

It gets lowered by

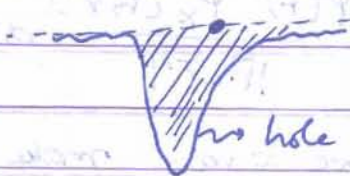
$$\frac{1}{P(\vec{r})} \sum_{\sigma} \sum_{j'} |\psi_{\sigma}(\vec{r}, \vec{r}')|^2$$

Note that it gets lowered by a more complicated function
By normalization (it is easy to show)

$$\frac{1}{P(\vec{r})} \int \sum_{\sigma} \sum_{j'} |\psi_{\sigma}(\vec{r}, \vec{r}')|^2 d\vec{r}' = 1$$

As total lowering of probability is precisely 1 so it must be

Thus we can think of an electron at \vec{r} as a hole around it due to antisymmetry of the wavefun



Half the hole comes from complete reduction of probability for electron of a particular spin. This is known as the Fermi or the exchange hole.

$$E_x = + \frac{1}{2} \int P(\vec{r}) \frac{\rho_x(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' d\vec{r}$$

$$\rho_x = - \frac{1}{P(\vec{r})} \sum_{\sigma} |\psi_{\sigma}(\vec{r}, \vec{r}')|^2$$

This exchange energy is nothing but lowering of energy due to deficit of electrons around each electron due to the antisymmetry of the wavefunction.

(4) Does $E_x = \frac{1}{2} \int \frac{\rho(\vec{r}) \rho_x(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'$

that the exchange potential is $\int \frac{\rho_x(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}'$

We will address this question later.

Hartree-Fock equations: We have the expectation value of the Hamiltonian

$$\langle H \rangle = \sum_i \int \frac{|\nabla \phi_i|^2}{2} d\vec{r} + \int V_{ext}(\vec{r}) \rho(\vec{r}) d\vec{r}$$

$$+ \frac{1}{2} \iint \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'$$

$$- \frac{1}{2} \iint \frac{\rho(\vec{r}) \rho_x(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'$$

To find the orbitals, we again make use of the variational principle and make

$$\langle H \rangle = \sum_i \epsilon_i \int |\phi_i|^2 d\vec{r} \quad \text{Stationary w.r.t}$$

$\phi_i^*(\vec{r})$ to get

$$-\frac{1}{2} \nabla^2 \phi_{i\sigma} + V_{ext}(\vec{r}) \phi_{i\sigma} + \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' \phi_{i\sigma}(\vec{r})$$

$$- \sum_j \int \frac{\phi_{j\sigma}^*(\vec{r}') \phi_{k\sigma}(\vec{r}') \phi_{j\sigma}(\vec{r})}{|\vec{r}-\vec{r}'|} d\vec{r}' = \epsilon_i \phi_{i\sigma}$$

exchange potential

Total energy:

$$E = T + \int_{\text{all}} U(\mathbf{r}) \rho(\mathbf{r}) + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

$$= \sum E_i - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \frac{1}{2} \sum \text{exchange term}$$

Koopmans' theorem:

$E_i \approx$ Removal energy of electron from the i^{th} orbital.

Question: How good is Hartree-Fock theory for total energies, removal energies, band gaps (excited-state energies) and other properties

Energy of some atoms within Hartree-Fock theory

	HF (eV)	$E_{\text{exp}}(eV)$	% Difference
H	-13.6	-13.6	0 %
He	-79.9	-79.0	1.4 %
Be	-396.5	-399.1	0.65 %
Ne	-3497.8	-3508.1	0.29 %
Mg	-5431.5	-5443.2	0.22 %
Ar	-14334.7	-14354.6	0.14 %

