

MSc Physics of Complex Systems - Advanced Experimental Physics

Lecture Notes: Density Functional Theory

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1. Introduction

Our starting point is the many-body hamiltonian for electrons and ions:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (1)$$

where i and I refer to electrons and ions respectively, while Z_I and M_I are the ionic charge and mass.

The standard quantum mechanical approach would require the solution of the Schroedinger equation for such many-body Hamiltonian:

$$\hat{H}\Psi = E\Psi \quad (2)$$

However such approach becomes unfeasible in solids due to the large number of particles ($\sim N_A \propto 10^{23}$, i.e. the Avogadro number) and due to the difficult many-body terms. In particular the electron-electron, the electron-ion and the ion-ion interactions: such terms will be referred to as **correlations**.

The central issue of electronic structure theory is the development of methods to treat electronic correlations with sufficient accuracy that one can predict different properties of a material. We will focus on an **ab-initio** method for solving the many-body problem, which is called **Density Functional Theory** (DFT). For “ab-initio” or “from first principles” we mean that the only information we need to study a material is simply the chemical nature of the atoms and the crystal structure (i.e. the symmetry properties of a material). No other assumption is made.

A first approximation to the many-body Hamiltonian is the **Born-Oppenheimer approximation** or the **adiabatic approximation**, which allows us to neglect ion-kinetic energy ($m_i/M_I \rightarrow 0$). By doing so we get:

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_{int} + E_{II} \quad (3)$$

which can be written in atomic units (i.e. $\hbar = m_e = e = 4\pi/\epsilon_0 = 1$) as:

- **Kinetic energy operator:**

$$\hat{T} = \sum_i \left(-\frac{1}{2} \nabla_i^2 \right) \quad (4)$$

- **Electron-ion interaction:**

$$\hat{V}_{ext} = \sum_{i,I} V_I(|\mathbf{r}_i - \mathbf{R}_I|) \quad (5)$$

- **Electron-electron interaction:**

$$\hat{V}_{int} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (6)$$

- E_{II} is the **classical ion-ion interaction**

Notice that the electron-ion interaction is include in a fixed external potential: in this term other external potentials can be included, such as an external electric or magnetic field.

In DFT we move the attention from the many-body wavefunction to the electronic density. Indeed in the Schroedinger approach we solve the eigenvalue problem and we obtain the eigenvalues and eigenvectors of our system. By the variational principle, if we use a trial wavefunction Ψ_{tr} :

$$\langle \Psi_{tr} | \hat{H} | \Psi_{tr} \rangle = E_{tr} \geq E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \quad (7)$$

where Ψ_0 is the true ground-state of our Hamiltonian.

We can therefore say that the energy is a **functional** of the wavefunction, $E[\Psi]$, and restate the variational principle as a minimization problem:

$$E_0 = \min_{\Psi \rightarrow N} E[\Psi] \quad (8)$$

This means that we search for the wavefunction that minimizes the energy with the constraint that Ψ gives the number N of electrons. Therefore, given a certain number of electrons N , the atomic charge Z_I and the atomic positions \mathbf{R}_I the problem is fully determined.

A different approach is based on the electron density whose properties are:

- it is positive;
- it depends only on the electrons' space variables $\mathbf{r} = \{x, y, z\}$;
- it goes to zero as $\mathbf{r} \rightarrow \infty$ asymptotically;
- if we integrate it over the whole space, it gives the total number of electrons N ;
- it has maxima only at nuclear positions \mathbf{R}_I ;

The electronic density, as the many-body wavefunction, has all the ingredients (i.e. N , Z_I and \mathbf{R}_I) needed for defining the Hamiltonian operator. We can define the energy as a functional of the density, $E[n(\mathbf{r})]$, and find the ground-state energy as the minimum of this functional over the physically acceptable electronic density:

$$E_0 = \min_{n \rightarrow \{N, V_{ext}\}} E[n(\mathbf{r})] \quad (9)$$

2. Density Functional Theory

2.1 Introduction

The basic idea of density functional theory (DFT) comes from Hohenberg and Kohn (1964): the electron density becomes the basic variable, meaning that all of the other quantities will be functionals of the density. They showed that the ground state of a quantum system can be determined by minimizing the energy as a functional of the density. However, even if it is an exact theory, it is unpractical as formulated by Hohenberg and Kohn.

In 1965, Kohn and Sham assumed an independent particle picture which lead to effective mean-field equations that can be solved self-consistently. The information regarding correlation among particles are put into an ad-hoc energy function (**exchange-correlation functional** or E_{XC}). In principle Kohn-Sham equations are exact, however there is no way to write exactly E_{XC} and some assumptions are needed.

2.2 Hohenberg-Kohn Theorems

The approach of HK is to formulate DFT as an exact theory of many-body systems. This formulation applies to any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i V_{ext}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (10)$$

I HK THEOREM

For any system of interacting particles in an external potential V_{ext} , the potential itself is determined uniquely (except for a constant) by the ground state particle density $n_0(\mathbf{r})$.

