LONI Institute workshop on

Density Functional Theory

Louisiana State University, Baton Rouge, LA, USA

July 23-27, 2011

CENTER FOR COMPUTATION & TECHNOLOGY

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Preface

It is our pleasure to welcome you to the LONI Institute workshop on

Density Functional Theory

We thank LONI Institute for its generous financial support and the Center for Computation & Technology and LSU High Performance Computing for their technical and logistical support.

This educational workshop will expose graduate students, postdocs, faculty, and staff to several flavors of electronic structure calculations in a holistic way. The workshop will be accessible to graduate students and postdocs in condensed matter physics, chemistry, and materials engineering, who may not have prior knowledge of DFT methods.

The invited speakers will provide pedagogical and expository lectures on the methods that they use, complemented by hands-on sessions. The format will allow plenty of time for discussions.

We hope you will benefit from the excellent lectures and inspiring discussions.

Conference Organizers:

Juana Moreno, Louisiana State University
John Perdew, Tulane University
Ramu Ramachandran, Louisiana Tech University
Randall Hall, Louisiana State University

High Performance Computing Support Team: Harsha Bhagawaty, Alexander Pacheco, Kathy Traxler, and Jim Lupo.

Special thanks to Bety Rodriguez-Milla, Leigh Townsend, and Shelley Lee for all their help in putting together this workshop.

Cover image credit: Ramu Ramachandran

LONI Institute
Density Functional Theory Workshop
Johnston Hall, Room 338
Louisiana State University
Baton Rouge, Louisiana, USA
July 23rd to 27th, 2011

	Saturday, July 23rd, 2011, Louisiana State University
9:00-10:00	Registration and Breakfast
10:00-10:10	Opening remarks, **Mark Jarrell** (Louisiana State University)
10:10-11:40	**John Perdew** (Tulane University) *Lecture 1: Introduction to Density Functional Theory*
12:00-1:00	Lunch break
1:00-2:30	**Melvyn Levy** (Duke University), *Lecture 1: Basic Existence Theorems*
2:30-2:45	Coffee break
2:45-4:15	**Weitao Yang** (Duke University) *Lecture 1: Free energies and mechanisms of chemical reactions in solution and in enzymes with DFT QM/MM method*
4:15-6:00	*HPC training* (Unix training: connect to LONI, soft env, running codes, etc.)

	Sunday, July 24th, 2011, Louisiana State University
8:30-9:00	Breakfast
9:00-10:30	**Melvyn Levy**, *Lecture 2: Properties of Exact Functionals*
10:30-10:45	Coffee break
10:45-12:15	**Weitao Yang**, *Lecture 2: Revealing Noncovalent interactions*
12:15-1:30	Lunch break
1:30-5:00	**Weitao Yang**, *Hands-on session* **Melvyn Levy**, *Hands-on session*

	Monday, July 25th, 2011, Louisiana State University
8:30-9:00	Breakfast
9:00-10:30	**John Perdew**, *Lecture 2: Advanced Density Functional Theory*
10:30-10:45	Coffee break
10:45-12:15	**Shobhana Narasimhan** (Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore), *Lecture 1: Plane Waves and Pseudopotentials*
12:15-1:30	Lunch break
1:30-5:00	**John Perdew**, *Hands-on session*

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	Tuesday, July 26th, 2011, Louisiana State University
8:30-9:00	Breakfast
9:00-10:30	**Shobhana Narasimhan** *Lecture 2: Practical Issues in Doing a DFT Calculation (with Plane Waves and Pseudopotentials)*
10:30-10:45	Coffee break
10:45-12:15	**Tanusri Saha-Dasgupta** (S.N. Bose National Centre for Basic Sciences, Calcutta), *Lecture 1: DFT Electronic Structure Calculations by Muffin Tin Orbital Based Basis*
12:15-1:30	Lunch break
1:30-5:00	**Shobhana Narasimhan**, *Hands-on session*

