1 Thomas-Fermi Theory

1.1 Introduction

In the previous session, we discussed jellium: the uniform interacting electron gas. This is instructive, but it is obvious that the density distribution of electrons in a real solid is far from uniform,
because there is a potential field $V(r)$ acting on the electrons. This field comes from the electrostatic interaction of the electrons with the nuclei. So a fundamental question is: if the interacting electron gas is subjected to a field $V(r)$, then in the ground state what is the density of electrons $\rho(r)$ as a function of position $r$? The Thomas-Fermi theory was an early attempt to answer this question\textsuperscript{1}.

\textbf{1.2 A simple example}

As an initial indication of the thinking behind the TF theory, consider a simple example: the non-interacting electron gas in a large box. The box consists of a left half and a right half, and the electrons experience a constant potential in each half, the values of the potential being $V_L$ and $V_R$ in the left and right halves. Clearly, the electrons will flow from the region of high potential to the region of low potential, so that the densities of electrons in the two halves are unequal; we will call these densities $\rho_L$ and $\rho_R$.

Now we saw in the first session that the Fermi energy (energy of highest occupied state) in a non-interacting gas of density $\rho$ is $\epsilon_F(\rho) = \frac{\hbar^2}{2m} \left(\frac{3}{\pi^2}\rho\right)^{2/3}$. But if the electrons are acted on by a constant potential $V$, then the energy of the highest occupied state becomes $\mu = \epsilon_F + V$. Now the energies of the highest occupied states must be equal in the left- and right-hand parts of the box, because otherwise the energy could be reduced by transferring electrons between the two halves. So in equilibrium the values of $\mu$ in the two halves must be equal:

$$\mu_L = V_L + \frac{\hbar^2}{2m} \left(\frac{3}{\pi^2}\rho_L\right)^{2/3} = \mu_R = V_R + \frac{\hbar^2}{2m} \left(\frac{3}{\pi^2}\rho_R\right)^{2/3}.$$ (1)

This tells us that the density varies throughout the system in such a way that the quantity $\mu = V(r) + \frac{\hbar^2}{2m} \left(\frac{3}{\pi^2}\rho(r)\right)^{2/3}$ is constant.

\textbf{1.3 Non-interacting jellium in a non-uniform field}

Now we apply this idea to a non-interacting electron gas subjected to a general non-uniform potential field $V(r)$. The total energy of the system is the sum of the kinetic energy $E_{\text{kin}}$ and the interaction energy $E_V$ of the electrons with the field. We saw in the previous session that in a uniform non-interacting electron gas of density $\rho$, the average kinetic energy per electron is $\epsilon_{\text{kin}} = (a\hbar^2/m)\rho^{2/3}$, where $a = (3/10)(3\pi^2)^{2/3}$. This means that the kinetic energy density (amount of kinetic energy per unit volume) is $(a\hbar^2/m)\rho^{5/3}$. The crucial approximation made by TF theory is that the total kinetic energy for the electron gas can be obtained by integrating this kinetic energy density over the volume of the non-uniform system, so that:

$$E_{\text{kin}} = \frac{a\hbar^2}{m} \int \rho(r)^{5/3} \, dr.$$ (2)

The interaction energy of the electrons with the external field is given by:

$$E_V = \int V(r)\rho(r) \, dr,$$ (3)

\textsuperscript{1} Remarkably, this theory was published in 1927
so that the total energy is:

$$E_{\text{tot}} = \frac{\alpha}{\bar{\hbar}} \, \frac{\hbar^2}{m} \int \rho(r)^{5/3} \, dr + \int V(r) \rho(r) \, dr .$$  \hspace{1cm} (4)

Now to obtain the ground-state energy, we must minimise $E_{\text{tot}}$ with respect to $\rho(r)$, subject to the constraint that the total number of electrons $N$ is fixed:

$$N = \int \rho(r) \, dr .$$  \hspace{1cm} (5)

Let us suppose we have found the density $\rho(r)$ that minimises $E_{\text{tot}}$, subject to this constraint. Then if we vary $\rho(r)$ away from this by a small amount $\delta \rho(r)$, the variation of $E_{\text{tot}}$ to linear order in $\delta \rho(r)$ must vanish. This variation is:

$$\delta E_{\text{tot}} = \frac{\alpha}{\bar{\hbar}} \, \frac{\hbar^2}{m} \cdot \frac{5}{3} \int \rho(r)^{2/3} \delta \rho(r) \, dr + \int V(r) \delta \rho(r) \, dr .$$  \hspace{1cm} (6)

If there were no constraint, this variation $\delta E_{\text{tot}}$ would have to be zero. To enforce the constraint, we use the technique of Lagrange undetermined multipliers. (If you are unfamiliar with this technique, you may find it helpful to look at the notes on this subject, which are provided in Appendix A; you should also read those notes in conjunction with the separate notes on functionals.) In the present case, the technique requires that $\delta E_{\text{tot}} - \mu \delta N = 0$, where $\mu$ is the undetermined multiplier. This gives:

$$\frac{\alpha}{\bar{\hbar}} \, \frac{\hbar^2}{m} \cdot \frac{5}{3} \int \rho(r)^{2/3} \delta \rho(r) \, dr + \int (V(r) - \mu) \delta \rho(r) \, dr = 0 .$$  \hspace{1cm} (7)

The only way that this can be zero for all variations $\delta \rho(r)$ is:

$$\frac{5 \alpha \hbar^2}{3m} \rho(r)^{2/3} + V(r) = \mu .$$  \hspace{1cm} (8)

This is precisely the same condition that we found when considering the box with two halves. To see that the agreement is precise, note that:

$$\frac{5 \alpha \hbar^2}{3m} = \frac{(3\pi^2)^{2/3} \hbar^2}{2m} ,$$  \hspace{1cm} (9)

which is exactly the constant appearing in eqn (1). It is interesting to note that the $5/3$ appearing in this equation is the same $5/3$ that relates the Fermi energy to the average kinetic energy in jellium (see eqn (47)) in Session 1.

