

I.D. #	
Name	Philip Phillips
Subject	
Course	Physics 560
Instructor	
Date	

Receiving or giving aid in a final examination is a cause for dismissal from the University.

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Lecture 9:

1.) Review

$$E_{HF} = \langle H_i \rangle + \frac{1}{2} \sum_{\lambda, \nu} U_{\lambda\nu} - J_{\lambda\nu}$$

$$U_{\lambda\nu} = \int dr_1 dr_2 |\phi_\lambda(r_1)|^2 \frac{e^2}{|r_1 - r_2|} |\phi_\nu(r_2)|^2$$

$$J_{\lambda\nu} = \int dr_1 dr_2 \phi_\lambda^*(r_1) \phi_\nu^*(r_2) \frac{e^2}{|r_1 - r_2|} \phi_\nu(r_1) \phi_\lambda(r_2)$$

The HF eqs. are

$$\frac{\delta E_{HF}}{\delta \phi_\nu^*(r)} = \epsilon_\nu \frac{\delta}{\delta \phi_\nu^*(r)} \int |\phi_\nu|^2 dr$$

$$\left[-\frac{k^2}{2m} \nabla^2 + \hat{V}_{ion}(r) + \sum_i \int \frac{dr' n_{\lambda}(r') e^2 |\phi_\lambda(r')|}{|r-r'|} \right] \phi_\nu(r) = \epsilon_\nu \phi_\nu(r)$$

$$- \sum_\lambda \int dr' \phi_\lambda^*(r') \phi_\nu(r') \frac{e^2}{|r-r'|} \phi_\lambda(r)$$

For the Jellium model $\hat{V}_{ion} + U_{direct}$ cancel. The eigenstates are $\phi_\nu = \phi_p = \frac{1}{V} e^{ip \cdot r / \hbar}$.

Exchange int.

$$\text{We showed that } E_p = \frac{p^2}{2m} - \underbrace{\int_0^{P_F} \frac{dp'}{(2\pi\hbar)^3} \int dx \frac{e^{-(p-p') \cdot x/\hbar}}{|x|}}$$

$$= \frac{p^2}{2m} - 2\frac{e^2 P_F}{\pi\hbar} \left(\frac{1}{2} + \frac{(P_F^2 - p^2)}{4PP_F} \ln \left| \frac{p+P_F}{p-P_F} \right| \right)$$

$$x = \frac{p}{P_F}$$

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

$$\frac{E(p)}{E_F} = x^2 - \frac{2e^2 P_F}{\pi\hbar} \frac{2m}{\hbar^2} F(x) ; \quad \boxed{\alpha_0^{-1} = \frac{mc^2}{\hbar^2}} \text{ and } \boxed{r_e = 1.92 \frac{\hbar}{P_F}}.$$

$$= x^2 - .663 r_s F(x)$$

$$F(x \rightarrow 0) = \frac{1}{2} + \underset{0}{\cancel{0}} \xrightarrow[\text{L'Hospitals rule}]{\text{L'Hospitals rule}} \frac{1}{2} + \frac{1}{4} \left(\frac{1}{1+0} + \frac{1}{1-0} \right) = 1.$$

$$F(x \rightarrow 1) = \frac{1}{2} \Rightarrow \Delta = E(P_F) - E(P=0)$$

$$= E(x=1) - E(x=0)$$

$$= E_F^0 (1 - .331 r_s + .663 r_s) = (1 + .331 r_s) E_F^0$$

\Rightarrow The H.F. bandwidth is larger than the N.I. value.

