

Electronic Structure

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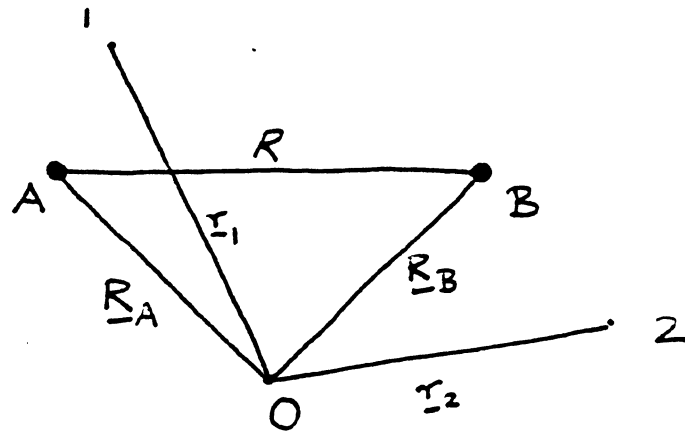
I can't remember when I taught this course or to whom. The first lecture is dated 1995 and the rest is 2004.

These notes may be useful as an introduction to the density functional theory. I know that I drew heavily on Parr and Yang, and Raimes's textbooks for a lot of the material.

1. H₂ molecule

Along with the He atom, this is the simplest “many-body” ($n > 2$) problem. It’s intractable in closed form, but can be converged numerically to an exact solution.

Geometry and coordinates of the problem are as FIG 1:



We will always use \mathbf{r} for electron positions and \mathbf{R} for coordinates of the nuclei. In FIG 1, $R = |\mathbf{R}_A - \mathbf{R}_B|$.

The hamiltonian (total energy operator—*cf* classical mechanics) for the system of electrons and fixed nuclei is:

$$\begin{aligned} \hat{H} &= \left(-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_A|} \right) + \left(-\frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_B|} \right) \\ &\quad - \frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_B|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_A|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{e^2}{R} \\ &\equiv \hat{H}_A + \hat{H}_B + \hat{V}_{\text{int}} \end{aligned}$$

NOTES:

1. In quantum mechanics, $p_x \rightarrow -i\hbar \frac{\partial}{\partial x}$.
2. The hamiltonian has electron (but not nucleus, because they’re fixed) kinetic energy, electron-nucleus, electron-electron and nucleus-nucleus terms.
3. \hat{H}_A and \hat{H}_B , the quantities in large parentheses, are the hamiltonians for the free hydrogen atoms labelled A and B.

We now use first-order perturbation theory of \hat{V}_{int} . We will only need to know the wavefunctions of the *unperturbed* system; namely the eigenfunctions of $\hat{H}_A + \hat{H}_B$ which are *products* of the eigenfunctions of the free hydrogen atoms (PROBLEM: Prove this). We will call these $\psi_A(\mathbf{r}_1)$ and $\psi_B(\mathbf{r}_2)$ respectively, where \mathbf{r}_1 labels the position of electron 1. But we CANNOT use $\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2)$ as a product wavefunction because it does not account for *indistinguishability*: *ie*, $\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2)$ cannot be distinguished from $\psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_1)$. Therefore the proper first order wavefunction is the linear combination,

$$\Psi(\mathbf{r}_1\mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2) \pm \psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_1)], \quad (1)$$

so that $\Psi^2(\mathbf{r}_1\mathbf{r}_2) = \Psi^2(\mathbf{r}_2\mathbf{r}_1)$ which is the *fundamental requirement*. Note: we will use Ψ for “many-body” wavefunctions and ψ or ϕ for “one-electron” or “single particle” wavefunctions.

Actually, we can write down from simple atomic theory that the 1s ground state wavefunctions for the free hydrogen atoms are $\psi_I(\mathbf{r}_i) = \frac{1}{\sqrt{\pi}} e^{-|\mathbf{r}_i - \mathbf{R}_I|/a_0}$, where a_0 is the Bohr radius and I is A or B and i is 1 or 2.

To first order, the *binding energy* is

$$E(R) = \frac{\iint d\mathbf{r}_1 d\mathbf{r}_2 \bar{\Psi} \hat{V}_{\text{int}} \Psi}{\iint d\mathbf{r}_1 d\mathbf{r}_2 \bar{\Psi} \Psi} \equiv \frac{\langle \Psi | \hat{V}_{\text{int}} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

NOTES:

1. The second identity introduces Dirac's bra-ket notation.
2. The bar indicates complex conjugate. But the wavefunctions in this case are real.

Now using

$$\hat{V}_{\text{int}} = -\frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_B|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_A|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{e^2}{R}$$

we get two solutions corresponding to the plus and minus signs in equation (1) respectively:

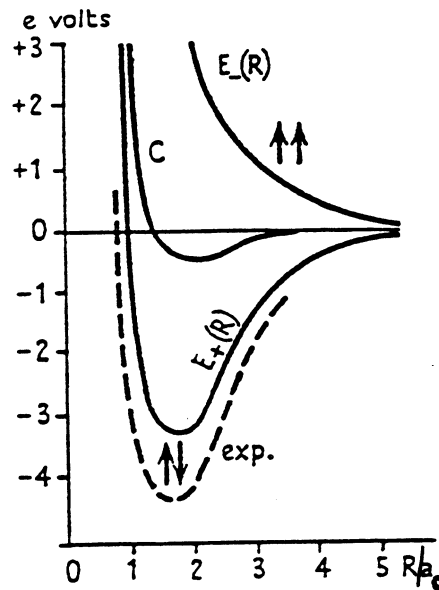
$$E_+(R) = \frac{C + A}{1 + S^2} \quad \text{and} \quad E_-(R) = \frac{C - A}{1 - S^2}$$

where

$$\begin{aligned} C &= \iint d\mathbf{r}_1 d\mathbf{r}_2 \bar{\psi}_A(\mathbf{r}_1) \bar{\psi}_B(\mathbf{r}_2) \left(-\frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_B|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_A|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{e^2}{R} \right) \psi_A(\mathbf{r}_1) \psi_B(\mathbf{r}_2) \\ A &= \iint d\mathbf{r}_1 d\mathbf{r}_2 \bar{\psi}_A(\mathbf{r}_1) \bar{\psi}_B(\mathbf{r}_2) \left(-\frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_B|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_A|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{e^2}{R} \right) \psi_A(\mathbf{r}_2) \psi_B(\mathbf{r}_1) \\ S^2 &= \iint d\mathbf{r}_1 d\mathbf{r}_2 \bar{\psi}_A(\mathbf{r}_1) \bar{\psi}_B(\mathbf{r}_2) \psi_A(\mathbf{r}_2) \psi_B(\mathbf{r}_1) \end{aligned}$$

(PROBLEM: Write these equations in bra-ket notation. For this and subsequent exercises you can use shorthand like $\psi_A(\mathbf{r}_1) \rightarrow a(1)$ etc...)

The binding energy as a function of R is shown in FIG 2:



NOTES:

1. The picture is essentially the same as in the Molecular Orbital Theory. There is an attractive “bonding” solution and a repulsive solution—called “antibonding” in MO Theory.
2. Neglecting the overlap S^2 (*ie*, to first order in S), the “bonding–antibonding splitting” is a consequence of the appearance of the integral A which is negative and much larger in magnitude than C .

C is easily interpreted: it is the interaction due to \hat{V}_{int} between the charge clouds $\psi_A^2(\mathbf{r}_1)$ and $\psi_B^2(\mathbf{r}_2)$ on the unperturbed atoms. C is called the “Coulomb integral.” Note that there is a self interaction (often called the “Hartree energy”) and interactions with the two nuclei (PROBLEM: Identify these).

The integral A which leads to the bonding is similarly interpreted as the interaction between the “exchange charge densities” $\bar{\psi}_A(\mathbf{r}_1)\psi_B(\mathbf{r}_1)$ and $\bar{\psi}_B(\mathbf{r}_2)\psi_A(\mathbf{r}_2)$. This is a wholly quantum mechanical effect arising from the indistinguishability principle.

Actually the condition $\Psi^2(\mathbf{r}_1\mathbf{r}_2) = \Psi^2(\mathbf{r}_2\mathbf{r}_1)$ is not the whole story. The Pauli exclusion principle states that the wavefunction for Fermions is *antisymmetric* under exchange of position *and* spin coordinates. That is,

$$\Psi(s_1\mathbf{r}_1s_2\mathbf{r}_2) = -\Psi(s_2\mathbf{r}_2s_1\mathbf{r}_1).$$

This is a more restrictive requirement. An electron spin s is either plus or minus one (in units of $\frac{1}{2}\hbar$) and the complete wavefunctions for the unperturbed atom are $\psi_A(\mathbf{r}_1)\alpha(s_1)$ or $\psi_A(\mathbf{r}_1)\beta(s_1)$ etc., where the factor $\alpha(s_i)$ is *one* if electron i has spin $+\frac{1}{2}\hbar$ and *zero* if it has spin $-\frac{1}{2}\hbar$, whereas $\beta(s_i)$ is *zero* if electron i has spin $+\frac{1}{2}\hbar$ and *one* otherwise:

$$\alpha(1) = 1 \quad \alpha(-1) = 0 \quad \beta(1) = 0 \quad \beta(-1) = 1 \quad (2)$$

To satisfy the Pauli principle, we must have for the wavefunction corresponding to $E_+(R)$

$$\Psi(\mathbf{r}_1 s_1 \mathbf{r}_2 s_2) = \left(\psi_A(\mathbf{r}_1) \psi_B(\mathbf{r}_2) + \psi_A(\mathbf{r}_2) \psi_B(\mathbf{r}_1) \right) \left(\alpha(s_1) \beta(s_2) - \alpha(s_2) \beta(s_1) \right) \quad (3)$$

and for that corresponding to $E_-(R)$

$$\Psi(\mathbf{r}_1 s_1 \mathbf{r}_2 s_2) = \left(\psi_A(\mathbf{r}_1) \psi_B(\mathbf{r}_2) - \psi_A(\mathbf{r}_2) \psi_B(\mathbf{r}_1) \right) \left\{ \begin{array}{l} \alpha(s_1) \alpha(s_2) \\ \beta(s_1) \beta(s_2) \\ \alpha(s_1) \beta(s_2) + \alpha(s_2) \beta(s_1) \end{array} \right\} \quad (4)$$

This will be demonstrated in a later problem. Note that the symmetric orbital function is multiplied by an antisymmetric spin function and *vice versa*. Spin factors with a single term *eg*, $\alpha(s_1) \alpha(s_2)$ indicate that electrons 1 and 2 both have the same spin (+1)—the total spin for these states is ± 1 in units of \hbar . Two term spin factors are interpreted as mixtures of states in which the two electrons have opposite spins and the total spin is zero. Equation (3) is called a “singlet” state. Equation (4) has three degenerate levels having total spin $-1, 0, +1$ in units of \hbar , but whose degeneracy is lifted in a magnetic field. It is called a “triplet” state.

(PROBLEM: Insert factors of $\frac{1}{2}$ and $1/\sqrt{2}$ that normalise equations (3) and (4). Integrals must be made over \mathbf{r} and the spin s . $\int ds$ has to be interpreted as a sum over spins, $\sum_{s=\pm 1}$)

- The **essential** conclusion from all this is that the *symmetric* orbital $\psi_A(\mathbf{r}_1) \psi_B(\mathbf{r}_2) + \psi_A(\mathbf{r}_2) \psi_B(\mathbf{r}_1)$ must have an *antisymmetric* spin function in which the spins have opposite signs and the *antisymmetric* orbital $\psi_A(\mathbf{r}_1) \psi_B(\mathbf{r}_2) - \psi_A(\mathbf{r}_2) \psi_B(\mathbf{r}_1)$ must be occupied by electrons with parallel spins. This is illustrated in FIG 2. *Only hydrogen atoms whose electrons have opposite spins will form a molecule.*

In this description of the H_2 molecule, the “exchange energy” A is identified as the origin of the the bonding. This is a quantum mechanical effect (*cf* the quantum mechanical interference in the MO picture—Appendix). The general definition of the exchange energy is half the energy difference between antiparallel and parallel spin states of a quantum mechanical system:

$$A_x \equiv \frac{1}{2} (E_{\uparrow\downarrow} - E_{\uparrow\uparrow}).$$

(PROBLEM: Show that for the Heitler–London H_2 molecule, neglecting S^2 , the exchange energy is

$$\begin{aligned} & \frac{1}{2} (E_- - E_+) \\ &= \iint d\mathbf{r}_1 d\mathbf{r}_2 \bar{\psi}_A(\mathbf{r}_1) \bar{\psi}_B(\mathbf{r}_2) \left(-\frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_B|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_A|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \psi_B(\mathbf{r}_1) \psi_A(\mathbf{r}_2) \\ &\equiv A_H. \end{aligned}$$

A_H is called the “Heisenberg exchange energy.” A positive exchange energy favours anti-symmetric or antiferromagnetic spin alignments. Ferromagnetism occurs when the exchange coupling is negative. More on that later when we discuss magnetism.)

2. The General Case

Our view of condensed matter involves the Born–Oppenheimer approximation that the motion of electrons is much faster than that of the nuclei. Therefore at any instant of time the problem is one of fixed nuclei and electrons in their ground state. We can separate out the Coulomb interactions between the nuclei, and for the electrons we have the hamiltonian for a system of N nuclei and n electrons as follows.

$$\begin{aligned}\hat{H} &= \sum_{i=1}^n \left(-\frac{\hbar^2}{2m} \nabla_i^2 + v_{\text{ext}}(\mathbf{r}_i) \right) + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &= \hat{T} + \hat{V}_{\text{en}} + \hat{V}_{\text{ee}}\end{aligned}\quad (5)$$

where

$$v_{\text{ext}}(\mathbf{r}_i) = - \sum_{I=1}^N \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}$$

is called the “external potential.”

The total electronic energy is $\langle \Psi | \hat{H} | \Psi \rangle$ where Ψ is the normalised many-body wavefunction, *ie* a function of all the electron coordinates and spins:

$$\Psi(s_1 \mathbf{r}_1 s_2 \mathbf{r}_2 \dots s_n \mathbf{r}_n)$$

the interpretation of which is that $\bar{\Psi} \Psi d\mathbf{r}_1 \dots d\mathbf{r}_n$ is the *probability* that electron 1, having spin s_1 is to be found in the volume element $d\mathbf{r}_1$ around \mathbf{r}_1 , while simultaneously electron 2, having spin s_2 is to be found in the volume element $d\mathbf{r}_2$ around \mathbf{r}_2 , and so on up to electron n having spin s_n and being found in the volume element $d\mathbf{r}_n$ around \mathbf{r}_n .[†] Below, I will use the shorthand “in $d\mathbf{r}$ ” to mean in the volume element $d\mathbf{r}$ around \mathbf{r} .

