorporating parameterized empirical basis functions suggested by chemical intuition such as using atomic orbitals, but the basis functions have to be tuned finely and manually in order to obtain comparable accuracy as that in uniform mesh. We present a new scheme that constructs the basis functions adaptively by using the eigenfunctions from Kohn-Sham theory defined on a local region. The resulting basis functions capture the localized feature of the global eigenfunctions by definition. The basis functions are local and are discontinuous in a global level, and the global eigenfunctions are reconstructed from these discontinuous basis functions in Discontinuous Galerkin framework. Numerical examples indicate that the new scheme achieves dimension reduction effectively and automatically. The local nature of the basis functions leads to a sparse matrix eigenvalue problem, which allows to be combined with the recently proposed sparse matrix technique (selected inversion technique) to further reduce the computational cost for both insulating and metallic systems. (Joint work with Weinan E, Jianfeng Lu and Lexing Ying)

Kenneth A. Lopata, Pacific Northwest National Laboratory. *Modeling fast electron dynamics with real-time time-dependent density-functional theory*: The response of matter to external fields forms the basis for a vast wealth of fundamental physical processes ranging from light harvesting to nanoscale electron transport. Accurately modeling ultrafast electron dynamics in excited systems thus offers unparalleled insight, but requires an inherently non-linear time-resolved approach. To this end, an efficient and massively parallel real-time real-space time-dependent density functional theory (RT-TDDFT) implementation in NWChem is presented. The implementation is first validated against linear-response TDDFT and experimental results for a series of molecules subjected to small electric field perturbations. Next, non-linear excitation of green fluorescent protein is studied, which shows a blue-shift in the spectrum with increasing perturbation, as well as a saturation in absorption. Finally, the charge dynamics of optically excited zinc porphyrin is presented in real-time and real-space, with relevance to charge injection in photovoltaic devices.

Gang Lu, Department of Physics, California State University Northridge. *Exciton Diffusion in Organic Solar Cells: First-Principles Investigations*: Exciton diffusion length and time are among the most important factors that govern the performance of organic solar cells and light-emitting diodes. Understanding exciton diffusion process in organic semiconductors such as conjugated polymers from first-principles represents a crucial aspect of designing high-efficiency solar cells. We have developed a first-principles approach based on time-dependent density functional linear response theory with the Casida's formalism to describe the energy and many-body wave-functions of excitons. The non-adiabatic ab initio molecular dynamics is used to calculate phonon-assisted transition rates between localized exciton states with the spontaneous emission determined by the dipole approximation. With Monte Carlo simulations, we are able to calculate the exciton diffusion length, time, and diffusivity for a prototype polymer system P3HT, and have obtained excellent results comparing to experiments as well as physical insight into the microscopic nature of exciton diffusion.

The work was partially supported by NSF-Solar grant DMR-1035480.

Yvon Maday, Laboratoire Jacques Louis Lions, Université Pierre et Marie Curie, Paris, France and Division of Applied Mathematics, Brown University, USA, *Two-grid method for the approximation of nonlinear eigenvalue problems*: Approximation of non linear eigenvalue problems represent the key ingredient in quantum chemistry. These approximation are much computer demanding and these approximations saturate the ressources of many HPC centers. Being nonlinear, the approximation methods are iterative and a way to reduce the cost is to use different grids as has been proposed in fluid mechanics for various non linear problems as the Navier Stokes problem. We explain the basics of the approximation, present the numerical analysis

and numerical results that illustrate the good behavior of the two grids scheme. This work has been done in collaboration with Eric Cancès and Rachida Chakir.

John E. Pask, Lawrence Livermore National Laboratory, USA. *Partition-of-unity finite elements for large, accurate quantum mechanical materials calculations*: Over the past few decades, the planewave (PW) pseudopotential method has established itself as the dominant method for large, accurate, density-functional calculations in condensed matter. However, due to its global Fourier basis, the PW method suffers from substantial inefficiencies in parallelization and applications involving highly localized states, such as those involving 1st-row or transition-metal atoms, or other atoms at extreme conditions. Modern "real space" approaches, such as finite-difference (FD) and finite-element (FE) methods, can address these deficiencies without sacrificing rigorous, systematic improvability but have until now required much larger bases to attain the required accuracy. Here, we present a new real-space FE based method [1,2] which employs modern partition-of-unity FE (PUFE) techniques to substantially increase the efficiency of the real-space representation, thus decreasing the number of basis functions required correspondingly, by building known atomic physics into the FE basis: without sacrificing locality or systematic improvability. We discuss the weak formulation of the required Poisson and Schroedinger problems in the Kohn-Sham solution and the imposition of Bloch-periodic boundary conditions. We present both pseudopotential and all-electron applications, with attention in the latter case to the approximation of the singular solution outside Sobolev space H^1 using a basis in H^1 . Finally, we highlight recent progress and open questions relating to generalized eigensolvers and parallelization. Initial results show order-of-magnitude improvements relative to current state-of-the-art PW and adaptive-mesh FE methods for systems involving localized states such as d- and f-electron metals and/or other atoms at extreme conditions.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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Kieron Burke, Department of Chemistry and Department of Physics, University of California, Irvine. *Density Functional Theory, and the Persistence of Chemistry in the Limit of Large Atomic Number*: This talk applies the orbital-based Kohn-Sham density functional theory to compute the first ionization energies of hypothetical non-relativistic neutral atoms with up to $Z=3000$ electrons, within the sp or main block of the periodic table [1]. The ionization energies and density changes upon ionization are extrapolated to the limit of infinite atomic number Z . We find well-defined limits that depend upon the chosen column of the periodic table. Thus the periodic table becomes perfectly periodic in this limit. The limiting ionization energies are smaller than those from the real periodic table, but still increase across a row or period. The finiteness of the limiting ionization energy is remarkable, because the total energy of the neutral atom varies as Z^{-1} . An sp chemistry of unusually long, weak bonds likely persists in the limit. The simple local density approximation for the exchange energy appears to give an exact or nearly-exact exchange contribution to the ionization energy averaged over a shell. Proving or disproving these conclusions rigorously is a challenge to mathematical physics.

