



Banff International Research Station

for Mathematical Innovation and Discovery

Density Functional Theory: Fundamentals and Applications in Condensed Matter Physics

Organized by Eric Cancès¹, Carlos J. García-Cervera², and Yan Alexander Wang³

January 23rd-28th, 2011

MEALS

*Breakfast (Buffet): 7:00–9:30 am, Sally Borden Building, Monday–Friday

*Lunch (Buffet): 11:30 am–1:30 pm, Sally Borden Building, Monday–Friday

*Dinner (Buffet): 5:30–7:30 pm, Sally Borden Building, Sunday–Thursday

Coffee Breaks: As per daily schedule, 2nd floor lounge, Corbett Hall

***Please remember to scan your meal card at the host/hostess station in the dining room for each meal.**

MEETING ROOMS

All lectures will be held in Max Bell 159 (Max Bell Building accessible by walkway on 2nd floor of Corbett Hall). LCD projector, overhead projectors and blackboards are available for presentations. Note that the meeting space designated for BIRS is the lower level of Max Bell, Rooms 155–159. Please respect that all other space has been contracted to other Banff Centre guests, including any Food and Beverage in those areas.

SCHEDULE

Sunday

- 16:00** Check-in begins (Front Desk - Professional Development Centre - open 24 hours)
Lecture rooms available after 16:00 (if desired)
- 17:30–19:30** Buffet Dinner, Sally Borden Building
- 20:00** Informal gathering in 2nd floor lounge, Corbett Hall (if desired)
Beverages and a small assortment of snacks are available on a cash honor system.

¹CERMICS-ENPC, Paris, France.

²Mathematics Department, University of California, Santa Barbara, USA

³Department of Chemistry, University of British Columbia, Vancouver, Canada.

Monday

7:00–8:45	Breakfast
8:45–9:00	Introduction and Welcome by BIRS Station Manager, Max Bell 159
9:00–10:30	Minicourse: Gero Friesecke
10:30–11:00	Coffee Break, 2nd floor lounge, Corbett Hall
11:00–11:45	Gustavo E. Scuseria
11:45–13:00	Lunch
13:00–14:00	Guided Tour of The Banff Centre; meet in the 2nd floor lounge, Corbett Hall
14:00	Group Photo; meet on the front steps of Corbett Hall
14:15–15:00	Matthias Ernzerhof
15:00–15:30	Coffee Break, 2nd floor lounge, Corbett Hall
15:30–17:00	Minicourse: Roberto Car
17:00–17:45	Kieron Burke
17:45–19:30	Dinner

Tuesday

7:00–9:00	Breakfast
9:00–10:30	Minicourse: Jianfeng Lu
10:30–11:00	Coffee Break, 2nd floor lounge, Corbett Hall
11:00–11:45	Virginie Ehrlacher
11:30–13:30	Lunch
13:30–15:00	Minicourse: Kieron Burke
15:00–15:30	Coffee Break, 2nd floor lounge, Corbett Hall
15:30–16:15	Pina Romaniello
16:15–17:00	Emil Prodan
17:00–17:45	Gang Lu
17:45–19:30	Dinner

Wednesday

7:00–9:00	Breakfast
9:00–9:45	Viktor Staroverov
9:45–10:30	Jan Philip Solovej
10:30–11:00	Coffee Break, 2nd floor lounge, Corbett Hall
11:00–11:45	DISCUSSION SESSION
11:45–13:30	Lunch
	Free Afternoon
17:30–19:30	Dinner

Thursday

7:00–9:00 Breakfast
9:00–9:45 Yvon Maday
9:45–10:30 John E. Pask
10:30–11:00 Coffee Break, 2nd floor lounge, Corbett Hall
11:00–11:45 Lin Lin
11:45–13:30 Lunch
13:30–14:15 Kenneth A. Lopata
14:15–15:00 Reinhold Schneider
15:00–15:30 Coffee Break, 2nd floor lounge, Corbett Hall
15:30–16:15 Xavier Andrade
16:15–17:00 Yakun Chen
17:30–19:30 Dinner

Friday

7:00–9:00 Breakfast
9:00–9:45 Yan Alexander Wang
9:45–10:30
Coffee Break, 2nd floor lounge, Corbett Hall
11:30–13:30 Lunch
Checkout by
12 noon.