Why do exchange interactions lead to an increase of the band width? The exchange int. decreases the likelihood that same spins are nearby. To understand this let's re-interpret the H.F. $E(p)$ in terms of the N.I. form but with $m \rightarrow m^*$. Let's say that

$$E(p) \rightarrow \frac{p^2}{2m^*}$$

$$\Rightarrow \frac{\partial E}{\partial p} \rightarrow \frac{p}{m^*} \rightarrow \frac{1}{m^*} = \frac{1}{P_F} \frac{\partial E}{\partial p} \Big|_{p \rightarrow P_F} .$$

We need $\ln \frac{\partial F}{\partial x}$.

$$x \rightarrow 1$$

$$\frac{\partial F}{\partial x} = -\frac{2x}{4x} \ln \left| \frac{1+x}{1-x} \right|_{x \rightarrow 1}$$

$$= \frac{1}{2} \ln \left| \frac{1-x}{2} \right| \Big|_{x \rightarrow 1} \rightarrow -\infty$$

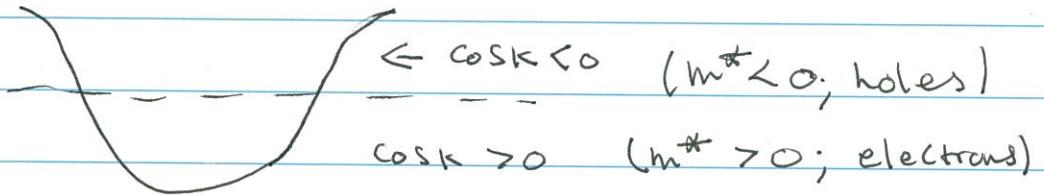
$$\Rightarrow m^* \sim \frac{1}{\ln|1-x|} \rightarrow 0 \text{ as } x \rightarrow 1.$$

\Rightarrow e's actually get lighter as a result of the exchange hole.

$\Rightarrow P^2/m^*$ increases and so does the bandwidth.

So at least HF is internally consistent.

In general $\frac{1}{m^*} \propto \frac{\partial^2 \Sigma}{\partial P^2}$



2.) Energy of Jellium.

$$E_{HF} = 2V \int_0^{P_F} \frac{d^3 p}{(2\pi\hbar)^3} \left[\frac{p^2}{2m} + \frac{1}{2} \epsilon_{\text{exch}}(p) \right].$$

You will show that $\int_0^{P_F} \epsilon_{\text{exch}}(p) = -\frac{C^2 P_F^4}{4\pi^3 \hbar^4}$.

recall $2V \int_0^{P_F} \frac{d^3 p}{(2\pi\hbar)^3} \frac{p^2}{2m} = \frac{\sqrt{V} P_F^5}{10\pi^2 \hbar^3 m}$.

$$\Rightarrow E_{HF} = V \left[\frac{P_F^5}{10m\pi^2 \hbar^3} - \frac{C^2 P_F^4}{4\pi^3 \hbar^4} \right].$$

recall $\frac{N}{V} \equiv n_e = \frac{P_F^3}{3\pi^2 k^3}$.

$$\Rightarrow P_F = \left(\frac{3\pi^2}{k^3}\right)^{1/3} n_e^{1/3}.$$

$$\Rightarrow \frac{E_{HF}}{V} = \frac{3\pi^2 k^3}{10m\pi^2 k^3} n_e^{5/3} - \frac{e^2 (3\pi^2 k^3)^4}{4\pi^3 k^4} n_e^{4/3}.$$

$\Rightarrow E_{kin} \sim n_e^{5/3}$ and $E_{ee} \sim n_e^{4/3}$. \Rightarrow at the HF level the energy is a unique fn. of the electron density. Is this true in general?

This is the claim of density functional theory.

Before we do this, let's write E_{HF} as an energy per particle.

$$\frac{E_{HF}}{N} = \frac{3\pi^2 k^3}{P_F^3} \left(\frac{P_F^5}{10m\pi^2 k^3} - \frac{e^2 P_F^4}{4\pi^3 k^4} \right).$$

$$= \frac{3 P_F^2}{10m} - \frac{3 e^2 P_F}{4\pi k} . \quad 1 \text{ Ry} = e^2/2a_0.$$

$$= \left[\frac{3 P_F^2}{10m} \frac{2a_0}{e^2} - \frac{3}{4} \frac{P_F e^2}{\pi k} \frac{2a_0}{e^2} \right] \frac{e^2}{2a_0} ; \quad m e^2 = \frac{k^2}{a_0}$$

