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

Plan for Lecture 11:
Reading: Chapter 9 in MPM
Approximations to the many electron problem

1. Hartree approximation
2. Hartree-Fock approximation
3. Density functional theory

Course schedule for Spring 2015

(Preliminary schedule -- subject to frequent adjustment.)

	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

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

Quantum Theory of materials

Electronic coordinates

Atomic coordinates

Exact Schrödinger equation:

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

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:

$$\Psi_{\alpha v}(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = X_{\alpha v}^{\text{Nuclei}}(\{\mathbf{R}^a\})\Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

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)

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

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

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

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

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

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

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

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

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

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

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

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

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 C of MPM

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

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:

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

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

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

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