PHY 752 Solid State Physics
11-11:50 AM MWF Olin 107

Plan for Lecture 13:
Reading: Chapter 9 in MPM
Density functional theory

1. Thomas-Fermi theory
2. Some practical considerations of density functional theory

Course schedule for Spring 2015

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	MPM Reading	Topic	Assign.	Due date
1	Mon: 01/12/2015	Chap. 1 & 2	Crystal structures	#1	01/23/2015
2	Wed: 01/14/2015	Chap. 1 & 2	Some group theory	#2	01/23/2015
	Fri: 01/16/2015	No class	NAWH out of town		
	Mon: 01/19/2015	No class	MLK Holiday		
3	Wed: 01/21/2015	Chap. 1 & 2	Some group theory	#3	01/23/2015
4	Fri: 01/23/2015	Chap. 1 & 2	Some more group theory	#4	01/26/2015
5	Mon: 01/26/2015	Chap. 7.3	Some more group theory	#5	01/28/2015
6	Wed: 01/28/2015	Chap. 6	Electronic structure; Free electron gas	#6	01/30/2015
7	Fri: 01/30/2015	Chap. 7	Electronic structure; Model potentials	#7	02/02/2015
8	Mon: 02/02/2015	Chap. 8	Electronic structure; LCAO	#8	02/04/2015
9	Wed: 02/04/2015	Chap. 8	Electronic structure; LCAO and tight binding	#9	02/06/2015
10	Fri: 02/06/2015	Chap. 8	Band structure examples	#10	02/09/2015
11	Mon: 02/09/2015	Chap. 9	Electron-electron interactions	#11	02/11/2015
12	Wed: 02/11/2015	Chap. 9	Electron-electron interactions	#12	02/13/2015
13	Fri: 02/13/2015	Chap. 9	Electron-electron interactions	#13	02/16/2015

Note: Take-home exam scheduled for the week of March 2nd.

Summary of results for expressing the electronic energy in terms of the density:

$$E_v[\Psi] \equiv E_v[n] = F[n] + \int d^3r\ v(\mathbf{r})\ n(\mathbf{r})$$

$$E_v[n] = T[n] + E_{ee}[n] + E_{ex}[n] + E_{ext}[n]$$

General forms:

$$E_{ext}[n] \equiv \int d^3r\ v(\mathbf{r})\ n(\mathbf{r})$$

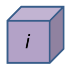
$$E_{ee} = \frac{e^2}{2}\int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Special for jellium:

$$T[n] = \frac{\hbar^2 \mathcal{V}}{2m}\frac{3}{5}\left(3\pi^2\right)^{2/3} n^{5/3}$$

$$E_{ex}[n] = -\frac{3\mathcal{V}e^2 n}{4\pi}\left(3\pi^2 n\right)^{1/3}$$

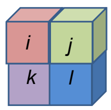
Jellium extension



Box of volume $\mathcal{V}$ containing N_i electrons

with energy $E_i = V_i + \frac{\hbar^2 \mathcal{V}}{2m} \frac{3}{5} \left(3\pi^2\right)^{2/3} n_i^{5/3}$

Local potential at site *i*



Slowly varying potential and electron density:

$$E(\mathbf{r}) = V(\mathbf{r}) + \frac{\hbar^2 \mathcal{V}}{2m} \frac{3}{5} \left(3\pi^2\right)^{2/3} n(\mathbf{r})^{5/3}$$

Explicit density functional based on extended jellium model

$$E_v[n] = T[n] + E_{ee}[n] + E_{ex}[n] + E_{ext}[n]$$

$$T[n] = \frac{\hbar^2}{2m} \frac{3}{5} \left(3\pi^2\right)^{2/3} \int d^3r \; n(\mathbf{r})^{5/3}$$

$$E_{ee} = \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$E_{ex}[n] = -\frac{3e^2}{4\pi} \left(3\pi^2\right)^{1/3} \int d^3r \; n(\mathbf{r})^{4/3}$$

$$E_{ext}[n] \equiv \int d^3r \; v(\mathbf{r}) \; n(\mathbf{r})$$

Thomas-Fermi theory

Thomas, *Proc. Cambridge Phil. Soc.* **23**, 542 (1927) Fermi, *Z. Physik* **48**, 73 (1928)