We can make the following identities and definitions by “integrating out” all the variables, or all but those that we care about, in $\bar{\Psi} \Psi$.

The probability that the electrons are all somewhere is 1. That is simply “normalisation:”

$$1 = \int \dots \int ds_1 d\mathbf{r}_1 ds_2 d\mathbf{r}_2 \dots ds_n d\mathbf{r}_n |\Psi(s_1 \mathbf{r}_1 s_2 \mathbf{r}_2 \dots s_n \mathbf{r}_n)|^2 \quad (6)$$

The probability that there is an electron in $d\mathbf{r}_1$ is $\rho(\mathbf{r}_1) d\mathbf{r}_1$, and the *charge density* at \mathbf{r}_1 is

$$\rho(\mathbf{r}_1) \doteq n \int \dots \int ds_1 ds_2 d\mathbf{r}_2 \dots ds_n d\mathbf{r}_n |\Psi(s_1 \mathbf{r}_1 s_2 \mathbf{r}_2 \dots s_n \mathbf{r}_n)|^2 \quad (7)$$

The probability that there is an electron in $d\mathbf{r}_1$ and an electron in $d\mathbf{r}_2$ is $2\rho_2(\mathbf{r}_1 \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$:

$$2\rho_2(\mathbf{r}_1 \mathbf{r}_2) \doteq n(n-1) \int \dots \int ds_1 ds_2 ds_3 d\mathbf{r}_3 \dots ds_n d\mathbf{r}_n |\Psi(s_1 \mathbf{r}_1 s_2 \mathbf{r}_2 \dots s_n \mathbf{r}_n)|^2 \quad (8)$$

NOTES:

[†] This rather glib statement must not be underestimated, although we won’t go into the meaning of $\bar{\Psi} \Psi$ any further here. But it represents the mean or “expectation” value resulting from a *measurement* of the position operator $\hat{\mathbf{r}}$; and the probabilistic rather than deterministic character of quantum mechanics itself is reflected here. See “Quantum theory and measurement,” eds Wheeler and Zurek, Princeton.

1. We can continue integrating out fewer and fewer “unimportant” events (Mike Finnis calls this *marginalisation*) to obtain further “density matrices,” but to evaluate the expectation value of \hat{H} we will only need ρ and ρ_2 since only one and two particle operators appear in equation (5).
2. We also integrate out the spins to obtain these because spin does not appear explicitly in the non-relativistic hamiltonian (5).

(PROBLEM: Just for fun write down the probability that there’s an electron in $d\mathbf{r}_1$, one in $d\mathbf{r}_2$ and one in $d\mathbf{r}_3$. Show that in general, the probability of there being electrons simultaneously in $d\mathbf{r}_1, d\mathbf{r}_2, \dots, d\mathbf{r}_p$ is $p! \rho_p(\mathbf{r}_1 \dots \mathbf{r}_p) d\mathbf{r}_1, d\mathbf{r}_2, \dots, d\mathbf{r}_p$, where

$$p! \rho_p(\mathbf{r}_1 \dots \mathbf{r}_p) = p! \binom{n}{p} \int \dots \int ds_1 ds_2 \dots ds_{p+1} d\mathbf{r}_{p+1} \dots ds_n d\mathbf{r}_n |\Psi(s_1 \mathbf{r}_1 s_2 \mathbf{r}_2 \dots s_n \mathbf{r}_n)|^2.$$

Then, using (6), integrate out the remaining coordinates, *ie*, work out

$$\int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_p \rho_p.$$

The answer is an integer. What is it, and what is it counting? Do it first for $p = 2$)

TOTAL ENERGY

The “total energy” $W = W(\mathbf{R}_1 \dots \mathbf{R}_N)$ is defined to be the zero temperature, ground state energy of the assembly of nuclei and electrons. It is the total electronic energy,

$$E[\Psi_0] = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \quad (9)$$

plus the energy of the Coulomb interaction between the nuclei whose atomic numbers are Z :

$$\hat{V}_{\text{nn}} = \sum_{I < J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Ψ_0 denotes the ground state wavefunction and

$$W = E + \hat{V}_{\text{nn}} \quad (10)$$

3. The Hartree–Fock approximation

We want to avoid like the plague dealing with many body wavefunctions; firstly because it is too complicated and secondly because we like to *think* in a one-electron picture, since this is the picture that leads to the notions of energy bands, Brillouin zones, densities of states, tight-binding and free-electron approximations, and the description of bonding. Not to mention optical properties and all the language of semiconductor engineering.

In the Hartree–Fock approximation, Ψ is expressed as a sum of products of one-electron wavefunctions much as in equation (1). When spin is included, this sum of products must be consistent with Pauli’s principle which states that the wavefunction must be *antisymmetric* under interchange of the coordinates:

$$\Psi(s_1\mathbf{r}_1 \dots s_i\mathbf{r}_i \dots s_j\mathbf{r}_j \dots s_n\mathbf{r}_n) = -\Psi(s_1\mathbf{r}_1 \dots s_j\mathbf{r}_j \dots s_i\mathbf{r}_i \dots s_n\mathbf{r}_n).$$

This can be achieved for n “trial” functions ϕ_i by constructing the “Slater determinant:”

$$\Psi_{\text{HF}} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(s_1\mathbf{r}_1) & \phi_2(s_1\mathbf{r}_1) & \dots & \phi_n(s_1\mathbf{r}_1) \\ \phi_1(s_2\mathbf{r}_2) & \phi_2(s_2\mathbf{r}_2) & \dots & \phi_n(s_2\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(s_n\mathbf{r}_n) & \phi_2(s_n\mathbf{r}_n) & \dots & \phi_n(s_n\mathbf{r}_n) \end{vmatrix} \quad (11)$$

Here the ϕ_i are products of orbital and spin functions as on page 4:

$$\phi_i(s_j\mathbf{r}_j) = \psi_i(\mathbf{r}_j)\chi_i(s_j),$$

where χ is either α or β .

This guarantees antisymmetry because interchanging rows or columns changes the sign of the determinant. It also guarantees that two identical one-electron states cannot be simultaneously occupied (a common statement of Pauli’s principle) because if two rows or columns are the same then the determinant is zero.

The n trial functions can be varied to find the lowest value of

$$\begin{aligned} E_{\text{HF}} &= \sum_{s_1, s_2, \dots} \int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_n \bar{\Psi}_{\text{HF}} \hat{H} \Psi_{\text{HF}} \\ &= \langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle \end{aligned} \quad (12)$$

according to the variational principle of quantum mechanics.

Putting equation (11) into equation (12) we get

$$E_{\text{HF}} = \sum_{i=1}^n h_i + \frac{1}{2} \sum_{i,j=1}^n (C_{ij} - A_{ij}) \quad (13)$$

where

$$\begin{aligned} h_i &= \int \bar{\psi}_i(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{ext}} \right] \psi_i(\mathbf{r}) d\mathbf{r} \\ C_{ij} &= \iint |\psi_i(\mathbf{r}_1)|^2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_j(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \\ A_{ij} &= \delta_{s_i s_j} \iint \bar{\psi}_i(\mathbf{r}_1) \psi_j(\mathbf{r}_1) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \bar{\psi}_i(\mathbf{r}_2) \psi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned}$$

NOTES:

1. Equation (13) is quite nice and simple: a sum of one-electron terms for the kinetic energy and electron–nucleus interaction; and the two-body electron–electron terms which comprise a direct Coulomb interaction and an exchange part.
2. Note that $A_{ii} = C_{ii}$ so that the unphysical Coulomb interaction of the electron with itself cancels out so that in equation (13) the second sum can be carried over all values of i and j including $i = j$. This is called “self-interaction cancellation” and we will return to this point later.
3. With Ψ_{HF} a single determinant, the *exchange energy is zero between two electrons with opposite spins*, as indicated by the Kronecker delta symbol which is zero unless $s_1 = s_2$. This is a consequence of equation (2) making K vanish for antiparallel spins. The exchange energy in Heitler–London H_2 is not zero in the ground state although the electron spins are opposite. This is because the ground state Heitler–London wavefunction, equation (3), cannot be written as a single determinant.

3.1 Hartree–Fock equations for “Jellium”

We don’t want to dwell on Hartree–Fock theory, but there is one case where the equations can be solved analytically and the outcome is very instructive. We consider a free-electron gas as in the well-known Sommerfeld theory, but including electron–electron interactions. In the absence of nuclei, the gas would simply fly apart, so in a first approximation we include a uniform distribution of positive background charge that neutralises the total charge. The electron density is measured conventionally by the parameter r_s defined such that the volume $\frac{4}{3}\pi r_s^3$ contains precisely one electron if the gas is homogeneously distributed in space. This model is called “Jellium” and has some properties similar to free-electron like metals (*eg*, Na).

Details of the calculation are in textbooks. I will only give the salient results.

NOTES:

1. The wavefunctions that solve the Hartree–Fock equations are the plane waves

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}}/\sqrt{V}$$

where V is the volume of the Jellium.

2. The direct Coulomb electron–electron interaction is exactly cancelled by the electron–positive background interaction since they are obviously identical but with opposite sign.
3. The remaining energy terms are the kinetic energy of free-electrons and the exchange energy:

$$E(k) = \frac{\hbar^2 k^2}{2m} + \varepsilon_x(k) \quad (14a)$$

where

$$\varepsilon_x(k) = -\frac{e^2 k_F}{2\pi} \left\{ 2 + \frac{k_F^2 - k^2}{kk_F} \log \left| \frac{k_F + k}{k_F - k} \right| \right\} \quad (14b)$$

$$< 0.$$

k_F is the Fermi wavevector, *ie*, the wavevector of the highest energy occupied state.

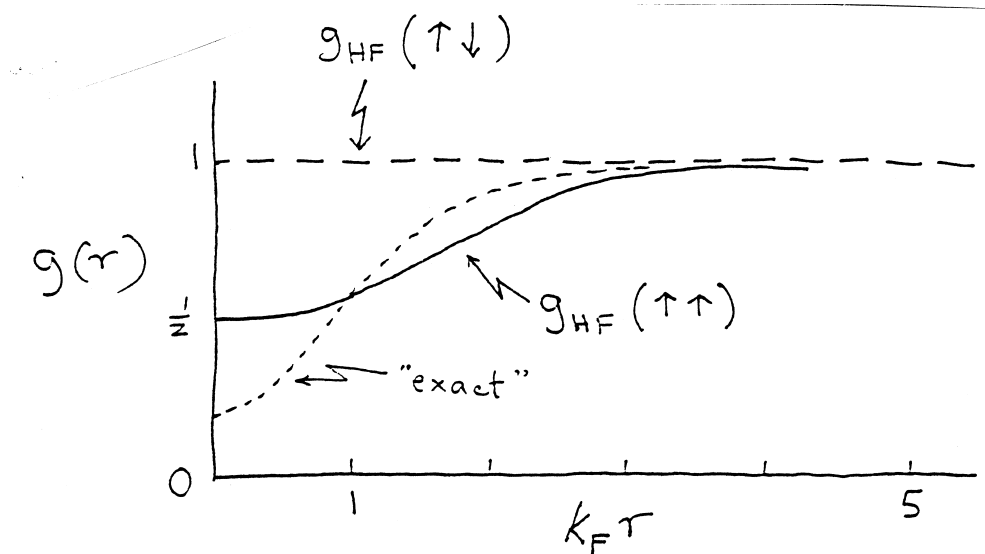
4. The extent to which electrons are *correlated* in their motion is described by the following quantity, see equations (7) and (8).

$$g(r) \equiv \frac{2\rho_2(0r)}{\rho(0)\rho(r)}.$$

This is called the “pair distribution function.” Remembering that $2\rho_2(0r)$ is the probability that there’s an electron at r and one at the origin, and $\rho(0)$ and $\rho(r)$ are the independent probabilities that there’s an electron at the origin or at r ; $g(r)$ is the probability of there being an electron at r if there’s already one at the origin, relative to the probability in the absence of that constraint. It is *one* in the absence of electron-electron interactions. In the Hartree–Fock approximation, $g(r)$ can be worked out exactly:

$$g_{\text{HF}}(r) = 1 - \frac{9}{2} \left(\frac{\sin k_F r - k_F r \cos k_F r}{(k_F r)^3} \right)^2.$$

Since the only electron-electron interaction is due to exchange, *only parallel spins are correlated* in the Hartree–Fock approximation. The pair distribution function



is sketched in FIG 3 (above). It is important to see what has happened. The electron at the origin has put an exclusion zone around it called an “exchange hole.” $g_{\text{HF}}(r)$ is exactly a half at $r = 0$ because all like spin *ie*, *half* the other electrons, are completely excluded (by Pauli’s principle) and this repulsion becomes weaker like $1/r^6$ as r increases. The radius of the exchange hole is roughly r_s and we shall see in a moment that the amount of charge excluded from the neighbourhood of a electron is exactly one electronic charge $-e$. This exposes an amount of the positive background that exactly neutralises the electron: *the electron and its exchange hole is a neutral quasiparticle*. This Hartree–Fock electron has a dispersion (14a) that implies an increased effective mass relative to the Hartree free electron.

5. Unlike spin electrons are uncorrelated in this approximation (FIG 3). The probability of there being an electron at the origin is not affected by whether there is one (of opposite spin) there already; *ie*, $2\rho_2(0r) = \rho(0)\rho(r)$. This quite unreal picture is responsible for the...