PROOF

Assume that there are two different external potentials $V_{ext}^{(1)}(\mathbf{r})$ and $V_{ext}^{(2)}(\mathbf{r})$ which differ by more than a constant and which lead to the same ground state density $n_0(\mathbf{r})$:

$$V_{ext}^{(1)}(\mathbf{r}) \Rightarrow \hat{H}^{(1)} \Rightarrow \psi^{(1)} \Rightarrow n_0(\mathbf{r})$$

$$V_{ext}^{(2)}(\mathbf{r}) \Rightarrow \hat{H}^{(2)} \Rightarrow \psi^{(2)} \Rightarrow n_0(\mathbf{r})$$

Since $\psi^{(2)}$ is not the ground state of $\hat{H}^{(1)}$, by the variational principle:

$$\langle \psi^{(2)} | \hat{H}^{(1)} | \psi^{(2)} \rangle > E^{(1)} = \langle \psi^{(1)} | \hat{H}^{(1)} | \psi^{(1)} \rangle$$

assuming that we don't have degenerate ground states. Then:

$$\begin{aligned}
\langle \psi^{(2)} | \hat{H}^{(1)} | \psi^{(2)} \rangle &= \langle \psi^{(2)} | \hat{H}^{(2)} | \psi^{(2)} \rangle + \langle \psi^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \psi^{(2)} \rangle = \\
&= E^{(2)} + \int d\mathbf{r} [V_{ext}^{(1)}(\mathbf{r}) - V_{ext}^{(2)}(\mathbf{r})] n_0(\mathbf{r}) \Rightarrow \\
&\Rightarrow E^{(1)} < E^{(2)} + \int d\mathbf{r} [V_{ext}^{(1)}(\mathbf{r}) - V_{ext}^{(2)}(\mathbf{r})] n_0(\mathbf{r})
\end{aligned} \tag{11}$$

On the other hand:

$$\begin{aligned}
\langle \psi^{(1)} | \hat{H}^{(2)} | \psi^{(1)} \rangle &> E^{(2)} = \langle \psi^{(2)} | \hat{H}^{(2)} | \psi^{(2)} \rangle \\
\langle \psi^{(1)} | \hat{H}^{(2)} | \psi^{(1)} \rangle &= \langle \psi^{(1)} | \hat{H}^{(1)} | \psi^{(1)} \rangle + \langle \psi^{(1)} | \hat{H}^{(2)} - \hat{H}^{(1)} | \psi^{(1)} \rangle = \\
&= E^{(1)} + \int d\mathbf{r} [V_{ext}^{(2)}(\mathbf{r}) - V_{ext}^{(1)}(\mathbf{r})] n_0(\mathbf{r}) \Rightarrow \\
&\Rightarrow E^{(2)} < E^{(1)} + \int d\mathbf{r} [V_{ext}^{(2)}(\mathbf{r}) - V_{ext}^{(1)}(\mathbf{r})] n_0(\mathbf{r})
\end{aligned} \tag{12}$$

If we add up Eq. 11 and Eq.12:

$$E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)}$$

which is a contradiction! There cannot be two different external potentials (differing by more than a constant) which give rise to the same non-degenerate ground state density $n_0(\mathbf{r})$. The density uniquely determines the external potential (within a constant). \square

COROLLARY I

Since \hat{H} is fully determined, it follows that the many-body wavefunction for all states are determined. Therefore, all properties of the system are completely determined given only the ground state density $n_0(\mathbf{r})$. \square

The original proof of HK is restricted to densities of the electron Hamiltonian with some external potential $V_{ext}(\mathbf{r})$: such densities are called **V-REPRESENTABLE**. This defines a space of possible densities within which we can construct functionals of the density.

Since all properties are uniquely determined if $n(\mathbf{r})$ is specified, then also the total energy can be considered a functional of the density:

$$\begin{aligned}
E_{HK}[n] &= T[n] + E_{int}[n] + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_H = \\
&= F_{HK}[n] + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_H
\end{aligned} \tag{13}$$

$F_{HK}[n]$ includes all internal energies (kinetic and potential) and is therefore a **universal functional**, meaning that it is the same for all electron systems since it is independent of the external potential $V_{ext}(\mathbf{r})$.

II HK THEOREM

A universal functional of the energy $E[n]$ in terms of the density $n(\mathbf{r})$ can be defined, valid for any external potential $V_{ext}(\mathbf{r})$. For any particular $V_{ext}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional and the density $n(\mathbf{r})$ which minimizes $E[n]$ is the exact ground state density $n_0(\mathbf{r})$.