	Wednesday, July 27th, 2011, Louisiana State University
8:30-9:00	Breakfast
9:00-10:30	**Tanusri Saha-Dasgupta**, *Lecture 2: Correlation Effects in Real Materials*
10:30-10:45	Coffee break
10:45-12:15	**Kieron Burke** (University of California, Irvine) *Special Lecture via videoconference: The Golden Age of Electronic Structure Theory*
12:15-1:30	Lunch break
1:30-4:30	**Tanusri Saha-Dasgupta**, *Hands-on session*

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Lectures and Hands-on Sessions

John Perdew (Tulane University)

Lecture 1: Introduction to Density Functional Theory
A density functional is a formula that expresses the ground-state energy of a many- electron system in terms of its electron density, facilitating the easy computation of both. In Kohn-Sham density functional theory (DFT), most of the energy is expressed exactly in terms of orbitals, leaving the exchange-correlation energy to be expressed exactly or approximately in terms of the density or the orbitals. This lecture will summarize the history of DFT, and explain why it is so widely used in quantum chemistry and condensed matter physics. The theorems and proofs that justify this approach to the ground-state energy and electron spin densities will be reviewed. The exchange-correlation energy will be defined, and the Jacob's ladder of approximations to it will be introduced. Finally, it will be explained why the lower-rung, computationally-efficient semilocal approximations are appropriate for some problems and not for others.

Lecture 2: Advanced Density Functional Theory
The adiabatic connection formula for the exchange-correlation energy as a functional of the density will be introduced, with the related idea of the exchange-correlation hole around an electron. Exact properties of the density functional and hole will be introduced, and used as exact constraints for the nonempirical or minimally empirical construction of density functional approximations. From this discussion, it will be clear why even the simple local density approximation works fairly well, and why higher-rung functionals can work better. The one- and many-electron self-interaction errors, which can be especially problematic for strongly-correlated systems, will be discussed.

Hands-on Session
Perdew may assign some DFT computations for atoms and small molecules using GAUSSIAN09, to illustrate what the theory and its approximations can or cannot do. He might also assign conceptual or pen-and-paper exercises.

Melvyn Levy (Duke University)

Lecture 1: Basic Existence Theorems
Comparisons of the theories of wave functions, density functionals, and density-matrix functionals will be discussed briefly. Then the basic existence theorems will be proven for degenerate and non-degenerate cases, and mathematical aspects of the self-consistent equations will be studied.

Lecture 2: Properties of Exact Functionals
Several fundamental properties of the exact functionals, such as those involving coordinate scaling, will be derived and discussed in terms of their use for obtaining approximations. Properties of the electron density, including its asymptotic decay, will also be discussed.

Hands-on Session
Discuss solutions to conceptual problems.

Weitao Yang (Duke University)

Lecture 1: Free energies and mechanisms of chemical reactions in solution and in enzymes with DFT QM/MM method
Multiscale modeling is an effective tool for extending the applicability of DFT to large and complex systems, in particular for processes in condensed environment. The multiscale combined QM/MM methods provide an accurate and efficient energetic description of complex chemical and biological systems, leading to significant advances in the understanding of chemical reactions in solution and in enzymes. Density functional theory based ab initio QM/MM methods capitalize on the accuracy and reliability of the associated quantum mechanical approaches, but at a much higher computational cost compared with semiempirical quantum mechanical approaches. Thus reaction path and activation free energy calculations encounter unique challenges in simulation timescales and phase space sampling. Recent developments of the DFT QM/MM minimum free energy path method overcome these challenges and enable accurate free energy determination for reaction and redox processes in solution and enzymes. Applications to several solution and enzyme reactions and redox processes will be highlighted.