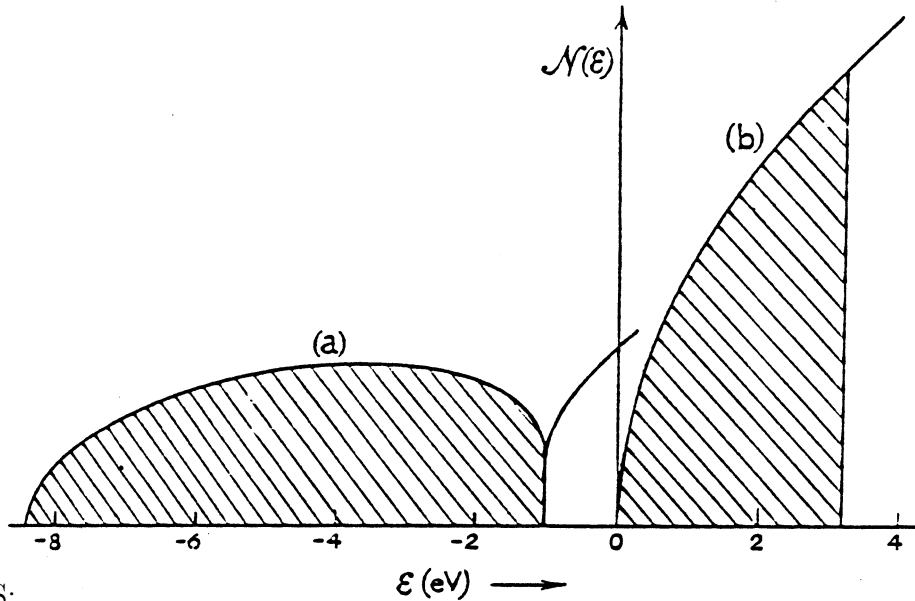
... Failure of the Hartree–Fock theory of the electron gas

The dispersion relation (14) has certain features quite different from the non-interacting, or Sommerfeld, or Hartree electron gas:

NOTES:

1. The energy (and also the density of states) depends on k_F (or equivalently r_s which is proportional to k_F).
2. The logarithmic singularity leads to the density of states going actually to zero at $k = k_F$ or $E = E_F$, where E_F is the Fermi energy.[†]

The densities of states of Hartree–Fock (a) and Hartree (b) Jellium are compared in FIG 4:



NOTES:

1. The pathological density of states at the Fermi energy leads to incorrect descriptions of many properties of metals, including electronic specific heat, X-ray emission, paramagnetic susceptibility. Also the bandwidth is too large. For example 4.1eV for $r_s = 4a_0$ compared to 3.2eV in Na.
2. The non-interacting picture is more respectable: bandwidths and the density of states at the Fermi level agree with measured values in simple metals.
3. However, the Hartree Jellium is *not bound*: the total energy of the electron gas, equation (14) summed over all k occupied up to the maximum, k_F , is

$$2 \sum_k \frac{\hbar^2 k^2}{2m} + \sum_k \varepsilon_x(k) = \frac{3\hbar^2}{10m} \left(\frac{9\pi}{4}\right)^{\frac{2}{3}} \frac{1}{r_s^2} - \frac{3e^2}{4} \left(\frac{9}{4\pi^2}\right)^{\frac{1}{3}} \frac{1}{r_s}.$$

In Rydberg atomic units, the first term is $2.21/r_s^2$, which is positive. The exchange term is $-0.916/r_s$. The total is $0.138 - 0.229 = -0.091$ Ryd in Na, compared to the experimental cohesive energy, -0.08 Ryd.

The failure of the Hartree–Fock approximation can be traced to the neglect of correlations between unlike spins, mentioned above.

[†] The relations between r_s , k_F and E_F for the free electron gas are:

$$k_F = \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{r_s} \quad \text{and} \quad E_F = \frac{\hbar^2}{2m} \left(\frac{9\pi}{4}\right)^{\frac{2}{3}} \frac{1}{r_s^2}$$

2. The General Case

Our view of condensed matter involves the Born–Oppenheimer approximation that the motion of electrons is much faster than that of the nuclei. Therefore at any instant of time the problem is one of fixed nuclei and electrons in their ground state. We can separate out the Coulomb interactions between the nuclei, and for the electrons we have the hamiltonian for a system of N nuclei and n electrons as follows.

$$\begin{aligned}\hat{H} &= \sum_{i=1}^n \left(-\frac{\hbar^2}{2m} \nabla_i^2 + v_{\text{ext}}(\mathbf{r}_i) \right) + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &= \hat{T} + \hat{V}_{\text{en}} + \hat{V}_{\text{ee}}\end{aligned}\quad (5)$$

where

$$v_{\text{ext}}(\mathbf{r}_i) = - \sum_{I=1}^N \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}$$

is called the “external potential.”

The total electronic energy is $\langle \Psi | \hat{H} | \Psi \rangle$ where Ψ is the normalised many-body wavefunction, *ie* a function of all the electron coordinates and spins:

$$\Psi(s_1 \mathbf{r}_1 s_2 \mathbf{r}_2 \dots s_n \mathbf{r}_n)$$

the interpretation of which is that $\overline{\Psi} \Psi d\mathbf{r}_1 \dots d\mathbf{r}_n$ is the *probability* that electron 1, having spin s_1 is to be found in the volume element $d\mathbf{r}_1$ around \mathbf{r}_1 , while simultaneously electron 2, having spin s_2 is to be found in the volume element $d\mathbf{r}_2$ around \mathbf{r}_2 , and so on up to electron n having spin s_n and being found in the volume element $d\mathbf{r}_n$ around \mathbf{r}_n .[†] Below, I will use the shorthand “in $d\mathbf{r}$ ” to mean in the volume element $d\mathbf{r}$ around \mathbf{r} .

We can make the following identities and definitions by “integrating out” all the variables, or all but those that we care about, in $\overline{\Psi} \Psi$.

The probability that the electrons are all somewhere is 1. That is simply “normalisation:”

$$1 = \int \dots \int ds_1 d\mathbf{r}_1 ds_2 d\mathbf{r}_2 \dots ds_n d\mathbf{r}_n |\Psi(s_1 \mathbf{r}_1 s_2 \mathbf{r}_2 \dots s_n \mathbf{r}_n)|^2 \quad (6)$$

The probability that there is an electron in $d\mathbf{r}_1$ is $\rho(\mathbf{r}_1) d\mathbf{r}_1$, and the *electron density* at \mathbf{r}_1 is

$$\rho(\mathbf{r}_1) \doteq n \int \dots \int ds_1 ds_2 d\mathbf{r}_2 \dots ds_n d\mathbf{r}_n |\Psi(s_1 \mathbf{r}_1 s_2 \mathbf{r}_2 \dots s_n \mathbf{r}_n)|^2 \quad (7)$$

The probability that there is an electron in $d\mathbf{r}_1$ and an electron in $d\mathbf{r}_2$ is $2\rho_2(\mathbf{r}_1 \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$:

$$2\rho_2(\mathbf{r}_1 \mathbf{r}_2) \doteq n(n-1) \int \dots \int ds_1 ds_2 ds_3 d\mathbf{r}_3 \dots ds_n d\mathbf{r}_n |\Psi(s_1 \mathbf{r}_1 s_2 \mathbf{r}_2 \dots s_n \mathbf{r}_n)|^2 \quad (8)$$

NOTES:

[†] This rather glib statement must not be underestimated, although we won’t go into the meaning of $\overline{\Psi} \Psi$ any further here. But it represents the mean or “expectation” value resulting from a *measurement* of the position operator $\hat{\mathbf{r}}$; and the probabilistic rather than deterministic character of quantum mechanics itself is reflected here. See “Quantum theory and measurement,” eds Wheeler and Zurek, Princeton.

1. We can continue integrating out fewer and fewer “unimportant” events (Mike Finnis calls this *marginalisation*) to obtain further “density matrices,” but to evaluate the expectation value of \hat{H} we will only need ρ and ρ_2 since only one and two particle operators appear in equation (5).
2. We also integrate out the spins to obtain these because spin does not appear explicitly in the non-relativistic hamiltonian (5).

(PROBLEM: Just for fun write down the probability that there’s an electron in $d\mathbf{r}_1$, one in $d\mathbf{r}_2$ and one in $d\mathbf{r}_3$. Show that in general, the probability of there being electrons simultaneously in $d\mathbf{r}_1, d\mathbf{r}_2, \dots, d\mathbf{r}_p$ is $p! \rho_p(\mathbf{r}_1 \dots \mathbf{r}_p) d\mathbf{r}_1, d\mathbf{r}_2, \dots, d\mathbf{r}_p$, where

$$p! \rho_p(\mathbf{r}_1 \dots \mathbf{r}_p) = p! \binom{n}{p} \int \dots \int ds_1 ds_2 \dots ds_{p+1} d\mathbf{r}_{p+1} \dots ds_n d\mathbf{r}_n |\Psi(s_1 \mathbf{r}_1 s_2 \mathbf{r}_2 \dots s_n \mathbf{r}_n)|^2.$$

Then, using (6), integrate out the remaining coordinates, *ie*, work out

$$\int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_p \rho_p.$$

The answer is an integer. What is it, and what is it counting? Do it first for $p = 2$)

TOTAL ENERGY

The “total energy” $W = W(\mathbf{R}_1 \dots \mathbf{R}_N)$ is defined to be the zero temperature, ground state energy of the assembly of nuclei and electrons. It is the total electronic energy,

$$E[\Psi_0] = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \quad (9)$$

plus the energy of the Coulomb interaction between the nuclei whose atomic numbers are Z :

$$\hat{V}_{\text{nn}} = \sum_{I < J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Ψ_0 denotes the ground state wavefunction and

$$W = E + \hat{V}_{\text{nn}} \quad (10)$$

3. The Hartree–Fock approximation

We want to avoid like the plague dealing with many body wavefunctions; firstly because it is too complicated and secondly because we like to *think* in a one-electron picture, since this is the picture that leads to the notions of energy bands, Brillouin zones, densities of states, tight-binding and free-electron approximations, and the description of bonding. Not to mention optical properties and all the language of semiconductor engineering.

In the Hartree–Fock approximation, Ψ is expressed as a sum of products of one-electron wavefunctions much as in equation (1). When spin is included, this sum of products must be consistent with Pauli’s principle which states that the wavefunction must be *antisymmetric* under interchange of the coordinates:

$$\Psi(s_1\mathbf{r}_1 \dots s_i\mathbf{r}_i \dots s_j\mathbf{r}_j \dots s_n\mathbf{r}_n) = -\Psi(s_1\mathbf{r}_1 \dots s_j\mathbf{r}_j \dots s_i\mathbf{r}_i \dots s_n\mathbf{r}_n).$$

This can be achieved for n “trial” functions ϕ_i by constructing the “Slater determinant:”

$$\Psi_{\text{HF}} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(s_1\mathbf{r}_1) & \phi_2(s_1\mathbf{r}_1) & \dots & \phi_n(s_1\mathbf{r}_1) \\ \phi_1(s_2\mathbf{r}_2) & \phi_2(s_2\mathbf{r}_2) & \dots & \phi_n(s_2\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(s_n\mathbf{r}_n) & \phi_2(s_n\mathbf{r}_n) & \dots & \phi_n(s_n\mathbf{r}_n) \end{vmatrix} \quad (11)$$

Here the ϕ_i are products of orbital and spin functions:

$$\phi_i(s_j\mathbf{r}_j) = \psi_i(\mathbf{r}_j)\chi_i(s_j),$$

where χ is either α or β .

This guarantees antisymmetry because interchanging rows or columns changes the sign of the determinant. It also guarantees that two identical one-electron states cannot be simultaneously occupied (a common statement of Pauli’s principle) because if two rows or columns are the same then the determinant is zero.

The n trial functions can be varied to find the lowest value of

$$\begin{aligned} E_{\text{HF}} &= \sum_{s_1, s_2, \dots} \int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_n \bar{\Psi}_{\text{HF}} \hat{H} \Psi_{\text{HF}} \\ &= \langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle \end{aligned} \quad (12)$$

according to the variational principle of quantum mechanics.

Putting equation (11) into equation (12) we get

$$E_{\text{HF}} = \sum_{i=1}^n h_i + \frac{1}{2} \sum_{i,j=1}^n (C_{ij} - A_{ij}) \quad (13)$$

where

$$\begin{aligned} h_i &= \int \bar{\psi}_i(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{ext}} \right] \psi_i(\mathbf{r}) d\mathbf{r} \\ C_{ij} &= \iint |\psi_i(\mathbf{r}_1)|^2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_j(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \\ A_{ij} &= \delta_{s_i s_j} \iint \bar{\psi}_i(\mathbf{r}_1) \psi_j(\mathbf{r}_1) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \bar{\psi}_i(\mathbf{r}_2) \psi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned}$$

NOTES:

1. Equation (13) is quite nice and simple: a sum of one-electron terms for the kinetic energy and electron–nucleus interaction; and the two-body electron–electron terms which comprise a direct Coulomb interaction and an exchange part.
2. Note that $A_{ii} = C_{ii}$ so that the unphysical Coulomb interaction of the electron with itself cancels out so that in equation (13) the second sum can be carried over all values of i and j including $i = j$. This is called “self-interaction cancellation” and we will return to this point later.
3. With Ψ_{HF} a single determinant, the *exchange energy is zero between two electrons with opposite spins*, as indicated by the Kronecker delta symbol which is zero unless $s_1 = s_2$. In the integral leading to A_{ij} , if the spins are parallel the spin functions will appear in the combinations $\alpha(i)^2\alpha(j)^2$ or $\beta(i)^2\beta(j)^2$ which both integrate to one; but if the spins are antiparallel then the spin functions will be $\alpha(j)\beta(i)\alpha(i)\beta(j)$ which integrates to zero.[†] The exchange energy in Heitler–London H_2 is not zero in the ground state although the electron spins are opposite. This is because the ground state Heitler–London wavefunction, equation (3), cannot be written as a single determinant.

3.1 Hartree–Fock equations for “Jellium”

We don’t want to dwell on Hartree–Fock theory, but there is one case where the equations can be solved analytically and the outcome is very instructive. We consider a free-electron gas as in the well-known Sommerfeld theory, but including electron–electron interactions. In the absence of nuclei, the gas would simply fly apart, so in a first approximation we include a uniform distribution of positive background charge that neutralises the total charge. The electron density is measured conventionally by the parameter r_s defined such that the volume $\frac{4}{3}\pi r_s^3$ contains precisely one electron if the gas is homogeneously distributed in space. This model is called “Jellium” and has some properties similar to free-electron like metals (*eg*, Na). Details of the calculation are in textbooks. I will only give the salient results.

NOTES:

1. The wavefunctions that solve the Hartree–Fock equations are the plane waves

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}}/\sqrt{V}$$

where V is the volume of the Jellium.

2. The direct Coulomb electron–electron interaction is exactly cancelled by the electron–positive background interaction since they are obviously identical but with opposite sign.
3. The remaining energy terms are the kinetic energy of free-electrons and the exchange energy:

$$E(k) = \frac{\hbar^2 k^2}{2m} + \varepsilon_x(k) \quad (14a)$$

where

$$\varepsilon_x(k) = -\frac{e^2 k_F}{2\pi} \left\{ 2 + \frac{k_F^2 - k^2}{kk_F} \log \left| \frac{k_F + k}{k_F - k} \right| \right\} \quad (14b)$$

< 0 .

k_F is the Fermi wavevector, *ie*, the wavevector of the highest energy occupied state.

[†] Remember the definitions: $\alpha(1) = 1$ $\alpha(-1) = 0$ $\beta(1) = 0$ $\beta(-1) = 1$.

