PHY 742 Quantum Mechanics II
1-1:50 AM MWF via video link:
https://wakeforest-university.zoom.us/my/natalie.holzwarth

Extra Notes for Lecture 30

Hartree-Fock approximation and other formalisms for treating multi electron systems

1. Summary of Hartree-Fock analysis
2. Other mean field treatments – density functional theory

Note that equations will be written for an atom, but can be extended to molecules and solids.

We will summarize and review the Hartree-Fock method and then talk about extensions

21	Mon: 03/23/2020	Chap. 17	Quantization of the Electromagnetic Field	#17	03/25/2020
22	Wed: 03/25/2020	Chap. 17	Quantization of the Electromagnetic Field	#18	03/27/2020
23	Fri: 03/27/2020	Chap. 17	Quantization of the Electromagnetic Field	#19	03/30/2020
24	Mon: 03/30/2020	Chap. 18	Photons and atoms		
25	Wed: 04/01/2020	Chap. 10	Multiparticle systems	#20	04/03/2020
26	Fri: 04/03/2020	Chap. 10	Multiparticle systems	#21	04/06/2020
27	Mon: 04/06/2020	Chap. 10	Multielectron atoms	#22	04/08/2020
28	Wed: 04/08/2020	Chap. 10	Multielectron atoms		
	Fri: 04/10/2020	No class	*Good Friday*		
29	Mon: 04/13/2020	Chap. 10	Multielectron atoms	#23	04/15/2020
30	Wed: 04/15/2020		Hartree-Fock and other formalisms	#24	04/17/2020
31	Fri: 04/17/2020				
32	Mon: 04/20/2020				
33	Wed: 04/22/2020				
34	Fri: 04/24/2020				
35	Mon: 04/27/2020				
36	Wed: 04/29/2020		Review		

This is the last homework assignment for the semester. It involves evaluating the exchange integral for a continuum of plane waves.

General equations for multi electron systems

We have established that in order to represent N indistinguisable Fermi particles:

the wave function must have the property:

$$\psi(\mathbf{r}_1,\mathbf{r}_2,..\mathbf{r}_i...\mathbf{r}_j...\mathbf{r}_N) = -\psi(\mathbf{r}_1,\mathbf{r}_2,..\mathbf{r}_j...\mathbf{r}_i...\mathbf{r}_N)$$

For example, we can construct a wave function that has the correct antisymmetry from combinations of single particle states $\varphi_a(\mathbf{r}),\varphi_b(\mathbf{r}),\varphi_c(\mathbf{r})....$

Example for N particles using Slater determinant:

$$\psi(\mathbf{r}_1,\mathbf{r}_2....\mathbf{r}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_a(\mathbf{r}_1) & \varphi_a(\mathbf{r}_2) & \varphi_a(\mathbf{r}_3) & \cdots & \varphi_a(\mathbf{r}_N) \\ \varphi_b(\mathbf{r}_1) & \varphi_b(\mathbf{r}_2) & \varphi_b(\mathbf{r}_3) & \cdots & \varphi_b(\mathbf{r}_N) \\ \varphi_c(\mathbf{r}_1) & \varphi_c(\mathbf{r}_2) & \varphi_c(\mathbf{r}_3) & \cdots & \varphi_c(\mathbf{r}_N) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \varphi_z(\mathbf{r}_1) & \varphi_z(\mathbf{r}_2) & \varphi_z(\mathbf{r}_3) & \cdots & \varphi_z(\mathbf{r}_N) \end{vmatrix}$$

Review of the properties of identical Fermi particles.

In general, the Hamiltonian of the system takes the form:

$$H(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) = \sum_{i=1}^{N} h(\mathbf{r}_i) + \frac{1}{2} \sum_{i,j=1 (i \neq j)}^{N} v(\mathbf{r}_i, \mathbf{r}_j)$$

Here $v(\mathbf{r}_i, \mathbf{r}_j) = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$ representing electron-electron repulsion

For an atom having atomic number Z, $h(\mathbf{r}_i) = -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i}$

Identification of one-electron and two-electron terms.

