PHY 741 Quantum Mechanics
12-12:50 PM MWF Olin 103

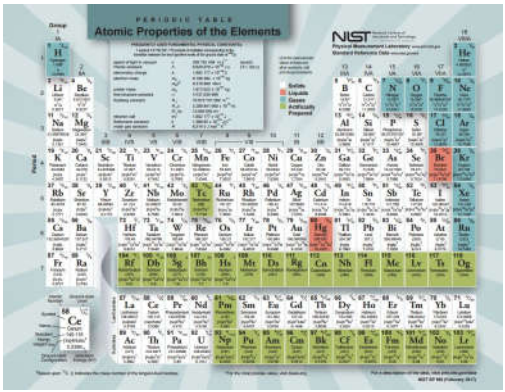
Plan for Lecture 18:
Shankar, Chapter 13

1. Approximate eigenstates of multielectron atoms
2. Hartree-Fock approximation
3. Density functional approximation

Course Schedule

(Preliminary schedule -- subject to frequent adjustment.)

	Date	F&W Reading	Topic	Assignment	Due
1	Mon, 8/28/2017	Chap. 1	Review of basic principles	#1	9/6/2017
2	Wed, 8/30/2017	Chap. 1	Linear vector spaces	#2	9/6/2017
3	Fri, 9/01/2017	Chap. 1	Linear vector spaces	#3	9/6/2017
7	Mon, 9/11/2017	Chap. 5	Schrödinger equation in one-dimension		
8	Wed, 9/13/2017	Chap. 7	Schrödinger equation in one-dimension	#6	9/15/2017
9	Fri, 9/15/2017	Chap. 7	Schrödinger equation in one-dimension	#7	9/20/2017
10	Mon, 9/18/2017	Chap. 5 and 7	Schrödinger equation in one-dimension		
11	Wed, 9/20/2017	Chap. 9	Commutator formalism	#8	9/22/2017
12	Fri, 9/22/2017	Chap. 10	Quantum mechanics of multiparticle systems	#9	9/25/2017
13	Mon, 9/25/2017	Chap. 10-12	Multiparticle systems and angular momentum		
14	Wed, 9/27/2017	Chap. 12	Eigenstates of angular momentum		
15	Fri, 9/29/2017	Chap. 1,4,5,7,9,10,12	Review		
	Mon, 10/02/2017		*Take-home exam -- No class*		
	Wed, 10/04/2017		*Take-home exam -- No class*		
16	Fri, 10/06/2017	Chap. 12-13	Spherically symmetric systems		
17	Mon, 10/09/2017	Chap. 13	Quantum mechanics of a hydrogen atom	#10	10/16/2017
18	Wed, 10/11/2017	Chap. 13	Quantum mechanics of multi-electron aotms		
	Fri, 10/13/2017		*Fall break -- No class*		
19	Mon, 10/16/2017				
20	Wed, 10/18/2017				
21	Fri, 10/20/2017				
22	Mon, 10/23/2017				
23	Wed, 10/25/2017				



For Hydrogen atom:

$$\left(-\frac{\hbar^2}{2m}\nabla_r^2-\frac{Ze^2}{r}\right)\psi(\mathbf{r})=E\psi(\mathbf{r})$$

$$\psi(\mathbf{r})=R_{El}(r)Y_{lm}\left(\hat{\mathbf{r}}\right)$$

Differential equation for radial wavefunction:

$$\left(-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}-\frac{l(l+1)}{r^2}\right]-\frac{Ze^2}{r}\right)R_{El}(r)=ER_{El}(r)$$

Hydrogen atom eigenvalues --

Example of normalized radial functions $R_{nl}(r)$:

$$R_{10}(r)=\left(\frac{Z}{a_0}\right)^{3/2}2e^{-Zr/a_0} \qquad E_1=-\frac{Z^2e^2}{2a_0}$$

$$R_{20}(r)=\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/(2a_0)}$$

$$R_{21}(r)=\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Zr}{\sqrt{3}a_0}e^{-Zr/(2a_0)} \qquad E_2=-\frac{Z^2e^2}{2a_0}\frac{1}{2^2}$$