$$= \left[\frac{3}{5} \left(\frac{P_F a_0}{k} \right)^2 - \frac{3}{2\pi} \left(\frac{P_F a_0}{k} \right) \right] \frac{e^2}{2a_0} ; \quad r_e = 1.92 \frac{k}{P_F}$$

$$= \left[\frac{3}{5} \left(1.92 \right)^2 \left(\frac{a_0}{r_e} \right)^2 - \frac{3}{2\pi} \cdot 1.92 \cdot \frac{a_0}{r_e} \right] \text{Ry}.$$

$$= \left[\frac{2 \cdot 21}{r_e^2} - 0.96 \right] \text{Ryd.}$$

$E_{kin} \propto 1/r_e^2$; $V_{ee} \propto 1/r_e^2$.

3.) Density Functional Theory

$$n(\vec{r}) = \left\langle \Psi \left| \sum_{i=1}^N \delta(\vec{r} - \vec{R}_i) \right| \Psi \right\rangle.$$

Q: Does n uniquely determine the density?

Here's the proof. Let

$$H = T + U(r) + V_{ee}$$

here $U(r)$ is a 1-body potential. The question is does $U(r)$ uniquely determine the density $n(r)$?

Let $|\psi\rangle$ and $|\psi'\rangle$ be the ground states of H and $H' = T + U' + V_{ee}$. Suppose \exists two potentials U, U' that generate the same densities. $\rho = |\psi|^2 = |\psi'|^2$.

$$E = \langle \psi | H | \psi \rangle$$

By the variational principle

$$\begin{aligned} E &\leq \langle \psi' | H | \psi' \rangle \\ &< \langle \psi' | H + H' - H' | \psi' \rangle \\ &< E' + \langle \psi' | H - H' | \psi' \rangle \\ &< E' + \int \rho(r) (U - U'). \end{aligned} \tag{1}$$

Now do the same thing for $|\psi\rangle$.

$$\begin{aligned} E' &\leq \langle \psi | H' | \psi \rangle \\ &< \langle \psi | H' + H - H | \psi \rangle \\ &< E + \int \rho(r) (U' - U) \end{aligned} \tag{2}$$

add $\textcircled{1} + \textcircled{2}$.

$$\Rightarrow E + E' < E' + E$$

$\rightarrow \leftarrow$.

$\Rightarrow E$ is a unique functional of the density.

$$\Rightarrow E[n] = T[n] + U[n] + V_{ee}[n],$$

Subject to the constraint that $\int n(r) = N$.

All of this started with Hohenberg-Kohn.

What they said is that

$$E(n) = \int dr n(r) U(r) + F_{HK}[n].$$

$$F_{HK} = T[n] + V_{ee}[n].$$

4.) Thomas-Fermi Approximation:

Look at n -dependence in Jellium model.

$$T = V \int d^3k \frac{(x_k)^3}{2m} = \frac{3}{5} V \frac{k^3}{2m} (3\pi^2)^{2/3} n^{5/3}$$

also $\epsilon_{\text{exch}} \propto n^{4/3}$.

$$\text{direct: } \frac{1}{2} \int dr_1 dr_2 \frac{n(r_1) n(r_2)}{|r_1 - r_2|}.$$

$$\Rightarrow E[n] = \frac{k^2}{2m} \frac{3}{5} (3\pi^2)^{2/3} \int dr n^{5/3} + \int dr n(r) U(r) \\ + Y_2 \int dr_1 dr_2 n(r_1) n(r_2) / |r_1 - r_2|$$

7.

$$-\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} e^2 \int dr n^{4/3}(r).$$

$$\mu = \frac{\delta E}{\delta n(r)} = \frac{k^2}{2m} (3\pi^2)^{2/3} n^{2/3} + \mu(r) + e^2 \int \frac{n(r') dr'}{|r-r'|}$$
$$- \left(\frac{3}{\pi}\right)^{1/3} e^2 n^{4/3},$$