** 5-day workshops are welcome to use BIRS facilities (2nd Floor Lounge, Max Bell Meeting Rooms, Reading Room) until 3 pm on Friday, although participants are still required to checkout of the guest rooms by 12 noon. **

TUTORIALS
(in alphabetic order by speaker surname)

Speaker: **Kieron Burke**¹

Title: *TDDFT - past, present, and future*

Abstract:

¹Department of Chemistry and Department of Physics, University of California, Irvine

Speaker: **Roberto Car**¹

Title: *TBA*

Abstract:

¹Department of Chemistry and Program in Applied and Computational Mathematics, Princeton University

Speaker: **Gero Friesecke**¹

Title: *Some mathematical challenges in quantum chemistry*

Abstract: 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.

¹TU Munich, Germany

Speaker: **Weinan E**¹ and **Jianfeng Lu**²

Title: *Density Functional Theory: Analysis and Algorithms*

Abstract: 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.

¹Mathematics Department and Program in Applied and Computational Mathematics, Princeton University

²Courant Institute of Mathematical Sciences, New York University

ABSTRACTS
(in alphabetic order by speaker surname)

Speaker: **Xavier Andrade**¹

Title: *Computationally efficient schemes for linear and non-linear response within time-dependent density functional theory*

Abstract: In this talk we discuss the application of time-dependent density functional theory (TDDFT) to the description of non-linear electronic and ionic phenomena of complex structures. This is framed in the general context of having an efficient formalism able to describe both the electronic and magnetic dynamical response properties of nanoscopic systems beyond the linear regime, including time-resolved spectroscopies.

As we are focusing on the modelling of realistic systems, emphasis is placed on formalisms that are suitable for efficient numerical implementation. Two basic formulations are considered: propagation in real-time of the TDDFT equations for arbitrary external perturbations and the frequency-dependent Sternheimer equation for linear and non-linear dynamical susceptibilities.

The real-time TDDFT formulation, already a popular method for the calculation of optical absorption spectra, is extended to deal with other responses like the chiro-optical activity. We also discuss the recently proposed modified Ehrenfest dynamics, a mixed classical-quantum dynamics where the ions are treated as classical particles. In the adiabatic regime this new ab-initio molecular dynamics approach becomes competitive with the widely used Car-Parrinello and Born-Oppenheimer methods. The scheme is ideally suited for massive parallel implementations and allows handling of thousands of atoms.

The Sternheimer equation is an alternative method for linear response in the frequency domain that, as the previous time-propagation scheme, does not need unoccupied states or response functions. It is based on the solution of a self-consistent set of linear equations for each frequency. We present a dynamic version of the Sternheimer formalism that can be used to calculate response in the resonant and non-resonant regimes. We apply this formalism to calculate different properties, including the magnetic response and the non-linear optical response.

Some examples of applications are shown, where the methods are used to calculate different properties of physical systems of interest, including small molecules and nano-clusters, highlighting the impact of the present work for future applications in nano and bio-sciences.

¹Department of Chemistry and Chemical Biology, Harvard University

Speaker: **Kieron Burke**¹

Title: *Non-empirical derivation of density and potential functional approximations*

Abstract: 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.

¹Department of Chemistry and Department of Physics, University of California, Irvine

Speaker: **Yakun Chen**¹ and **Yan Alexander Wang**¹

Title: *Linear-expansion Shooting Technique for Accelerating Self-consistent Field Convergence*

Abstract: 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].

1. B. Zhou and Y. A. Wang, J. Chem. Phys. 128, 084101 (2008).
2. Y. A. Zhang and Y. A. Wang, J. Chem. Phys. 130, 144116 (2009).
3. P. Pulay, Chem. Phys. Lett. 73, 393 (1980).
4. P. Pulay, J. Comput. Chem. 3, 556 (1982).
5. E. Cancès and C. Le Bris, Int. J. Quant. Chem. 79, 82 (2000).
6. K. N. Kudin, G. E. Scuseria, and E. Cancès, J. Chem. Phys. 116, 8255 (2002).
7. X. Hu and W. Yang, J. Chem. Phys. 132, 054109 (2010).

¹Department of Chemistry, University of British Columbia, Vancouver, Canada

Speaker: **Eric Cancès**¹, **Virginie Ehrlacher**¹

Title: *Local defects are always neutral in the Thomas-Fermi-von Weiszcker theory of crystals*

Abstract: 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.

¹CERMICS - Ecole des Ponts ParisTech, France

Speaker: **Matthias Ernzerhof**¹

Title: *Density functional theory for open systems: Theory and applications*

Abstract: 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.