1.4 Interacting jellium in a non-uniform field

It is straightforward to generalise this idea to the system of interacting electrons. To do this, we have to add two terms to the total energy. Clearly, the non-uniform density distribution creates a non-uniform charge distribution $-e \rho(r)$, and this has a Coulomb energy, because the different parts of the charge distribution interact with each other. This part of the total energy is called Hartree energy, $E_{\text{Har}}$:

$$E_{\text{Har}} = \frac{\epsilon^2}{8\pi e_0^2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(r) \rho(r')}{|\mathbf{r} - \mathbf{r}'|} .$$  \hspace{1cm} (10)
In addition, there is exchange energy $E_x$. We saw in Session 1 that in uniform jellium of density $\rho$ the exchange energy per electron is $\epsilon_x = - (\beta e^2 / 4 \pi \varepsilon_0) \rho^{1/3}$, where $\beta = (3/4)(3/\pi)^{1/3}$. The exchange energy per unit volume is therefore $- (\beta e^2 / 4 \pi \varepsilon_0) \rho^{4/3}$.

Thomas-Fermi theory then makes the approximation that in the non-uniform situation the total exchange energy is:

\[
E_x = - \frac{\beta e^2}{4 \pi \varepsilon_0} \int \rho(r)^{4/3} \, dr .
\]

Adding the contributions, the total energy is now:

\[
E_{\text{tot}} = \frac{\alpha \hbar^2}{m} \int \rho(r)^{5/3} \, dr + \int V(r) \rho(r) \, dr + \frac{\beta^2}{8 \pi \varepsilon_0} \int dr \int d'r \frac{\rho(r) \rho(r')}{|r - r'|} + \frac{\beta e^2}{4 \pi \varepsilon_0} \int \rho(r)^{4/3} \, dr .
\]

Performing the first-order variation, as before, the minimisation condition is now:

\[
0 = \delta E_{\text{tot}} - \mu \delta N
\]

\[
= \frac{5 \alpha \hbar^2}{3m} \int \rho(r)^{2/3} \delta \rho(r) \, dr + \int \left( V(r) - \mu \right) \delta \rho(r) \, dr + \frac{\beta^2}{8 \pi \varepsilon_0} \int dr \int d'r \frac{\rho(r')}{|r - r'|} \delta \rho(r)
\]

\[
- \frac{4 \beta e^2}{12 \pi \varepsilon_0} \int \rho(r)^{1/3} \delta \rho(r) \, dr .
\]

This condition can be written more simply if we define the Hartree and exchange-correlation potentials as:

\[
V_{\text{Har}}(r) = \frac{\alpha \hbar^2}{4 \pi \varepsilon_0} \int dr' \frac{\rho(r')}{|r - r'|}
\]

\[
V_x(r) = - \frac{4 \beta e^2}{12 \pi \varepsilon_0} \rho(r)^{1/3} .
\]

Then the minimum condition is:

\[
\frac{5 \alpha \hbar^2}{3m} \rho(r)^{2/3} + (V(r) + V_{\text{Har}}(r) + V_x(r)) = \mu .
\]

We can write the minimum condition even more simply as:

\[
\frac{5 \alpha \hbar^2}{3m} \rho(r)^{2/3} + V_{\text{eff}}(r) = \mu ,
\]

where the "effective" potential $V_{\text{eff}}(r)$ is given by:

\[
V_{\text{eff}}(r) = V(r) + V_{\text{Har}}(r) + V_x(r) .
\]

This is a really remarkable equation, because it tells us that the ground-state density distribution $\rho(r)$ of the system of interacting electrons in the presence of the field $V(r)$ is exactly the same as that of a non-interacting system in the field $V_{\text{eff}}(r)$, where $V_{\text{eff}}(r)$ is obtained from $V(r)$ by adding the Hartree potential $V_{\text{Har}}(r)$ and the exchange-correlation potential $V_x(r)$.

Note a very important fact. The potential $V_{\text{eff}}(r)$ depends on the density distribution $\rho(r)$. But $\rho(r)$ in turn depends on $V_{\text{eff}}(r)$, by eqn (16). The practical solution of the TF equations therefore involves self-consistency: The potential $V_{\text{eff}}(r)$ must be such that the density $\rho(r)$ that it yields, when used to construct the effective potential through eqns (14), gives exactly the same $V_{\text{eff}}(r)$.
1.5 Practical usefulness of Thomas-Fermi theory

TF theory gives correct results only in rather limited circumstances. For example, one theoretically important question about atoms is: for a sequence of neutral atoms of increasing atomic number \( Z \) in the ground state, what is the asymptotic dependence of the total energy \( E_{\text{tot}} \) on \( Z \)? The answer to this is that \( E_{\text{tot}} \) goes asymptotically as \(-\gamma Z^{7/3}\), where \( \gamma \) is a constant. TF theory correctly predicts this asymptotic dependence, and even gives the correct value of \( \gamma \). However, this is of somewhat academic interest. The dependence of \( E_{\text{tot}} \) on \( Z \) predicted by TF theory is completely monotonic, and it fails to predict the special stability of closed-shell atoms. Even more seriously, it was shown by Teller that the theory is incapable of accounting for the binding energy of molecules. So for practical purposes, TF theory is more or less useless. Nonetheless, it points the way to density functional theory, which is introduced in the next section.