Bohr radius:

$$a_0\equiv\frac{\hbar^2}{me^2}=0.529\ 177\ 210\ 67\ \text{x}\ 10^{-10}\text{m}$$

Consider the case of He (Z=2):

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

Estimating the ground state of the He atom:

$$f(\psi)\equiv\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \qquad \min_\psi f(\psi)\geq E_0$$

Trial wavefunction: $|\psi\rangle=e^{-\gamma(r_1+r_2)/a_0}$

Variational methods for estimating ground state energy:

Define $f(\psi) \equiv \dfrac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$ $\quad \min_\psi f(\psi) \geq E_0$

$f(\psi) = \dfrac{e^2}{a_0}\left(\gamma^2 - \dfrac{27}{8}\gamma\right)$ $\quad \min_\psi f(\psi) = -\dfrac{e^2}{a_0}\left(\dfrac{27}{16}\right)^2$

$\dfrac{df}{d\psi} = 0 \quad \Rightarrow \gamma_{opt} = \dfrac{27}{16}$ $\quad = -\dfrac{e^2}{2a_0} 5.695$

Experimental

value $\approx -\dfrac{e^2}{2a_0} 5.807$

Systemmatic approach for studying the 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:

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

Quantum Theory of materials -- continued

Electronic Schrödinger equation:

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

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

Nuclear Hamiltonian: (Often treated classically)

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

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

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

Electronic wavefunctions

$$\phi_{n_i\mathbf{k}_i\sigma_i}(\mathbf{r}_i)$$

electron spin ↑ or ↓

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 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

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

Hartree-Fock approximation to electronic wavefunction -- 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:

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

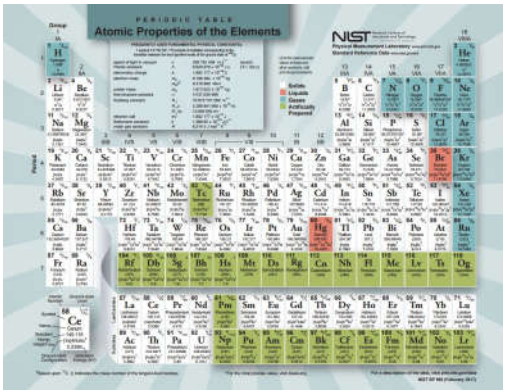
Note that in the Hartree-Fock formalism, there is no spurious electron self-interaction.

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

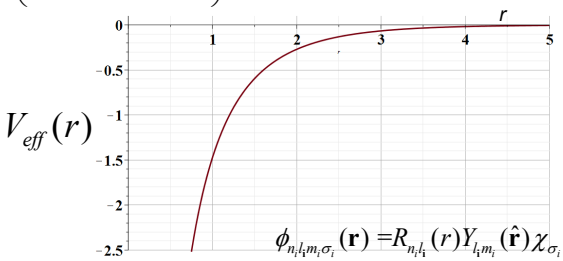
$$E_{HF} = E_K + E_{Ne} + E_{ee} + E_{ex}$$

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



Shell structure of atoms based on Hartree and Hartree-Fock treatments

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V_{eff}(\mathbf{r})\right)\phi_{n_i l_i m_i \sigma_i}(\mathbf{r})=\epsilon_{n_i l_i}\phi_{n_i l_i m_i \sigma_i}(\mathbf{r})$$



$$\phi_{n_i l_i m_i \sigma_i}(\mathbf{r})=R_{n_i l_i}(r)Y_{l_i m_i}(\hat{\mathbf{r}})\chi_{\sigma_i}$$

Equation for radial functions

$$\left(-\frac{\hbar^2}{2m}\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l_i(l_i+1)}{r^2}\right]+V_{eff}(\mathbf{r})\right)R_{n_i l_i}(r)$$
$$=\epsilon_{n_i l_i}R_{n_i l_i}(r)$$