

PHY 742 Quantum Mechanics II

1-1:50 AM MWF via video link:

<https://wakeforest-university.zoom.us/my/natalie.holzwarth>

Plan 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.**

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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	<i>Good Friday</i>		
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 indistinguishable Fermi particles: the wave function must have the property:

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

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

Example for N particles using Slater determinant:

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

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Review of the properties of identical Fermi particles.

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

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

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:

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

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

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

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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

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

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

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

Variational approximation.

The Hartree-Fock approximation is based on the choice of

$$|\Psi_{trial}\rangle = \prod_{i=1}^N f_i^\dagger |0\rangle$$

using the second quantized notation or

the equivalent Slater determinant based on the single particle functions $\varphi_i(\mathbf{r})$

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

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

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

Hartree-Fock approximation

Matrix elements

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

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

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

Constrained optimization

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

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

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Writing out the integrals.

Coupled Hartree-Fock equations to solve

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

Define: Exchange integral form:

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

Coupled integral-differential equations:

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

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

Form of coupled equations

Self-consistent solution of the Hartree-Fock equations

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

Count=0

Solve differential integral equations

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

Count=Count+1

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

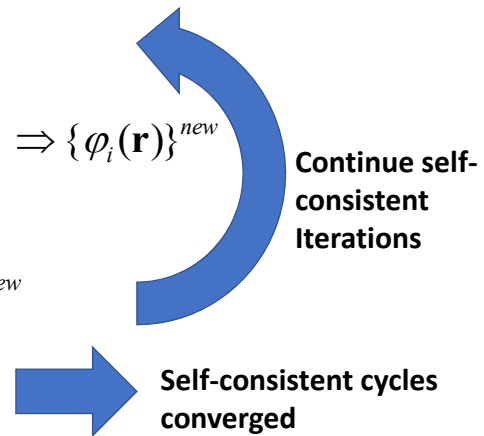
test: if $|\{\varphi_i(\mathbf{r})\}^{Count-1} - \{\varphi_i(\mathbf{r})\}^{Count}| > \epsilon$

if $|\{\varphi_i(\mathbf{r})\}^{Count-1} - \{\varphi_i(\mathbf{r})\}^{Count}| < \epsilon$

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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

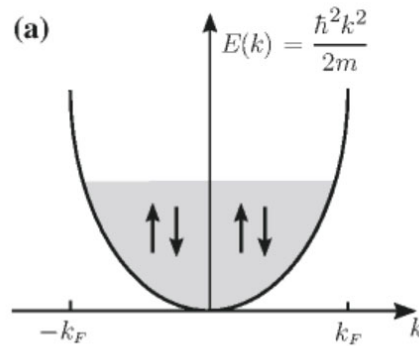
- A. Attempts to solve #1**
- B. Reduces the pain of #2**
- C. Physicists are happier than chemists**

Perspective on the state of the formalism.

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

Prelude to DFT --

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



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

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

$$\begin{aligned} V_{\text{exch}} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} &= - \sum_{\mathbf{q}}^{(\text{occ})} \frac{1}{\sqrt{V}} e^{i\mathbf{q}\cdot\mathbf{r}} \int \frac{1}{\sqrt{V}} e^{-i\mathbf{q}\cdot\mathbf{r}'} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}'} d\mathbf{r}' \\ &= - \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \sum_{\mathbf{q}}^{(\text{occ})} \int \frac{1}{V} e^{-i(\mathbf{k}-\mathbf{q})\cdot(\mathbf{r}-\mathbf{r}')} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &= - \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \frac{1}{V} \sum_{\mathbf{q} < k_F} \frac{4\pi e^2}{|\mathbf{k} - \mathbf{q}|^2}. \end{aligned}$$

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Some details

Some details --

$$\begin{aligned}
 V_{\text{exch}} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} &= - \sum_{\mathbf{q}}^{(\text{occ})} \frac{1}{\sqrt{V}} e^{i\mathbf{q}\cdot\mathbf{r}} \int \frac{1}{\sqrt{V}} e^{-i\mathbf{q}\cdot\mathbf{r}'} \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}'} d\mathbf{r}' \\
 &= - \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \sum_{\mathbf{q}}^{(\text{occ})} \int \frac{1}{V} e^{-i(\mathbf{k}-\mathbf{q})\cdot(\mathbf{r}-\mathbf{r}')} \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \\
 &= - \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \frac{1}{V} \sum_{q < k_F} \frac{4\pi e^2}{|\mathbf{k}-\mathbf{q}|^2}.
 \end{aligned}$$

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

$$\begin{aligned}
 \int e^{-i\mathbf{Q}\cdot\mathbf{r}-\epsilon r} \frac{1}{r} d^3r &= \int e^{-iQr-\epsilon r} \frac{1}{r} r^2 dr d\cos\theta d\phi = -2\pi \int_0^\infty r dr e^{-\epsilon r} \int_{-1}^1 d\cos\theta e^{-iQr\cos\theta} \\
 &= -2\pi \int_0^\infty r dr e^{-\epsilon r} \left(\frac{e^{-iQr} - e^{iQr}}{-iQr} \right) = \frac{4\pi}{Q^2 + \epsilon^2}
 \end{aligned}$$

More details.

More details

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

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

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

We thus obtain

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

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:

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

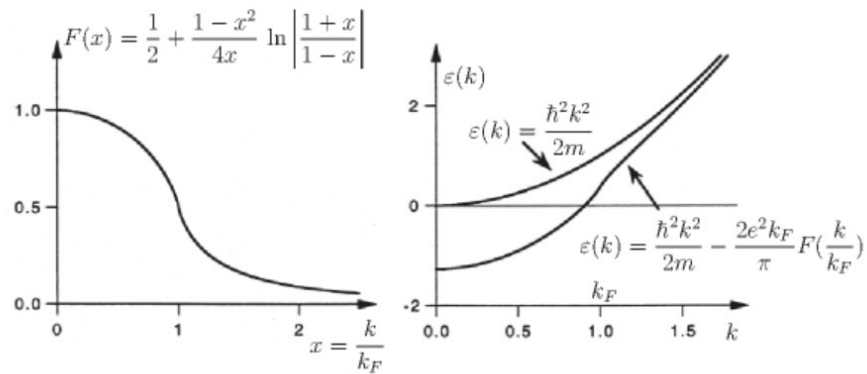


Figure 4.4 (a) Schematic plot of the function $F(x)$. (b) Kinetic energy and Hartree-Fock orbital energy as a function of the wavevector k for the homogeneous electron gas. Energies are in Rydbergs, k is in units of a_B^{-1} (inverse Bohr radius), and we have taken $k_F = 1/a_B$.

Plots of results.

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

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

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

Some details:

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

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

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

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

For a electron gas of density n :

$$\langle V_{\text{jellium exchange}} \rangle = -\frac{2e^2 k_F}{\pi} \frac{3}{4} \quad k_F = (3\pi^2 n)^{1/3}$$

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

More details

Kohn-Sham's approximate exchange

Total exchange energy per unit volume of jellium model

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


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

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

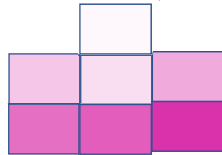
$$V_{\text{ex}}^{KS}(\mathbf{r}) = -\frac{e^2 (3\pi^2 n(\mathbf{r}))^{1/3}}{\pi} \quad V_{\text{ex}}^{\text{Slater}}(\mathbf{r}) = -\frac{3 e^2 (3\pi^2 n(\mathbf{r}))^{1/3}}{2 \pi}$$

This slide is the focus of HW #24.

Comment on the spatial dependence of these approximations

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

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



Cheating.