PROOF

Consider a system with ground state density $n^{(1)}(\mathbf{r})$ corresponding to $V_{ext}^{(1)}(\mathbf{r})$:

$$E^{(1)} = E_{HK}[n^{(1)}] = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle$$

Consider a different system with ground state density $n^{(2)}(\mathbf{r})$ corresponding to $V_{ext}^{(2)}(\mathbf{r})$:

$$E^{(2)} = \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle > \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle = E^{(1)}$$

due to variational principle. Thus the energy given in terms of $E_{HK}[n]$ evaluated for the correct ground state density $n_0(\mathbf{r})$ is the lowest. If $F_{HK}[n]$ was known, minimizing $E_{HK}[n]$ with respect to small variations of the density (i.e. $\delta E[n]/\delta n(\mathbf{r})$) would give the correct ground state density and energy. \square

COROLLARY II

The functional $E[n]$ alone is sufficient to determine the exact ground state energy and density. In general, excited states must be determined by other means. \square

2.3 Levy-Lieb Formulation

An alternative definition has been given by Levy (1979-1985) and Lieb (1982-1985) which:

- clarifies the definition of the energy functional;
- provides a way to determine it (in principle);
- leads to the same ground state density and energy at the minimum as HK;
- applies also to degenerate ground states;

We want to minimize the energy:

$$E = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \quad (14)$$

In the first step we pick a density $n(\mathbf{r})$ and we minimize E within the subset of wavefunctions that yields this density:

$$E_{LL}[n] = \min_{\Psi \rightarrow n(\mathbf{r})} \langle \Psi | \hat{H} | \Psi \rangle = F_{LL} + \int V_{EXT}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{II} \quad (15)$$

where $F_{LL} = \min_{\Psi \rightarrow n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{V}_{INT} | \Psi \rangle$, i.e. we search for the minimum restricted to the antisymmetric wavefunction Ψ which yield $n(\mathbf{r})$.

$E_{LL}[n]$ is now manifestly a functional of the density. Moreover, the meaning of the universal functional $F_{LL}[n]$ is now clear: the minimum of the sum of the kinetic energy plus the interaction energies for all possible wavefunctions having the given density $n(\mathbf{r})$. This is termed **N-REPRESENTIBILITY**.

In the second step we minimize $E_{LL}[n]$ with respect to that density:

$$E = \min_{n(\mathbf{r})} \left\{ F_{LL} + \int V_{EXT}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{II} \right\} \quad (16)$$

Now it is clear that $F_{LL}[n]$ is universal, regardless the choice of $V_{EXT}(\mathbf{r})$. Therefore:

$$E_{LL}[n + \delta n] - E_{LL}[n] = \int \left[\frac{\delta F[n]}{\delta n(\mathbf{r})} + V(\mathbf{r}) \right] \delta n(\mathbf{r})d\mathbf{r} + O(\delta n^2) \Rightarrow \frac{\delta F[n]}{\delta n(\mathbf{r})} = -V(\mathbf{r}) \quad (17)$$

subjected to the constraint that $\int n(\mathbf{r})d\mathbf{r} = N$. If we find many $n(\mathbf{r})$ satisfying this condition (degenerate case), the one with the minimum energy must be selected.

2.4 Limitations of HK Theorems

Even if the HK formulation of DFT is exact, it has two major problems:

- There is no prescription on how we can write the universal functional $F_{HK}[n]$;
- Even if we could find an analytical formulation of $F_{HK}[n]$, once we have obtained $n_0(\mathbf{r})$ (i.e. the ground state electronic density) we have no clue on how we can extract material properties. For example, we have no information on whether the system is metallic or an insulator.

3. The Kohn-Sham Equations

3.1 Introduction

In order to find a way to write the energy functional $F[n]$, Kohn and Sham reformulated the DFT problem in an independent particle picture. In this way, we obtain a set of equations to be solved self-consistently that is also practical to implement in a computer software.

3.2 The Kohn-Sham Ansatz

The idea of Kohn and Sham was to replace the difficult many-body interacting problem with a simpler non-interacting system.

ANSATZ

Assume that the system of interacting electrons can be mapped onto an auxiliary system of non-interacting particles having the same ground state density of the original problem. As a result we will obtain an exactly soluble problem of independent particles where all the information regarding the interactions are incorporated in an **exchange-correlation functional**. Then, according to the HK theorems, we can minimize the new energy functional and obtain the ground state density of the original problem. In practical calculations, the accuracy of this approach is limited only by the approximations on the E_{XC} functional.

3.3 The Auxiliary System

Consider a system of $N = N^\uparrow + N^\downarrow$ independent electrons. The ground state will have one electron for each N^σ orbitals $\Psi_i^\sigma(\mathbf{r})$ with the lowest energy eigenvalue ϵ_i^σ . The density of a non-interacting ground state can be written as:

$$n(\mathbf{r}) = \sum_{\sigma} n(\mathbf{r}, \sigma) = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} |\Psi_i^\sigma(\mathbf{r})|^2 \quad (18)$$

On the other hand, the problem with the kinetic energy of an interacting many-body problem is that:

$$T_{HK} = -\frac{\hbar^2}{2m_e} \sum_i \int d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N \Psi^\sigma(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)^* \nabla_i^2 \Psi^\sigma(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (19)$$

Since in the many-body interacting problem we don't know how the orbital wavefunction depends on \mathbf{r}_i (i.e. the position upon which ∇_i^2 acts) due to the fact that it is correlated in some way to the other electrons' positions, we cannot express T_{HK} in terms of the density.