2 Density functional theory: the basics

2.1 Formulation of the problem

A system of \( N \) interacting electrons acted on by the electrostatic field of the nuclei is described by the Hamiltonian \( H \):

\[
H = T + U + V = H_0 + V. \tag{18}
\]

Here, \( T \) is the kinetic energy of the electrons:

\[
T = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2, \tag{19}
\]

\( U \) is the sum of all the Coulomb interactions of the electrons with each other:

\[
U = \frac{e^2}{8\pi\varepsilon_0} \sum_{i \neq j} \frac{1}{|r_i - r_j|}, \tag{20}
\]

and \( V \) is the sum of all the Coulomb interactions of the electrons with the nuclei, which we can write as:

\[
V = \sum_{i=1}^{N} v(r_i). \tag{21}
\]

The position of electron \( i \) is denoted by \( r_i \). It is sometimes helpful to consider separately the total energy of the electrons without the "external" field due to the nuclei, and that is why in eqn (18) we have introduced the notation \( H_0 \) to mean \( T + U \). Note that the field \( v(r) \) acting on the individual electrons can be written in terms of the charges on the nuclei and the electron-nucleus distances.

Our aim is to calculate the ground-state energy \( E_g \) of the system and the density distribution \( \rho_g(r) \) in the ground state. (Note that to get the total energy, we also need to add the Coulomb interaction of all the nuclei with each other, but we assume that the nuclei
are fixed here, so this energy is just a constant.) The ground-state energy $E_g$ is the expectation value of $H = H_0 + V$ computed with the many-electron ground-state wavefunction $\Psi$:

$$E_g = \langle \Psi | H_0 + V | \Psi \rangle ,$$

where we assume the wavefunction to be normalised: $\langle \Psi | \Psi \rangle = 1$.

The electron density is also an expectation value:

$$\rho(r) = \langle \Psi | \hat{n}(r) | \Psi \rangle ,$$

where $\hat{n}(r)$ is the operator defined as:

$$\hat{n}(r) = \sum_{i=1}^{N} \delta(r - r_i) .$$

The many-electron wavefunction $\Psi$ is appallingly complicated, and no-one knows how to solve Schrödinger’s equation to determine it exactly (except for the hydrogen atom, of course). But DFT gives us a way of avoiding the need to compute the many-electron wavefunction. The whole idea is to follow the Thomas-Fermi strategy of expressing the total energy as a functional of the electron density $\rho(r)$.

### 2.2 Energy as a functional of density: The first Hohenberg-Kohn theorem

It is intuitively obvious that if we specify the “external” potential $v(r)$ then this determines the ground state of the system (we assume throughout that the ground state is non-degenerate). This means that the many-electron wavefunction $\Psi$, the ground-state energy $E_g$ and the electron density distribution $\rho(r)$ are in principle uniquely determined (even though in practice it is too hard to solve Schrödinger’s equation). But Thomas-Fermi theory assumes something completely different: it assumes that specifying the electron density $\rho(r)$ is by itself enough to uniquely determine the ground-state properties, including the ground-state energy $E_g$. But is it justified to assume this?

The first Hohenberg-Kohn theorem says essentially that it is justified. More precisely, it states that:

**Theorem 1:** It is impossible that two external potentials $v(r)$ and $v'(r)$ whose difference $v'(r) - v(r)$ is not a constant give rise to the same ground-state density distribution $\rho(r)$.

The corollary of this is that the ground-state density $\rho(r)$ uniquely determines the external potential $v(r)$, apart from an additive constant, and hence it determines the many-electron wavefunction $\Psi$ and the ground-state energy $E_g$. The proviso about the additive constant simply reflects the fact that if the external potential is changed by adding a constant to it (equivalent to shifting the zero of energy), this does not change the ground-state $\Psi$ or the ground-state $\rho(r)$. 

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The proof of this Theorem 1 is simple, and is given in Appendix C. The theorem is very important, because it implies that the ground-state energy can be expressed as:

\[ E_g = \int d\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r}) + F[\rho(\mathbf{r})] , \]  

(25)

where \( F[\rho(\mathbf{r})] \) is a universal functional of the density \( \rho(\mathbf{r}) \) representing the expectation value of \( H_0 = T + U \) (i.e. the total kinetic energy plus the total electron-electron interaction energy) when the ground-state density is \( \rho(\mathbf{r}) \).

Because of Theorem 1, specifying the ground-state density \( \rho(\mathbf{r}) \) uniquely determines the value of \( F \) and hence the total ground-state energy.

