

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 32

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

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

We will illustrate the details of density functional theory for atoms.

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		Density functional theory for atoms		
33	Wed: 04/22/2020				
34	Fri: 04/24/2020				
35	Mon: 04/27/2020				
36	Wed: 04/29/2020		Review		

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Ongoing schedule

Your questions –

From Trevor

1. On slide 8 we consider a carbon atom, and the assumption is made that it is spherically symmetric. Is this a safe assumption for atoms in general, and if not, what conditions need to be met for an atom to be asymmetric?

From Surya

1. I know in DFT people used terms like "exchange-correlation hole" and local exchange-correlation, can you plz. enlighten these terms?

Comments – will be made in context

Summary of results for density functional theory –

For a system with a given one-electron potential $v(r)$, there is a unique density $n(r)$ which describes the system in its ground state. Although the density $n(r)$ is a collective property of the system, it can be described by a single particle function and it implies that the task of finding the electronic ground state of the multi electron system can be mapped to a process of solving a related single particle problem self-consistently.

Total energy

$$E_{KS}(n(\mathbf{r})) = E_{kin}(n(\mathbf{r})) + E_v(n(\mathbf{r})) + E_{Hartree}(n(\mathbf{r})) + E_{xc}(n(\mathbf{r}))$$



Kinetic energy

**Single particle
interaction**

**Electron-electron
repulsion**

**Exchange-correlation
energy**

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Summary of the theorem and of the various energy contributions.

Kohn-Sham scheme supposes that we can represent the density as a sum over one-electron orbitals

$$n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$

Here we are sweeping some details like spin under the rug....

$$E_{kin}(n(\mathbf{r})) = \sum_{i=1}^N \int d^3r \phi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \phi_i(\mathbf{r})$$

$$E_v(n(\mathbf{r})) = \int d^3r v(\mathbf{r})n(\mathbf{r})$$

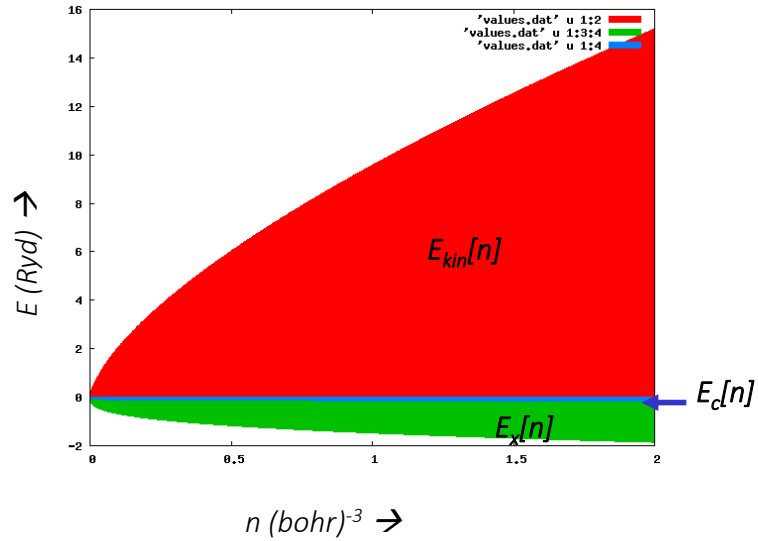
$$E_{Hartree}(n(\mathbf{r})) = \frac{e^2}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$E_{xc}(n(\mathbf{r})) = \int d^3r f_{xc}(n(\mathbf{r}))$$

Here are the formulas for the various contributions

Digression: Jellium energies

Question:
What about E_V ?



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This gives an idea of the order of magnitude of the terms as a function of density for the jellium model

Optimizing the energy with respect to the density,
maintaining orbital normalization:

$$\frac{\delta E_{KS}}{\delta \phi_i^*} = H_{KS} \phi_i = \epsilon_i \phi_i$$

$$H_{KS} = -\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}(\mathbf{r})$$

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

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n} \quad V_{xc} = V_x + V_c$$

Original Kohn-Sham exchange: $V_x(\mathbf{r}) = -\frac{e^2}{\pi} (3\pi^2)^{1/3} n(\mathbf{r})^{1/3}$

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Various potential terms.

Digression – notion of an exchange-correlation “hole”


Note that the notion of a “hole” in condensed matter physics usually means the absence of an electron in some region of space which would generally provide an attractive interaction for electrons.