However in the KS approach:

$$\Psi^\sigma(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Psi^\sigma(\mathbf{r}_1)\Psi^\sigma(\mathbf{r}_2) \cdots \Psi^\sigma(\mathbf{r}_N) = \prod_i \Psi_i^\sigma(\mathbf{r}) \quad (20)$$

Therefore, the kinetic energy operator can be easily expressed as:

$$T_{KS}[n] = -\frac{\hbar^2}{2m_e} \sum_\sigma \sum_i^{N_\sigma} \int d\mathbf{r} |\nabla \Psi_i^\sigma(\mathbf{r})|^2 \quad (21)$$

Notice that T_{KS} is not explicitly given in terms of $n(\mathbf{r})$ but it is an implicit functional of the density.

The electron-electron Coulomb interaction of an independent particle system coincide with the Hartree repulsion energy:

$$E_{HARTREE}[n] = \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (22)$$

Finally, any external potential (like the potential due to ions or due to a magnetic or electric field) can be incorporated as:

$$E_{EXT}[n] = \int n(\mathbf{r}) V_{EXT}(\mathbf{r}) d\mathbf{r} \quad (23)$$

All of the many-body interaction terms will be put into the exchange-correlation functional $E_{XC}[n]$. As a consequence, the KS energy functional will be written as:

$$E_{KS}[n] = T_{KS}[n] + E_{HARTREE}[n] + E_{EXT}[n] + E_{XC}[n] \quad (24)$$

Recall that the HK energy functional was:

$$E_{HK}[n] = \langle \hat{T} \rangle + \langle \hat{V}_{int} \rangle + E_{EXT}[n] \quad (25)$$

By comparing E_{HK} with E_{KS} we can see that:

$$E_{XC} = \{ \langle \hat{T} \rangle - T_{KS}[n] \} + \{ \langle \hat{V}_{int} \rangle - E_{HARTREE}[n] \} \quad (26)$$

So that the $E_{XC}[n]$:

- must be a functional of the density because all of the other quantities are functionals of $n(\mathbf{r})$;
- corresponds to the difference between the interacting and non-interacting kinetic energy plus Coulomb interaction, therefore representing the correlation part of the problem.

3.4 The Kohn-Sham Equations

We would like to obtain an effective on-particle Hamiltonian of the form:

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{KS}^\sigma(\mathbf{r}) \right] \Psi_i^\sigma(\mathbf{r}) = \varepsilon_i^\sigma \Psi_i^\sigma(\mathbf{r}) \quad (27)$$

subjected to the orthonormality condition:

$$\int d\mathbf{r} \Psi_i^\sigma(\mathbf{r})^* \Psi_j^{\sigma'}(\mathbf{r}) = \delta_{ij} \delta_{\sigma\sigma'} \quad (28)$$

So the problem relies on finding $V_{KS}^\sigma(\mathbf{r})$ for a given $n(\mathbf{r})$. We can exploit the variational property of the energy. Therefore we can define:

$$E'[n] = E_{KS}[n] - \sum_{ij} \sum_{\sigma\sigma'} \lambda_{ij,\sigma\sigma'} \int d\mathbf{r} \Psi_i^\sigma(\mathbf{r})^* \Psi_j^{\sigma'}(\mathbf{r}) \quad (29)$$

where $\lambda_{ij,\sigma\sigma'}$ are Lagrange multipliers. Then, we impose:

$$\frac{\delta E'[n]}{\delta \Psi_i^\sigma(\mathbf{r})^*} = \frac{\delta E'[n]}{\delta \Psi_i^\sigma(\mathbf{r})^*} = 0 \quad (30)$$

Therefore:

$$\begin{aligned} \frac{\delta E'[n]}{\delta \Psi_i^\sigma(\mathbf{r})^*} = & -\frac{\hbar^2}{2m_e} \sum_{l\mu} \int d\mathbf{r}' \frac{\delta \Psi_l^\mu(\mathbf{r}')^*}{\delta \Psi_i^\sigma(\mathbf{r})^*} \nabla^2 \Psi_l^\mu(\mathbf{r}') + \\ & + \frac{e^2}{2} \times 2 \int d\mathbf{r}' d\mathbf{r}'' \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}''|} \cdot \frac{\delta n(\mathbf{r}'')}{\delta \Psi_i^\sigma(\mathbf{r})^*} + \\ & + \int d\mathbf{r}' V_{EXT}(\mathbf{r}') \frac{\delta n(\mathbf{r}')}{\delta \Psi_i^\sigma(\mathbf{r})^*} + \frac{\delta E_{XC}[n]}{\delta \Psi_i^\sigma(\mathbf{r})^*} + \\ & - \sum_{ll'} \sum_{\mu\mu'} \lambda_{ll',\mu\mu'} \int d\mathbf{r}' \frac{\delta \Psi_l^\mu(\mathbf{r}')^*}{\delta \Psi_i^\sigma(\mathbf{r})^*} \Psi_{l'}^{\mu'}(\mathbf{r}') = 0 \end{aligned}$$