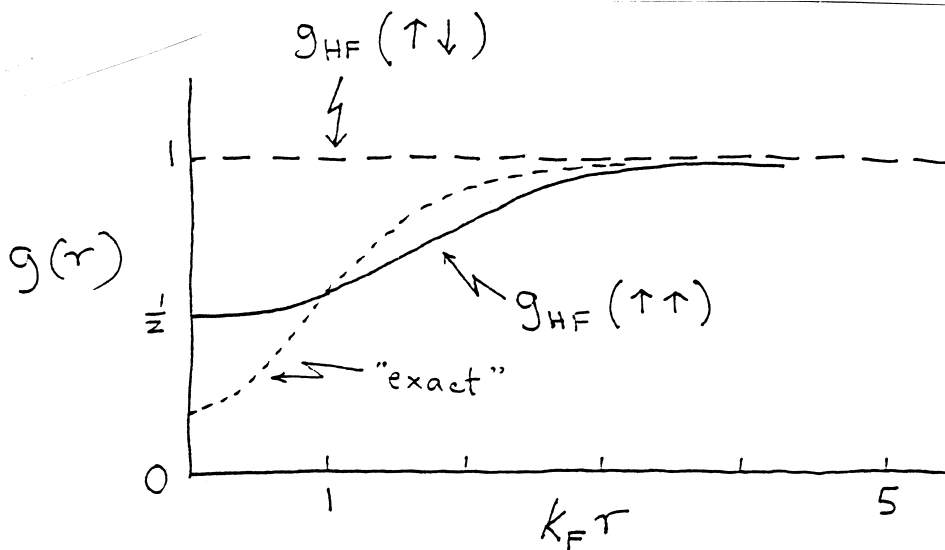
4. The extent to which electrons are *correlated* in their motion is described by the following quantity, see equations (7) and (8).

$$g(r) \equiv \frac{2\rho_2(0r)}{\rho(0)\rho(r)}.$$

This is called the “pair distribution function.” Remembering that $2\rho_2(0r)$ is the probability that there’s an electron at r and one at the origin, and $\rho(0)$ and $\rho(r)$ are the independent probabilities that there’s an electron at the origin or at r ; $g(r)$ is the probability of there being an electron at r if there’s already one at the origin, relative to the probability in the absence of that constraint. It is *one* in the absence of electron-electron interactions. In the Hartree–Fock approximation, $g(r)$ can be worked out exactly:

$$g_{\text{HF}}(r) = 1 - \frac{9}{2} \left(\frac{\sin k_F r - k_F r \cos k_F r}{(k_F r)^3} \right)^2.$$

Since the only electron-electron interaction is due to exchange, *only parallel spins are correlated* in the Hartree–Fock approximation. The pair distribution function



is sketched in FIG 3 (above). It is important to see what has happened. The electron at the origin has put an exclusion zone around it called an “exchange hole.” $g_{\text{HF}}(r)$ is exactly a half at $r = 0$ because all like spin *ie*, *half* the other electrons, are completely excluded (by Pauli’s principle) and this repulsion becomes weaker like $1/r^6$ as r increases. The radius of the exchange hole is roughly r_s and we shall see in a moment that the amount of charge excluded from the neighbourhood of a electron is exactly one electronic charge $-e$. This exposes an amount of the positive background that exactly neutralises the electron: *the electron and its exchange hole is a neutral quasiparticle*. This Hartree–Fock electron has a dispersion (14a) that implies an increased effective mass relative to the Hartree free electron.

5. Unlike spin electrons are uncorrelated in this approximation (FIG 3). The probability of there being an electron at the origin is not affected by whether there is one (of opposite spin) there already; *ie*, $2\rho_2(0r) = \rho(0)\rho(r)$. This quite unreal picture is responsible for the...

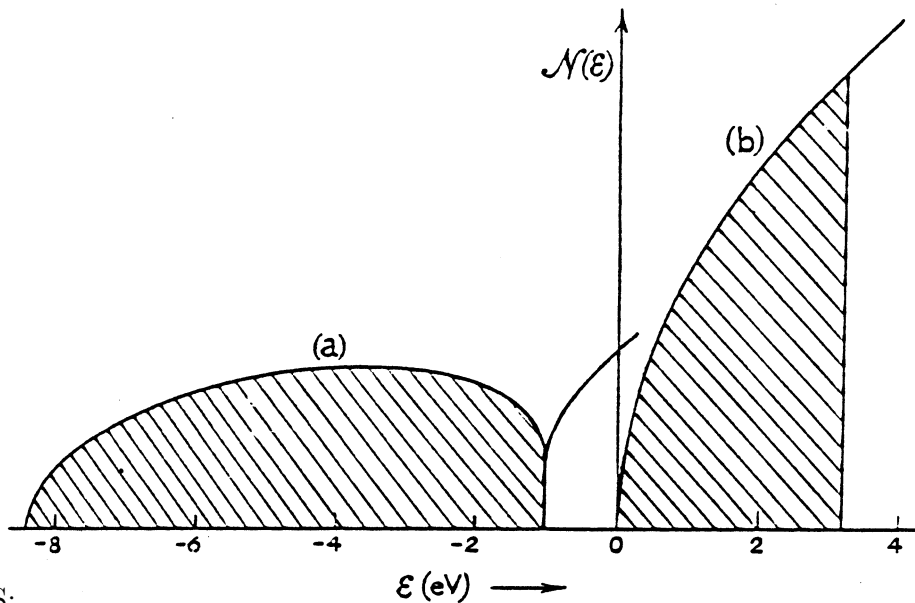
... **Failure of the Hartree–Fock theory of the electron gas**

The dispersion relation (14) has certain features quite different from the non-interacting, or Sommerfeld, or Hartree electron gas:

NOTES:

1. The energy (and also the density of states) depends on k_F (or equivalently r_s which is proportional to k_F).
2. The logarithmic singularity leads to the density of states going actually to zero at $k = k_F$ or $E = E_F$, where E_F is the Fermi energy.[†]

The densities of states of Hartree–Fock (a) and Hartree (b) Jellium are compared in FIG 4:



NOTES:

1. The pathological density of states at the Fermi energy leads to incorrect descriptions of many properties of metals, including electronic specific heat, X-ray emission, paramagnetic susceptibility. Also the bandwidth is too large. For example 4.1eV for $r_s = 4a_0$ compared to 3.2eV in Na.
2. The non-interacting picture is more respectable: bandwidths and the density of states at the Fermi level agree with measured values in simple metals.
3. However, the Hartree Jellium is *not bound*: the total energy of the electron gas, equation (14) summed over all k occupied up to the maximum, k_F , is

$$2 \sum_k \frac{\hbar^2 k^2}{2m} + \sum_k \varepsilon_x(k) = \frac{3\hbar^2}{10m} \left(\frac{9\pi}{4}\right)^{\frac{2}{3}} \frac{1}{r_s^2} - \frac{3e^2}{4} \left(\frac{9}{4\pi^2}\right)^{\frac{1}{3}} \frac{1}{r_s}.$$

In Rydberg atomic units, the first term is $2.21/r_s^2$, which is positive. The exchange

[†] The relations between r_s , k_F and E_F for the free electron gas are:

$$k_F = \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{r_s} \quad \text{and} \quad E_F = \frac{\hbar^2}{2m} \left(\frac{9\pi}{4}\right)^{\frac{2}{3}} \frac{1}{r_s^2}$$

term is $-0.916/r_s$. The total is $0.138 - 0.229 = -0.091\text{Ryd}$ in Na, compared to the experimental cohesive energy, -0.08Ryd .

The failure of the Hartree–Fock approximation can be traced to the neglect of correlations between unlike spins, mentioned above.

4. Electron correlations

We have seen the following picture emerge. The electron-electron interaction, \hat{V}_{ee} , introduces two energy terms. The *direct* Coulomb energy (also called the “Hartree energy”) which can be written

$$C[\rho] = \frac{1}{2}e^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (15)$$

is the classical electrostatic energy of the electron distribution $\rho(\mathbf{r})$. However this neglects fluctuations in the electron coordinates occurring such that *electrons keep out of each other’s way*. One reason for this is the Pauli principle that leads to the exchange hole that we saw in the free electron gas; another is simply the Coulomb repulsion which act to further deepen the exchange hole as seen in figure 3. This is *correlated motion* and acts to reduce the electron-electron interaction energy relative to its Hartree average.

It was mentioned at the end of page 1 that the total energy only depends on ρ and ρ_2 . For the expectation value of the two-electron operator \hat{V}_{ee} we can write

$$\langle \Psi | \hat{V}_{ee} | \Psi \rangle = \iint \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \rho_2(\mathbf{r}_1 \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (16)$$

which we can separate into a classical part— $C[\rho]$ —and the remaining part due to electron correlations. Comparing the integrands of equations (15) and (16) we are tempted to write[†]

$$\rho_2(\mathbf{r}_1 \mathbf{r}_2) = \frac{1}{2}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)g(\mathbf{r}_1 \mathbf{r}_2) = \frac{1}{2}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) [1 + h(\mathbf{r}_1 \mathbf{r}_2)] \quad (17)$$

which defines the “pair correlation function” $h(\mathbf{r}_1 \mathbf{r}_2)$ which is related to the pair distribution function: $h(\mathbf{r}_1 \mathbf{r}_2) = g(\mathbf{r}_1 \mathbf{r}_2) - 1$, and indicates how the integrand in (15) must be modified to correct the classical expression and account for electron correlations.

In the Hartree–Fock approximation only like spin electrons are correlated and the electron-electron interaction between like spins has come to be known as **exchange**. The error due to the neglect of unlike spin correlations has come to be called **correlation** so that

$$E_{\text{correlation}} \equiv E_{\text{exact}} - E_{\text{HF}}. \quad (18)$$

From now on, I will stick to this usage, and refer to electron correlation as “exchange and correlation” (xc). One reason for this artificial separation is that, as we have seen, for the homogeneous electron gas, the exchange energy can be calculated exactly from equation (14b) and is $-0.916/r_s$ [Ryd.]. On the other hand the calculation of the correlation energy has not yet been made in closed form except for asymptotic results for large and small r_s and very accurate parameterisations for intermediate values of r_s . The effect on $g(r)$ of including correlation is expected to be roughly as shown by the dotted line in figure 3. There is one very important result. Like the exchange hole, the “exchange and correlation hole” is neutral. *The electron behaves as a neutral quasiparticle with increased effective mass*. When we think in terms of the one-electron picture, possibly without knowing it, we are thinking of these, so-called Landau quasiparticles. They behave independently because they are neutral and so their interaction is short ranged. Electron correlations are not negligible. The reason electrons behave as independent particles is that they carry with them their “xc-hole.” You can say that as it moves, an electrons digs

[†] Recalling the pair distribution function, $g(\mathbf{r}_1 \mathbf{r}_2) = 2\rho_2(\mathbf{r}_1 \mathbf{r}_2)/\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)$.

itself a hole in the surrounding electron distribution large enough to expose exactly one unit of the background positive charge. In Jellium, the xc-hole is naturally spherical and centred at the electron. In a non-uniform system, the xc-hole may have quite a peculiar shape and may not even be centered at the electron or may not contain the electron at all in extreme cases.[†] A remarkable result is that the exchange and correlation energy is *independent* of the shape of the xc-hole and depends only on its spherical average. We will return to this point when we discuss density functional theory.

Let us now *prove* that the electron plus xc-hole is neutral. The proof is independent of the detailed nature of the electron-electron interaction, which is why it was true in the Hartree-Fock Jellium and is also true in the exact treatment.

It follows immediately from equations (7) and (8) that

$$\rho(\mathbf{r}_1) = \frac{2}{n-1} \int \rho_2(\mathbf{r}_1\mathbf{r}_2) d\mathbf{r}_2. \quad (19)$$

The pair distribution function is

$$g(\mathbf{r}_1\mathbf{r}_2) = \frac{2\rho_2(\mathbf{r}_1\mathbf{r}_2)}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}.$$

If there is an electron at \mathbf{r}_1 , then the probability of finding one at \mathbf{r}_2 is *reduced* by the factor $g(\mathbf{r}_1\mathbf{r}_2)$. Therefore the change in the density at \mathbf{r}_2 due to the presence of the electron at \mathbf{r}_1 is $\rho(\mathbf{r}_2)[g(\mathbf{r}_1\mathbf{r}_2) - 1]$. It is a function of \mathbf{r}_1 and the distance between \mathbf{r}_1 and \mathbf{r}_2 . This is called the exchange and correlation charge, or xc-hole, and is (in units of the electron charge)

$$\begin{aligned} \rho_{xc}(\mathbf{r}_1, \mathbf{r}_1 - \mathbf{r}_2) &= \rho(\mathbf{r}_2)[g(\mathbf{r}_1\mathbf{r}_2) - 1] \\ &= \rho(\mathbf{r}_2)h(\mathbf{r}_1\mathbf{r}_2) \end{aligned} \quad (20).$$

The total charge excluded by an electron at \mathbf{r}_1 is

$$\int \rho_{xc}(\mathbf{r}_1, \mathbf{r}_1 - \mathbf{r}_2) d\mathbf{r}_2 = \int \rho(\mathbf{r}_2) \left[\frac{2\rho_2(\mathbf{r}_1\mathbf{r}_2)}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} - 1 \right] d\mathbf{r}_2,$$

and using equation (19)

$$\int \rho_{xc}(\mathbf{r}_1, \mathbf{r}_1 - \mathbf{r}_2) d\mathbf{r}_2 = -1$$

for any \mathbf{r}_1 . This completes the proof. The electron, whose charge is *one* in units of electron charge, carries a depletion region about it whose charge is *minus one*. The quasiparticle is neutral.

Now we can use equations (15), (16), (17) and (20) to write

$$\begin{aligned} \langle \Psi | \hat{V}_{ee} | \Psi \rangle &= C[\rho] + \frac{1}{2} \iint \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)h(\mathbf{r}_1\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= C[\rho] + \frac{1}{2} \iint \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \rho(\mathbf{r}_1)\rho_{xc}(\mathbf{r}_1, \mathbf{r}_1 - \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (21)$$

which exposes the exchange and correlation energy as the *electrostatic interaction energy between the electrons and their xc-holes*.

[†] For an electron outside a metal surface, its xc-hole is in the metal; it is in fact the so-called “image charge.”

5. Density Functional Theory

The principal motivation behind the foregoing development has been to assemble the machinery necessary to tackle density functional theory. Let us proceed to do this.

It is clear that the electron density is determined completely by the number of electrons n and the external potential v_{ext} . The converse can be demonstrated, namely that v_{ext} is determined by a knowledge of the density $\rho(\mathbf{r})$.

The proof is by contradiction: suppose there *were* two external potentials, v_1 and v_2 both giving rise to identical charge densities ρ . Then each external potential will define a different hamiltonian \hat{H}_1 and \hat{H}_2 which differ only in their external potentials (since they give rise to the same densities, the electron-electron and kinetic energy terms must be the same). Each hamiltonian would have its own ground state wavefunction Ψ_1 and Ψ_2 and corresponding total energies E_1 and E_2 .