For the more general choice of single particle basis $\varphi_a(\mathbf{r})$:

(note the basis functions must be orthonormal: $\langle \varphi_a(\mathbf{r}) | \varphi_b(\mathbf{r}) \rangle = \delta_{ab}$)

Second quantized version of the multi electron system:

$$H(\mathbf{r}_1, \mathbf{r}_2, ..\mathbf{r}_N) \Rightarrow \sum_i h_{ii} f_i^\dagger f_i + \sum_{ijkl} v_{ijkl} f_i^\dagger f_j^\dagger f_l f_k$$

Here h_{ii} denotes single particle matrix elements

$$h_{ii} = \langle \varphi_i(\mathbf{r}) | h(\mathbf{r}) | \varphi_i(\mathbf{r}) \rangle$$

Here v_{ijkl} denotes two particle matrix elements

$$v_{ijkl} = \langle \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) | v(\mathbf{r}_1 - \mathbf{r}_2) | \varphi_k(\mathbf{r}_1) \varphi_l(\mathbf{r}_2) \rangle$$

Review of second quantization formalism

In order to estimate the lowest energy state (ground state) of our system, we can use the variational principle to optimize a trial wave function which minimizes the expectation value

$$E_{trial} = \frac{\left\langle \Psi_{trial} \middle| H \middle| \Psi_{trial} \right\rangle}{\left\langle \Psi_{trial} \middle| \Psi_{trial} \right\rangle} = \sum_{i=1}^{N} h_{ii} + \frac{1}{2} \sum_{i,j=1}^{N} \left(v_{ijij} - v_{ijji} \right)$$

$$h_{ii} = \left\langle \varphi_i(\mathbf{r}) \middle| h(\mathbf{r}) \middle| \varphi_i(\mathbf{r}) \right\rangle$$

$$v_{ijkl} = \left\langle \varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2) \middle| v(\mathbf{r}_1 - \mathbf{r}_2) \middle| \varphi_k(\mathbf{r}_1)\varphi_l(\mathbf{r}_2) \right\rangle$$

Note that we have assumed here that $\left\langle \Psi_{trial} \middle| \Psi_{trial} \right\rangle = 1$

Variational approximation.

The Hartree-Fock approximation is based on the choice of

$\left|\Psi_{trial}\right\rangle = \prod_{i=1}^{N} f_i^\dagger \left|0\right\rangle$ using the second quantized notation or

the equivalent Slater determinant based on the single particle functions $\varphi_i(\mathbf{r})$ with the constraint $\left\langle \varphi_i(\mathbf{r}) \middle| \varphi_j(\mathbf{r}) \right\rangle = \delta_{ij}$

$$E_{trial} = \sum_{i=1}^{N} h_{ii} + \frac{1}{2}\sum_{i,j=1}^{N}\left(v_{ijij} - v_{ijji}\right)$$

Note that the *i=j* contribution cancels out.

Hartree-Fock approximation

Matrix elements

$$h_{ii} = \int d^3r \; h(\mathbf{r}) \left|\varphi_i(\mathbf{r})\right|^2$$

$$v_{ijij} = e^2 \int d^3r \int d^3r' \frac{\left|\varphi_i(\mathbf{r})\right|^2 \left|\varphi_j(\mathbf{r}')\right|^2}{\left|\mathbf{r}-\mathbf{r}'\right|}$$

$$v_{ijji} = e^2 \delta_{\sigma_i \sigma_j} \int d^3r \int d^3r' \frac{\left(\varphi_i(\mathbf{r})\varphi^*{}_j(\mathbf{r})\right)\left(\varphi^*{}_i(\mathbf{r}')\varphi_j(\mathbf{r}')\right)}{\left|\mathbf{r}-\mathbf{r}'\right|}$$

Constrained optimization

$$\delta\left(E_{trial}\left(\{\varphi_i\}\right) - \sum_{i,j=1}^{N} \lambda_{ij} \left\langle \varphi_i \middle| \varphi_j \right\rangle \right) = 0$$

$$\varphi_i \rightarrow \varphi_i + \delta\varphi_i$$

Writing out the integrals.

Coupled Hartree-Fock equations to solve

Define: $V_{Hartree}(\mathbf{r}) = e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$ where $n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$

Define: Exchange integral form:

$$\Sigma_i(\mathbf{r}) = -e^2 \sum_{j=1}^{N} \delta_{\sigma_i \sigma_j} \int d^3r' \frac{\left(\varphi_i(\mathbf{r}')\varphi^*{}_j(\mathbf{r}')\right)}{|\mathbf{r}-\mathbf{r}'|} \varphi_j(\mathbf{r})$$

Coupled integral-differential equations:

$$\left(h(\mathbf{r}) + V_{Hartree}(\mathbf{r})\right)\varphi_i(\mathbf{r}) + \Sigma_i(\mathbf{r}) = \sum_{i=1}^{N} \lambda_{ij}\varphi_j(\mathbf{r})$$

where $\langle \varphi_i(\mathbf{r}) | \varphi_j(\mathbf{r}) \rangle = \delta_{ij}$

