

PHY 742 Quantum Mechanics II

1-1:50 AM MWF via video link:

<https://wakeforest-university.zoom.us/my/natalie.holzwarth>

Extra notes for Lecture 31

**Density functional formalism for treating
multi electron systems**

- 1. General theorem**
- 2. Practical calculation schemes**
- 3. Examples**

04/17/2020

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We will discuss the density functional theorem and its proof.

21	Mon: 03/23/2020	Chap. 17	Quantization of the Electromagnetic Field	#17	03/25/2020
22	Wed: 03/25/2020	Chap. 17	Quantization of the Electromagnetic Field	#18	03/27/2020
23	Fri: 03/27/2020	Chap. 17	Quantization of the Electromagnetic Field	#19	03/30/2020
24	Mon: 03/30/2020	Chap. 18	Photons and atoms		
25	Wed: 04/01/2020	Chap. 10	Multiparticle systems	#20	04/03/2020
26	Fri: 04/03/2020	Chap. 10	Multiparticle systems	#21	04/06/2020
27	Mon: 04/06/2020	Chap. 10	Multielectron atoms	#22	04/08/2020
28	Wed: 04/08/2020	Chap. 10	Multielectron atoms		
	Fri: 04/10/2020	No class	<i>Good Friday</i>		
29	Mon: 04/13/2020	Chap. 10	Multielectron atoms	#23	04/15/2020
30	Wed: 04/15/2020		Hartree-Fock and other formalisms	#24	04/17/2020
31	Fri: 04/17/2020		Density functional theory		
32	Mon: 04/20/2020				
33	Wed: 04/22/2020				
34	Fri: 04/24/2020				
35	Mon: 04/27/2020				
36	Wed: 04/29/2020		Review		

Ongoing schedule

Your questions –

From Trevor

1. I'm not sure what slide 14 is trying to imply.
2. On slide 16, what do the alpha's and beta's represent?

Comments – will be made in context --

Density functional theory

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

Proof of theorem behind density functional theory

Estimates of $F[n]$.

Overview

Density functional theory -- continued

PHYSICAL REVIEW

VOLUME 136, NUMBER 3B

9 NOVEMBER 1964

Inhomogeneous Electron Gas*

P. HOHENBERG†

École Normale Supérieure, Paris, France

AND

W. KOHN‡

École Normale Supérieure, 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 $v(r)$. It is proved that there exists a universal functional of the density, $F[n(r)]$, independent of $v(r)$, such that the expression $E = \int v(r)n(r)dr + F[n(r)]$ has as its minimum value the correct ground-state energy associated with $v(r)$. The functional $F[n(r)]$ is then discussed for two situations: (1) $n(r) = n_0 + \delta n(r)$, $\delta n/n_0 \ll 1$, and (2) $n(r) = \varphi(r/r_0)$ with φ arbitrary and $r_0 \rightarrow \infty$. 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 $\frac{1}{2}$.) 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.

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Original papers

The Nobel Prize in Chemistry 1998

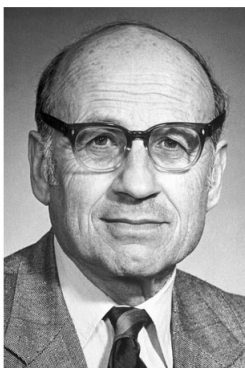


Photo from the Nobel Foundation archive.

Walter Kohn

Prize share: 1/2

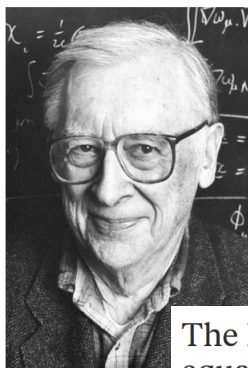


Photo from the Nobel F archive.

John A. Pople

Prize share: 1/2

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry."

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Nobel prize for Walter Kohn

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 $v(\mathbf{r})$.

$$H = \underbrace{T}_{\text{Kinetic energy}} + \underbrace{V}_{\text{External potential}} + \underbrace{U}_{\text{Coulomb interaction}}$$

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

The (many electron) density can be calculated

$$\begin{aligned} \text{from } n(\mathbf{r}) &= \langle \Psi | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle \\ &= N \int d^3 r_1 \dots d^3 r_N \Psi^*(r_1, r_2, \dots, r_N) \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \Psi(r_1, r_2, \dots, r_N) \end{aligned}$$

Setting up the problem.

Theorem: The density $n(\mathbf{r})$ of the ground state of the system is a unique functional of the external potential $v(\mathbf{r})$.

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

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

Suppose $n(\mathbf{r})$ is the same for H and H' .