1. M. Ernzerhof, J. Chem. Phys. 125, 124104 (2006).
2. F. Goyer, M. Ernzerhof, and M. Zhuang, J. Chem. Phys. 126, 144104 (2007); M. Ernzerhof, J. Chem. Phys. 127, 204709 (2007).
3. Y. Zhou and M. Ernzerhof, in preparation.

¹Department of Chemistry, University of Montreal

Speaker: **Lin Lin**¹

Title: *Adaptive local basis for Kohn-Sham density functional theory in Discontinuous Galerkin framework*

Abstract: 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)

¹Program in Applied and Computational Mathematics, Princeton University

Speaker: **Kenneth A. Lopata**¹

Title: *Modeling fast electron dynamics with real-time time-dependent density-functional theory*

Abstract: 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.

¹Pacific Northwest National Laboratory

Speaker: **Xu Zhang**¹, **Zi Li**¹ and **Gang Lu**¹

Title: *Exciton Diffusion in Organic Solar Cells: First-Principles Investigations*

Abstract: 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 firstprinciples 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.

¹Department of Physics, California State University Northridge

Speaker: **Yvon Maday**¹

Title: *Two-grid method for the approximation of nonlinear eigenvalue problems*

Abstract: TBA

¹Laboratoire Jacques Louis Lions, Université Pierre et Marie Curie, Paris, France

Speaker: **John E. Pask**¹

Title: *Partition-of-unity finite elements for large, accurate quantum mechanical materials calculations*

Abstract: 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.

1. N. Sukumar and J.E. Pask, *Int. J. Numer. Meth. Eng.* 77, 1121 (2009).
2. J.E. Pask, N. Sukumar, and S.E. Mousavi, arXiv:1004.1765 (2010).

¹Lawrence Livermore National Laboratory, USA

Speaker: **John P. Perdew**¹, **Lucian A. Constantin**², **John C. Snyder**², and **Kieron Burke**³

Title: *Density Functional Theory, and the Persistence of Chemistry in the Limit of Large Atomic Number*

Abstract: 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.

1. L.A. Constantin, J.C. Snyder, J.P. Perdew, and K. Burke, J. Chem. Phys. (Communication, to appear).

¹Department of Physics, Tulane University, New Orleans, LA 70118

²Department of Chemistry, University of California, Irvine

³Department of Chemistry and Department of Physics, University of California, Irvine

Speaker: **Emil Prodan**¹

Title: *Predictive ab-initio simulations of Topological Insulators: Fundamental Challenges*

Abstract: 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.

¹Department of Physics, Yeshiva University

Speaker: **Pina Romaniello**¹

Title: *DFT: insight from MBPT*

Abstract: 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.

1. A. L. Fetter and J. D. Walencka, Quantum Theory of Many-particle Systems, W. A. Benjamin, Inc. New York, (1964).
2. P. Romaniello, F. Bechstedt, and L. Reining, in preparation.
3. G. Lani, P. Romaniello, and Lucia Reining, in preparation.

¹Universit e Paul Sabatier, Toulouse, France and European Theoretical Spectroscopy Facilities (ETSF), F-91128 Palaiseau, France

Speaker: **Reinhold Schneider**¹ and **S. Schwinger**²

Title: *A posteriori error estimators in Density Functional Theory and Hartree-Fock*

Abstract: 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. Cances 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.

¹TU Berlin

²MIS- Max Planck Institute Leipzig

Speaker: **Gustavo E. Scuseria**¹

Title: *Strong Correlations from Constrained Mean-Field Approaches*

Abstract: 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.

1. Strong correlations via constrained-pairing mean-field theory, T. Tsuchimochi and G. E. Scuseria, *J. Chem. Phys.* 131, 121102 (2009).
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

¹Department of Chemistry, Department of Physics and Astronomy, Rice University, Houston, Texas 77005, USA, guscus@rice.edu

Speaker: **Jan Phillip Solovej**¹

Title: *The Scott correction in different models of atoms and molecules*

Abstract: 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.

¹Department of Mathematics, University of Copenhagen, Denmark

Speaker: **Viktor N. Staroverov**¹

Title: *Solved and unsolved problems in the theory of model Kohn-Sham potentials*

Abstract: 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.

¹Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7

Speaker: **Yan Alexander Wang**¹

Title: *Functional Derivatives and Differentiability in Density-Functional Theory*

Abstract: 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.

¹Department of Chemistry, University of British Columbia, Vancouver, Canada, yawang@chem.ubc.ca