Form of coupled equations

Digression – why is it necessary to have the orthonormality constraint?

$$\left\langle \varphi_i(\mathbf{r}) \middle| \varphi_j(\mathbf{r}) \right\rangle = \delta_{ij}$$

1. **It is not necessary**
2. **It is not necessary and a bad idea**
3. **It is not necessary but a good idea**
4. **It just is necessary**

Self-consistent solution of the Hartree-Fock equations

Guess one electron functions $\{\varphi_i(\mathbf{r})\}^0$

Count=0

Solve differential integral equations

$$\left(h(\mathbf{r}) + V_{Hartree}(\mathbf{r})\right)\varphi_i(\mathbf{r}) + \Sigma_i(\mathbf{r}) = \sum_{i=1}^{N} \lambda_{ij}\varphi_j(\mathbf{r}) \quad \Rightarrow \{\varphi_i(\mathbf{r})\}^{new}$$

Count=Count+1

$$\{\varphi_i(\mathbf{r})\}^{\text{Count}} = \alpha\{\varphi_i(\mathbf{r})\}^{\text{Count-1}} + (1-\alpha)\{\varphi_i(\mathbf{r})\}^{new}$$

test: if $\left|\{\varphi_i(\mathbf{r})\}^{\text{Count-1}} - \{\varphi_i(\mathbf{r})\}^{\text{Count}}\right| > \epsilon$ → **Continue self-consistent Iterations**

if $\left|\{\varphi_i(\mathbf{r})\}^{\text{Count-1}} - \{\varphi_i(\mathbf{r})\}^{\text{Count}}\right| < \epsilon$ → **Self-consistent cycles converged**

Iteration process in order to achieve self-consistency.

Problem with Hartree-Fock approach

1. **Solutions do not have correlation effects.***
2. **Solutions are slightly painful (integral-differential equations are painful)**
3. **Chemists are happier than physicists**

Density functional theory

A. **Attempts to solve #1**
B. **Reduces the pain of #2**
C. **Physicists are happier than chemists**

*The definition of electron correlation energy is

$$E_{correlation} \equiv E_{exact} - E_{Hartree-Fock}$$

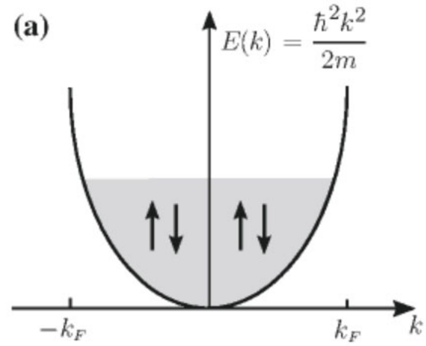
Perspective on the state of the formalism.

Prelude to DFT --

Evaluation of the Hartree-Fock equations for the jellium model – homogeneous electron gas

$$\Psi_0 = \mathcal{A}\{W_{\mathbf{k}_1}\alpha\ W_{\mathbf{k}_1}\beta \cdots W_{\mathbf{k}_{N/2}}\alpha\ W_{\mathbf{k}_{N/2}}\beta\} \quad \text{with} \quad W(\mathbf{k}_i, \mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_i \cdot \mathbf{r}}.$$

Jellium is the "hydrogen atom" of condensed matter physics. It consists of an infinite volume of non-interacting electrons with a density of N/V. It is evaluated for fixed volume V and it is assumed that V is very large. The system is assumed to be neutral due to a uniform positive compensation charge also having a density N/V.



Preparing to evaluate the exchange interaction for a convenient analytical case -- jellium

What do you think about the Jellium model?

1. **A totally bad idea**
2. **A somewhat reasonable idea**
3. **There are some materials for which jellium provides a reasonably accurate description.**

Hartree-Fock Equations

$$\left[\frac{\mathbf{p}^2}{2m} + V_{\text{nucl}}(\mathbf{r}) + V_{\text{coul}}(\mathbf{r}) + V_{\text{exch}}\right]\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

$$V_{\text{coul}}(\mathbf{r}) = 2\sum_j^{N/2} \langle \phi_j(\mathbf{r}')| \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} |\phi_j(\mathbf{r}')\rangle,$$

$$V_{\text{exch}}\phi_i(\mathbf{r}) = -\sum_j^{N/2} \langle \phi_j(\mathbf{r}')| \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} |\phi_i(\mathbf{r}')\rangle \phi_j(\mathbf{r}).$$

