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

### Plan for Lecture 14:
**Reading: Chapter 10 in MPM**
**Numerical Realizations of Density functional theory**

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



| | 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 |
| 14 | Mon: 02/16/2015 | Chap. 10 | Electronic structure calculation methods | #14 | 02/18/2015 |
| 15 | Wed: 02/18/2015 | Chap. 10 | Electronic structure calculation methods | #15 | 02/20/2015 |
| 16 | Fri: 02/20/2015 | Chap. 10 | Electronic structure calculation methods | #16 | 02/23/2015 |

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



Numerical methods for solving the Kohn-Sham equations

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

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

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

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

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

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

Numerical methods for solving the Kohn-Sham equations

Self-consistent solution

Iteration $\alpha = 0$

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

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

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

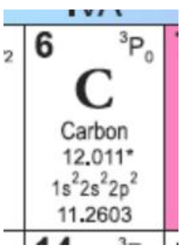
$$n_{temp}^{\alpha+1}(\mathbf{r}) = \sum_i \left|\phi_i^{\alpha+1}(\mathbf{r})\right|^2$$

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

$$\alpha + 1 \Rightarrow \alpha$$



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.




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

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

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

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



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:

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

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

Notes on numerical integration of differential equations

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

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 |