2.3 Minimising the energy: The second Hohenberg-Kohn theorem

In Thomas-Fermi theory, we find the ground state by minimising the total energy with respect to \( \rho(\mathbf{r}) \), subject to fixed total number of electrons \( N \). This is intuitively reasonable, but we did not attempt to justify it. The justification is provided by the second Hohenberg-Kohn theorem:

**Theorem 2:** The ground-state energy for a given external potential \( v(\mathbf{r}) \) is correctly obtained by minimising the functional \( E_g = \int d\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r}) + F[\rho(\mathbf{r})] \) with respect to \( \rho(\mathbf{r}) \) for fixed \( v(\mathbf{r}) \) and fixed \( N \), and the resulting \( \rho(\mathbf{r}) \) gives the correct density distribution of the ground state.

The proof of this Theorem is straightforward, and is given in Appendix D.

2.4 Terms in the total energy

Exactly as in Thomas-Fermi theory, we want to express the total energy as a sum of terms. Specifically, we would like to express \( F[\rho(\mathbf{r})] \) as a sum of kinetic energy, Hartree energy, exchange energy and correlation energy. It is usual to lump exchange and correlation together into a term called “exchange-correlation energy”. We therefore express the energy as:

\[ E_g = \int d\mathbf{r} \rho(\mathbf{r}) v(\mathbf{r}) + E_{\text{kin}}[\rho(\mathbf{r})] + E_{\text{Har}}[\rho(\mathbf{r})] + E_{\text{xc}}[\rho(\mathbf{r})] . \]  

(26)

Now let’s clearly define what the terms in eqn (26) are. The first term on the right is the exact expression for the interaction of the electrons with the external potential, and needs no further comment. However, the kinetic-energy term \( E_{\text{kin}} \) definitely does need comment, because it is defined in a somewhat unexpected way. It is defined to be the kinetic energy of the system of non-interacting electrons having the density distribution \( \rho(\mathbf{r}) \). It does not mean the expectation value \( \langle T \rangle \) of the true kinetic energy of the system of interacting electrons. It is deliberately defined like this for a very good reason, which will become clear below. The third term
on the right is our friend the Hartree energy:

\[ E_{\text{Har}}[\rho(r)] = \frac{e^2}{8\pi\varepsilon_0} \int dr \, d\mathbf{r} \frac{\rho(r)\rho(\mathbf{r}')}{| \mathbf{r} - \mathbf{r}' |}, \quad (27) \]

exactly as in Thomas-Fermi theory. The final term \( E_{\text{xc}}[\rho(r)] \) is simply defined to be the part of the energy that is not accounted for by the other terms \( E_V = \int d\mathbf{r} \rho(\mathbf{r})v(\mathbf{r}), E_{\text{kin}} \) and \( E_{\text{Har}} \).

### 2.5 The local density approximation

Since all the other terms in eqn (26) are well defined functionals of \( \rho(r) \), the first Hohenberg-Kohn theorem assures us that the exchange-correlation energy \( E_{\text{xc}}[\rho(r)] \) is a unique and universal functional of the electron density. Our problem is that we do not have an exact formula for it. However, there is a very simple approximation for \( E_{\text{xc}}[\rho(r)] \) which works surprisingly well in practice. This makes use of the fact that we know \( E_{\text{xc}} \) almost exactly for the uniform electron gas. This system has been intensively studied by many methods, and there are extremely accurate formulas for its exchange-correlation energy per electron \( \varepsilon_{\text{xc}}^0(\rho) \) as a function of density \( \rho \) (the density in this case does not depend on position, of course). So then, following Thomas-Fermi ideas, it seems reasonable for a non-uniform system, where \( \rho(r) \) does depend on position, to say that at every point \( r \) there is a density of exchange-correlation energy given by \( \rho(r)\varepsilon_{\text{xc}}^0(\rho(r)) \). That being so, the total exchange-correlation energy in the whole system is:

\[ E_{\text{xc}}[\rho(r)] = \int d\mathbf{r} \rho(r)\varepsilon_{\text{xc}}^0(\rho(r)). \quad (28) \]

This is called the Local Density Approximation (LDA). In evaluating \( E_{\text{xc}} \) with the LDA, we use one of the very accurate formulas for \( \varepsilon_{\text{xc}}^0(\rho) \) in the uniform electron gas.

### 2.6 The Kohn-Sham equation

The ground state is now determined by minimising the total energy with respect to \( \rho(r) \), while holding \( N \) constant. This is done exactly as in Thomas-Fermi theory: at the ground state, the energy must be stationary with respect to variations of \( \rho(r) \). As usual, this means that if we start from the ground-state density \( \rho_0(r) \), and make a small change to \( \rho(r) = \rho_0(r) + \delta \rho(r) \), the resulting change \( \delta E \) of the total energy must be zero to linear order in \( \delta \rho(r) \).

To put this into practice, write the total energy as:

\[ E = \int d\mathbf{r} \rho(\mathbf{r})v(\mathbf{r}) + T[\rho(\mathbf{r})] + G[\rho(\mathbf{r})], \quad (29) \]

where \( G = E_{\text{Har}} + E_{\text{xc}} \). Then:

\[ \delta E = 0 = \int d\mathbf{r} \left[ v(\mathbf{r}) + \frac{\delta T}{\delta \rho(\mathbf{r})} + \frac{\delta G}{\delta \rho(\mathbf{r})} \right] \delta \rho(\mathbf{r}), \quad (30) \]
subject to the constraint:

$$\int d\mathbf{r} \delta \rho(\mathbf{r}) = 0 . \quad (31)$$

The notation used here employs functional derivatives, for example $\delta T/\delta \rho(\mathbf{r})$. If you are unfamiliar with this, please see the notes on “Functional and functional derivatives” in Appendix B.

