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

Plan for Lecture 11:

Reading: Chap. 4 in GGGPP;

One-electron approximations to the many electron problem

1. **Hartree approximation**
2. **Hartree-Fock approximation**

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			
13	Wed, 9/23/2015			
14	Fri, 9/25/2015			
15	Mon, 9/28/2015			

Quantum Theory of materials

Electronic coordinates

Atomic coordinates

Exact Schrödinger equation:

$$\mathcal{H}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\Psi_{\alpha\nu}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = E_{\alpha\nu}\Psi_{\alpha\nu}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

where

$$\mathcal{H}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = \mathcal{H}^{\text{Nuclei}}(\{\mathbf{R}^a\}) + \mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

Born-Oppenheimer approximation

Born & Huang, **Dynamical Theory of Crystal Lattices**, Oxford (1954)

Approximate factorization:

$$\Psi_{\alpha\nu}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = X^{\text{Nuclei}}_{\alpha\nu}(\{\mathbf{R}^a\})\Upsilon^{\text{Electrons}}_{\alpha}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

Quantum Theory of materials -- continued

Electronic Schrödinger equation:

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = U_\alpha(\{\mathbf{R}^a\})\Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_{a,i}\frac{Z^a e^2}{|\mathbf{r}_i - \mathbf{R}^a|} + \sum_{i<j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Nuclear Hamiltonian: (Often treated classically)

$$\mathcal{H}^{\text{Nuclei}}\left(\{\mathbf{R}^a\}\right)X_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\}) = W_{\alpha\nu}X_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Nuclei}}\left(\{\mathbf{R}^a\}\right) = \sum_a \frac{\mathbf{P}^{a2}}{2M^a} + U_\alpha(\{\mathbf{R}^a\})$$

Effective nuclear interaction provided by electrons

Consider electronic Hamiltonian

Electronic Schrödinger equation:

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = U_\alpha(\{\mathbf{R}^a\})\Upsilon_\alpha^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_{a,i}\frac{Z^a e^2}{|\mathbf{r}_i - \mathbf{R}^a|} + \sum_{i<j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Electron-electron interaction term prevents exactly separable electron wavefunction

Hartree approximation to electronic wavefunction

$$\Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = \phi_{n_1\mathbf{k}_1\sigma_1}(\mathbf{r}_1)\phi_{n_2\mathbf{k}_2\sigma_2}(\mathbf{r}_2)....\phi_{n_N\mathbf{k}_N\sigma_N}(\mathbf{r}_N)$$

$$= \prod_{i=1}^{N}\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r}_i)$$

Variational estimate of electron energy in Hartree approximation

$$E_H = \frac{\left\langle \Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\middle| H \middle|\Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right\rangle}{\left\langle \Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\middle|\Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right\rangle}$$

Let $\mathcal{F}_H \equiv \left\langle \Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\middle| H \middle|\Upsilon_{\alpha H}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right\rangle$

and require $\left\langle \phi_{n_i\mathbf{k}_i\sigma_i}\middle|\phi_{n_i\mathbf{k}_i\sigma_i}\right\rangle = 1$, then the variational equations for the Hartree orbitals are:

$$\frac{\partial \mathcal{F}_H}{\partial \phi_{n_i\mathbf{k}_i\sigma_i}^*} = \epsilon_i\phi_{n_i\mathbf{k}_i\sigma_i}$$

Variational equation for Hartree approximation -- continued

$$\frac{\partial \mathcal{F}_H}{\partial \phi^*_{n_i \mathbf{k}_i \sigma_i}} = \epsilon_i \phi_{n_i \mathbf{k}_i \sigma_i}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{Ne}(\mathbf{r}) + V_{ee}(\mathbf{r}) \right) \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}) = \epsilon_i \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r})$$

Nuclear-electron interaction:

$$V_{Ne}(\mathbf{r}) \equiv -\sum_a \frac{Z^a e^2}{|\mathbf{r} - \mathbf{R}^a|}$$

Electron-electron interaction:

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

where $n(\mathbf{r}') \equiv \sum_{n_i \mathbf{k}_i \sigma_i} \left| \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}') \right|^2$

Note: In principle, the self interaction term should be omitted from $V_{ee}(r)$, but often it is included.