For jellium model: $V_{\text{coul}}(\mathbf{r}) = -V_{\text{nucl}}(\mathbf{r})$ $\phi_i(r) = \frac{1}{\sqrt{V}} e^{i\mathbf{q}\cdot\mathbf{r}}$

$$V_{\text{exch}} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} = -\sum_{\mathbf{q}}^{(\text{occ})} \frac{1}{\sqrt{V}} e^{i\mathbf{q}\cdot\mathbf{r}} \int \frac{1}{\sqrt{V}} e^{-i\mathbf{q}\cdot\mathbf{r}'} \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}'}\, d\mathbf{r}'$$

$$= -\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \sum_{\mathbf{q}}^{(\text{occ})} \int \frac{1}{V} e^{-i(\mathbf{k}-\mathbf{q})\cdot(\mathbf{r}-\mathbf{r}')} \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}'$$

$$= -\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \frac{1}{V} \sum_{q<k_F} \frac{4\pi e^2}{|\mathbf{k}-\mathbf{q}|^2}.$$

Some details

Some details --

$$V_{\text{exch}}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} = -\sum_{\mathbf{q}}^{(\text{occ})}\frac{1}{\sqrt{V}}e^{i\mathbf{q}\cdot\mathbf{r}}\int\frac{1}{\sqrt{V}}e^{-i\mathbf{q}\cdot\mathbf{r}'}\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}'}\,d\mathbf{r}'$$

$$= -\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}}\sum_{\mathbf{q}}^{(\text{occ})}\int\frac{1}{V}\,e^{-i(\mathbf{k}-\mathbf{q})\cdot(\mathbf{r}-\mathbf{r}')}\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'$$

$$= -\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}}\frac{1}{V}\sum_{q<k_F}\frac{4\pi e^2}{|\mathbf{k}-\mathbf{q}|^2}.$$

Note that: $\int e^{-i\mathbf{Q}\cdot\mathbf{r}}\frac{1}{r}d^3r = \lim_{\epsilon\to 0}\left(\int e^{-i\mathbf{Q}\cdot\mathbf{r}-\epsilon r}\frac{1}{r}d^3r\right)$

$$\int e^{-i\mathbf{Q}\cdot\mathbf{r}-\epsilon r}\frac{1}{r}d^3r = \int e^{-i\mathbf{Q}\cdot\mathbf{r}-\epsilon r}\frac{1}{r}r^2dr\ d\cos\theta\ \mathrm{d}\phi = -2\pi\int_0^\infty rdre^{-\epsilon r}\int_{-1}^{1}d\cos\theta\ e^{-iQr\cos\theta}$$

$$= -2\pi\int_0^\infty rdre^{-\epsilon r}\left(\frac{e^{-iQr}-e^{iQr}}{-iQr}\right) = \frac{4\pi}{Q^2+\epsilon^2}$$

More details.

More details

$$I(k) = \frac{1}{V}\sum_{q<k_F}\frac{4\pi e^2}{|\mathbf{k}-\mathbf{q}|^2} = \frac{4\pi e^2}{(2\pi)^3}\int_{q<k_F}\frac{1}{|\mathbf{k}-\mathbf{q}|^2}\,d\mathbf{q}.$$

$$I(k) = \frac{4\pi e^2}{(2\pi)^3}\int_{q<k_F}\frac{1}{q^2-2kq\cos\theta+k^2}\,q^2\sin\theta\,d\theta\,d\phi\,dq.$$

$$I(k) = \frac{e^2}{\pi}\frac{1}{k}\int_0^{k_F} q\ln\frac{k+q}{k-q}\,dq = \frac{e^2}{\pi}\frac{1}{k}\left[kq-\frac{1}{2}(k^2-q^2)\ln\frac{k+q}{k-q}\right]_0^{k_F}.$$

We thus obtain

$$\boxed{I(k) = \frac{2e^2k_F}{\pi}F\left(\frac{k}{k_F}\right)},$$

where the function $F(x)$ is given by

$$F(x) = \frac{1}{2}+\frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|$$

Not totally trivial.