Now if we use Ψ_2 as a trial wavefunction for \hat{H}_1 , then the expectation value formed must be greater than the actual energy E_1 because of the variational principle. So we can write

$$\begin{aligned} E_1 &< \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle \\ \Rightarrow E_1 &< \langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle \\ \Rightarrow E_1 &< E_2 + \int d\mathbf{r} (v_1 - v_2) \end{aligned}$$

In the second line we just added and subtracted $E_2 = \langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle$ and in the third we used that the difference in the two hamiltonians lies only in their external potentials.

Now we can also do the same starting with Ψ_1 as a trial function in the expectation value of \hat{H}_2 which must be greater than E_2 . We then get exactly the same development except all the subscripts 1 and 2 are interchanged. This leads to

$$E_2 < E_1 + \int d\mathbf{r} (v_2 - v_1)$$

If we add this to the final inequality in the first development we get

$$E_1 + E_2 < E_2 + E_1$$

which is absurd.

Therefore there cannot be two external potentials leading to the same charge density. It follows that in the *ground state* the total energy depends only on the charge density. This is the first theorem of Hohenberg and Kohn produced in 1964.

The second theorem of Hohenberg and Kohn states that for all densities $\tilde{\rho}(\mathbf{r})$ having the properties $\tilde{\rho}(\mathbf{r}) \geq 0$ and $\int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = n$, $E[\tilde{\rho}(\mathbf{r})]$ is a minimum for $\tilde{\rho}(\mathbf{r}) = \rho(\mathbf{r})$, the ground state density. This is a statement of the variational principle.

We conclude that in the ground state, $E[\Psi_0(\mathbf{r}_1 \dots \mathbf{r}_n)]$ —equation (9)—can be determined from $\rho(\mathbf{r})$ without knowing the many-electron wavefunction itself. This is a very radical simplification of the problem, hugely reducing the number of variables. Instead of equation (9) we write $E = E[\rho(\mathbf{r})]$. Moreover, we can determine the ground state energy and density by minimising the energy functional in the space of all correctly normalised, non negative densities.

5.1 Functionals and functional derivatives

This is a digression to present some mathematical detail. We have said that E depends on ρ which itself depends on \mathbf{r} . E is said to be a functional of ρ : a function of a function.

A function $f(x)$ takes a number x and turns it into another number. A functional $F[f(x)]$ takes a function $f(x)$ and turns it into a number (or into another function).

Think of the number $F[\rho(\mathbf{r})]$ as a function of many variables, $f(\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\cdots\rho(\mathbf{r}_m))$. Then a small change in F is

$$\begin{aligned}\delta F &= F[\rho(\mathbf{r}) + \delta\rho(\mathbf{r})] - F[\rho(\mathbf{r})] \\ &= \sum_{i=1}^m \frac{\partial f}{\partial \rho(\mathbf{r}_i)} \delta\rho(\mathbf{r}_i)\end{aligned}$$

taking the limit as $m \rightarrow \infty$

$$\delta F = \int \xi(\mathbf{r}) \delta\rho(\mathbf{r}) \, d\mathbf{r}.$$

This defines the functional derivative

$$\xi(\mathbf{r}) \equiv \frac{\delta F}{\delta \rho}(\mathbf{r}). \quad (22)$$

For example, to get the functional derivative of the Hartree energy

$$\begin{aligned}C[\rho] &= \frac{1}{2}e^2 \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 \, d\mathbf{r}_2, \\ \delta C[\rho] &= C[\rho + \delta\rho] - C[\rho] \\ &= \frac{1}{2}e^2 \iint \frac{[\rho(\mathbf{r}_1) + \delta\rho(\mathbf{r}_1)][\rho(\mathbf{r}_2) + \delta\rho(\mathbf{r}_2)]}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \\ &\quad - \frac{1}{2}e^2 \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \\ &= e^2 \iint \frac{\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 \, d\mathbf{r}_2 + \mathcal{O}(\delta\rho)^2\end{aligned}$$

Comparing with equation (22) we get

$$\begin{aligned}\frac{\delta C}{\delta \rho}(\mathbf{r}_2) &= e^2 \int \frac{\rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 \\ &\equiv \phi_{\text{H}}, \quad \text{the "Hartree potential"}\end{aligned} \quad (23)$$

5.2 Back to density functional theory

Our proven postulate is that the ground state expectation value of \hat{H} —equation (5)—is a *unique functional* of $\rho(\mathbf{r})$. Therefore from (5) we can write

$$E[\rho] = T[\rho] + V_{\text{en}}[\rho] + V_{\text{ee}}[\rho], \quad (24)$$

where an operator without its hat means its expectation value: $V = \langle \Psi | \hat{V} | \Psi \rangle$. Taking out the interaction with the external potential, we have

$$E[\rho] = F[\rho] + \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \, \text{d}\mathbf{r} \quad (25a)$$

where

$$F[\rho] = \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle \quad (25b)$$

is a universal functional of ρ . That is to say, it doesn't depend on v_{ext} : if we know ρ we can get F .

We take out that part of V_{ee} that we know about: the classical self-energy of the electrons:

$$\begin{aligned} F[\rho] &= \frac{1}{2} e^2 \iint \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, \text{d}\mathbf{r}_1 \, \text{d}\mathbf{r}_2 + G[\rho] \\ &= C + G. \end{aligned} \quad (26)$$

We now need to find the value of $E[\rho]$ that is minimised with respect to $\rho(\mathbf{r})$ according to the variational principle. The minimisation must be done subject to the constraint that the number of electrons is conserved:

$$n = \int \rho(\mathbf{r}) \, \text{d}\mathbf{r}.$$

We introduce a Lagrange “undetermined multiplier” and get

$$\frac{\delta}{\delta \rho} \left\{ E[\rho] - \mu \left(\int \rho(\mathbf{r}) \, \text{d}\mathbf{r} - n \right) \right\} = 0.$$

Using equations (24), (23), (25) and (26), this leads to

$$\frac{\delta E}{\delta \rho} = \mu = v_{\text{ext}} + \phi_{\text{H}} + \frac{\delta G}{\delta \rho} \quad (27)$$

called the “Euler–Lagrange” equation. We have also used $(\delta/\delta \rho) \int \rho(\mathbf{r}) \, \text{d}\mathbf{r} = 1$. (See the problem sheet.) We shall see later that μ is the chemical potential, since

$$\mu = \left(\frac{\partial E}{\partial n} \right)_{v_{\text{ext}}; T=0K}. \quad (28)$$

After some *ad hoc* manipulation of the energy terms, we now have an exact formulation of the total energy problem in terms of $\rho(\mathbf{r})$ only. We now need a way of solving the Euler–Lagrange equation. We will see that there *is* a way which moreover resembles the one-electron scheme we are looking for.

5.3 The Kohn–Sham equations

We are looking for that density $\rho(\mathbf{r})$ that minimises the total electronic energy E for a given external potential (*ie*, fixed nuclei). First imagine, if you can, a system of non interacting electrons, *ie*, for which $\hat{V}_{ee} = 0$, that has the same density $\rho(\mathbf{r})$ that we’re looking for. These “electrons” are seeing an external potential $v_0(\mathbf{r}) \neq v_{\text{ext}}(\mathbf{r})$. Their ground state energy functional is

$$E_0[\rho] = T_0[\rho] + \int \rho(\mathbf{r})v_0(\mathbf{r}) \, \text{d}\mathbf{r}.$$

$T_0[\rho]$ is the kinetic energy of a non interacting “electron” gas of density $\rho(\mathbf{r})$. It’s not likely to be very much different from $T[\rho]$ in equation (24). The Euler–Lagrange equation for the “electrons” is

$$\mu_0 = v_0(\mathbf{r}) + \frac{\delta T_0}{\delta \rho}. \quad (29)$$

Because $\hat{V}_{ee} = 0$, the Hartree–Fock equations are exact. The many-electron wavefunction is a single Slater determinant of one-electron (single-particle) wavefunctions $\{\phi_i^0(\mathbf{sr}), i = 1 \dots n\}$ which are given by solutions of the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_0(\mathbf{r})\right) \phi_i^0(\mathbf{sr}) = \varepsilon_i^0 \phi_i^0(\mathbf{sr})$$

and the density we are looking for is

$$\rho(\mathbf{r}) = \sum_{i=1}^n \sum_s |\phi_i^0(\mathbf{sr})|^2. \quad (30)$$

This shows that there *is* a way to solve the Euler–Lagrange equation using a one-electron Schrödinger equation from which ρ can be obtained as in (30). Furthermore the trick doesn’t depend on the particular form of v_0 .

What we do is this. First take out of $G[\rho]$ —defined in equation (26)—the kinetic energy of the non interacting gas:

$$G[\rho] = T_0[\rho] + E_{\text{xc}}[\rho]$$

This identifies the “exchange and correlation (xc) energy” as

$$E_{\text{xc}} = (T - T_0) + (V_{ee} - C). \quad (31)$$

This seems to be at odds with equation (21) on account of the inclusion of the term $T - T_0$. But in density functional theory, we want to lump *all* the many-electron interaction terms into the xc-energy. This means *another* redefinition of exchange and correlation energy as the expectation value of \hat{V}_{ee} (16) take away the Hartree energy (15) *plus* the interaction part of the kinetic energy, $T - T_0$. In the next section we will derive an equation like (21) for our newly defined E_{xc} . Meanwhile note that in density functional theory, what is meant by “kinetic energy” is actually $T_0[\rho]$, the kinetic energy of non interacting “electrons” having a density $\rho(\mathbf{r})$. We don’t expect it to be too different from the actual kinetic energy T , but the missing bit due to electron–electron interaction is actually in E_{xc} .

To continue the present argument, we return to the Euler–Lagrange equation (27)—for the *interacting* problem—by replacing v_0 in (29) by the effective potential:

$$v_{\text{eff}}[\rho, \mathbf{r}] = v_{\text{ext}}(\mathbf{r}) + \phi_{\text{H}}(\mathbf{r}) + \frac{\delta E_{\text{xc}}}{\delta \rho}, \quad (32)$$

and solve the “Kohn–Sham equations:”

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}[\rho, \mathbf{r}]\right)\phi_i(\mathbf{sr}) = \varepsilon_i\phi_i(\mathbf{sr}). \quad (33)$$

Again, $\rho(\mathbf{r})$ is given by summing the squared single-particle wavefunctions

$$\rho(\mathbf{r}) = \sum_{i=1}^n \sum_s |\phi_i(\mathbf{sr})|^2. \quad (34)$$

We *have* lost *something*. The $\{\phi^0\}$ and $\{\varepsilon^0\}$ are the correct wavefunctions and energies of the non interacting “electrons” in the potential v_0 because the Hartree–Fock equations are exact *in this case*. The Kohn–Sham wavefunctions produce the correct density because they solve the correct Euler–Lagrange equation (27), but no significance can be attached to the $\{\phi\}$ and $\{\varepsilon\}$ as these are merely *constructs* on the way to solving equation (27). I should say that the Kohn–Sham eigenvalues $\{\varepsilon\}$ are usually interpreted as the bandstructure, and comparison with optical spectra is often very good. It can be shown that the highest occupied Kohn–Sham eigenvalue *is* the exact ionisation energy of the system.

Finally we can obtain the kinetic energy from equation (33) (PROBLEM: derive this):

$$T_0[\rho] = \sum_{i=1}^n \varepsilon_i - \int v_{\text{eff}}[\rho, \mathbf{r}]\rho(\mathbf{r}) \, d\mathbf{r}. \quad (35)$$

This completes the basic description of density functional theory. It is an *exact* re-working of the many-electron problem of determining the ground state total energy—equation (9)—from the hamiltonian (5). Because it is a statement of the exact many-electron problem you will rightly suspect that it is still not soluble. Next we have to introduce the “local density approximation” based on what we know about the properties of the exchange and correlation energy—the quantity that is so elusive in the theory.

5.4 The exchange and correlation energy

Before doing that, I want to return to the point made under equation (31). First in this section, an equation like (21) is derived for the density functional theory case in which the interaction part of the kinetic energy is to be included in the xc-energy; and then we go on to demonstrate a result given earlier without proof that the xc-energy depends only on the spherical average of the xc-hole and not on its detailed shape.

To get an equation like (21) for our new xc-energy E_{XC} requires a method called “adiabatic connection.” We have already thought about the interacting electron gas with density $\rho(\mathbf{r})$ —the fundamental subject of these lectures,—and about an “electron” gas of the same density without the electron–electron interaction. In the adiabatic connection we imagine continuously moving from the latter to the former by slowly turning on the electron–electron interaction while keeping the density the same. The hamiltonian that will do this for us is

$$\hat{H}_\lambda = \hat{T} + \lambda\hat{V}_{\text{ee}} + V_\lambda \quad (36a)$$

$$V_\lambda = \sum_{i=1}^n v_\lambda(\mathbf{r}_i) \quad (36b)$$

where λ varies smoothly between zero and one, and V_λ is defined as that external potential, different for each λ , that maintains $\rho(\mathbf{r})$ the same as when $\lambda = 1$. When $\lambda = 0$, $\lambda\hat{V}_{ee} = 0$ and we have non interacting “electrons” in an external potential V_0 as used in the derivation of the Kohn–Sham equations. When $\lambda = 1$, \hat{H}_1 is our hamiltonian from equation (5). Now, \hat{H}_λ has eigenfunctions Ψ_λ and eigenvalues E_λ :

$$\hat{H}_\lambda |\Psi_\lambda\rangle = E_\lambda |\Psi_\lambda\rangle \quad (37a)$$

$$E_\lambda = \langle \Psi_\lambda | \hat{T} + \lambda\hat{V}_{ee} + V_\lambda | \Psi_\lambda \rangle \quad (37b)$$

and for all λ

$$\rho(\mathbf{r}_1) = n \int \dots \int d\mathbf{r}_2 \dots d\mathbf{r}_n |\Psi_\lambda(\mathbf{r}_1 \dots \mathbf{r}_n)|^2 \quad (38)$$

which is equation (7) for Ψ_λ (omitting spins for simplicity). As in equation (25b), we have

$$F_\lambda = \langle \Psi_\lambda | \hat{T} + \lambda\hat{V}_{ee} | \Psi_\lambda \rangle;$$

clearly, F_1 is equation (25b) (fully interacting electrons):

$$F_1 = F = T + V_{ee},$$

and $F_0 = T_0$ for the non interacting case ($\lambda = 0$) in which $V_{ee} = 0$. Then equation (31) becomes

$$\begin{aligned} E_{xc} &= V_{ee} - C + T - T_0 \\ &= F_1 - F_0 - C \\ &= \int_0^1 \frac{\partial F_\lambda}{\partial \lambda} d\lambda - C \end{aligned} \quad (39)$$

which is like equation (21) in that the electron-electron interaction is divided into classical and non classical parts $C + E_{xc}$, except that now the interaction is V_{ee} , plus $(T - T_0)$ —the interaction part of the kinetic energy. So what is $(\partial F_\lambda / \partial \lambda)$?