References
H. Hu, Z. Y. Lu, and W. T. Yang,"QM/MM minimum free-energy path: Methodology and application to triosephosphate isomerase," Journal of Chemical Theory and Computation, vol. 3, pp. 390-406, 2007.
H. Hu, Z. Y. Lu, J. M. Parks, S. K. Burger, and W. T. Yang, "Quantum Mechanics/Molecular Mechanics minimum free-energy path for accurate reaction energetics in solution and enzymes: Sequential sampling and optimization on the potential of mean force surface," Journal of Chemical Physics, vol. 128, p. 034105, 2008.
H. Hu and W. T. Yang,"Free energies of chemical reactions in solution and in enzymes with ab initio Quantum Mechanics/Molecular Mechanics methods," Annual Review of Physical Chemistry, vol. 59, pp. 573-601, 2008.
H. Hu, A. Boone, and W. T. Yang, "Mechanism of omp decarboxylation in orotidine 5 '-monophosphate decarboxylase," Journal of the American Chemical Society, vol. 130, pp. 14493-14503, 2008.
X. C. Zeng, H. Hu, X. Q. Hu, A. J. Cohen, and W. T. Yang, "Ab initio Quantum Mechanical/Molecular Mechanical simulation of electron transfer process: Fractional electron approach," Journal of Chemical Physics, vol. 128, p. 124510, 2008.
X. C. Zeng, H. Hu, X. Q. Hu, and W. T. Yang, "Calculating solution redox free energies with ab initio Quantum Mechanical/Molecular Mechanical minimum free energy path method," Journal of Chemical Physics, vol. 130, p. 164111, 2009.

Xiangqian Hu, Hao Hu, Jeffrey A. Melvin, Kathleen W. Clancy, Dewey G. McCafferty, and Weitao Yang, "Autocatalytic Intramolecular Isopeptide Bond Formation in Gram-Positive Bacterial Pili: A QM/MM Simulation", J. Am. Chem. Soc., 133, 478-485, 2011.

Lecture 2: Revealing Noncovalent interactions
Molecular or bulk structure does not easily identify the intricate noncovalent interactions that govern many areas of physics, biology and chemistry, including design of new materials and drugs. We develop an approach to detect noncovalent interactions (NCI) in real space, based on the electron density and its derivatives. Our approach reveals the underlying chemistry that compliments the covalent structure. It provides a rich representation of van der Waals interactions, hydrogen bonds, and steric repulsion in small molecules, molecular complexes, and solids. Most importantly, the method, requiring only knowledge of the atomic coordinates, is efficient and applicable to large systems, such as nanostructures, bulk solids, proteins or DNA. Across these applications, a view of nonbonded interactions emerges as continuous surfaces rather than close contacts between atom pairs, offering rich insight into the design of new and improved ligands. We will describe the NCI computational algorithms and their implementation for the analysis and visualization of weak interactions, using both self-consistent fully quantum-mechanical as well as promolecular densities. A wide range of options for tuning the range of interactions to be plotted is also presented. To demonstrate the capabilities of our approach, several examples are given from organic, inorganic, solid state, and macromolecular chemistry, including cases where NCI analysis gives insight into unconventional chemical bonding. The NCI code and its manual are available for download at `http://www.chem.duke.edu/~yang/software.htm`

References
E. R. Johnson, S. Keinan, P. Mori-Sanchez, J. Contreras-Garcia, A. J. Cohen, and W. T. Yang. "Revealing noncovalent interactions." Journal of the American Chemical Society, 132:6498, 2010.
Julia Contreras-Garcia, Erin R. Johnson, Shahar Keinan, Robin Chaudret, Jean-Philip Piquemal, David N. Beratan, and W. T. Yang, "NCIPLOT: A Program for Plotting Noncovalent Interaction Region," J. Chem. Theory Comput. 7: 625, 2011.

Hands-on Session
Using the Noncovalent Interaction Index (NCI).