In terms of the one electron orbitals $\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r})$ the exchange interaction:

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

Functional derivative:

$$V_x(\mathbf{r}) = \frac{\delta E_x}{\delta \phi_{n_i\mathbf{k}_i\sigma_i}^*} = -e^2 \sum_j \delta_{\sigma_i\sigma_j} \phi_{n_j\mathbf{k}_j\sigma_j}(\mathbf{r}) \int d^3r' \frac{\phi_{n_j\mathbf{k}_j\sigma_j}^*(\mathbf{r}') \phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

 **Attractive interaction**

Numerical methods for solving the Kohn-Sham equations

Self-consistent solution

Iteration $\alpha = 0$

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

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

$$H_{KS}^\alpha(\mathbf{r})\phi_i^{\alpha+1}(\mathbf{r}) = \epsilon_i\phi_i^{\alpha+1}(\mathbf{r})$$

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

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

$\alpha + 1 \Rightarrow \alpha$

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Iteration scheme

Numerical methods for solving the Kohn-Sham equations –
Consider the case of a single atom, choosing the coordinate
system at the center of the nucleus. We will further assume
that the atom is spherically symmetric, averaging over the
multiplet configurations.

2	6	³ P ₀
C		
Carbon		
12.011*		
1s ² 2s ² 2p ²		
11.2603		

$$n(\mathbf{r}) = n(r)$$

$$\phi_i(\mathbf{r}) = \phi_{n_i l_i}(r) Y_{l_i m_i}(\hat{\mathbf{r}})$$

$$n(r) = 4\pi \sum_i w_{n_i l_i} |\phi_{n_i l_i}(r)|^2$$

$$\text{where } 0 \leq w_{n_i l_i} \leq 2(2l_i + 1)$$

Example of Carbon atom

Digression – why might we think that the atom is spherically symmetric?

- 1. If the atom is isolated (as in a monoatomic gas), there should be no preferred direction in space**
- 2. If the atom were bonded as in a molecule or solid, the atom is typically not in a spherical environment**

In case #1, how do we reconcile the notion of spherical symmetry with the atomic terms which in this are 3P , 1D , 1S ?

- 1. This is a problem?**
- 2. No problem?**

Kohn-Sham equations for spherical atom

Equations for radial orbitals $\phi_{n,l_i}(r)$:

$$\left(-\frac{\hbar^2}{2m} \left(\frac{1}{r} \frac{d^2}{dr^2} r - \frac{l_i(l_i+1)}{r^2} \right) + v(r) + V_{Hartree}(r) + V_{xc}(r) \right) \phi_{n,l_i}(r) = \epsilon_{n,l_i} \phi_{n,l_i}(r)$$

$$v(r) = -\frac{Ze^2}{r}$$

$$V_{Hartree}(r) = \frac{\delta E_{Hartree}[n]}{\delta n} = e^2 \left(\frac{1}{r} \int_0^r r'^2 dr' n(r') + \int_r^\infty r' dr' n(r') \right)$$

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

Detailed equations

Kohn-Sham equations for spherical atom -- continued

$$\text{Let } \phi_{n_i l_i}(r) = \frac{P_{n_i l_i}(r)}{r} :$$

$$\left(-\frac{\hbar^2}{2m} \left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} \right) + v(r) + V_{Hartree}(r) + V_{xc}(r) \right) P_{n_i l_i}(r) = \epsilon_{n_i l_i} P_{n_i l_i}(r)$$

Convenient units:

$$\text{Bohr radius } a_B = \frac{\hbar^2}{me^2}$$

$$\text{Rydberg energy } E_R = \frac{\hbar^2}{2ma_B^2} = \frac{e^2}{2a_B} = 13.60569253 \text{ eV}$$

$$r \leftarrow r / a_B \quad \epsilon_{n_i l_i} \leftarrow \epsilon_{n_i l_i} / E_R$$

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Simplifying the differential equation and choosing convenient units.

Kohn-Sham equations for spherical atom -- continued

Equations in Rydberg units

$$\left(-\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} \right) + v(r) + V_{Hartree}(r) + V_{xc}(r) \right) P_{n,l_i}(r) = \epsilon_{n,l_i} P_{n,l_i}(r)$$

$$v(r) = -\frac{2Z}{r}$$

$$V_{Hartree}(r) = \frac{\delta E_{Hartree}[n]}{\delta n} = 2 \left(\frac{1}{r} \int_0^r r'^2 dr' n(r') + \int_r^\infty r' dr' n(r') \right)$$

$$V_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n} = -\frac{2}{\pi} (3\pi^2)^{1/3} n(r)^{1/3} + V_c(r)$$

