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

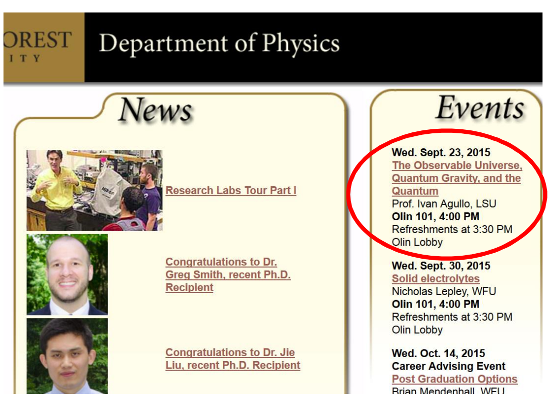
Plan for Lecture 13:
Reading: Chapter 4 in GGGPP
Approximations to the many electron problem -- Density functional theory

1. General theorem
2. Practical calculation scheme
3. Some results

Course schedule

(Preliminary schedule -- subject to frequent adjustment.)

	Date	F&W Reading	Topic	Assignment
1	Wed, 8/26/2015	Chap. 1.1-1.2	Electrons in a periodic one-dimensional potential	#1
2	Fri, 8/28/2015	Chap. 1.3	Electrons in a periodic one-dimensional potential	#2
3	Mon, 8/31/2015	Chap. 1.4	Tight binding models	#3
4	Wed, 9/02/2015	Chap. 1.6, 2.1	Crystal structures	#4
5	Fri, 9/04/2015	Chap. 2	Group theory	#5
6	Mon, 9/07/2015	Chap. 2	Group theory	#6
7	Wed, 9/09/2015	Chap. 2	Group theory	#7
8	Fri, 9/11/2015	Chap. 2	Group theory	#7
9	Mon, 9/14/2015	Chap. 2.4-2.7	Densities of states	#8`
10	Wed, 9/16/2015	Chap. 3	Free electron model	#9
11	Fri, 9/18/2015	Chap. 4	One electron approximations to the many electron problem	#10
12	Mon, 9/21/2015	Chap. 4	One electron approximations to the many electron problem	#11
13	Wed, 9/23/2015	Chap. 4	Density functional theory	#12
14	Fri, 9/25/2015			
15	Mon, 9/28/2015			
16	Wed, 9/30/2015			
17	Fri, 10/02/2015			



WFU Physics Colloquium

TITLE: The Observable Universe, Gravity, and the Quantum

SPEAKER: Professor Ivan Agullo,

Department of Physics and Astronomy,
Louisiana State University

TIME: Wednesday September 23, 2015 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

ABSTRACT

An important difficulty in the search for a satisfactory theory of quantum gravity is the absence of experimental guidance. The astonishing improvement in cosmological observations attained in the last years offers an exciting opportunity to change this situation. It is believed that the anisotropies observed in the cosmic microwave background were originated in the very early universe. Observing their details could therefore tell us about physics in such extreme conditions.

In this talk, I will review the physics of the genesis of cosmic non-uniformities, paying special attention to the interplay between quantum effects and gravitation. I will describe how the forthcoming observations could provide detailed information about processes where the relationship between gravity and quantum mechanics plays a crucial role.

Density functional theory

Describes the relationship between the many electron problem and independent electron treatments.

Proof of theorem

Estimates of *F[n].*

Density functional theory -- continued

PHYSICAL REVIEW VOLUME 136, NUMBER 3B 9 NOVEMEBR 1964

Inhomogeneous Electron Gas*

P. Hohenberg†
École Normale Superieure, Paris, France
AND
W. Kohn‡
École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France
and
University of California at San Diego, La Jolla, California
(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$, $\tilde{n}/n_0 << 1$, and (2) $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \to \infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

PHYSICAL REVIEW VOLUME 140, NUMBER 4A 15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

W. Kohn and L. J. Sham
University of California, San Diego, La Jolla, California
(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

Hohenberg and Kohn: formal proof of basic theorem

The system consists of N electrons interacting via their mutual Coulomb repulsion in the presence of an "external" single particle potential $v(\mathbf{r})$.

$$H = T \quad + \quad V \quad + \quad U$$

Kinetic energy — External potential — Coulomb interaction

Consider a many Fermion wavefunction $|\Psi\rangle$.