Hartree approximation -- continued

In practice, the equations must be solved self-consistently

One possible procedure would start with a guess of the one-electron functions $\left\{ \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}) \right\}$ and the electron density

where $n(\mathbf{r}') \equiv \sum_{n_i \mathbf{k}_i \sigma_i} \left| \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}') \right|^2$

Next, find new one electron functions from:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{Ne}(\mathbf{r}) + V_{ee}(\mathbf{r}) \right) \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}) = \epsilon_i \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r})$$

and determine the new electron density $n(\mathbf{r})$. At convergence the electron density is stable.

Hartree approximation -- continued

At convergence, the Hartree electronic energy can be computed from one-electron functions $\left\{ \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}) \right\}$ and the electron density

where $n(\mathbf{r}') \equiv \sum_{n_i \mathbf{k}_i \sigma_i} \left| \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}') \right|^2$

$$E_H = E_K + E_{Ne} + E_{ee}$$

$$E_K = -\frac{\hbar^2}{2m} \sum_{n_i \mathbf{k}_i \sigma_i} \int d^3r \, \phi^*_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}) \nabla^2 \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r})$$

$$E_{Ne} = \int d^3r \, V_{Ne}(\mathbf{r}) n(\mathbf{r})$$

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

Comment about homework problem

1. This problem is concerned with variationally estimating the ground state electronic energy of a two-electron atom with nuclear charge Ze in the Hartree-Fock approximation. The Hamiltonian for the two-electron system is

$$H(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - Ze^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

Assume that the spatial part of the two-electron wavefunction can be written in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(r_1)\phi(r_2),$$

where

$$\phi(r) = \mathcal{N}\mathrm{e}^{-\alpha r/a},$$

where $\mathcal{N}$ is the normalization factor, $a = \hbar^2/(me^2)$ is the Bohr radius, and α is a variational parameter.

Comment about homework problem -- continued

(a) Show that

$$E(\alpha) \equiv \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\hbar^2}{2ma^2}\left(\alpha^2 - 2\alpha\left(Z - \frac{5}{8}\right)\right).$$

Hint: Show that the two electron term involves the integral

$$\int_0^\infty dr r^2 \mathrm{e}^{-2\alpha r/a}\left(\frac{1}{r}\int_0^r dr' r'^2 \mathrm{e}^{-2\alpha r'/a} + \int_r^\infty dr' r' \mathrm{e}^{-2\alpha r'/a}\right) = 2\int_0^\infty dr r \mathrm{e}^{-2\alpha r/a}\int_0^r dr' r'^2 \mathrm{e}^{-2\alpha r'/a}$$

(b) Find the value of α that minimizes the Hartree Fock energy $E(\alpha)$ and the corresponding estimate of the ground state energy of the two-electron system.

Comment about electron-electron interaction in the Hartree approximation

Note that we have shown that in the Hartree approximation, the electron electron term can be evaluated as:

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

In the following, we will see that is form is a consequence of the Hartree approximation, so that in the following we will call this the "Hartree" energy:

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

Hartree-Fock approximation to electronic wavefunction

Fermi symmetry

$$\Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i ... \mathbf{r}_k\},\{\mathbf{R}^a\}) = -\Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_k ... \mathbf{r}_i\},\{\mathbf{R}^a\})$$

$$\Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = \mathcal{A}\left(\phi_{n_1\mathbf{k}_1\sigma_1}(\mathbf{r}_1)\phi_{n_2\mathbf{k}_2\sigma_2}(\mathbf{r}_2)....\phi_{n_N\mathbf{k}_N\sigma_N}(\mathbf{r}_N)\right)$$

$$= \mathcal{A}\left(\prod_{i=1}^{N}\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r}_i)\right)$$