Shobhana Narasimhan (Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore)

Lecture 1: Plane Waves and Pseudopotentials

- Plane Wave Basis
- Problems for Core and Valence Wavefunctions
- The Pseudopotential Approximation
- Generating an Ab initio Pseudopotential
- Norm Conservation: Advantages and Disadvantages
- Transferability
- Smoothness
- Ultrasoft Pseudopotentials

Lecture 2: Practical Issues in Doing a DFT Calculation (with Plane Waves and Pseudopotentials)

- Iterative Solution: The Self-Consistent Loop
- Convergence with Respect to Cut-off
- Brillouin Zone Sampling
- Metals and Smearing
- Mixing
- Output Quantities

Hands-on Session
Simple self-consistent-field calculations on silicon (and, if time permits, aluminum) with the Quantum ESPRESSO code.

Tanusri Saha-Dasgupta (S.N. Bose National Centre for Basic Sciences, Calcutta)

Lecture 1: DFT Electronic Structure Calculations by Muffin Tin Orbital Based Basis

- Introduction to Basis Sets
- Muffin-Tin Approximation
- Envelope Function, Screening and Augmentation: Muffin Tin Orbitals
- Tail Cancellation and KKR
- Linearization: Linear Muffin Tin Orbital (LMTO)
- Improved LMTO – N-th Order MTO (NMTO) Method
- Applications of NMTO in Deriving Few Band Hamiltonians

Lecture 2: Correlation Effects in Real Materials

- Introduction: Why Strong Correlations?
  - Failure of One-Electron Theories
  - Hesitant Electrons: Delocalized Waves or Localized Particles?
  - Examples of Strongly Correlated Materials
  - Different Energy Scales and MIT in TMO
- Methods to Deal with Correlations in Realistic Ways
  - Concepts (LDA+U, LDA+DMFT)
  - Practical Details
  - Examples
- Spin-Physics out of Correlation
  - t-J and Heisenberg
  - Super-Exchange

Hands-on Session
Calculation of electronic structure of Si and $CaMnO_3$ using LMTO method.

Kieron Burke (University of California, Irvine)

Special Videoconference Lecture: The Golden Age of Electronic Structure Theory
The ever increasing power of computers and algorithms have made it possible to calculate the properties of collections of hundreds of atoms using density functional theory. This capability has already transformed chemistry, and is about to revolutionize materials science. It is a wonderful time to be entering this field and this workshop is a great introduction from the leaders, including several who made this revolution possible.

However, we are still far from providing a turn-key tool to solve all problems of materials design, and thus usher in a new age of human control over our environment. While our methods work for many generic cases, failures abound, and we often have no good solution in these cases. Woe betide the naive student who ignores these dangers. My lecture will discuss the past, present, and future of the field.

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Invited Speakers

Kieron Burke (University of California, Irvine)

Kieron Burke[1] is a professor in both the chemistry and physics departments at UC Irvine. He began his checkered academic career as a chemical engineering student at University College Dublin, but was drawn to the study of quantum mechanics by Dirac's monograph. He is one of the leading developers of density functional theory, a method for solving the Schroedinger equation for electrons that can be easily applied to molecules with hundreds of atoms which has transformed modern chemistry. His current interests include removing empiricism from the theory, the foundations of the time-dependent theory, molecular electronics, electron-atom scattering, including nuclear motion beyond Born-Oppenheimer, and open quantum systems. He has won several awards for teaching and research, and was recently elected a fellow of the American Physical Society.

Melvyn Levy (Duke University)

Prof. Mel Levy[2], who was born in Brooklyn, New York, in 1941, is a Visiting Professor at Duke University and a Professor Emeritus at both Tulane University and North Carolina Agricultural and Technical State University. For over thirty-five years, he has made important contributions to the foundations and mathematical structures of density-functional and density-matrix functional theories. He is an elected Fellow of the American Physical Society, and an elected member of the International Academy of Quantum Molecular Science and of the International Academy of Mathematical Chemistry. He has served on the Editorial Boards of Advances in Quantum Chemistry, Theoretical Chemistry Accounts, and Progress in Theoretical Chemistry.