Eigenvalues of the plane wave orbitals:

$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m} - \frac{2e^2 k_F}{\pi} F\left(\frac{k}{k_F}\right).$$

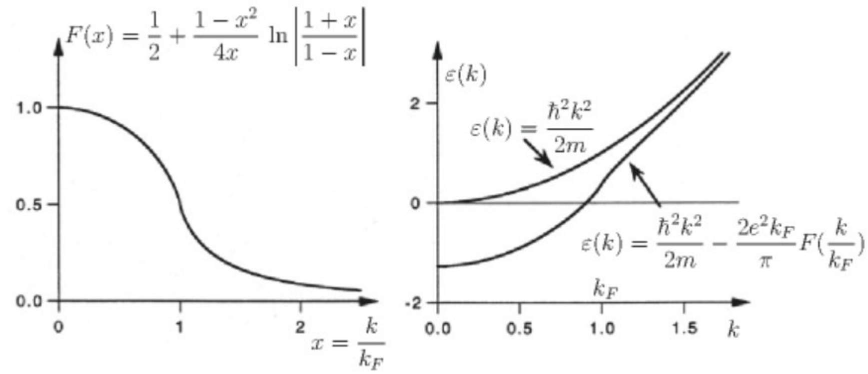


Figure 4.4 (a) Schematic plot of the function $F(x)$. (b) Kinetic energy and Hartree-Fock orbital energy as a function of the wavevector k for the homogeneous electron gas. Energies are in Rydbergs, k is in units of a_B^{-1} (inverse Bohr radius), and we have taken $k_F = 1/a_B$.

Plots of results.

Total electronic energy of homogeneous electron gas in Hartree-Fock approximation

$$E_0^{(\mathrm{HF})} = 2\sum_{k<k_F} \frac{\hbar^2 k^2}{2m} - 2\sum_{k<k_F} \frac{1}{2}\,\frac{2e^2 k_F}{\pi} F\left(\frac{k}{k_F}\right),$$

$$E_0^{(\mathrm{HF})} = N\left[\frac{3}{5}\frac{\hbar^2 k_F^2}{2m} - \frac{3}{4}\frac{e^2 k_F}{\pi}\right].$$

Some details:

$$F_{\mathrm{av}} = \int_0^1 x^2 F(x)\,dx \bigg/ \int_0^1 x^2\,dx = 3\int_0^1 x^2 F(x)\,dx = \frac{3}{4}.$$

The indefinite integral

$$\int x(1-x^2)\ln\frac{1+x}{1-x}\,dx = \frac{1}{2}x - \frac{1}{6}x^3 - \frac{1}{4}(1-x^2)^2\ln\frac{1+x}{1-x}$$

Some details.

Some ideas –

John Slater suggested that the average exchange potential of the homogeneous electron gas could be used to estimate the exchange interaction of a material

$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m} - \frac{2e^2 k_F}{\pi} F\left(\frac{k}{k_F}\right).$$

$$V_{\text{jellium exchange}} = -\frac{2e^2 k_F}{\pi} F\left(\frac{k}{k_F}\right)$$

$$\left\langle V_{\text{jellium exchange}} \right\rangle = -\frac{2e^2 k_F}{\pi}\frac{3}{4}$$

For a electron gas of density n:

$$k_F = \left(3\pi^2 n\right)^{1/3}$$

$$V_{\text{exch}}^{(\text{Slater})}(\mathbf{r}) = -\frac{3}{2}\frac{e^2}{\pi}[3\pi^2 n(\mathbf{r})]^{1/3}.$$

More details

Kohn-Sham's approximate exchange

Total exchange energy per unit volume of jellium model

$$E_{\text{jellium exchange}} = -\frac{N}{V}\frac{3}{4}\frac{e^2\left(3\pi^2 n\right)^{1/3}}{\pi} = -\frac{3}{4}\frac{e^2\left(3\pi^2\right)^{1/3} n^{4/3}}{\pi}$$

Kohn & Sham argued that the effective exchange potential should be determined from the density derivative:

$$V_{\text{jellium exchange}} = \frac{\partial E_{\text{jellium exchange}}(n)}{\partial n} = -\frac{e^2\left(3\pi^2 n\right)^{1/3}}{\pi}$$

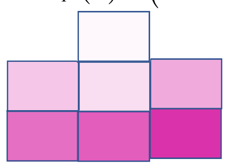
$$V_{ex}^{KS}(\mathbf{r}) = -\frac{e^2\left(3\pi^2 n(\mathbf{r})\right)^{1/3}}{\pi} \qquad V_{ex}^{Slater}(\mathbf{r}) = -\frac{3}{2}\frac{e^2\left(3\pi^2 n(\mathbf{r})\right)^{1/3}}{\pi}$$

This slide is the focus of HW #24.

Comment on the spatial dependence of these approximations

For a electron gas of density n: $k_F = \left(3\pi^2 n\right)^{1/3}$

$$\Rightarrow k_F(\mathbf{r}) = \left(3\pi^2 n(\mathbf{r})\right)^{1/3}$$



Cheating.