The (many electron) density can be calculated from $n(\mathbf{r}) = \langle\Psi|\sum_i \delta(\mathbf{r}-\mathbf{r}_i)|\Psi\rangle$

$$= N\int d^3r_1....d^3r_N \Psi^*(r_1,r_2.....r_N)\sum_i \delta(\mathbf{r}-\mathbf{r}_i)\Psi(r_1,r_2.....r_N)$$

Theorem: The density *n(r)* of the ground state of the system is a unique functional of the external potential *v(r)*.

Proof: Consider two Hamiltonians *H* and *H'* differing only by external potentials *v* and *v'*.

Ground state energies: $E = \langle\Psi|H|\Psi\rangle$

and $E' = \langle\Psi'|H'|\Psi'\rangle$

Note that $E' = \langle\Psi'|H'|\Psi'\rangle \le \langle\Psi|H'|\Psi\rangle$

$$\langle\Psi|H'|\Psi\rangle = \langle\Psi|H + V' - V|\Psi\rangle$$

$$= \langle\Psi|H|\Psi\rangle + \langle\Psi|V' - V|\Psi\rangle$$

$$= E + \int d^3r\; n(\mathbf{r})\left(v'(\mathbf{r}) - v(\mathbf{r})\right)$$

$$\Rightarrow E' \le E + \int d^3r\; n(\mathbf{r})\left(v'(\mathbf{r}) - v(\mathbf{r})\right)$$

We can also show:

Note that $E = \langle\Psi|H|\Psi\rangle \le \langle\Psi'|H|\Psi'\rangle$

$$\langle\Psi'|H|\Psi'\rangle = \langle\Psi'|H' + V - V'|\Psi'\rangle$$

$$= \langle\Psi|H|\Psi\rangle + \langle\Psi|V' - V|\Psi\rangle$$

$$= E' + \int d^3r\; n'(\mathbf{r})\left(v(\mathbf{r}) - v'(\mathbf{r})\right)$$

$$\Rightarrow E \le E' + \int d^3r\; n'(\mathbf{r})\left(v(\mathbf{r}) - v'(\mathbf{r})\right)$$

$$E' \le E + \int d^3r\; n(\mathbf{r})\left(v'(\mathbf{r}) - v(\mathbf{r})\right)$$

$$E \le E' + \int d^3r\; n'(\mathbf{r})\left(v(\mathbf{r}) - v'(\mathbf{r})\right)$$

$$\Rightarrow n(\mathbf{r}) \equiv n'(\mathbf{r}) \quad \text{if} \quad v(\mathbf{r}) \equiv v'(\mathbf{r})$$

The theorem implies that the ground state energy *E* can be considered as a functional of the density *n(**r**)*

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

Thus, the determination of the ground state energy E is transformed into a minimization of the functional with respect to the density *n(**r**)*, transforming a many particle minimization into a single particle minimization.

In practice, the functional form of *F[n]* is not known, but if it were, we could use optimization methods to determine the ground state energy $E_v[n]$.

Kohn-Sham scheme to find ground state energy $E_v[n]$

Assume that the electron density can be expressed in terms of *N* independent electron orbitals

$$n(\mathbf{r}) = \sum_i \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}),$$

For a given external potential $v_{ext}(\mathbf{r})$ the ground state energy is given by

$$E^{(\mathrm{HK})}[n(\mathbf{r}); v_{\mathrm{ext}}(\mathbf{r})] = T_0[n] + E_H[n] + \int v_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r})\,d\mathbf{r} + E_{\mathrm{xc}}[n],$$

$$T_0[n] = \sum_i \langle\phi_i| - \frac{\hbar^2\nabla^2}{2m}|\phi_i\rangle. \quad E_H[n] = \frac{1}{2}\int n(\mathbf{r})\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}n(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'$$