Well, from equation (37), $\langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle = E_\lambda$, and

$$\frac{\partial E_\lambda}{\partial \lambda} = \frac{\partial}{\partial \lambda} \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle = \left\langle \Psi_\lambda \left| \frac{\partial \hat{H}_\lambda}{\partial \lambda} \right| \Psi_\lambda \right\rangle \quad (40)$$

$$\begin{aligned} &= \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle + \left\langle \Psi_\lambda \left| \frac{\partial V_\lambda}{\partial \lambda} \right| \Psi_\lambda \right\rangle \\ &= \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle + \int \rho(\mathbf{r}) \frac{\partial}{\partial \lambda} v_\lambda(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (41)$$

The first line, equation (40), is a statement of the very important “Hellmann–Feynman theorem” (PROBLEM: derive it, or find a derivation in the literature). The second line follows by differentiating equation (36a) with respect to λ . The third line is obtained using equations (36b) and (38). (PROBLEM: can you see this?)

Now, from equation (37b), $E_\lambda = F_\lambda + \int \rho(\mathbf{r}) v_\lambda(\mathbf{r}) d\mathbf{r}$, also using equations (36b) and (38), therefore

$$\frac{\partial E_\lambda}{\partial \lambda} = \frac{\partial F_\lambda}{\partial \lambda} + \int \rho(\mathbf{r}) \frac{\partial}{\partial \lambda} v_\lambda(\mathbf{r}) d\mathbf{r}$$

which, when compared with equation (41), gives us the expression for $(\partial F_\lambda / \partial \lambda)$ we’re looking for:

$$\frac{\partial F_\lambda}{\partial \lambda} = \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle.$$

This is not the expectation value of \hat{V}_{ee} because the operator is taken between the states Ψ_λ which are the eigenfunctions of the hamiltonian \hat{H}_λ . You can see that it *is* V_{ee} if $\lambda = 1$. The expression (39) for E_{xc} is now therefore,

$$E_{xc} = \int_0^1 \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle d\lambda - C.$$

Looking at equations (16) and (17), the integral here suggests to us that we define a density matrix $\rho_2(\mathbf{r}_1\mathbf{r}_2, \lambda)$ as in equation (8) but using Ψ_λ in place of Ψ . Associated with this density matrix will be an *average pair correlation function*, \bar{h} :

$$\int_0^1 \rho_2(\mathbf{r}_1\mathbf{r}_2, \lambda) d\lambda \equiv \frac{1}{2} \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) [1 + \bar{h}(\mathbf{r}_1\mathbf{r}_2)].$$

We arrive finally at the required analogue of equation (21), in which \hat{V}_{ee} is replaced by $\hat{V}_{ee} + (\hat{T} - \hat{T}_0)$:

$$\int_0^1 \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle d\lambda = C[\rho] + E_{xc}[\rho] \quad (42a)$$

where

$$\begin{aligned} E_{xc}[\rho] &= \frac{1}{2} \iint \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\bar{h}(\mathbf{r}_1\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{2} \iint \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \rho(\mathbf{r}_1)\bar{\rho}_{xc}(\mathbf{r}_1, \mathbf{r}_1 - \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (42b)$$

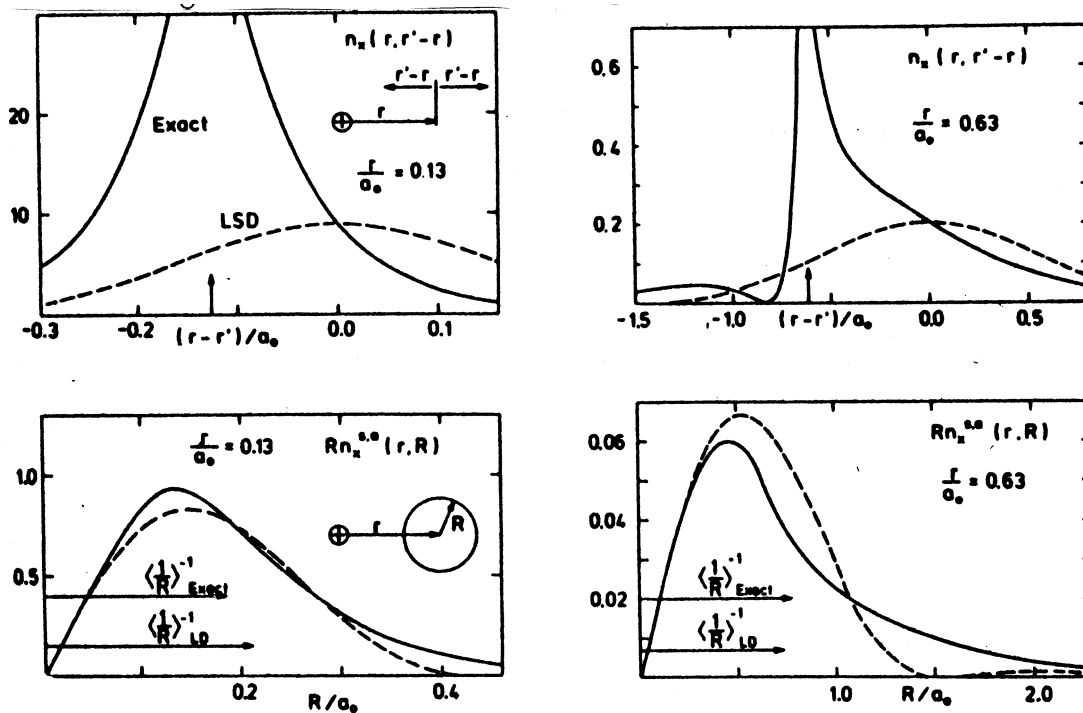
In density functional theory, where we want to put the interaction part of the kinetic energy $T - T_0$ into the exchange and correlation energy, we can do this if we reinterpret the xc-hole as an average over the interaction parameter λ . E_{xc} then emerges as the electrostatic interaction between the electrons and their xc-holes *averaged over the coupling constant* λ ; that is to say averaged over an imaginary mechanism that adiabatically “turns on” the electron-electron interaction from nothing to its full strength e^2/r while at the same time adjusting the external potential so as to keep the charge density unchanged and equal to the density of the fully interacting electron gas. The argument on page 13 leading to the conclusion that the xc-charge is exactly *minus one* electron remains in place for the averaged xc-hole $\bar{\rho}_{xc}$, because the argument was independent of the nature of the electron-electron interaction, and rested only on equation (19) which holds also for density matrices of the hamiltonian \hat{H}_λ .

Not only is the electron plus xc-hole neutral, we can also prove that E_{xc} only depends on the spherical average of $\bar{\rho}_{xc}$ and not on its detailed shape. In equation (42b), make the substitution, $\mathbf{R} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{r} = \mathbf{r}_1$. Then

$$E_{xc}[\rho] = \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \int_0^\infty dR R^2 \frac{e^2}{R} \int d\Omega \bar{\rho}_{xc}(\mathbf{r}, \mathbf{R}); \quad (43)$$

The third integral, over the solid angle Ω , is the *spherical average* of the xc-hole.

A final point that can be made, is that since the pair correlation function tends to zero as $|\mathbf{r}_1 - \mathbf{r}_2| \rightarrow \infty$, the two terms in equations (21) and (42) represent an approximate separation into long and short ranged effects of the Coulomb interaction. The xc-interaction can therefore be thought of a short ranged, or *local*, as well as being insensitive to the detailed shape of the average xc-hole.



This is illustrated above, which shows the exact exchange-only hole for an electron in the nitrogen atom, when the electron is at a distance $0.13a_0$ and $0.63a_0$ from the nucleus. The dotted lines are calculated in the *local density approximation* which we will discuss in detail soon. The important point to see is that whereas the exact and approximate holes are very different, their *spherical averages* are similar.

Finally, we can take equation (42b) a little further making a point due to Olle Gunnarsson. The sum rule is

$$\int \bar{\rho}_{\text{XC}}(\mathbf{r}_1, \mathbf{r}_1 - \mathbf{r}_2) d\mathbf{r}_2 = -1$$

which identifies $-\bar{\rho}_{\text{XC}}$ a normalised weighting function which can be used to *define* the mean radius of the xc-hole at \mathbf{r} :

$$\left\langle \frac{1}{\mathbf{R}} \right\rangle_{\mathbf{r}} = - \int d\mathbf{r} \frac{\bar{\rho}_{\text{XC}}(\mathbf{r}, \mathbf{R})}{|\mathbf{R}|}$$

from which we can obtain using (42b) and the previous substitution $\mathbf{R} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{r} = \mathbf{r}_1$

$$E_{\text{XC}}[\rho] = -\frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \left\langle \frac{1}{\mathbf{R}} \right\rangle_{\mathbf{r}}.$$

This is quite a though provoking formula for E_{XC} and, as Gunnarsson points out, it shows that E_{XC} is given by the first moment of a function whose second moment we know exactly.

6. First and second order changes in E

This section incorporates some developments in Parr and Yang, in which a rigorous contact is made between density functional theory and chemical principles of (principally, ionic) bond formation. It should be useful in interpreting density functional theory calculations of chemical reactions and interactions of molecules and atoms with surfaces. In this section, we will take it that we have solved a problem of interest, specified by a given v_{ext} and n , and that we are interested in the system's response to external perturbations: either changes in v_{ext} or changes in n . The results in this section are exact, and independent of the local density approximation to exchange and correlation. We will neglect spin in what follows.

6.1 The linear response function

Suppose we make a change in the external potential,

$$\Delta V = \sum_i \Delta v(\mathbf{r}_i).$$

In other words each of the electrons i experiences a small change $\Delta v(\mathbf{r}_i)$. We don't need to consider only the ground state in this development. If the solutions to the Schrödinger equation without the perturbation (superscript 0) are labelled k :

$$\hat{H}\Psi_k^0 = E_k^0\Psi_k^0,$$

then the first order change in the energy E_k when the change in v_{ext} is applied is,

$$\begin{aligned} \Delta E_k &= \langle \Psi_k^0 | \Delta V | \Psi_k^0 \rangle \\ &= \int \rho_k(\mathbf{r}_1) \Delta v(\mathbf{r}_1) \, d\mathbf{r}_1. \end{aligned}$$

In the ground state, $k = 0$, this is the Hellmann–Feynman theorem. You should be able to see how to get the second line from the first. It's exactly the same way as you get from equation (24) to equation (25a):

$$\sum_{i=1}^n \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_n \bar{\Psi} \Psi v(\mathbf{r}_i) = n \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_n \bar{\Psi} \Psi v(\mathbf{r}_1)$$

that is, n identical terms, because all the \mathbf{r}_i are dummy variables of integration and can be interchanged freely because $\bar{\Psi}\Psi$ doesn't change when you interchange variables. Then use equation (7) to get the second line.

The other standard result from perturbation theory is that the change in the wavefunction from Ψ_k^0 to Ψ_k when the perturbation is applied is, to first order in ΔV ,

$$\Psi_k - \Psi_k^0 = \sum_{\substack{j \\ j \neq k}} \Psi_j^0 \frac{\langle \Psi_j^0 | \Delta V | \Psi_k^0 \rangle}{E_k^0 - E_j^0}. \quad (52)$$

If we want to know the change in the charge density in state k , then from what we know about functional derivatives, this will be (to first order)

$$\Delta \rho_k(\mathbf{r}_1) = \int \frac{\delta \rho_k(\mathbf{r}_1)}{\delta v(\mathbf{r}_2)} \Delta v(\mathbf{r}_2) \, d\mathbf{r}_2. \quad (53)$$

But it is also the difference in charge densities obtained from Ψ_k and Ψ_k^0 in equation (52):

$$\begin{aligned}
\Delta\rho_k(\mathbf{r}'_1) &= n \int \cdots \int d\mathbf{r}'_2 \cdots d\mathbf{r}'_n \left(\bar{\Psi}_k \Psi_k - \bar{\Psi}_k^0 \Psi_k^0 \right) \\
&= 2n \operatorname{Re} \left\{ \sum_{\substack{j \\ j \neq k}} \frac{\langle \Psi_j^0 | \Delta V | \Psi_k^0 \rangle}{E_k^0 - E_j^0} \int \cdots \int d\mathbf{r}'_2 \cdots d\mathbf{r}'_n \bar{\Psi}_k^0 \Psi_j^0 \right\} \\
&= 2n \operatorname{Re} \left\{ \sum_{\substack{j \\ j \neq k}} \frac{1}{E_k^0 - E_j^0} \left[n \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_n \Delta v(\mathbf{r}_2) \bar{\Psi}_j^0 \Psi_k^0 \right] \right. \\
&\quad \left. \times \left[\int \cdots \int d\mathbf{r}'_2 \cdots d\mathbf{r}'_n \bar{\Psi}_j^0 \Psi_k^0 \right] \right\} \\
&= 2n^2 \operatorname{Re} \int \Delta v(\mathbf{r}_2) d\mathbf{r}_2 \sum_{\substack{j \\ j \neq k}} \frac{1}{E_k^0 - E_j^0} \left[\int \cdots \int d\mathbf{r}_1 d\mathbf{r}_3 \cdots d\mathbf{r}_n \bar{\Psi}_j^0 \Psi_k^0 \right] \\
&\quad \times \left[\int \cdots \int d\mathbf{r}'_2 \cdots d\mathbf{r}'_n \bar{\Psi}_j^0 \Psi_k^0 \right]
\end{aligned}$$

“Re” means real part. The point of all this mess is that we can compare it with equation (53) to get an expression for the *linear response function*:

$$\frac{\delta\rho_k(\mathbf{r}_1)}{\delta v(\mathbf{r}_2)} = \frac{\delta\rho_k(\mathbf{r}_2)}{\delta v(\mathbf{r}_1)} = 2n^2 \sum_{\substack{j \\ j \neq k}} \frac{\left[\int \cdots \int d\mathbf{r}_1 d\mathbf{r}_3 \cdots d\mathbf{r}_n \bar{\Psi}_j^0 \Psi_k^0 \right] \left[\int \cdots \int d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_n \bar{\Psi}_j^0 \Psi_k^0 \right]}{E_k^0 - E_j^0}$$

There are only two important things to know about all this.

1. The response function is symmetric in the variables \mathbf{r}_1 and \mathbf{r}_2 . (PROBLEM, what does this imply, physically?)
2. If you want to know the linear response of the system to a perturbation in the external potential, even if the system is in the ground state ($k = 0$), you need to know the excited states of the unperturbed system.