Since eqn (30) must be true for any arbitrary $\delta \rho(\mathbf{r})$ that satisfies eqn (31), the ground-state condition is:

$$\frac{\delta T}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) + \frac{\delta G}{\delta \rho(\mathbf{r})} = \mu , \quad (32)$$

where $\mu$ is the Lagrange undetermined multiplier (see notes on Thomas-Fermi theory. If you want a more detailed discussion of Lagrange undetermined multiplier, please see the notes “Lagrange undetermined multipliers” on the moodle pages.)

Following what we did for Thomas-Fermi theory, it is convenient to write eqn (32) as:

$$\frac{\delta T}{\delta \rho(\mathbf{r})} + v_{\text{eff}}(\mathbf{r}) = \mu , \quad (33)$$

where the “effective” potential $v_{\text{eff}}(\mathbf{r})$ is $v(\mathbf{r}) + \delta G/\delta \rho(\mathbf{r})$. Now this equation may seem a bit obscure, because the quantity $\delta T/\delta \rho(\mathbf{r})$ looks mysterious. However, there is a wonderful way of re-interpreting this equation, which makes it easy to deal with. For non-interacting electrons, $G = 0$, since $G$ is the sum of Hartree and exchange-correlation energies, and both of these vanish for non-interacting electrons. In this case, the minimum condition becomes:

$$\frac{\delta T}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) = \mu . \quad (34)$$

This means that the ground-state density of the interacting system with the external potential $v(\mathbf{r})$ is identical to the ground-state density of the non-interacting system with the external potential $v_{\text{eff}}(\mathbf{r})$. But we know perfectly well how to find the ground-state density of a system of non-interacting electrons in potential $v_{\text{eff}}(\mathbf{r})$. All we have to do is to solve the Schrödinger equation:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r}) , \quad (35)$$

then fill up the lowest $1/2N$ states $\psi_n(\mathbf{r})$ (each with a spin-up and a spin-down electron), and then obtain the density as:

$$\rho(\mathbf{r}) = 2 \sum_{n \in \text{occ}} |\psi_n(\mathbf{r})|^2 , \quad (36)$$

where the sum goes over occupied states. In the context of DFT, eqn (35) is usually called the Kohn-Sham equation, and the effective potential $v_{\text{eff}}$ is called the Kohn-Sham potential, often denoted by $v_{\text{KS}}(\mathbf{r})$. 
2.7 The Kohn-Sham potential

The final question to be addressed is: what is the quantity $\delta G / \delta \rho(r)$ that appears in the Kohn-Sham potential $v_{KS}(r)$ and how do we calculate it? Fortunately, we have answered almost exactly this question already in the Thomas-Fermi theory. Since $G = E_{\text{Har}} + E_{\text{xc}}$, we have the sum of two terms:

$$\frac{\delta G}{\delta \rho(r)} = \frac{\delta E_{\text{Har}}}{\delta \rho(r)} + \frac{\delta E_{\text{xc}}}{\delta \rho(r)} .$$  \hspace{1cm} (37)

But $\delta E_{\text{Har}} / \delta \rho(r)$ is exactly the Hartree potential that we discussed before:

$$\frac{\delta E_{\text{Har}}}{\delta \rho(r)} = \frac{e^2}{4\pi\epsilon_0} \int dr' \frac{\rho(r')}{|r-r'|} = v_{\text{Har}}(r) .$$  \hspace{1cm} (38)

Likewise, $\delta E_{\text{xc}} / \delta \rho(r)$ is the same kind of thing as the exchange potential dealt with in Thomas-Fermi theory, but now it is based not on the total exchange energy, but on the total exchange-correlation energy. If we adopt the Local Density Approximation, it is given by:

$$\frac{\delta E_{\text{xc}}}{\delta \rho(r)} = \frac{d}{d\rho(r)} \left[ \rho(r) e_{\text{xc}}^0(\rho(r)) \right] = v_{\text{xc}}(r) .$$  \hspace{1cm} (39)

This can be evaluated using whatever formula we choose to adopt for $e_{\text{xc}}^0(\rho)$. The quantity $v_{\text{xc}}(r)$ in eqn (39) is called the exchange-correlation potential.

**Conclusion:** the Kohn-Sham potential appearing in the Kohn-Sham equation is given by:

$$v_{KS}(r) = v(r) + v_{\text{Har}}(r) + v_{\text{xc}}(r) ,$$  \hspace{1cm} (40)

so that it is the sum of the “external” potential $v(r)$, the Hartree potential $v_{\text{Har}}(r)$ and the exchange-correlation potential $v_{\text{xc}}(r)$.

2.8 Summary of density functional theory

We can now give a complete outline of a calculation of the ground-state energy of an assembly of atoms using DFT. Since the terms $v_{\text{Har}}$ and $v_{\text{xc}}$ in the Kohn-Sham potential depend on $\rho(r)$, which is what we want to determine, there is a requirement of self-consistency. A DFT calculation proceeds thus:

- Assume an initial density distribution $\rho_{\text{in}}(r)$ – this is sometimes chosen to be a superposition of atomic electron densities.
- Use this $\rho_{\text{in}}(r)$ to compute $v_{\text{Har}}(r)$ and $v_{\text{xc}}(r)$, and hence $v_{KS}(r)$.
- Solve the Kohn-Sham equation to obtain the Kohn-Sham orbitals $\psi_n(r)$ and the Kohn-Sham orbital energies $\epsilon_n$.
- Fill up the lowest $\frac{1}{2}N$ states and compute the “output” density $\rho_{\text{out}}(r)$ using eqn (36).
- In general, $\rho_{\text{out}}(r)$ will not agree with $\rho_{\text{in}}(r)$, so we have to iterate the process to self-consistency, i.e. until $\rho_{\text{out}}(r) = \rho_{\text{in}}(r)$ to within a specified tolerance.
Finally, use the self-consistent ground-state density to compute the ground-state energy.

