Physics 8990-016 Density Functional Theory Fall 2012
Independent Study
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References: Density Functional Theory: A practical introduction by D.S. Sholl and J.A. Steckel (Wiley) + prepared notes

The purpose of this course is to provide a general background to the theoretical ideas underlying the density functional theory approach to electronic structure calculation, as well as an understanding of the advantages and limitations of different density functional theory methods, along with a practical introduction to density functional theory calculations using the VASP (Vienna Ab-Initio Simulation Package) software in the case of bulk solids, surfaces, and interfaces.

The following topics will be included.

I. Theoretical Background
Atomic Units
Hartree equations and Hartree-Fock equations
Kohn-Sham Theorems (I + II)
Kohn-Sham equations

Definition of local density functional $E_{xc}[\rho] = \int \rho(\mathbf{r})\, \varepsilon_{xc}(\rho(\mathbf{r}))\, d\mathbf{r}$ and division of

$\varepsilon_{xc}(\rho(\mathbf{r})) = \varepsilon_x(\rho) + \varepsilon_c(\rho)$ where $\varepsilon_x(\rho)$ is the exchange integral and $\varepsilon_c(\rho)$ is the universal but unknown "correlation" correction

Derivation of Dirac form for the exchange integral: $\varepsilon_x(\rho) = -C\,\rho^{1/3}$

Derivation of LDA form: $\varepsilon_x(\rho) = -(81/64\pi)^{1/3}\,\rho^{1/3}$

LDA form for $\varepsilon_c(\rho)$ [obtained from quantum Monte Carlo simulations and fits]
See: M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980)
J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981)
Perdew and Wang, Phys. Rev. B **45**, 13244 (1992) [PW91], also PBE

GGA approximation to $\varepsilon_c(\rho)$

Higher order approximations to $\varepsilon_c(\rho)$ (Meta-GGA, Hybrid, B3LYP)
Hybrid: A.D. Becke, J. Chem. Phys. 98, 1372 (1993), ibid, 98, 5648 (1993), ibid 88, 1053 (1988)
(obtained from linear interpolation between Hartree-Fock and DFT)

Derivation of the kinetic energy term for non-interacting electron gas:

$T[\rho] = A \int \rho^{5/3}(\mathbf{r})\, d\mathbf{r}$

Derivation of exchange term for non-interacting electron gas LDA $\varepsilon_x(\rho)$):

$E_x[\rho] = -C \int \rho^{4/3}(\mathbf{r})\, d\mathbf{r}$

Use of pseudopotentials – why they are used and advantages – ["PracticalconcernsDFT.pdf"]

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I. Theoretical Background (continued)

Definition of Brillouin zone and irreducible Brillouin zone - ["PracticalconcernsDFT.pdf"]
Monkhorst-Pack approach to efficient numerical integration in k-space (k-point sampling):
Monkhorst and Pack, Phys. Rev. B **13**, 5188 (1976)
Smearing Method of Methfessel and Paxton, Phys. Rev. B **40**, 3616 (1989)

II. Practical DFT calculations

Energy cutoff, k-space sampling, testing for convergence
Use of VASP package: INCAR, OUTCAR, POTCAR etc.
Energy minimization
Bulk lattice constants
Bulk compressibility
Tutorial calculations for bulk metals and semiconductors
Surface energy and structure and adsorbates on surfaces
Calculation of activation barriers using the nudged elastic band (NEB) method

III. Additional topics

Calculation of density of states
Phonons
Ab-initio molecular dynamics
DFT + X: Methods for improved treatment of electron correlation
(DFT+U, GW)
Linear scaling methods
Van der Waals interactions (Ruiz, Liu, Zojer, Scheffler, Tkatchenko, Phys. Rev. Lett. **108**, 146103 (2012) and Tkatchenko and Scheffler, Phys. Rev. Lett. **102**, 073005 (2009))