Electronic Structure Lectures

Telluride School on Theoretical Chemistry 2013

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In my series of lectures, I will attempt to paint a picture of the current state of the art in electronic structure theory. By necessity, this will involve three key ingredients 1) Discussion of the fundamental questions typically studied in electronic structure 2) Consideration of the types of problems one would ideally like to solve with electronic structure tools and 3) The nuts and bolts of how one uses and abuses electronic structure techniques to actually get things done.

In the first lecture, we will discuss the quantities of common interest in electronic structure. We will outline the structure of the many electron wave function, molecular orbitals, the electron density and density matrices, the potential energy surface and molecular forces. In part, this lecture will serve to lay out the notation for the subsequent lectures. Good preparatory readings for this will be some combination of: Szabo&Ostlund Chapters 1&2, Parr and Yang Chapters 1&2 and/or McWeeny Chapters 1,2,3&5.

In the second lecture, we will summarize important approximations to the electronic wave function. We will begin with a study of the mean field approximation, as illustrated by the Hartree-Fock method, and introduce the concept of electron correlation. We will then briefly outline beyond mean field methods like perturbation theory, configuration interaction and coupled cluster theory. As an illustration of how these methods work, we will discuss applications to thermochemistry. Good background reading here would be Szabo&Ostlund Chapter 3 and/or McWeeny Chapter 6.

In the third lecture, we will cover density functional theory. Beginning with the Hohenberg Kohn theorem, we will show how one can develop an in principle exact theory based on the density alone. We will then outline the Kohn-Sham formulation of DFT in terms of orbitals and the resulting popular generalized gradient approximation. We will also discuss the invention of hybrid density functionals, which mix some ingredients of wave function theory with DFT. As a illustration of how these methods work, we will discuss the utility of DFT in describing molecular dynamics. We will also cover some of the outstanding challenges in DFT, including electron delocalization, band gaps and intermolecular forces. Good companion reading here is Parr&Yang chapters 7&8.

In the fourth lecture, we will discuss practical considerations concerning electronic structure calculations. We will cover the use of basis sets, mostly focusing on Gaussian type orbitals, but also with some discussion of plane waves. We will derive the asymptotic scaling of different methods with system size, including the computational bottlenecks for commonly used approximations. Finally, we will discuss the expected accuracy of different properties with various methods. Time permitting, we will discuss some applications to charge transfer and/or catalysis as illustrations at this point.

In the fifth lecture, we will outline the description of excited states. We will discuss the use of dynamic linear response to generate electronic excited states based on a ground state calculation. We will also describe the utility of single- versus multi-reference calculations for electronically excited states. Finally, we will illustrate how electronic excited states help us understand absorption spectra, energy transfer and nonradiative relaxation. We will spend a significant portion of this lecture discussing what we cannot at present do with electronic excited state calculations. The list of unsolved problems for excited states is far longer than the corresponding list for ground states.

The sixth lecture will be a special topics lecture. Possible topics of interest include: Intermolecular interactions, electron transfer, diabatic states, electron transport, localization and screening, energy transfer and local correlation models. The content of this final lecture will be chosen based on the interests of the students on hand.