Appendices

A Lagrange undetermined multipliers

Suppose we have a function \( f(x_1, x_2, \ldots, x_P) \) depending on \( P \) variables \( x_i \) \((i = 1, 2, \ldots, P)\). Then the condition that \( f \) has a stationary point (i.e. a minimum, a maximum, or a saddle point) for given values of the variables \( x_i \) is that:

\[
\frac{\partial f}{\partial x_i} = 0 \quad \text{for all} \quad x_i .
\]  

(41)

For brevity, let \( x = (x_1, x_2, \ldots, x_P) \) denote the \( P \)-dimensional vector whose components are \( x_i \). Let \( x^* \) be a stationary point. Then if we go to a neighbouring point \( x = x^* + \delta x \), a Taylor series expansion shows that the change of \( f \) is:

\[
\delta f = f(x^* + \delta x) - f(x^*) = \sum_{i=1}^{P} \frac{\partial f}{\partial x_i} \delta x_i + O(\delta x^2) .
\]  

(42)

The term linear in \( \delta x_i \) vanishes, because \( \frac{\partial f}{\partial x_i} = 0 \) for all \( i \).

Now let us suppose that the values of \( x_i \) are constrained by the condition that another function \( \phi(x_1, x_2, \ldots, x_P) \) has the fixed value \( c \). In the \( P \)-dimensional space of vectors \( x \), there is some surface on which \( \phi(x_1, x_2, \ldots, x_P) = c \). We seek the stationary points of \( f \) subject to this constraint. Because of the constraint, it is no longer true that \( \frac{\partial f}{\partial x_i} = 0 \) for all \( i \) at a stationary point. Instead, we can show that the constrained stationary point is an unconstrained stationary point of the function \( f - \mu \phi \) for an appropriate value of \( \mu \). The parameter \( \mu \) is called the Lagrange undetermined multiplier, because initially we do not know what value it should have. The value that should be chosen for \( \mu \) depends on the constant \( c \), and in practice we have to search for the value of \( \mu \) that gives the desired value of \( c \).

To see that all this is true, let \( x^* \) be an unconstrained stationary point of the function \( f - \mu \phi \). At this stationary point, we have:

\[
\frac{\partial f}{\partial x_i} - \mu \frac{\partial \phi}{\partial x_i} = 0 .
\]  

(43)

Now let us make a small displacement \( \delta x \) to the neighbouring point \( x = x^* + \delta x \). Then the change \( \delta f \) is given to linear order by eqn (42). But if \( \frac{\partial f}{\partial x_i} = \mu \frac{\partial \phi}{\partial x_i} \) for all \( i \), then the change of \( f \) is:

\[
\delta f = \sum_{i=1}^{P} \frac{\partial f}{\partial x_i} \delta x_i = \mu \sum_{i=1}^{P} \frac{\partial \phi}{\partial x_i} \delta x_i .
\]  

(44)

Now for all displacements satisfying the constraint, there is no change of \( \phi \) to linear order in \( \delta x \), so that \( \sum_{i=1}^{P} (\frac{\partial \phi}{\partial x_i}) \delta x_i = 0 \), which implies that:

\[
\sum_{i=1}^{P} \frac{\partial f}{\partial x_i} \delta x_i = 0 ,
\]  

(45)
so that $\mathbf{x}^\star$ is, indeed, a constrained stationary point.

A more pictorial way of considering this is to note that $\partial f / \partial x_i$ are the components of the gradient vector $\nabla f$ in the $P$-dimensional space. Similarly, $\partial \phi / \partial x_i$ are the components of the gradient $\nabla \phi$. But $\nabla \phi$ is perpendicular to the iso-value surface of $\phi$. So the condition written in eqn (43) simply says that at a constrained stationary point the $\nabla f$ must be perpendicular to the iso-value surface of $\phi$. But it is intuitively obvious that this must be true, because if it were not so, then there would be displacements $\delta \mathbf{x}$ lying in the constraint surface which are not perpendicular to $\nabla f$, which would mean that $\sum_{i=1}^{P} (\partial f / \partial x_i) \delta x_i \neq 0$, so that we could not be at a constrained stationary point.

### B Functionals and functional derivatives

In physics, chemistry and other scientific areas, one often has to consider quantities that depend on more than one variable. For example, the pressure in a gas depends on both volume and temperature. So the concept of a function $f(x_1, x_2, \ldots x_P)$ which depends on a set of variables $x_1, x_2, \ldots x_P$ is a familiar one. Also familiar is the idea of partial derivatives $\partial f / \partial x_i$, which is the rate of change of $f$ with variation of a chosen variable $x_i$, when the values of all the other variables $x_j$ ($j \neq i$) are held fixed. But in Thomas-Fermi theory and in density functional theory (DFT), the total energy $E_{\text{tot}}$ depends on the density distribution $\rho(r)$. We also have to consider the variation of $E_{\text{tot}}$ when $\rho(r)$ changes. So we need the mathematical tools to discuss quantities that depend not on a discrete set of variables, but on a function. Such a quantity is called a functional. The rate of change of a functional with variation of the function on which it depends is called a functional derivative.