Slater determinant

$$\Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_{n_1\mathbf{k}_1\sigma_1}(\mathbf{r}_1) & \phi_{n_1\mathbf{k}_1\sigma_1}(\mathbf{r}_2) & \cdots & \phi_{n_1\mathbf{k}_1\sigma_1}(\mathbf{r}_N) \\ \phi_{n_2\mathbf{k}_2\sigma_2}(\mathbf{r}_1) & \phi_{n_{12}\mathbf{k}_2\sigma_2}(\mathbf{r}_2) & \cdots & \phi_{n_2\mathbf{k}_2\sigma_2}(\mathbf{r}_N) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_{n_N\mathbf{k}_N\sigma_N}(\mathbf{r}_1) & \phi_{n_N\mathbf{k}_N\sigma_N}(\mathbf{r}_2) & \cdots & \phi_{n_N\mathbf{k}_N\sigma_N}(\mathbf{r}_N) \end{vmatrix}$$

Hartree-Fock approximation to electronic wavefunction Second quantization formalism

$$\Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = \mathcal{A}\left(\phi_{n_1\mathbf{k}_1\sigma_1}(\mathbf{r}_1)\phi_{n_2\mathbf{k}_2\sigma_2}(\mathbf{r}_2)....\phi_{n_N\mathbf{k}_N\sigma_N}(\mathbf{r}_N)\right)$$

$$\equiv \hat{c}^{\dagger}_{n_1\mathbf{k}_1\sigma_1}\hat{c}^{\dagger}_{n_2\mathbf{k}_2\sigma_2}\cdots\hat{c}^{\dagger}_{n_N\mathbf{k}_N\sigma_{1N}}\left|\Psi^0\right\rangle$$

Properties of Fermi operators:

$$\hat{c}_l^{\dagger}\hat{c}_{l'}^{\dagger} = -\hat{c}_{l'}^{\dagger}\hat{c}_l^{\dagger}$$

$$\hat{c}_l\,\hat{c}_{l'} = -\hat{c}_{l'}\hat{c}_l$$

$$\hat{c}_l\,\hat{c}_{l'}^{\dagger} = -\hat{c}_{l'}^{\dagger}c_l + \delta_{ll'}$$

See Appendix B of GGGPP

Hartree-Fock approximation to electronic wavefunction -- continued

Variational estimate of electron energy in Hartree-Fock approximation

$$E = \frac{\left\langle \Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\middle| H \middle|\Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right\rangle}{\left\langle \Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\middle|\Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right\rangle}$$

Let $\mathcal{F}_{HF} \equiv \left\langle \Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\middle| H \middle|\Upsilon_{\alpha HF}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\right\rangle$

and require $\left\langle \phi_{n_i\mathbf{k}_i\sigma_i}\middle|\phi_{n_j\mathbf{k}_j\sigma_j}\right\rangle = \delta_{ij}$, then the variational equations for the Hartree Fock orbitals are:

$$\frac{\partial \mathcal{F}_{HF}}{\partial \phi^{*}_{n_i\mathbf{k}_i\sigma_i}} = \sum_j \lambda_{ij}\phi_{n_j\mathbf{k}_j\sigma_j}$$

Variational equation for Hartree-Fock approximation -- continued

$$\frac{\partial \mathcal{F}_{HF}}{\partial \phi^*_{n_i \mathbf{k}_i \sigma_i}} = \sum_j \lambda_{ij} \phi_{n_j \mathbf{k}_j \sigma_j}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{Ne}(\mathbf{r}) + V_{ee}(\mathbf{r}) + V_{ex}(\mathbf{r}) \right) \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}) = \sum_j \lambda_{ij} \phi_{n_j \mathbf{k}_j \sigma_j}$$

Electron-exchange interaction:

$$V_{ex}(\mathbf{r}) \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}) \equiv -e^2 \sum_j \delta_{\sigma_i \sigma_j} \phi_{n_j \mathbf{k}_j \sigma_j}(\mathbf{r}) \int d^3 r' \frac{\phi^*_{n_j \mathbf{k}_j \sigma_j}(\mathbf{r}') \phi_{n_i \mathbf{k}_i \sigma_i}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Note that in the Hartree-Fock formalism, there is no spurious electron self-interaction.

Hartree-Fock approximation – continued

As for the Hartree formulation, the Hartree-Fock equations must be solved iteratively. At convergence, the Hartree-Fock electronic energy can be calculated from the one-electron orbitals and the charge density

$$E_{HF} = E_K + E_{Ne} + E_{ee} + E_{ex}$$

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