Using the fact that:

$$\frac{\delta n(\mathbf{r}')}{\delta \Psi_i^\sigma(\mathbf{r})^*} = \sum_{l\mu} \frac{\delta \Psi_l^\mu(\mathbf{r}')^*}{\delta \Psi_i^\sigma(\mathbf{r})^*} \Psi_l^\mu(\mathbf{r}') = \Psi_i^\sigma(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')$$

We obtain:

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + e^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} + V_{EXT}(\mathbf{r}) + V_{XC}^\sigma(\mathbf{r}) \right] \Psi_i^\sigma(\mathbf{r}) = \sum_{j\sigma'} \lambda_{ij,\sigma\sigma'} \Psi_j^{\sigma'}(\mathbf{r}) \quad (31)$$

In order to find $\lambda_{ij,\sigma\sigma'}$, multiply left and right hand side by $\Psi_k^\mu(\mathbf{r})^*$ and integrate over \mathbf{r} :

$$\begin{aligned} \sum_{j\sigma'} \lambda_{ij,\sigma\sigma'} \int d\mathbf{r} \Psi_k^\mu(\mathbf{r})^* \Psi_j^{\sigma'}(\mathbf{r}) &= \int d\mathbf{r} \Psi_k^\mu(\mathbf{r})^* \left[-\frac{\hbar^2}{2m_e} \nabla^2 + e^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} + V_{EXT}(\mathbf{r}) + V_{XC}^\sigma(\mathbf{r}) \right] \Psi_i^\sigma(\mathbf{r}) \Rightarrow \\ &\Rightarrow \sum_{j\sigma'} \lambda_{ij,\sigma\sigma'} \delta_{jk} \delta_{\mu\sigma'} = \varepsilon_i^\sigma \delta_{ik} \delta_{\mu\sigma} \Rightarrow \end{aligned}$$

So that:

$$\lambda_{ik,\sigma\mu} = \varepsilon_i^\sigma \delta_{ik} \delta_{\mu\sigma} \quad (32)$$

which is diagonal and represents the KS eigenvalues. Finally we can write the Kohn-Sham equations as:

$$\left[-\frac{\hbar^2}{2m_e} \nabla_i^2 + V_{KS}^\sigma(\mathbf{r}) \right] \Psi_i^\sigma(\mathbf{r}) = \varepsilon_i^\sigma \Psi_i^\sigma(\mathbf{r}) \quad (33)$$

$$V_{KS}^\sigma(\mathbf{r}) = V_{HARTREE}(\mathbf{r}) + V_{EXT}(\mathbf{r}) + V_{XC}^\sigma(\mathbf{r}) \quad (34)$$

$$n(\mathbf{r}) = \sum_{i\sigma} |\Psi_i^\sigma(\mathbf{r})|^2 \quad (35)$$

These equations have the form of independent particle equations with a potential that must be found self-consistently together with the resulting density. These equations are independent of any approximation and therefore the KS formulation is still exact, leading to the correct ground state density if $E_{XC}[n]$ was known.

Due to the HK theorems, the ground state density uniquely determines the potential at the minimum, so that there is a unique KS potential $V_{KS}^\sigma(\mathbf{r})$ associated with any given interacting electron system.

3.5 Total Energy Functional

The Kohn-Sham total energy functional can be written as:

$$E_{KS}[n] = T_{KS}[n] + E_{POT}[n] = T_{KS}[n] + E_{EXT}[n] + E_{HARTREE}[n] + E_{XC}[n] + E_{II} \quad (36)$$

The KS eigenvalues are given by:

$$\langle \Psi_i^\sigma | H_{KS}^\sigma | \Psi_i^\sigma \rangle = \varepsilon_i^\sigma \quad (37)$$

As a consequence, we can express the kinetic energy as:

$$T_{KS}[n] = \sum_{i\sigma} \varepsilon_i^\sigma - \sum_{\sigma} \int d\mathbf{r} V_{KS}^{\sigma,in}(\mathbf{r}) n^{out}(\mathbf{r}) \quad (38)$$

where *in* (*out*) denotes input (output) quantities of the KS equations. T_{KS} is the ground state kinetic energy of a non-interacting electron system but it is not the energy of our original problem. In order to find it we notice that, at any stage of a KS calculation which is not at the minimum, $V_{KS}^{\sigma,in}$ determines all the quantity in the energy as:

$$E_{KS}[V^{\sigma,in}] = \sum_{i\sigma} \varepsilon_i[V^{\sigma,in}]^\sigma - \sum_{\sigma} \int d\mathbf{r} V^{\sigma,in}(\mathbf{r}) n^{out}(\mathbf{r}) + E_{POT}[V^{\sigma,in}] \quad (39)$$