#### B.1 Example of functionals

For simplicity, I consider a quantity $E$ that depends on a function $f(x)$, with this function $f$ depending on a single variable $x$. To indicate that $E$ depends on $f(x)$, it is usual to write $E = E[f(x)]$, with square brackets around the function $f(x)$. Here are some simple examples (the function $p(x)$ in the following is a chosen fixed function):

\begin{align*}
E[f(x)] &= \int p(x)f(x) \, dx \\
E[f(x)] &= \int f(x)^2 \, dx \\
E[f(x)] &= \int f(x)^{5/3} \, dx \\
E[f(x)] &= \int \frac{f(x)f(x')}{|x - x'|} \, dx \, dx',
\end{align*}

where all integrals are taken over some chosen interval, for example the range $(-\infty, \infty)$. In each case, for any chosen function $f(x)$, $E$ has some numerical value.
B.2 Functional derivative

The idea of functional derivative is a generalisation of the usual idea of derivative. But a functional derivative, instead of being a number (or a set of numbers, in the case of partial derivatives), is actually a function. Let us take the first example above \( E[f(x)] = \int p(x)f(x) \, dx \). If we change the function \( f(x) \) so that it becomes \( f(x) + \delta f(x) \), then the change of \( E \) is:

\[
\delta E = \int p(x)\delta f(x) \, dx .
\] (50)

We see that \( \delta E \) can be expressed as an integral involving \( \delta f(x) \). This is true in all the other cases too. In the second, third and fourth examples given above, we have:

\[
\delta E = \int 2f(x)\delta f(x) \, dx
\] (51)

\[
\delta E = \int \frac{5}{3}f(x)^{2/3}\delta f(x) \, dx
\] (52)

\[
\delta E = 2\int \left( \frac{f(x')}{|x-x'|} \right) \delta f(x') \, dx .
\] (53)

(The fourth example is not quite straightforward, and you might like to verify that it is correct.)

So it is clear that with a functional \( E \), when we change infinitesimally the function \( f(x) \) on which it depends, the change \( \delta E \) can be expressed as an integral of some function times the change \( \delta f(x) \). That function appearing in the integral is called the functional derivative, and is written \( \frac{\delta E}{\delta f(x)} \). The functional derivative is thus defined by:

\[
\delta E = \int \frac{\delta E}{\delta f(x)} \delta f(x) \, dx ,
\] (54)

in the limit that \( \delta f(x) \) becomes infinitesimally small. In the examples given above, the functional derivatives are:

\[
\frac{\delta E}{\delta f(x)} = p(x) \]
(55)

\[
\frac{\delta E}{\delta f(x)} = 2f(x)
\] (56)

\[
\frac{\delta E}{\delta f(x)} = \frac{5}{3}f(x)^{2/3}
\] (57)

\[
\frac{\delta E}{\delta f(x)} = 2\int \frac{f(x')}{|x-x'|} \, dx' .
\] (58)

Often in practice, when we have to do practical computations on a functional \( E[f(x)] \), we do not allow \( f(x) \) to be completely arbitrary. For example, we might want to consider only those functions \( f(x) \) that can be expressed as a linear combination of fixed “basis” functions. Suppose we have a finite set of functions \( \phi_i(x) \) \((i = 1, 2, \ldots, P)\), which are not allowed to change. Then consider all functions \( f(x) \) that can be expressed as:

\[
f(x) = \sum_{i=1}^{P} c_i \phi_i(x) ,
\] (59)
where the \( c_i \) are coefficients. In such a case, \( E[f(x)] \) actually depends only on the finite set of coefficients \( c_i \). In this case, the only allowed changes \( \delta f(x) \) have the form:

\[
\delta f(x) = \sum_{i=1}^{P} \delta c_i \phi_i(x) , \tag{60}
\]

so that the resulting change of \( E \) is:

\[
\delta E = \int \frac{\delta E}{\delta f(x)} \delta f(x) \, dx = \sum_{i=1}^{P} \delta c_i \int \frac{\delta E}{\delta f(x)} \phi_i(x) \, dx . \tag{61}
\]

From this, the partial derivative of \( E \) with respect to \( c_i \) is expressed in terms of the functional derivative as:

\[
\frac{\partial E}{\partial c_i} = \int \frac{\delta E}{\delta f(x)} \phi_i(x) \, dx . \tag{62}
\]

### B.3 Stationary point of a functional

In Thomas-Fermi theory and DFT, we need to consider the minimisation of the total energy with respect to the density distribution. For a general functional \( E[f(x)] \), the functional is stationary with respect to variation of \( f(x) \) when the functional derivative is zero: \( \frac{\delta E}{\delta f(x)} = 0 \) for all \( x \). This means that the variation of \( E \) to linear order in \( \delta f(x) \) is zero:

\[
\delta E = \int \frac{\delta E}{\delta f(x)} \delta f(x) \, dx = 0 . \tag{63}
\]

In practical computations, if the possible forms of \( f(x) \) are restricted by expressing \( f(x) \) as a superposition of a finite set of basis functions, as in eqn (59), then we have a stationary point when \( \partial E/\partial c_i = 0 \) for all \( i \), so the whole problem becomes exactly equivalent to minimising a function of \( P \) variables \( c_i \).

