PHY 752 Solid State Physics
11-11:50 AM MWF Olin 103

Plan for Lecture 14:

Reading: Chapter 5 in GGGPP

Numerical Realizations of Density functional theory

1. Electronic structure of atoms
2. Integration of the radial equations
3. Frozen core approximation

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	Chap. 5	Implementation of density functional theory	#13
15	Mon, 9/28/2015			
16	Wed, 9/30/2015			
17	Fri, 10/02/2015			
18	Mon, 10/05/2015			
19	Wed, 10/07/2015			
20	Fri, 10/09/2015			
	Mon, 10/12/2015		No class	Take-home exam
	Wed, 10/14/2015		No class	Take-home exam due
	Fri, 10/16/2015		Fall break -- no class	
23	Mon, 10/19/2015			

Numerical methods for solving the Kohn-Sham equations

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

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

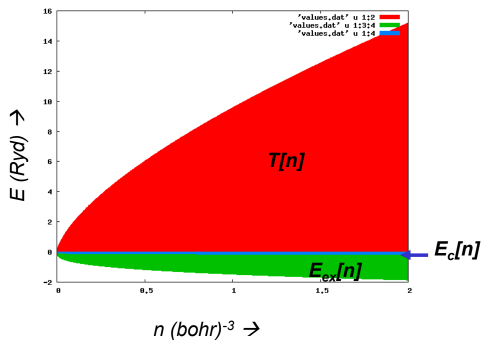
$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{ee}(\mathbf{r}) + V_{ex}(\mathbf{r}) + v(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

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

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

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

Digression: Jellium energies



Numerical methods for solving the Kohn-Sham equations

Self-consistent solution

Iteration $\alpha = 0$

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

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

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

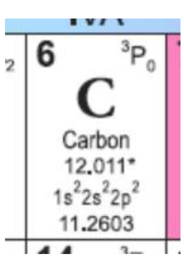
$n^{\alpha+1}_{temp}(\mathbf{r}) = \sum_i |\phi_i^{\alpha+1}(\mathbf{r})|^2$

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

$\alpha + 1 \Rightarrow \alpha$

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.



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

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

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

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

Kohn-Sham equations for spherical atom

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

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

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

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

$$V_{ext}(r)=\frac{\delta E_{ext}[n]}{\delta n}=v(r)=-\frac{Ze^2}{r}$$

Kohn-Sham equations for spherical atom -- continued

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

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

Convenient units:

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

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

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

Kohn-Sham equations for spherical atom -- continued

Equations in Rydberg units

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

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

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

$$V_{ext}(r)=\frac{\delta E_{ext}[n]}{\delta n}=v(r)=-\frac{2Z}{r}$$

Note that another convention differs by a factor of 2:

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

Kohn-Sham equations for spherical atom -- continued

Differential equations:

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

Boundary behaviors:

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

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

Notes on numerical integration of differential equations

Digression on numerical integration

Consider the differential equation

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

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
ν=1	9.54915028	9.7697954	9.869604404
ν=2	34.54915031	37.9008002	39.47841762

Numerical results from Numerov approximation:

	N=4	Exact
ν=1	9.863097625	9.869604404
ν=2	39.04581620	39.47841762

Some details:

Consider the differential equation

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

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

$$-\frac{d^2P_\nu(r)}{dr^2}=E_\nu P_\nu(r)$$

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

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

with $P_\nu(r_0)=P_\nu(r_N)=0$

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

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*));

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

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