6.2 The chemical potential

Let us now concentrate on the ground state—the only state accessible in density functional theory. We have just seen that for a change ΔV in the external potential, the first order change in the electronic energy is

$$\delta E = \langle \Psi_0 | \Delta V | \Psi_0 \rangle = \int \rho(\mathbf{r}) \Delta v(\mathbf{r}) d\mathbf{r}.$$

From our rules for functional derivatives, we then have

$$\left(\frac{\delta E}{\delta v} \right)_\rho = \left(\frac{\delta E}{\delta v} \right)_n = \rho(\mathbf{r}). \tag{54}$$

We know that $E = E[n, v(\mathbf{r})]$, so

$$dE = \left(\frac{\partial E}{\partial n} \right)_v dn + \int \left(\frac{\delta E}{\delta v(\mathbf{r})} \right)_n dv(\mathbf{r}) d\mathbf{r} \tag{55}$$

and also, from equation (25a), ($E[\rho] = F[\rho] + \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}$)

$$dE = \int \left(\frac{\delta E}{\delta \rho(\mathbf{r})} \right)_v d\rho(\mathbf{r}) d\mathbf{r} + \int \left(\frac{\delta E}{\delta v(\mathbf{r})} \right)_\rho dv(\mathbf{r}) d\mathbf{r}. \tag{56}$$

We also have the Euler–Lagrange equation (27):

$$\left(\frac{\delta E}{\delta \rho}\right)_v = \mu$$

and

$$dn = \int d\rho(\mathbf{r}) d\mathbf{r}.$$

Putting these last two into equation (56) and using equation (54) we get

$$dE = \mu dn + \int \rho(\mathbf{r}) dv(\mathbf{r}) d\mathbf{r}$$

and comparing this with equation (55) we find that as in equation (28)

$$\mu = \left(\frac{\partial E}{\partial n}\right)_v$$

which is the *chemical potential*. It plays the same rôle in quantum mechanics as in classical thermodynamics. That is to say, in equilibrium, μ must be the same everywhere; and in chemical reactions electrons will flow to where the chemical potential is lowest so as to equalise the chemical potential. In fact $-\mu = \chi$ is the *electronegativity*.

6.3 Second derivatives of the energy: hardness and the Fukui function

We can also ask, what is the change in chemical potential associated with a change in n or $v(\mathbf{r})$?

$$\begin{aligned} d\mu &= \left(\frac{\partial \mu}{\partial n}\right)_v dn + \int \left(\frac{\delta \mu}{\delta v(\mathbf{r})}\right)_n dv(\mathbf{r}) d\mathbf{r} \\ &= 2\eta dn + \int f(\mathbf{r}) dv(\mathbf{r}) d\mathbf{r}. \end{aligned}$$

where the “hardness” is defined as

$$\eta = \frac{1}{2} \left(\frac{\partial \mu}{\partial n}\right)_v$$

and

$$f(\mathbf{r}) = \left(\frac{\delta \mu}{\delta v(\mathbf{r})}\right)_n = \left(\frac{\partial \rho(\mathbf{r})}{\partial n}\right)_v \quad (57)$$

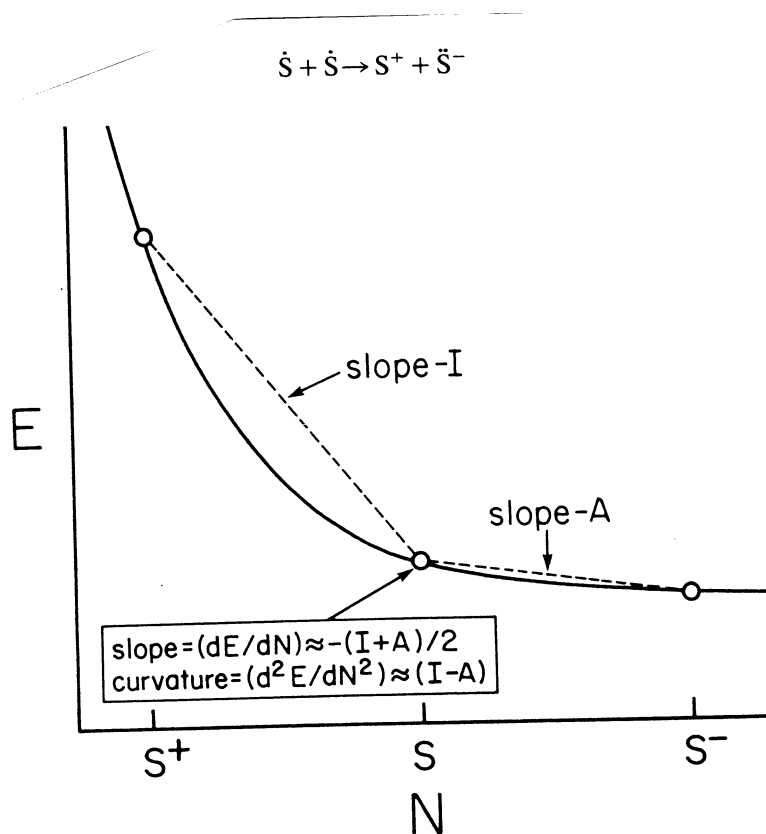
is called the “Fukui function,” or “reactivity index.” (PROBLEM, the identity in equation (57) is a “Maxwell relation,” can you derive it?)

Another second derivative quantity is

$$\frac{\delta^2 E}{\delta v(\mathbf{r}_1)\delta v(\mathbf{r}_2)} = \frac{\delta^2 E}{\delta v(\mathbf{r}_2)\delta v(\mathbf{r}_1)} = \frac{\delta \rho(\mathbf{r}_1)}{\delta v(\mathbf{r}_2)}$$

which you can see from equation (54); this is the linear response function for which an explicit expression was given in the previous section, (6.1). Because the order in the differentiation of the *total differential* dE is immaterial, the symmetry in the coordinates is elegantly demonstrated.

The object of section 6 has been to provide an introduction to the quantities in density functional theory that relate to chemical concepts of reactivity, electronegativity and hardness. To complete the subject, you should look in Parr and Yang, chapter 5. The figure below (from Parr and Yang) shows a schematic of the energy of a "typical species" as a function of the number of electrons:



7. Magnetism

This section contains a brief and incomplete description of ferromagnetism. The purpose is firstly to indicate the importance of *exchange energy* in the criteria for ferromagnetism. This emphasises the point that if the non relativistic many-body hamiltonian (5) has solutions that develop an imbalance between the numbers of up and down spins (*ie a magnetic moment*) then this must arise entirely from electrostatic origins. As I have stressed before, equation (5) does not contain the spin explicitly, so the electron-electron interaction energy, including exchange and correlation is entirely electrostatic in origin. The magnetic interactions are much much weaker and can be ignored, especially in a qualitative treatment but also in quantitative calculations. The second purpose in this section is to introduce the *local spin density approximation* and to show how a simple model based on this and the “rigid band approximation” can lead to a quantitative discussion of the ferromagnetic transition elements.

7.1 Qualitative arguments—the localised picture

In the treatment of the Heitler–London H_2 molecule a negative exchange energy favours the singlet state with antiparallel spins. In one of the problems we mentioned this as a fairly general result. In fact, since we wrote $A_x = \frac{1}{2}(E_{\uparrow\downarrow} - E_{\uparrow\uparrow}) = \frac{1}{2}(\varepsilon_1 - \varepsilon_3)$, the energy levels of the H_2 molecule can be written

$$\begin{aligned}\varepsilon &= \frac{1}{2}(\varepsilon_1 + \varepsilon_3) - \frac{1}{2}\kappa(\varepsilon_1 - \varepsilon_3), \quad \kappa = \pm 1 \\ &= \frac{1}{2}(\varepsilon_1 + \varepsilon_3) - \frac{1}{2}\kappa 2A_x.\end{aligned}\tag{58}$$

Now, you remember from your quantum mechanics that the eigenvalue of the spin operator \mathbf{S} squared is $S^2 = S(S+1)$, in units of \hbar . For the electron having spin one-half, $s_i^2 = s_i(s_i+1) = 3/4$. The total spin operator for the two-electron system is $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$, and the eigenvalue of the total spin squared is,

$$S^2 = s_1^2 + s_2^2 + 2\mathbf{s}_1 \cdot \mathbf{s}_2 = \frac{3}{2} + 2\mathbf{s}_1 \cdot \mathbf{s}_2 = S(S+1).$$

Therefore if we write down the operator

$$\left(\frac{1}{2} + 2\mathbf{s}_1 \cdot \mathbf{s}_2\right)$$

we can see immediately that it has an eigenvalue $[S(S+1) - 1]$, which is $+1$ for $S = 1$, the triplet state and -1 for $S = 0$, the singlet state. It therefore has the same properties as the number κ in equation (58) and can be substituted into that equation to give

$$\begin{aligned}\varepsilon &= \frac{1}{2}(\varepsilon_1 + \varepsilon_3) - \frac{1}{2}\left(\frac{1}{2} + 2\mathbf{s}_1 \cdot \mathbf{s}_2\right)(\varepsilon_1 - \varepsilon_3) \\ &= \frac{1}{2}(\varepsilon_1 + \varepsilon_3) - A_x\left(\frac{1}{2} + 2\mathbf{s}_1 \cdot \mathbf{s}_2\right) \\ &= \varepsilon_0 - 2A_x\mathbf{s}_1 \cdot \mathbf{s}_2,\end{aligned}\tag{59}$$

where $\varepsilon_0 = (\varepsilon_1 + 3\varepsilon_3)/4$ is the average energy of all four spin states of the system.

Equation (59) is nothing else except a rewriting of the equation we originally got for the Heitler–London H_2 molecule:

$$E_{\pm} = \varepsilon_{1,3} = \frac{C \pm A}{1 \pm S^2}$$

which has the singlet and triplet solutions that we found. But it exposes nicely the shifts away from the mean that occur as a result of *exchange splitting*. In fact equation (59) can be readily generalised to the many-electron case to give the “Heisenberg exchange hamiltonian:”

$$\hat{H}_{\text{ex}} = \varepsilon_0 - 2 \sum_{i < j} A_{ij} \mathbf{s}_i \cdot \mathbf{s}_j.$$

Here, the electrons are labelled i , and A_{ij} are exchange coupling integrals. This model is the starting point for the treatment of “localised” magnetism, the Ising model, and so on. You can see that this is essentially a picture of spins localised on atomic sites. In fact it is built in to the Heitler–London wavefunction—equation (1)—that while electron 1 is associated with atom 1 then electron 2 is associated with atom 2, or while electron 1 is associated with atom 2 then electron 2 is associated with atom 1; that is to say a highly correlated state.[†]

Unfortunately, the Heisenberg hamiltonian is not suitable for describing ferromagnetism in metals. In fact, whereas $A < 0$ in the Heitler–London H_2 molecule—which has the antiferromagnetic ground state—you can see that you will need $A > 0$ to stabilise the ferromagnetic state. It turns out that invariably A is *negative* when calculated between one-electron states on neighbouring atomic sites, and it is difficult to see how this picture can describe ferromagnetism.

Actually, A is positive when calculated between states on the same atom. The same method we used for H_2 applied to He, results in $A > 0$. Whereas in the Heitler–London H_2 molecule, $A < 0$ and the ground state energy is $C + A$ (to first order) requiring the spin function to be antisymmetric and hence a singlet; in He, $A > 0$ and the first excited state energy is $C - A$ and the wavefunction calls for the triplet spin function. This result is the basis for the well-known Hund’s rule which states that in an unfilled atomic shell, the spins will align parallel, as far as possible, to maximise the benefit from the exchange energy gain. (The ground state of He is, of course, a singlet as two electrons occupy a $1s$ orbital.)

Our problem, in α -Fe for example, is: given we can understand why the spins align within the atom, why do they also couple from atomic site to site collectively to align parallel?

Another way to see why the antiferromagnetic state is expected between two atomic sites, is that an electron will prefer to hop to a neighbouring atom if, when it gets there, it finds the electron already there has opposite spin (then it is not repelled by the Pauli principle). So there is a greater amplitude for hopping between atomic sites whose electrons are aligned antiparallel. This greater amplitude smears out the position of the electron and lowers its kinetic energy according to the Heisenberg uncertainty principle. Stronger hopping also leads to stronger covalent bonding as is clear from the usual tight binding or molecular orbital picture. You can expect there always to be a competition between ferromagnetism and covalency.

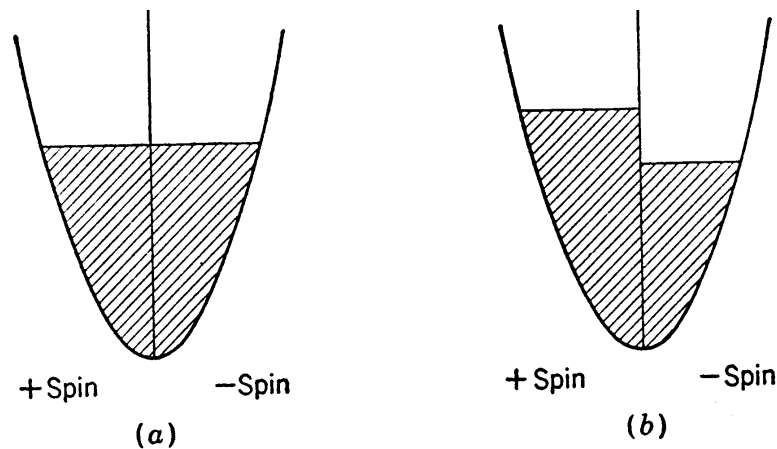
[†] Conversely, the molecular orbital picture is quite uncorrelated, the electrons together occupy a “delocalised” molecular orbital.

All these considerations have got us so far: we don't yet have a model that can describe magnetism in metals, but we have convinced ourselves that *exchange*, the quantity we have described at such length up till now, is at the bottom of magnetic phenomena. So where do we go from here to get a description of the ferromagnetic state?

7.2 Qualitative arguments—the itinerant picture

How does the spin alignment propagate itself throughout a crystal? The mechanism that gives rise to localised spins in *f*-metals (rare-earths) is not overlap of the atomic *f*-electron states because that is very small. Instead, the picture is one in which the moment in the atomic *f*-shell polarises the electron gas in its neighbourhood and this propagates the exchange interaction to the next atom. It is called “indirect exchange.” So here the important exchange integrals are between the localised atomic *f*-states and the free-electron like *s* and *p* band states. This is an appropriate description when the electrons carrying the moment are in completely localised states, but is still not what we want for transition metals where we know that the *d*-electrons are in approximately one-electron bands—they are “itinerant.”