Note that another convention differs by a factor of 2:

$$\text{Hartree energy } E_H = \frac{\hbar^2}{ma_B^2} = \frac{e^2}{a_B} = 27.21138505 \text{ eV}$$

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Some detailed equations

Kohn-Sham equations for spherical atom -- continued

Differential equations:

$$\left(-\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} \right) + \underbrace{v(r) + V_{Hartree}(r) + V_{xc}(r)}_{V(r)} \right) P_{n_i l_i}(r) = \epsilon_{n_i l_i} P_{n_i l_i}(r)$$

Boundary behaviors:

$$P_{n_i l_i}(r) \xrightarrow{r=0} C r^{l_i+1}$$

$$P_{n_i l_i}(r) \xrightarrow{r=\infty} C' e^{-\sqrt{|\epsilon_{n_i l_i}|} r}$$

Notes on numerical integration of differential equations

Please read numerov.pdf and then continue with this power point.

In order to solve these equations numerically we need to do two things

- 1. Change the differential equation into an algebraic equation, in this case, using finite difference methods**
- 2. Determine the “eigenvalues” ϵ_i .**

Digression on numerical integration

Consider the differential equation

$$-\frac{d^2 P_\nu(r)}{dr^2} = E_\nu P_\nu(r) \quad \text{with } P_\nu(0) = P_\nu(1) = 0$$

$$\text{Exact solution: } P_\nu(r) = C \sin(\nu\pi r) \quad E_\nu = \nu^2 \pi^2$$

Numerical results from second-order approximation:

	N=4	N=8	Exact
$\nu=1$	9.54915028	9.7697954	9.869604404
$\nu=2$	34.54915031	37.9008002	39.47841762

Numerical results from Numerov approximation:

	N=4	Exact
$\nu=1$	9.863097625	9.869604404
$\nu=2$	39.04581620	39.47841762

Some details about numerical integration

Some details:

Consider the differential equation

$$-\frac{d^2 P_v(r)}{dr^2} = E_v P_v(r) \quad \text{with } P_v(0) = P_v(1) = 0$$

$$\text{Exact solution: } P_v(r) = C \sin(\nu\pi r) \quad E_v = \nu^2 \pi^2$$

$$-\frac{d^2 P_v(r)}{dr^2} = E_v P_v(r)$$

$$r \rightarrow r_n \equiv ns \quad \text{for } n = 0, 1, 2, \dots, N \quad s = 1/N$$

$$-\frac{d^2 P_v(r_n)}{dr^2} \approx \frac{2P_v(r_n) - P_v(r_{n+1}) - P_v(r_{n-1}))}{s^2}$$

$$\text{with } P_v(r_0) = P_v(r_N) = 0$$

Set up matrix problem for $(N-1)$ unknown values;
 $s^2 E_v$ are matrix eigenvalues

Details of the setup

Example for $N=7$:

$$M := \begin{bmatrix} 2 & -1 & 0 & 0 & 0 & 0 \\ -1 & 2 & -1 & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & 0 & 0 \\ 0 & 0 & -1 & 2 & -1 & 0 \\ 0 & 0 & 0 & -1 & 2 & -1 \\ 0 & 0 & 0 & 0 & -1 & 2 \end{bmatrix};$$

`evalf(Eigenvalues(M));`

**Tiny complex contributions
are due to Maple. Perhaps
Mathematica will do
better??**

$$\begin{bmatrix} 3.801937736 + 3. \cdot 10^{-10} I \\ 0.7530203960 + 7.32050808 \cdot 10^{-11} I \\ 2.445041868 - 2.732050808 \cdot 10^{-10} I \\ 3.246979605 + 1. \cdot 10^{-10} I \\ 0.1980622645 - 1.866025404 \cdot 10^{-10} I \\ 1.554958132 - 1.339745960 \cdot 10^{-11} I \end{bmatrix}$$

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Results using Maple

Example for $N=7$: -- continue

ν	λ	λ/s^2	E_ν
1	0.1980622645	9.7050509605	9.869604401
2	0.7530203960	36.897999404	39.47841760
3	1.554958132	76.192948468	88.82643960
4	2.445041868	119.80705153	157.9136704
5	3.246979605	159.10200064	246.7401100
6	3.801937736	186.29494906	355.3057584

Summary. Notice that lowest eigenvalues are estimated the best.

Opinions about numerical solutions for differential equations

- 1. Beautiful! I want to try it myself.**
- 2. Beautiful or at least OK, but I will never try it myself.**
- 3. Terrible pain and suffering. Please don't mention it again.**