Kohn-Sham equations

$$\boxed{\left[-\frac{\hbar^2\nabla^2}{2m} + V_{\mathrm{nucl}}(\mathbf{r}) + V_{\mathrm{coul}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})},$$

where

$$V_{\mathrm{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})} \qquad v_{\mathrm{ext}}(\mathbf{r}) = -\sum_I \frac{z_I e^2}{|\mathbf{r}-\mathbf{R}_I|} \equiv V_{\mathrm{nucl}}(\mathbf{r}).$$

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

Estimate of the exchange-correlation contribution

$$E_{exc}[n] = E_{ex}[n] + E_c[n]$$

$$E_{ex} = -\frac{e^2}{2}\sum_{i,j}\delta_{\sigma_i\sigma_j}\int d^3r\,\phi_{n_i\mathbf{k}_i\sigma_i}{}^*(\mathbf{r})\phi_{n_j\mathbf{k}_j\sigma_j}(\mathbf{r})\int d^3r'\,\frac{\phi_{n_j\mathbf{k}_j\sigma_j}{}^*(\mathbf{r}')\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

For jellium:

$$\phi_{n_j\mathbf{k}_j\sigma_j}(\mathbf{r}) = \frac{1}{\sqrt{\mathcal{V}}}e^{i\mathbf{k}_j\cdot\mathbf{r}}$$

It can be shown that

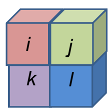
$$E_{ex}[n] = -\frac{2e^2k_F^4}{(2\pi)^3} = -\frac{2e^2\left(3\pi^2 n\right)^{4/3}}{(2\pi)^3} = -\frac{3e^2 n}{4\pi}\left(3\pi^2 n\right)^{1/3}$$

Note that in this case:

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

Digression on spatially varying electron density

$$k_F^i = \left(3\pi^2 n_i\right)^{1/3}$$



$$\Rightarrow \quad k_F(\mathbf{r}) = \left(3\pi^2 n(\mathbf{r})\right)^{1/3}$$

Correlation functionals
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.

Interpolation function for LDA:

$$E_c[n] = -2A(1+\alpha_1 r_s)\ln\left\{1+\frac{1}{2A(\beta_1 r_s^{1/2}+\beta_2 r_s+\beta_3 r_s^{3/2}+\beta_4 r_s^{P+1})}\right\}.$$

Where: $n = \frac{1}{\frac{4\pi r_s^3}{3a_B^3}}$

More complicated exchange-correlation functionals

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]

$$E_{\rm XC}^{\rm GGA}[n_\uparrow, n_\downarrow] = \int d^3r\, f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow).$$

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

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

Summary: 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 --

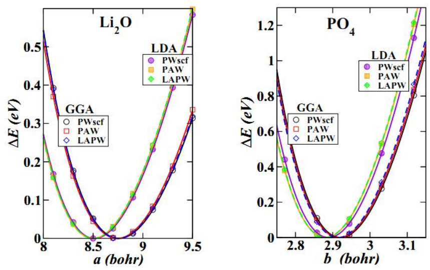
Ground state energy $E_v[n]$

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

Comparison of LDA and GGA binding energy curves

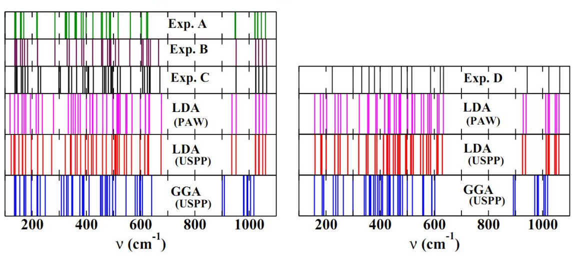
Test results for simple oxides



Fluorite structure — Tetrahedral molecule

LDA vs GGA performance wrt normal modes of vibration

Raman spectra – Experiment & Calculation



γ-Li$_3$PO$_4$ — β-Li$_3$PO$_4$

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).