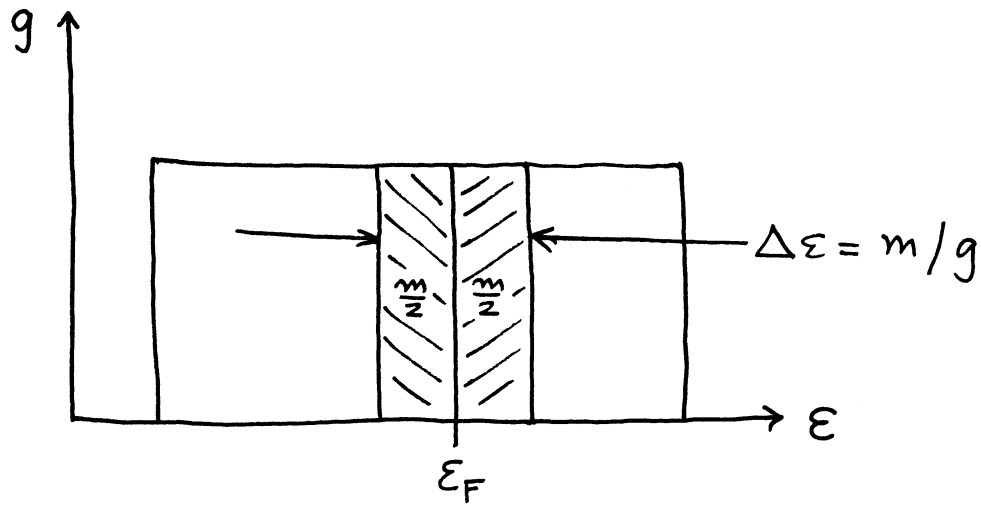
So let us first ask the following important question: can the free-electron gas become spontaneously spin polarised at any density? In other words, what is the ground state in the following figure, (a) or (b)?



The figure shows, back-to-back, the free-electron densities of states for spin-up (+) and spin-down (-) electrons. If we transfer $\frac{1}{2}m$ spin-down electrons into the spin-up band (*ie*, flip the spins of $\frac{1}{2}m$ electrons), there will be m more spin-up than spin-down electrons—a magnetic moment of $\mu_B m$, where $\mu_B = e\hbar/2mc$ is the Bohr magneton. The system will gain exchange energy as a result of the lowering due to exchange, but the process will cost kinetic energy since higher energy band states need to be occupied. For the case of Jellium, both contributions can be worked out in the Hartree–Fock approximation and it turns out that only at very low densities does the exchange term win out, and the Jellium becomes ferromagnetic.[†] The critical density is so low, however, that it is only realised in very few metals (for example Cs) but at these low densities correlation effects that have been ignored become overwhelmingly important.

[†] See J.C.Slater, “Quantum Theory of Matter,” 1st ed., pp. 418ff.

The d -electrons in transition metals are neither fully localised as are f -electrons nor free-electron like as are the s and p band states. But we need to treat the d -electrons in a band, or itinerant picture. As in the previous paragraph we have to think of the energy bands as two degenerate sets, spin-up and spin-down, which can split under the action of a magnetic or exchange field. The “exchange field,” which comes from *within* the crystal, will be explained in section 7.2. This brings us, then, to the “Stoner model” of itinerant ferromagnetism that draws on the ideas given up to now. As in the previous paragraph, we imagine flipping the spins of $\frac{1}{2}m$ electrons. The magnetic moment (in units of μ_B) is then $m = n_+ - n_-$ where $n_+ = \frac{1}{2}(n + m)$ is the number of up spins and $n_- = \frac{1}{2}(n - m)$ if n is the total number of electrons. The easiest way to calculate the change in the kinetic energy is to consider a rectangular, *ie* constant, density of states $g(\varepsilon) = g$.



We need to calculate

$$\int_{\varepsilon_F - \Delta\varepsilon}^{\varepsilon_F + \Delta\varepsilon} \varepsilon g(\varepsilon) d\varepsilon + \int_{\varepsilon_F + \Delta\varepsilon}^{\varepsilon_F + \Delta\varepsilon} \varepsilon g(\varepsilon) d\varepsilon - 2 \int_{\varepsilon_F}^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon$$

which is simply

$$g(\Delta\varepsilon)^2 = \frac{1}{4} \frac{m^2}{g(\varepsilon_F)} \quad (60)$$

and this is also approximately true if $g(\varepsilon)$ does not vary too much in the range of energy splitting $2\Delta\varepsilon$ around ε_F , the Fermi level.

This is an energy penalty; what about the energy gain from exchange? Here we postulate a repulsive energy between pairs of *unlike* spins, In_+n_- where I represents roughly the exchange energy penalty when unlike spin electrons find themselves, say, together in the d -shell of the same atom. It cannot necessarily be written as an exchange integral like A_x : as we have seen these are usually negative. Within this model, it is easy to work out the energy gain from flipping $\frac{1}{2}m$ spins: $I\frac{1}{2}(n+m)\frac{1}{2}(n-m) - I\frac{1}{2}n\frac{1}{2}n = \frac{1}{4}Im^2$. This is an energy gain, so the total (kinetic plus exchange) energy change on flipping $\frac{1}{2}m$ spins is

$$\frac{1}{4} \frac{m^2}{g(\varepsilon_F)} - \frac{1}{4} Im^2 = \frac{1}{4} \frac{m^2}{g(\varepsilon_F)} [1 - Ig(\varepsilon_F)]$$

which leaves a net energy *gain* if

$$Ig(\varepsilon_F) > 1 \quad (61)$$

which is called the Stoner Criterion for ferromagnetism. There is not any obviously new idea here, compared to the argument over the free electron gas; and indeed, the quantity I , the “Stoner parameter,” is not clearly defined yet. But it can be thought of in terms of the discussion in section 6.3 and the figure on p. 35 as the *difference* in the quantity U (or hardness) when an electron is put into an atomic shell where there is already one with the same spin and when there is one there with opposite spin. You expect, therefore $I \ll U$. We will get an expression for I involving the energy bands and crystal wavefunctions in the next section. Meanwhile note that the Stoner criterion calls for a large I *and* a large density of states at the Fermi level. We see here the competition between magnetism and covalency. Central bcc transition metals characteristically have the Fermi level at a *minimum* in the density of states separating occupied bonding from unoccupied antibonding states—a typical covalent picture, and non magnetic. α -Fe, on the other hand, has the Fermi level at a peak in the density of states and is stabilised in the bcc structure not by covalency but by the exchange energy—a typical picture of ferromagnetism.

7.3 Local spin density functional theory

The simplest extension of local density functional theory to magnetic systems is to consider a uniform magnetic field \mathcal{H} applied along the z -direction. The z -component of the spin, σ may be $+1$ or -1 , in units of $\frac{1}{2}\hbar$. The Kohn–Sham effective potential is now

$$v_{\text{eff}}^{\sigma}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \phi_{\text{H}}(\mathbf{r}) + \mu_{\text{xc}}^{\sigma}(\mathbf{r}) - \sigma\mu_B\mathcal{H}.$$

Now the exchange and correlation potential is different for different spins. The electrons see an exchange field from the other electrons in the crystal, and this is embodied in μ_{xc}^{σ} .

In practice, the K–S equations are solved separately for the separate spins, but self consistently, since μ_{xc}^{σ} depends on the density $\rho(\mathbf{r}) = \rho_+(\mathbf{r}) + \rho_-(\mathbf{r})$ and the spin density $m(\mathbf{r}) = \rho_+(\mathbf{r}) - \rho_-(\mathbf{r})$. The magnetic moment is (in units of μ_B)

$$m = \int m(\mathbf{r}) \, d\mathbf{r}.$$

In the *local spin density approximation*, we use the xc-potential of a uniform, spin polarised Jellium. Just as the Coulomb interaction is balanced by a uniform background, so the moment is balanced by an applied external magnetic field. As before, exchange can be done exactly. A parameterisation of μ_{xc}^{σ} for the homogeneous electron gas, due to Ulf Von Barth and Lars Hedin (1972) is,

$$\mu_{\text{xc}}^{\pm}(\rho) = \mu_{\text{x}}^{\text{P}}(\rho) \left[B(\rho) \pm \frac{1}{3} \frac{D(\rho)m/n}{1 \pm \gamma m/n} \right] \quad [\text{Ryd.}] \quad (62)$$

The constants, in terms of the density parameter

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

are

$$\begin{aligned} B(r_s) &= 1 + 0.0545r_s \ln(1 + 11.4/r_s) \\ D(r_s) &= 1 - 0.036r_s + 1.36r_s/(1 + 10r_s) \\ \gamma &= 0.297 \end{aligned}$$

Note, that $D = B = 1$ are the exchange-only potentials, and μ_x^P is the paramagnetic exchange potential.

Suppose, now, that we do a calculation for Fe, say, including spin polarisation. The energy bands will split just like we had a $\Delta\varepsilon$ when we did the rectangular band in section 7.2.

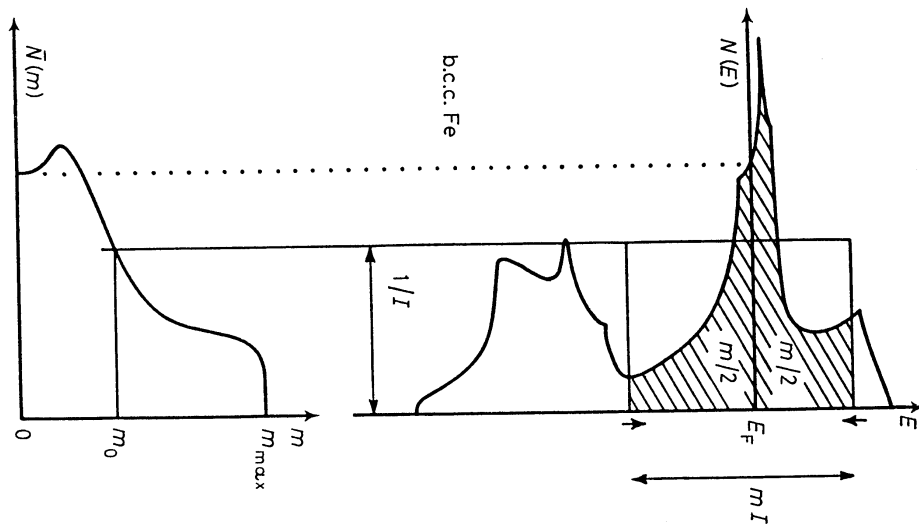
$$\begin{aligned}\Delta\varepsilon(j, \mathbf{k}) &= \varepsilon_{j+}(\mathbf{k}) - \varepsilon_{j-}(\mathbf{k}) \\ &= 2\mu_B\mathcal{H} + mI(j, \mathbf{k})\end{aligned}\quad (63)$$

which introduces the exchange splitting parameter I , a function of the band index j and the wavevector \mathbf{k} . We now want to do first order perturbation theory, so supposing we know the Kohn–Sham orbitals $\phi_j(\mathbf{k})$ from a non magnetic calculation, turning on the spin dependent part of the xc-potential can be thought of as a perturbation: $\mu_{xc}^+ - \mu_{xc}^-$. Then to first order in this potential, the splitting will be

$$\begin{aligned}mI(j, \mathbf{k}) &= -\langle \phi_j(\mathbf{k}) | \mu_{xc}^+ - \mu_{xc}^- | \phi_j(\mathbf{k}) \rangle \\ &= -\langle \phi_j(\mathbf{k}) | \frac{2}{3}\mu_x^P(\rho)D(\rho)\frac{m(\mathbf{r})}{n(\mathbf{r})} | \phi_j(\mathbf{k}) \rangle,\end{aligned}$$

the second line following from the difference between equation (62) with the plus sign and with the minus sign, keeping only terms to first order in m/n .

This suggests that a good estimate of the the exchange splitting and magnetic moment can be obtained from a knowledge of the Kohn–Sham wavefunctions and eigenvalues of the non magnetic crystal. $I(j, \mathbf{k})$ can be averaged over the Fermi surface to get an average splitting mI . In fact, once I is known (and this is essentially an *atomic* property as was discussed in the last section, only very weakly dependent on the crystal volume or environment) then the non magnetic density of states is all that is needed. For example, the non magnetic density of states of α -Fe (from a local density calculation) is shown here:



If the exchange splitting of the bands is $\Delta\varepsilon$, then just as in the qualitative description in section 7.2,

$$m = \int_{\varepsilon_F - \Delta\varepsilon/2}^{\varepsilon_F + \Delta\varepsilon/2} g(\varepsilon) d\varepsilon.$$

Define $\bar{g}(\varepsilon_F, m)$ as the density of states averaged in this range, so that

$$\Delta\varepsilon\bar{g} = m \quad ie, \quad \Delta\varepsilon = \frac{m}{\bar{g}}.$$

From equation (63) we have

$$\frac{m}{\bar{g}} = 2\mu_B\mathcal{H} + mI \quad \text{or} \quad m = \frac{2\mu_B\mathcal{H}\bar{g}}{1 - \bar{g}I}.$$

The *magnetic susceptibility* χ is the linear response of the magnetisation M as a function of applied field:

$$\chi \doteq \frac{M}{\mathcal{H}} = \frac{\mu_B m}{\mathcal{H}} = \frac{2\mu_B^2 \bar{g}}{1 - \bar{g}I}.$$

When this is negative, you expect spontaneous magnetisation, *ie* ferromagnetism in the absence of an applied field, and the condition for this to occur, you can see, is

$$\bar{g}I > 1$$

which is the Stoner Criterion, that we obtained as equation (61) from more qualitative arguments. This model is called the “generalised Stoner model,” because it does not require the density of states to be fairly constant around ε_F . The appearance of the average density of states \bar{g} is not an added approximation at this stage, but a legitimate construction.

In fact once I is given, the method can be used to determine the ferromagnetic moment *graphically* from the non magnetic density of states. Given the tabulated density of states, you can make a table for increasing splitting $\Delta\varepsilon$ of the moment m that that splitting would give (this is found from the area under the density of states in the range $\varepsilon_F - \Delta\varepsilon$ to $\varepsilon_F + \Delta\varepsilon$). At each value, you calculate a \bar{g} which is then plotted against m alongside a plot of the density of states. When $\bar{g} = 1/I$, you read off the magnetic moment m_0 . This construction is illustrated for α -Fe below. It is found that the method predicts that only Fe, Co and Ni are ferromagnetic (as it should) and the calculated moments are in good agreement with experiment. We might add that in the Hartree–Fock approximation magnetism is overstated and some non magnetic metals such as Pd are found to be magnetic. However a number of transition metals are “nearly magnetic” and moments can be induced, say at surfaces and defects, when the coordination number is reduced and thereby the density of states at the Fermi level is raised. Moments can also be induced on non magnetic elements when their atoms find themselves surrounded by magnetic atoms in, say, an alloy. Atomic values of I have been calculated and tabulated for many elements by Janak and others and can be found in the literature; using these and your calculated density of states at the Fermi level in a non magnetic calculation, you can estimate whether you’d expect your system to become ferromagnetic.