E_{KS} can be formally regarded as a functional of $n^{out}(\mathbf{r})$ since $V^{\sigma,in} \rightarrow n^{out}(\mathbf{r})$. However, KS equations provide no way to choose $n^{out}(\mathbf{r})$ except as a result of $V^{\sigma,in}$. The solution of KS equations is then for the potential $V^{\sigma,in}$ that minimizes $E_{KS}[V^{\sigma,in}]$. At the minimum:

- $V^{\sigma,in} = V_{KS}^\sigma$;
- $n^{out}(\mathbf{r}) = n_0(\mathbf{r})$;
- $E_{KS}[V^{\sigma,in}] - E_{KS}[V_{KS}^\sigma] = O[(V^{\sigma,in} - V_{KS}^\sigma)^2]$;
- $E_{KS}[n^{out}(\mathbf{r})] - E_{KS}[n_0(\mathbf{r})] = O[(n^{out}(\mathbf{r}) - n_0(\mathbf{r}))^2]$

3.6 Meaning of KS Eigenvalues

Neither the KS orbitals Ψ_i^σ nor the KS eigenvalues ε_i^σ have a compelling physical significance. In particular the KS eigenvalues do not correspond to physical excitation energies, i.e. the energy we need to add or subtract electrons from the interacting many-body problem. Nevertheless the eigenvalues can be used to construct meaningful quantities.

There are some exceptions:

- In finite systems (atoms or molecules) the negative of the highest occupied KS eigenvalue ε_N coincides with the ionization potential I ;
- In metallic extended systems, the highest occupied level gives the true Fermi energy. However, the shape of the KS Fermi surface in momentum space differs in general from the true one.

3.7 The Bandgap Problem

If one electron in state v is removed from the system:

$$\varepsilon_v = E_N - E_{N-1} \quad (40)$$

If one electron is added in state c to the system:

$$\epsilon_c = E_{N+1} - E_N \quad (41)$$

The band gap is defined as:

$$\epsilon_g = \epsilon_c - \epsilon_v = E_{N+1} + E_{N-1} - 2E_N \quad (42)$$

In solids ϵ_g represents the direct optical band gap. Nevertheless, as we have studied before, in DFT the KS eigenvalues cannot be seen as true excitation energies. As a consequence one may define DFT as a **ground state theory**. The reason for the band gap problem lies in the dependence of the exact energy functional upon the number of electrons and the inability of approximate functionals to reproduce it.

The basic variational property of DFT can be expressed as:

$$\frac{\delta}{\delta n(\mathbf{r})} \left\{ E - \mu \left[\int n(\mathbf{r}) d\mathbf{r} - N \right] \right\} \quad (43)$$

where μ is a Lagrange multiplier and N is the total number of electrons (which is an integer number).

Let D be the set of all density matrices of the form:

$$\hat{\rho} = (1-x) |\Psi_N\rangle \langle \Psi_N| + x |\Psi_{N+1}\rangle \langle \Psi_{N+1}| \quad (44)$$

obtained by mixing an N -particle state and an $(N+1)$ -particle state with weights $(1-x)$ and x . The expectation value of \hat{N} for any density matrix in this set is:

$$Tr \hat{\rho} \hat{N} = (1-x)N + x(N+1) = N + x \quad (45)$$

Therefore, we can extend the DFT formulation to non-integer number of electrons via the definition of:

$$\tilde{F}[n(\mathbf{r})] = \min_{\hat{\rho} \rightarrow n(\mathbf{r})} Tr \left\{ \hat{\rho} (\hat{T} + \hat{H}_{e-e}) \right\} \quad (46)$$

where the minimum must be searched among the set D that yield the prescribed density $n(\mathbf{r})$.

From the variational principle:

$$\frac{\delta E[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \mu \rightarrow \text{chemical potential} \quad (47)$$

and if we call E_N the energy of the ground state of N electrons:

$$\mu(N) = \frac{\partial E_N}{\partial N} \quad (48)$$

If we explicitly write down:

$$E_{N+x} = (1-x)E_N + xE_{N+1} \quad (49)$$

$$n_{N+x} = (1-x)n_N + xn_{N+1} \quad (50)$$

that is both energy and density are linear interpolations between the end points. However, μ and $\delta E / \delta n(\mathbf{r})$ are discontinuous at integer N . This is an important characteristic of the exact energy functional.