Shobhana Narasimhan (Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore)

Prof. Shobhana Narasimhan[3] received a M.Sc. at the Indian Institute of Technology, Bombay, India, 1985, an A.M. at Harvard University, 1988, and a Ph.D. at Harvard University, 1991 with Professor David Vanderbilt. She held postdoctoral appointments at Brookhaven National Lab and the Fritz-Haber-Institute in Berlin. Since 1996 she has been on the Faculty of the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India, where she is currently Professor and Chairperson of the Theoretical Sciences Unit.

[1] http://www.chem.uci.edu/faculty/kieron/
[2] http://fds.duke.edu/db/aas/Chemistry/faculty/mel.levy
[3] http://www.jncasr.ac.in/shobhana/

John Perdew (Tulane University)

John P. Perdew[4] is a Professor of Physics at Tulane University. His research in the density-functional theory of electronic structure has helped to establish this theory as the most widely-used method to predict the properties of atoms, molecules, and solids from the principles of quantum mechanics. He has published 250 research articles and his work has been cited 76,000 times. He is an elected Fellow of the American Physical Society, and an elected member of the International Academy of Quantum Molecular Science and the National Academy of Sciences (U.S.). Born in 1943 in western Maryland, Perdew received a B.S. in Physics and Mathematics from Gettysburg College in 1965, and a Ph.D. in Physics from Cornell University in 1971. After postdoctoral work at the University of Toronto and Rutgers University, he joined the Department of Physics at Tulane University in 1977, was promoted to full professor in 1982, and served two terms as Department Chair. His research has been supported by the NSF since 1978.

Tanusri Saha-Dasgupta (S.N. Bose National Centre for Basic Sciences, Calcutta)

Prof. Tanusri Saha-Dasgupta[5] received her PhD from Calcutta University in 1995. She did post-doctoral research at ONERA in Paris, University of Cergy-Pontoise in Paris and the Max-Planck Institute for Solid State Physics in Stuttgart. She joined the Indian Institute of Science, Bangalore as a research associate in 1999 and moved to the S.N. Bose National Centre for Basic Sciences as a faculty member in 2000. She is currently a Professor in the Department of Material Science and also the head of the Advanced Materials Research Unit. Her expertise is in electronic structure of complex materials, strongly correlated electron systems, phase stability in disordered alloys and electronic structure of nanomaterials. She has received the Swarnajayanti fellowship in 2006, has been appointed the head of Max-Planck partner group in 2005. She is a fellow of the Indian Academy of Sciences and the National Academy of Sciences, India.

Weitao Yang (Duke University)

Prof. Weitao Yang[6] was born in Chaozhou, China. He received his B.S. degree from Peking University and Ph.D. degree from the University of North Carolina at Chapel Hill. He is currently the Philip Handler Professor of Chemistry at Duke University. Yang's interests are in developing density functional theory and applying it to complex problems. Professor Yang has held visiting professorships from the Japanese Society for Promotion of Science, Kyoto University, and Hong Kong University, and Tsinghua University. He received the 1997 Annual Medal of the International Academy of Quantum Molecular Science, and the 2006 Humboldt Research Award for Senior U.S. Scientists. He has held Sloan fellowship, and is the co- author (with Robert G. Parr) of one of the leading textbooks on density-functional theory. He is an elected member of the International Academy of Quantum Molecular Science, `http://www.IAQMS.org/`, an elected fellow of American Association for the Advancement of Science and of the American Physical Society. Yang is recognized by the Institute for Scientific Information as a Highly Cited Researcher. In 2010, Yang was the International Solvay Chair in Chemistry, International Solvay Institutes for Physics and Chemistry, Brussels, Belgium.

[4] `http://www.physics.tulane.edu/Faculty/PerdewInfo.shtml`
[5] `http://www.bose.res.in/~tanusri/`
[6] `http://www.chem.duke.edu/~yang/`