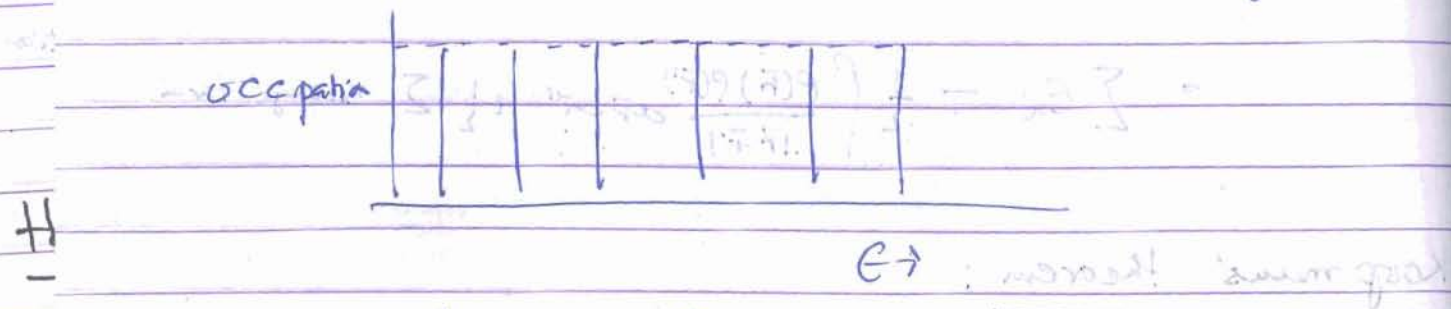
Koopmans

25

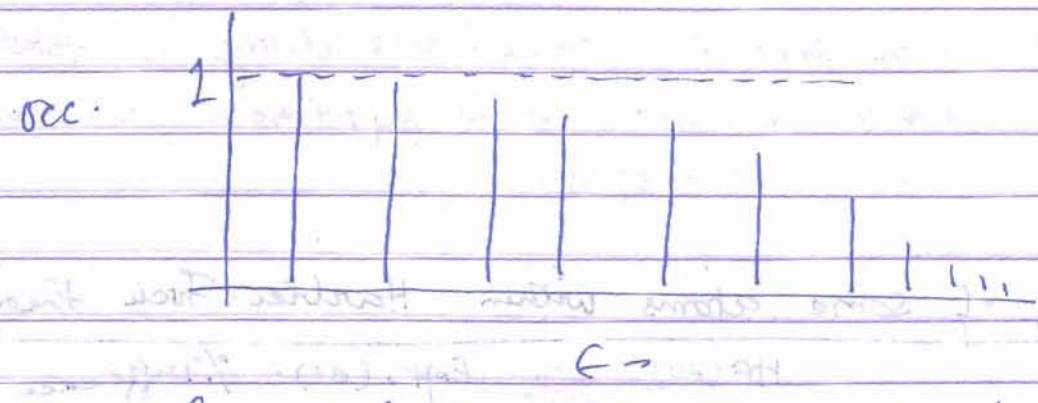
How to make energies more accurate?

Go beyond Hartree-Fock

In HF theory all orbitals below E_{max} are filled



This is because electrons are moving in mean field. However instantaneous collisions may excite electron out of the Fermi sea. This leads to lowering of energy



So a wavefunction will be a linear combination of many determinants

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N) = \sum c_i |\Psi_{HF}^i| \quad (c_i \text{ determined variationally})$$

$c_i \sim 1$ for HF configurations

\sim very small for higher energy configurations

OR make explicitly correlated wavefunctions (Jastron wavefn eg.)

Question: Why worry about such difficult calculations if energies are accurate enough

Gain in energy in going beyond HF is called

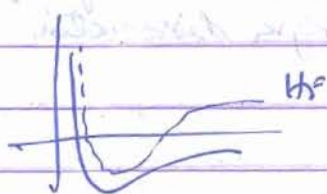
$$\Delta E = E_{\text{true}} - E_{\text{HF}} = E_{\text{CORRELATION}}$$

Now the question: Why worry if $E_{\text{correlation}}$ is so small?

How CORRELATIONS CHANGE PROPERTIES OF A SYSTEM.
(Why Hartree-Fock is not alright all the time?)

(1) H^- has energy higher than H^0 in HF theory. This implies H^- is unstable. Experimentally H^- is found in nature.

(2) H_2 molecule, calculate in HF theory, does not dissociate properly. The energy of separated atoms goes to greater than zero.



This is because in HF theory on an average, electrons can come close to each other.

(3) Density of states for free electron gas (alkali metals) vanishes at the Fermi level in HF theory. This implies that

$$C_V \propto 0 \text{ as } T \rightarrow 0 \text{ as } \frac{T}{\mu T} \text{ contrary to experiment}$$

where C_V & T_V calculated with free electron theory.