The energy gap can be written as:

$$E_g = \lim_{\delta \rightarrow 0} \{ \mu(N+\delta) - \mu(N-\delta) \} = \lim_{\delta \rightarrow 0} \left\{ \left. \frac{\delta E}{\delta n(\mathbf{r})} \right|_{N+\delta} - \left. \frac{\delta E}{\delta n(\mathbf{r})} \right|_{N-\delta} \right\} \quad (51)$$

For a non-interacting system only the kinetic energy contributes and:

$$E_g = \lim_{\delta \rightarrow 0} \left\{ \left. \frac{\delta T_{KS}}{\delta n(\mathbf{r})} \right|_{N+\delta} - \left. \frac{\delta T_{KS}}{\delta n(\mathbf{r})} \right|_{N-\delta} \right\} \quad (52)$$

For an interacting system, $E_{HARTREE}$ and E_{EXT} do not show any discontinuity, therefore E_{XC} must have a derivative discontinuity:

$$E_{XC}[n] = \tilde{F}[n] - T_{KS}[n] - E_{HARTREE}[n] - E_{EXT}[n] \quad (53)$$

$$\begin{aligned} E_g^{XC} &= \lim_{\delta \rightarrow 0} \left\{ \left. \frac{\delta E_{XC}}{\delta n(\mathbf{r})} \right|_{N+\delta} - \left. \frac{\delta E_{XC}}{\delta n(\mathbf{r})} \right|_{N-\delta} \right\} = \\ &= \lim_{\delta \rightarrow 0} \left\{ \left. \frac{\delta \tilde{F}}{\delta n(\mathbf{r})} \right|_{N+\delta} - \left. \frac{\delta \tilde{F}}{\delta n(\mathbf{r})} \right|_{N-\delta} - \left. \frac{\delta T_{KS}}{\delta n(\mathbf{r})} \right|_{N+\delta} + \left. \frac{\delta T_{KS}}{\delta n(\mathbf{r})} \right|_{N-\delta} \right\} = E_g - E_g^{KS} \Rightarrow \\ &\Rightarrow E_g^{XC} = E_g - E_g^{KS} \end{aligned} \quad (54)$$

The problem in practical DFT calculations is that the most popular approximations to E_{XC} do not show such discontinuity, yielding wrong energy gaps. If one knew how to add to the approximated E_{XC} the appropriate N -dependent constant as a functional of the ground state density then one would improve the calculation of the gap.

4. The Exchange-Correlation Functional

5. Plane Waves

6. Pseudopotentials

7. Density Functional Perturbation Theory

8. Ab-Intio Thermodynamics

References

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Appendix A: Theoretical Background

Functionals and functional derivative

The concept of a **functional** is the generalization of the concept of a function. A function associates a value with another value, while a functional associates a value with a function or a field:

- Function:

$$(x \xrightarrow{h} h(x)) \xrightarrow{F} F[h(x)] \in \mathcal{R}$$

- Field:

$$(x \xrightarrow{h} h(\mathbf{r})) \xrightarrow{F} F[h(\mathbf{r})] \in \mathcal{R}$$

If we have a functional $f[h]$, where $h : x \rightarrow h(x)$ and $f : h(x) \rightarrow f[h]$, the procedure to compute a **functional derivative** is:

- Consider a small variation of the function:

$$h \rightarrow h + \delta h \Rightarrow \delta f = f[h + \delta h] - f[h]$$

- Put δf in the form of a Taylor expansion:

$$\delta f = \int dx \alpha(x) \delta h(x) + \frac{1}{2} \int dx dy \beta(x, y) \delta h(x) \delta h(y) + \frac{1}{3!} \int dx dy dz \gamma(x, y, z) \delta h(x) \delta h(y) \delta h(z) \dots$$

By definition:

$$\alpha(x) = \frac{\delta f}{\delta h(x)}$$

$$\beta(x, y) = \frac{\delta^2 f}{\delta h(x) \delta h(y)}$$

Some properties:

- $f, g, \in \mathcal{F} \Rightarrow \frac{\delta(f+g)}{\delta h(x)} = \frac{\delta f}{\delta h(x)} + \frac{\delta g}{\delta h(x)}$
- $\alpha \in \mathcal{R}, u \in \mathcal{F} \Rightarrow \frac{\delta(\alpha u)}{\delta h(x)} = \alpha \frac{\delta u}{\delta h(x)}$
- $f, g, \in \mathcal{F} \Rightarrow \frac{\delta(f \cdot g)}{\delta h(x)} = \frac{\delta f}{\delta h(x)} \cdot g + \frac{\delta g}{\delta h(x)} \cdot f$
- Composition rule: $f[h] = g(u[h])$, with g a function and u a functional $\Rightarrow \frac{\delta f}{\delta h(x)} = g'(u[h]) \frac{\delta u}{\delta h(x)}$