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

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

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

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

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

$$\Rightarrow E' \leq E + \int d^3r n(\mathbf{r})(v'(\mathbf{r}) - v(\mathbf{r}))$$

Proof of theorem

We can also show:

$$\begin{aligned}\text{Note that } E &= \langle \Psi | H | \Psi \rangle \leq \langle \Psi' | H | \Psi' \rangle \\ \langle \Psi' | H | \Psi' \rangle &= \langle \Psi' | H' + V - V' | \Psi' \rangle \\ &= \langle \Psi' | H | \Psi' \rangle + \langle \Psi' | V' - V | \Psi' \rangle \\ &= E' + \int d^3r n'(\mathbf{r})(v(\mathbf{r}) - v'(\mathbf{r})) \\ \Rightarrow E &\leq E' + \int d^3r n'(\mathbf{r})(v(\mathbf{r}) - v'(\mathbf{r})) \\ E' &\leq E + \int d^3r n(\mathbf{r})(v'(\mathbf{r}) - v(\mathbf{r})) \\ E &\leq E' + \int d^3r n'(\mathbf{r})(v(\mathbf{r}) - v'(\mathbf{r}))\end{aligned}$$

Continued

$$E' \leq E + \int d^3r n(\mathbf{r})(v'(\mathbf{r}) - v(\mathbf{r}))$$

$$E \leq E' + \int d^3r n'(\mathbf{r})(v(\mathbf{r}) - v'(\mathbf{r}))$$

Now suppose that $n(\mathbf{r}) \equiv n'(\mathbf{r})$

It follows that $E + E' \leq E + E'$

From what we can conclude that

$$E = E' \quad \text{and} \quad v(\mathbf{r}) = v'(\mathbf{r}).$$

$\Rightarrow n(\mathbf{r})$ is an unique functional of $v(\mathbf{r})$.

Punch line

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 $E_v[n]$.

Significance of theorem

What is the big fuss over this theorem?

- 1. Overrated, overblown, ignorable...**
- 2. Enables practical simulations of otherwise numerically difficult exact equations.**

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 $v_{\text{ext}}(\mathbf{r})$ the ground state energy is given by

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

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

Underlying assumption: If we represent the electron density correctly, we can solve the multi electron physics correctly.

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Kohn Sham equations

In practice, we use single particle analysis to treat the many electron systems --

Kohn-Sham equations

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V_{\text{nuc1}}(\mathbf{r}) + V_{\text{coul}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}),$$

where

$$V_{\text{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \quad v_{\text{ext}}(\mathbf{r}) = - \sum_I \frac{z_I e^2}{|\mathbf{r} - \mathbf{R}_I|} \equiv V_{\text{nuc1}}(\mathbf{r}).$$

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

Estimate of the exchange-correlation contribution

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

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

For jellium:

It can be shown that

$$\phi_{n, \mathbf{k}_j, \sigma_j}(\mathbf{r}) = \frac{1}{\sqrt{\mathcal{V}}} e^{i\mathbf{k}_j \cdot \mathbf{r}} \quad E_{ex}[n] = -\frac{2e^2 k_F^4}{(2\pi)^3} = -\frac{2e^2 (3\pi^2 n)^{4/3}}{(2\pi)^3}$$
$$= -\frac{3e^2 n}{4\pi} (3\pi^2 n)^{1/3}$$


Note that in this case:

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

Practical implementations

Digression – How is the electron density related to the Fermi wave vector k_F ?

For a free electron system of N spin 1/2 particles, the Fermi sphere times 2 can accommodate those electrons:

$$\frac{\Omega}{(2\pi)^3} 2 \left(\frac{4\pi k_F^3}{3} \right) = N \quad k_F = \left(3\pi^2 \frac{N}{\Omega} \right)^{1/3} \equiv (3\pi^2 n)^{1/3}$$


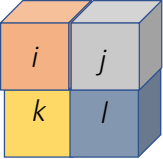
Here Ω represents the volume of the box containing N electrons

Factor that accounts for the number of wave vectors within the Fourier space (reciprocal space) increment

Digression – How is the electron density related to the Fermi wave vector k_F ?

The previous analysis assumed that we have a very large volume to contain our free electrons. Now imagine that we have several such boxes i, j, k, \dots with electron numbers N_i, N_j, \dots

Digression on spatially varying electron density

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


For a free electron system of N spin 1/2 particles, the Fermi sphere times 2 can accommodate those electrons:

$$\frac{\Omega}{(2\pi)^3} 2 \left(\frac{4\pi k_F^3}{3} \right) = N \quad k_F = \left(3\pi^2 \frac{N}{\Omega} \right)^{1/3} \equiv (3\pi^2 n)^{1/3}$$

How to cheat position dependence.

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

John P. Perdew and Yue Wang*

Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118
(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 $r_s \rightarrow \infty$. Close agreement with numerical RPA values for $\epsilon_c(r_s, 0)$, $\epsilon_c(r_s, 1)$, and the spin stiffness $\alpha_c(r_s) = \partial^2 \epsilon_c(r_s, \zeta=0) / \delta \zeta^2$, and recovery of the correct $r_s \ln r_s$ term for $r_s \rightarrow 0$, 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 $\mu_c^s(r_s, \zeta)$ is evaluated for use in self-consistent density-functional calculations.

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Correlations affecta

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

Here the coefficients α_i β_j etc. are fitting parameters to an accurate many electron calculation (determined by David Ceperly using Monte Carlo methods).

Some details

More complicated exchange-correlation functionals

VOLUME 77, NUMBER 18

PHYSICAL REVIEW LETTERS

28 OCTOBER 1996

Generalized Gradient Approximation Made Simple

John P. Perdew, Kieron Burke,* Matthias Ernzerhof

Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118
(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]

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

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More complication

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

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

Necessary details.

Summary: Kohn-Sham formulation of density functional theory

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

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

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

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

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

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

Practical implementation

Self-consistent solution

Iteration $\alpha = 0$

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

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

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

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

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

$\alpha + 1 \Rightarrow \alpha$

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Iteration scheme.

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

Perspective.