Minimize $E_v[n]$ subject to the constraint

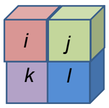
$$\int d^3r \; n(\mathbf{r}) = N[n]$$

$$\frac{\delta E_v[n]}{\delta n} = \mu \frac{\delta N[n]}{\delta n}$$

Fermi-Thomas-Dirac equation:

$$\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3} n(\mathbf{r})^{2/3} + e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$-\frac{e^2}{\pi}\left(3\pi^2\right)^{1/3} n(\mathbf{r})^{1/3} + v(\mathbf{r}) = \mu$$



Relationship of electron density $n(\mathbf{r})$ to local potential $V(\mathbf{r})$ in Fermi-Thomas picture:

$$\frac{\hbar^2\left(3\pi^2 n(\mathbf{r})\right)^{2/3}}{2m} + V(\mathbf{r}) = 0$$

Unfortunately, Thomas-Fermi theory predicts that atoms never bind into molecules.

Modern extensions – Orbital Free DFT

PRL **111,** 066402 (2013) PHYSICAL REVIEW LETTERS week ending 9 AUGUST 2013

Angular-Momentum-Dependent Orbital-Free Density Functional Theory

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Orbital-free (OF) density functional theory (DFT) directly solves for the electron density rather than the wave function of many electron systems, greatly simplifying and enabling large scale first principles simulations. However, the required approximate noninteracting kinetic energy density functionals and local electron-ion pseudopotentials severely restrict the general applicability of conventional OFDFT. Here, we present a new generation of OFDFT called angular-momentum-dependent (AMD)-OFDFT to harness the accuracy of Kohn-Sham DFT and the simplicity of OFDFT. The angular momenta of electrons are explicitly introduced within atom-centered spheres so that the important ionic core region can be accurately described. In addition to conventional OF total energy functionals, we introduce a crucial nonlocal energy term with a set of AMD energies to correct errors due to the kinetic energy density functional and the local pseudopotential. We find that our AMD-OFDFT formalism offers substantial improvements over conventional OFDFT, as we show for various properties of the transition metal titanium.

DOI: 10.1103/PhysRevLett.111.066402 PACS numbers: 71.15.Mb, 71.20.Be

Kohn-Sham formulation of density functional theory

Let $n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$

Resulting equations for orbitals $\phi_i(\mathbf{r})$:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{ee}(\mathbf{r}) + V_{ex}(\mathbf{r}) + v(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$V_{ee}(\mathbf{r}) = \frac{\delta E_{ee}[n]}{\delta n} = e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$V_{ex}(\mathbf{r}) = \frac{\delta E_{ex}[n]}{\delta n} = -\frac{e^2}{\pi}\left(3\pi^2\right)^{1/3} n(\mathbf{r})^{1/3}$$

$$V_{ext}(\mathbf{r}) = \frac{\delta E_{ext}[n]}{\delta n} = v(\mathbf{r})$$

Self-consistent solution

Iteration $\alpha = 0$

$\{\phi_i^\alpha(\mathbf{r})\}$

$n^\alpha(\mathbf{r}) = \sum_i |\phi_i^\alpha(\mathbf{r})|^2$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V^\alpha{}_{ee}(\mathbf{r}) + V^\alpha{}_{ex}(\mathbf{r}) + v(\mathbf{r})\right)\phi_i^{\alpha+1}(\mathbf{r}) = \epsilon_i \phi_i^{\alpha+1}(\mathbf{r})$$

$n_{temp}^{\alpha+1}(\mathbf{r}) = \sum_i |\phi_i^{\alpha+1}(\mathbf{r})|^2$

$n^{\alpha+1}(\mathbf{r}) = x n_{temp}^{\alpha+1}(\mathbf{r}) + (1-x) n^{\text{\alpha}}(\mathbf{r})$

$\alpha + 1 \Rightarrow \alpha$

Kohn-Sham formulation of density functional theory
Results of self-consistent calculations

Variationally determined --

Ground state energy $E_v[n]$

Electron density $n(\mathbf{r})$

Some remaining issues

- Theory for $E_{exc}[n]$ still underdevelopment
- This formalism does not access excited states
- Strongly correlated electron systems are not well approximated

Examples of E_{exc} -- Local Density Approximation (LDA)

PHYSICAL REVIEW B VOLUME 45, NUMBER 23 15 JUNE 1992-I

Accurate and simple analytic representation of the electron-gas correlation energy

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(Received 31 January 1992)