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Emil Prodan, Department of Physics, Yeshiva University. *Predictive ab-initio simulations of Topological Insulators: Fundamental Challenges*: Topological Insulators represent a new class of materials displaying robust physical properties triggered by a strong spin-orbit interaction. Based on qualitative and sometime empirical models, several topological insulating materials have been predicted and then discovered experimentally. Ab-initio simulations of such materials have start appearing in the literature and some of these simulations were even used to predict new classes of topological insulators. However, the ab-initio simulations of these systems with strong spin-orbit interaction are facing daunting challenges, especially when predictive power is needed.

In this talk I will first briefly summarize the status of the field, touching on the following points: what is a topological insulator, what are the robust properties and how are they triggered by the spin-orbit interaction, what materials are known to display the effect? Then I will discuss the status of the existing ab-initio simulations and start listing the emerging challenges. I will present the status of the Density Functional Theory

for systems with strong spin-orbit interaction and touch on several key points that need practical solutions in order to efficiently apply the theory to the complex topological materials.

Pina Romaniello, Universit e Paul Sabatier, Toulouse, France and European Theoretical Spectroscopy Facilities (ETSF), F-91128 Palaiseau, France. *DFT: insight from MBPT*: Density functional theory (DFT) has become over the years one of the few well-established theoretical approaches for calculations on realistic systems. The basic idea of DFT is to replace the many-body problem with an effective one-particle description in which the many-body effects of the system enter through an exchange-correlation potential that is a functional of the density of the system. This functional is not known and needs to be approximated. Designing new functionals that are generally applicable is an hard task. A way to follow is to pass through Many-Body Perturbation Theory (MBPT) [1]. In this framework, the many-body effects of the system are contained in the self-energy, which thus plays a similar role as the exchange-correlation potential in a density-functional context. Also the self-energy needs to be approximated. However in MBPT approximations can be found in a systematic way, although MBPT in itself is too costly for realistic systems. Therefore, passing through MBPT has the advantage that approximations with a clear physical meaning can be designed more easily than in the context of density functionals and introduced in a second-step into the computationally more efficient DFT. In this work I will focus on MBPT and I will show how one can improve the currently used approximations [2,3]; I will also discuss how to translate the physical insight acquired in MBPT into DFT.

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Reinhold Schneider, TU Berlin. *A posteriori error estimators in Density Functional Theory and Hartree-Fock*: We present an a posteriori error analysis of the discretization of error in the Kohn Sham energies, resp. the Hartree Fock energy. The analysis is based on duality techniques as developed for goal oriented error estimators. Basic assumptions are similar to those imposed for a priori estimates, e.g. Canc es et al.. We consider the error estimators for the orbital functions, taking the unitary invariance into account, as well as for the density matrix directly. This is joint work with S. Schwinger (MPI Leipzig), and most material is from his recent PhD thesis.

Gustavo E. Scuseria, Department of Chemistry, Department of Physics and Astronomy, Rice University, Houston, Texas 77005, USA, guscus@rice.edu. *Strong Correlations from Constrained Mean-Field Approaches*: This presentation will discuss mean-field approaches for describing strong correlations. The methods that we have developed allow for symmetry breaking followed by a restoration step. We work both with wavefunctions and density matrix functionals. In both cases, symmetry breaking is constrained to an active space. Constrained-pairing mean-field theory (CPMFT) [1-4] yields a two-particle density matrix ansatz that exclusively describes strong correlations. The model wavefunction breaks electron number conservation and is correct only on average but expectation values calculated from the effective two-particle density matrix contain no particle number fluctuations. On the other hand, Constrained Unrestricted Hartree-Fock (CUHF) theory [5, 6] limits spin and space symmetry breaking to an active space. Based on it, we have recently proposed a novel approach for obtaining high-spin ROHF wave functions by imposing constraints to UHF. The constraints can be selectively released in an active space but imposed elsewhere. If the active space is properly chosen, our CUHF method greatly benefits from a controlled broken-symmetry effect while avoiding the massive spin contamination of traditional UHF. We have also applied Lowdin's projection operator method to CUHF and obtain multireference wave functions with moderate computational cost. Singlet-triplet energy splittings show that our constrained scheme outperforms fully unrestricted methods. This constrained approach can be used in spin density functional theory with similar favorable effects.