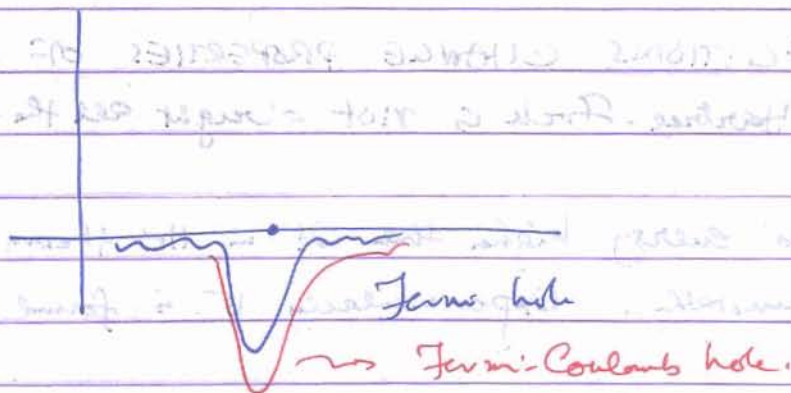
(4) In HF theory, free electron gas for density greater than $\nu_s > 5.65$ will be in ferromagnetic state (all parallel spins) whereas this is not the experimental case.

(5) ΔE_i gas band gaps that are too high.

(26)

Effect of Correlations:

- (1) Makes wavefunction more diffused. This results in a deeper hole (recall exchange hole) than H^+ and leads to further reduction in the energy



- (2) As a Corollary of (1) in the far distance limit, keeps electrons apart as two nuclei of H_2 molecule are pulled apart. Give proper dissociation limit

- (3) In homogeneous electron gas - gives rise to plasma oscillations by correlation motion of a large number of electrons.

So we see that correlations make qualitative difference in ~~study~~ describing behaviour of a system.

(*) In HEG, write the Hamiltonian as

$$H = \frac{1}{2} \int \frac{p_+ p_+}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \frac{1}{2} \int \frac{p_- p_-}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int \frac{p_+ p_-}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' = 0$$

(27)

LECTURE 2

We start this lecture by doing Hartree-Fock theory for Homogeneous electron gas.

(1) Homogeneous electron gas without interaction

$$-\frac{1}{2} \nabla^2 \psi = \epsilon \psi$$

$$\Rightarrow \psi = \int \frac{1}{L} e^{i\mathbf{k} \cdot \mathbf{r}} \quad \epsilon_k = \frac{\hbar^2 k^2}{2m}$$

has been done in previous lecture. It gives a ground state when occupation of orbitals is a Θ function.

(2) Homogeneous electron gas in HF approximation

$$-\frac{1}{2} \nabla^2 \phi_i = \int \frac{p_+(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \int \frac{p_-(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$

$$\int \frac{\phi_j^*(\mathbf{r}') \phi_j(\mathbf{r}) \phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' = \epsilon_i \phi_i(\mathbf{r})$$

We show that plane waves are self-consistent solution of HF for HEG

For plane waves p_+ & p_- cancel

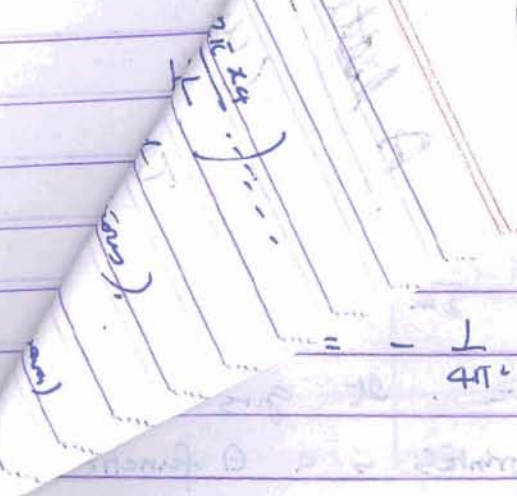
$$\sum_{\mathbf{k}'} \int \frac{e^{-i\mathbf{k}' \cdot \mathbf{r}'} e^{i\mathbf{k} \cdot \mathbf{r}} e^{i\mathbf{k}' \cdot \mathbf{r}'}}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$

$$= e^{i\mathbf{k} \cdot \mathbf{r}} \sum_{\mathbf{k}'} \int \frac{e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}'} e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}}}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$

$$= e^{i\mathbf{k} \cdot \mathbf{r}} \sum_{\mathbf{k}'} \int \frac{e^{i(\mathbf{k}-\mathbf{k}') \cdot (\mathbf{r}-\mathbf{r}')}}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$

②

Solution of term:



③

$$= \epsilon_0 \Phi_1$$

$$\frac{v(\vec{k}-\vec{k}') \cdot (\vec{r}-\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}'$$

$$\frac{\epsilon_0 v(\vec{k}-\vec{k}') \cdot \vec{R}}{R} \int_0^R \int_0^{2\pi} d\phi dR$$

$$= -\frac{1}{4\pi^2} \int d^3\vec{k}' R dR \int_{-1}^1 e^{-i|\vec{k}-\vec{k}'| R x} dx$$

$$= -\frac{1}{4\pi^2} \int d\vec{k}' R dR - \frac{1}{2|\vec{k}-\vec{k}'| R} \left. e^{-i|\vec{k}-\vec{k}'| R x} \right|_{-1}^1$$

$$= +\frac{1}{4\pi^2} \int d\vec{k}' \int_0^{\infty} \frac{2}{|\vec{k}-\vec{k}'|} \sin|\vec{k}-\vec{k}'| R dR$$

$$= -\frac{1}{2\pi^2} \int d\vec{k}' \frac{1}{|\vec{k}-\vec{k}'|^2} \left[\begin{matrix} \cos(k-k')R \rightarrow 0 \\ \text{as } R \rightarrow \infty \end{matrix} \right]$$

$$\int \frac{d\vec{k}'}{k-k'} = 2\pi \left[k_f + \frac{k_f^2 - k^2}{2k} \ln\left(\frac{k_f+k}{k_f-k}\right) \right]$$

$$\Rightarrow \epsilon_x(k) = -\frac{1}{\pi} \left[k_f + \frac{k_f^2 - k^2}{2k} \ln\left(\frac{k_f+k}{k_f-k}\right) \right]$$

$$\Rightarrow \epsilon(k) = \frac{k^2}{2} - \frac{1}{\pi} \left[k_f + \frac{(k_f^2 - k^2)}{2k} \ln\left(\frac{k_f+k}{k_f-k}\right) \right]$$

Density of states = $\int \frac{d\epsilon}{|D_\epsilon|} \rightarrow 0$ as $k \rightarrow k_f$

Total Exchange energy :

$$E_x = \frac{1}{2} \times \frac{2V}{8\pi^3} E_x(k) \cdot 4\pi k^2 dk$$

$$= - \left(\frac{3k_F}{4\pi} \right) \cdot \frac{k_F^3}{3\pi^2} V$$

$$= - \left(\frac{k_F^4}{4\pi^3} \right) V$$

$$\frac{E_x}{V} = - \left(\frac{k_F^4}{4\pi^3} \right) = - \rho(r) \left(\frac{k_F}{4\pi} \right) V$$

Exchange energy per electron = $-\left(\frac{3k_F}{4\pi}\right)$

How about correlation energy for HEG?

Different Approaches

- (i) Ligner Crystal at low density
- (ii) Perturbative calculation of Gellman & Brueckner at high density
- (iii) Bohm-Pines calculation by separating collective & single particle excitation
- (iv) Monte carlo simulation of Cepaly, Alda & and the parametrization of resulting energy

Different parametrization

Gunnarsson Lundquist parametrization

$$E_c^{hom} = C \left\{ (1+x^2) \ln \left(1 + \frac{1}{x} \right) + \frac{x}{2} - x^2 - \frac{1}{3} \right\}$$

$$C = -0.0333$$

$$x = \frac{r_s}{11.4} \quad r_s = \left(\frac{3\rho}{4\pi} \right)^{1/3}$$

Early attempts to do calculations in terms of electronic density (Thomas Fermi theory):

As we have already seen, for the homogeneous electron gas, the kinetic energy, the exchange energy and the correlation energy can all be expressed in terms of the density. A subtle point is that the kinetic energy is that of non-interacting electrons

$$KE = \left(\frac{3}{10} \frac{2}{k_F} \right) N = \frac{3}{10} (3\pi^2)^{2/3} \rho^{2/3} N \text{ eV/elec}$$

$$E_x = \left(\frac{36\pi}{4\pi} \right) N = - \frac{3}{4\pi} (3\pi^2)^{1/3} \rho^{1/3} N$$

$$= - \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \rho^{1/3} N \text{ eV/elec}$$

Now consider an inhomogeneous system of electrons like a molecule.

Write energy in terms of local density

$$KE = \int \frac{3}{10} (3\pi^2)^{2/3} \rho^{2/3}(\vec{r}) \rho(\vec{r}) dV$$

$$\text{External energy} = \int U(\vec{r}) \rho(\vec{r}) d\vec{r}$$

$$\text{Coulomb energy} = \frac{1}{2} \iint \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$$

$$\text{Exchange energy} = - \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int \rho^{4/3}(\vec{r}) d\vec{r}$$

$$\text{Correlation energy} = \int \epsilon_c(\rho) \rho(\vec{r}) d\vec{r}$$