We propose a simple analytic representation of the correlation energy ε_c for a uniform electron gas, as a function of density parameter r_s and relative spin polarization ζ. Within the random-phase approximation (RPA), this representation allows for the $r_s^{-3/4}$ behavior as $r_s \to \infty$. Close agreement with numerical RPA values for $\varepsilon_c(r_s,0)$, $\varepsilon_c(r_s,1)$, and the spin stiffness $\alpha_c(r_s) = \partial^2\varepsilon_c(r_s, \zeta=0)/\delta\zeta^2$, and recovery of the correct $r_s \ln r_s$ term for $r_s \to 0$, indicate the appropriateness of the chosen analytic form. Beyond RPA, different parameters for the same analytic form are found by fitting to the Green's-function Monte Carlo data of Ceperley and Alder [Phys. Rev. Lett. **45**, 566 (1980)], taking into account data uncertainties that have been ignored in earlier fits by Vosko, Wilk, and Nusair (VWN) [Can. J. Phys. **58**, 1200 (1980)] or by Perdew and Zunger (PZ) [Phys. Rev. B **23**, 5048 (1981)]. While we confirm the practical accuracy of the VWN and PZ representations, we eliminate some minor problems with these forms. We study the ζ-dependent coefficients in the high- and low-density expansions, and the r_s-dependent spin susceptibility. We also present a conjecture for the exact low-density limit. The correlation potential $\mu_c^\sigma(r_s,\zeta)$ is evaluated for use in self-consistent density-functional calculations.

Examples of E_{exc} -- Generalized Gradient Approximation (GGA)

VOLUME 77, NUMBER 18 PHYSICAL REVIEW LETTERS 28 OCTOBER 1996

Generalized Gradient Approximation Made Simple

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(Received 21 May 1996)

Generalized gradient approximations (GGA's) for the exchange-correlation energy improve upon the local spin density (LSD) description of atoms, molecules, and solids. We present a simple derivation of a simple GGA, in which all parameters (other than those in LSD) are fundamental constants. Only general features of the detailed construction underlying the Perdew-Wang 1991 (PW91) GGA are invoked. Improvements over PW91 include an accurate description of the linear response of the uniform electron gas, correct behavior under uniform scaling, and a smoother potential. [S0031-9007(96)01479-2]

Some details of the Generalized Gradient Approximation

$$E_{xc} = \int d^3r\, f(n(\mathbf{r}), |\nabla n(\mathbf{r})|).$$

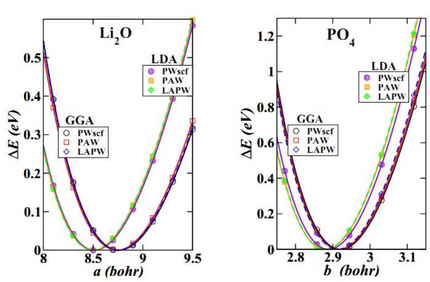
$$v_{xc}(\mathbf{r}) = \frac{\partial f(n, |\nabla n|)}{\partial n} - \nabla \cdot \left(\frac{\partial f(n, |\nabla n|)}{\partial |\nabla n|} \frac{\nabla n}{|\nabla n|} \right).$$

Note that $|\nabla n| \equiv \sqrt{\left(\frac{\partial n}{\partial x}\right)^2 + \left(\frac{\partial n}{\partial y}\right)^2 + \left(\frac{\partial n}{\partial z}\right)^2}$

$$\frac{\partial |\nabla n|}{\partial (\partial n / \partial x)} = \frac{\partial n / \partial x}{|\nabla n|}$$

Comparison of LDA and GGA binding energy curves

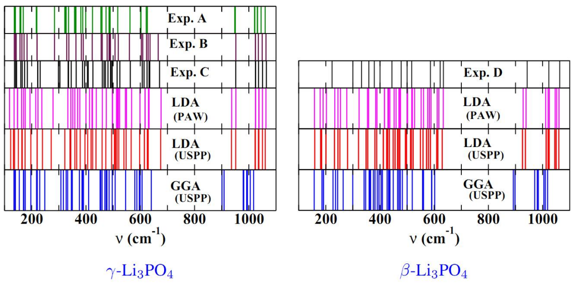
Test results for simple oxides



Fluorite structure Tetrahedral molecule

LDA vs GGA performance wrt normal modes of vibration

Raman spectra – Experiment & Calculation



A: B. N. Mavrin et al, J. Exp. Theor. Phys. **96**,53 (2003); B: F. Harbach and F. Fischer, Phys. Status Solidi B **66**, 237 (1974) – room temp. C: Ref. B at liquid nitrogen temp.; D: L. Popović et al, J. Raman Spectrosc. **34**,77 (2003).

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