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2. Constrained-Pairing Mean-Field Theory. II. Exact treatment of dissociations to non-degenerate orbitals, G. E. Scuseria and T. Tsuchimochi, J. Chem. Phys. 131, 164119 (2009).

3. Constrained-Pairing Mean-Field Theory. III. Inclusion of Density Functional Exchange and Correlation Effects via Alternative Densities, T. Tsuchimochi, G. E. Scuseria, and A. Savin, *J. Chem. Phys.* 132, 024111 (2010).
4. Constrained-Pairing Mean-Field Theory. IV. Inclusion of corresponding pair constraints and connection to unrestricted Hartree-Fock theory, T. Tsuchimochi, T. M. Henderson, G. E. Scuseria, and A. Savin, *J. Chem. Phys.* 133, 134108 (2010).
5. ROHF Theory Made Simple, T. Tsuchimochi and G. E. Scuseria, *J. Chem. Phys.* 133, 141102 (2010).
6. Constrained Active Space Unrestricted Mean-Field Methods for Controlling Spin-Contamination, T. Tsuchimochi and G. E. Scuseria, *J. Chem. Phys.* submitted

Jan Phillip Solovej, Department of Mathematics, University of Copenhagen, Denmark. *The Scott correction in different models of atoms and molecules*: The topic of this talk is the energy asymptotics of large atoms and molecules. I will discuss joint work with Ostergaard-Sorensen and Spitzer on relativistic corrections to the energy and recent joint work with Erdos and Fournais on corrections to the energy due to magnetic self-interactions. In both cases the leading order of the energy (as the atomic number gets large) is not affected by the corrections. It is given by the classical Thomas-Fermi energy. The corrections come in the next order: the Scott order.

Viktor N. Staroverov, Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7. *Solved and unsolved problems in the theory of model Kohn-Sham potentials*: Direct approximation of Kohn-Sham potentials is an intriguing alternative to the usual pursuit of density-functional approximations for the exchange-correlation (xc) energy. The two central issues of potential-driven DFT are inversion of functional differentiation (how to recover the energy functional from a given Kohn-Sham potential) and the problem of integrability (how to ensure that a directly approximated potential is a functional derivative of some functional). The inversion problem was solved by van Leeuwen and Baerends [*Phys. Rev. A* 51, 170 (1995)]. More recently [*J. Chem. Phys.* 133, 101104 (2010)], we found a way to construct integrable model potentials without knowing their parent functionals. Integrability matters more than is often assumed since non-integrable model potentials can lead to unphysical results. Model Kohn-Sham potentials proposed to date (e.g., the xc-potential of van Leeuwen and Baerends, numerous approximations to the optimized effective potential, the exchange potential of Becke and Johnson, and its various extensions) have limited use precisely because they are non-integrable. I will overview the recent progress in the methodology of potential-driven DFT and discuss the current challenges for the development of practical Kohn-Sham potential approximations.

Yan Alexander Wang, Department of Chemistry, University of British Columbia, Vancouver, Canada, yawang@chem.ubc.ca. *Functional Derivatives and Differentiability in Density-Functional Theory*: Based on Lindgren and Salomonsons analysis on Fréchet differentiability [*Phys. Rev. A* 67, 056501 (2003)], we showed a specific variational path along which the Fréchet derivative of the Levy-Lieb functional does not exist in the unnormalized density domain. This conclusion still holds even when the density is restricted within a normalized space. Furthermore, we extended our analysis to the Lieb functional and demonstrated that the Lieb functional is not Fréchet differentiable. Along our proposed variational path, the Gâteaux derivative of the Levy-Lieb functional or the Lieb functional takes a different form from the corresponding one along other more conventional variational paths. This fact prompted us to define a new class of unconventional density variations and inspired us to present a modified density variation domain to eliminate the problems associated with such unconventional density variations.

Aihui Zhou, LSEC, Institute of Computational Mathematics and Scientific/Engineering Computing, Academy of Mathematics and Systems Science, Chinese Academy of Sciences, Beijing 100190, China, Email: azhou@lsec.cc.ac.cn. *Finite Element Approximations of Nonlinear Eigenvalue Problems in Density Functional Models*: In this presentation, we will talk about finite element approximations of nonlinear eigenvalue problems in density functional theory. We will present a priori and a posteriori error estimates of finite element approximations of both orbital-free type and Kohn-Sham density functional models. We will also show the convergence and complexity of adaptive finite element approximations and report some numerical results of finite element electronic structure calculations that support our theory. This presentation is based on some joint works with Huajie Chen, Xingao Gong, Lianhua He, and Zhang Yang.

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