Now consider the search for stationary points of \( E \) subject to a constraint that is imposed. As a simple example, I take the following constraint:

\[
\int f(x) \, dx = N , \tag{64}
\]

where \( N \) is a chosen constant. If \( f(x) \) is represented in terms of basis functions, as in eqn (59), then this constraint has the form:

\[
\sum_i c_i \int \phi_i(x) \, dx = N , \tag{65}
\]

so that there is a single constraint on the possible values of the coefficients \( c_i \). But we know from the separate notes on “Lagrange undetermined multipliers” how to minimise a function of \( P \) variables subject to this kind of constraint: we have to minimise the quantity \( E - \mu N \), where \( \mu \) is the undetermined multiplier. The condition for the minimum is:

\[
\frac{\partial E}{\partial c_i} = \mu \frac{\partial N}{\partial c_i} , \tag{66}
\]
which in the present case is:

\[
\int \frac{\delta E}{\delta f(x)} \phi_i(x) \, dx = \mu \int \phi_i(x) \, dx \quad (67)
\]

for all \(i\). In the limit of a complete basis set, when the \(\phi_i(x)\) form a complete set of functions as \(P \to \infty\), eqn (67) can only be true if:

\[
\frac{\delta E}{\delta f(x)} = \mu, \quad (68)
\]

which is the general condition for a stationary point of \(E\), subject to the particular kind of constraint given in eqn (68).

### B.4 Functional of a function of more than one variable

In Thomas-Fermi theory and DFT, the function \(\rho(r)\) on which \(E_{\text{tot}}\) depends itself depends on a vector position \(r\), consisting of three variables \((x, y, z)\). However, this does not make any essential difference to the ideas outlined above. We write the functional dependence \(E_{\text{tot}} = E_{\text{tot}}[\rho(r)]\). If \(\rho(r)\) changes by an infinitesimal amount, we have:

\[
\delta E_{\text{tot}} = \int \frac{\delta E_{\text{tot}}}{\delta \rho(r)} \delta \rho(r) \, dr, \quad (69)
\]

where the integral is taken over the volume of the system. The condition for a stationary point of \(E_{\text{tot}}\), with no constraint, is:

\[
\frac{\delta E_{\text{tot}}}{\delta \rho(r)} = 0. \quad (70)
\]

But if there is a constraint of the form

\[
\int \rho(r) = N, \quad (71)
\]

then, following eqn (68), the condition for the stationary point is:

\[
\frac{\delta E_{\text{tot}}}{\delta \rho(r)} = \mu. \quad (72)
\]

### C Proof of HK Theorem 1

If we have two external potentials \(v(r)\) and \(v'(r)\) that differ by more than an additive constant, then we want to show that the resulting ground-state densities \(\rho(r)\) and \(\rho'(r)\) cannot be the same.

We denote by \(H = H_0 + V\) and \(H' = H_0 + V'\) the Hamiltonians associated with the two potentials \(v\) and \(v'\). Let their ground-state many-electron wavefunctions be called \(\Psi\) and \(\Psi'\); these wave functions are necessarily different. Then by the variational principle we have:

\[
E' = \langle \Psi'|[H']|\Psi'\rangle < \langle \Psi'|H'|\Psi\rangle = \langle \Psi'|H_0 + V + (V' - V)|\Psi\rangle. \quad (73)
\]

Hence:

\[
E' < E + \langle \Psi|V' - V|\Psi\rangle = E + \int d r \rho(r)(v'(r) - v(r)). \quad (74)
\]
We can use the same argument to prove that:

$$E < E' + \int d\mathbf{r} \rho'(\mathbf{r})(v(\mathbf{r}) - v'(\mathbf{r})).$$  \hspace{1cm} (75)$$

Adding the two equations, we get:

$$E' + E < E + E' - \int d\mathbf{r} (\rho'(\mathbf{r}) - \rho(\mathbf{r})(v' (\mathbf{r}) - v(\mathbf{r})).$$  \hspace{1cm} (76)$$

But since this is a strict inequality, we cannot have $\rho'(\mathbf{r}) = \rho(\mathbf{r})$.

**D Proof of HK Theorem 2**

If $E_g$ is the ground-state energy associated with external potential $v(\mathbf{r})$, then we have to show that:

$$E_g \leq \int d\mathbf{r} v(\mathbf{r})\rho'(\mathbf{r}) + F[\rho'(\mathbf{r})],$$  \hspace{1cm} (77)$$

where $\rho'(\mathbf{r})$ is the density associated with any arbitrary external potential $v'(\mathbf{r})$. Equality holds only if $\rho'(\mathbf{r}) = \rho(\mathbf{r})$, which by theorem 1 occurs only if $v'(\mathbf{r})$ and $v(\mathbf{r})$ differ by at most an additive constant.

The proof follows immediately from the variational principle. Let $\Psi$ and $\Psi'$ be the many-electron ground-state wave functions associated with $v(\mathbf{r})$ and $v'(\mathbf{r})$. Then:

$$E_g < \langle \Psi' | H_0 + V | \Psi' \rangle = \int d\mathbf{r} v(\mathbf{r})\rho'(\mathbf{r}) + F[\rho'(\mathbf{r})],$$  \hspace{1cm} (78)$$

which proves the theorem.