- Chain rule: $f[u[h]]$, f is a functional of u and it depends on all the $u(x)$ but each $u(x)$ is a functional of the function $h(x) \Rightarrow \frac{\delta f}{\delta h(x)} = \int dy \frac{\delta f}{\delta u(y)} \frac{\delta u(y)}{\delta h(x)}$

Examples:

- $f[h] = h(x_0)$

$$h \rightarrow h + \delta h, \quad f \rightarrow f + \delta f$$

$$f[h + \delta h] = (h + \delta h) \Big|_{x_0} = h(x_0) + \delta h(x_0) \Rightarrow \delta f = \delta h(x_0) = \int dx \delta h(x) \delta(x - x_0)$$

$$\frac{\delta f}{\delta h(x)} = \delta(x - x_0)$$

- $f[h] = \int dx \frac{1}{2} a h^2(x)$

$$\begin{aligned} \frac{\delta f}{\delta h(x)} &= \frac{\delta}{\delta h(x)} \int dy \frac{1}{2} a h^2(y) = \int dy \frac{1}{2} a \frac{\delta h^2(y)}{\delta h(x)} = \int dy a h(y) \frac{\delta h(y)}{\delta h(x)} = \\ &= \int dy a h(y) \delta(x - y) = a h(x) \end{aligned}$$

- $f[h] = h'(y)$, y fixed

$$f[h + \delta h] = (h + \delta h)' \Big|_y = h'(y) + \delta h'(y)$$

$$\delta f = \delta h'(y) = \int dx \delta(x - y) \delta h'(x) = - \int dx \delta'(x - y) \delta h(x) + B.T. \Rightarrow$$

$$\frac{\delta f}{\delta h(x)} = -\delta'(x - y)$$

- $f[h] = \int d^d y \frac{1}{2} a (\nabla h)^2 = \int d^d y \frac{1}{2} a (\partial_i h)(\partial_i h)$

$$f[h + \delta h] = \int d^d y \frac{1}{2} a (\partial_i h + \partial_i \delta h)(\partial_i h + \partial_i \delta h) = f[h] + \int d^d y a (\partial_i h)(\partial_i \delta h) + O(\delta h^2) =$$

$$= f[h] - \int d^d y a (\partial_i \partial_i h) \delta h + B.T. \Rightarrow \frac{\delta f}{\delta h(x)} = -a \nabla^2 h(x)$$

Variational principle

We will employ the method of **Lagrange multipliers**. This method deals with the problem of finding stationary conditions for an integral I_0 while keeping at the same time constant other integrals I_1, I_2, \dots, I_k . One then wants to solve the equivalent problem:

$$\delta \{I_0 + \sum_k \lambda_k I_k\} = 0$$

where λ_k are constants to be determined and are called **Lagrange multipliers**.

Consider a Hamiltonian H and a function Ψ that can be varied with the sole condition that it stays normalized: $\langle \Psi | \Psi \rangle = 1$. In general Ψ is not eigenfunction of H , but we use it to calculate the expectation value of the energy:

$$\langle H \rangle = \int \Psi^* H \Psi d\mathbf{r}$$

Then we have:

$$I_0 = \int \Psi^* H \Psi d\mathbf{r}, \quad I_1 = \int \Psi^* \Psi d\mathbf{r}$$

$$\delta(I_0 - \lambda I_1) = 0, \quad \lambda \text{ to be determined}$$

If $\Psi \rightarrow \Psi + \delta\Psi$ and $\langle H \rangle \rightarrow \langle H \rangle + \langle \delta H \rangle$:

$$I_0 \rightarrow I_0 + \delta I_0 = \int (\Psi^* + \delta\Psi^*) H (\Psi + \delta\Psi) = I_0 + \int \Psi^* H \delta\Psi + \int \delta\Psi^* H \Psi + O(\delta\Psi^2) \Rightarrow$$

$$\Rightarrow \delta I_0 = \int \delta\Psi^* H \Psi + c.c.$$

$$I_1 \rightarrow I_1 + \delta I_1 = \int (\Psi^* + \delta\Psi^*) (\Psi + \delta\Psi) = I_1 + \int \Psi^* \delta\Psi + \int \delta\Psi^* \Psi + O(\delta\Psi^2) \Rightarrow$$

$$\Rightarrow \delta I_1 = \int \delta\Psi^* \Psi + c.c.$$

Then:

$$\delta(I_0 - \lambda I_1) = \int \delta\Psi^* [H - \lambda] \Psi + c.c. = 0 \Rightarrow H\Psi = \lambda\Psi$$

The Lagrange multiplier is equal to the energy eigenvalue. The variational principle states that the functions Ψ for which $\langle H \rangle$ is **stationary** (i.e. doesn't vary to first order in small variations of Ψ) are the eigenfunctions of the energy.

Consider now a different function Φ and expand it in terms of the energy eigenfunctions Ψ_n , which form a complete orthonormal basis:

$$\Phi = \sum_n c_n \Psi_n$$

Now take the expectation value of the Hamiltonian w.r.t. this new function:

$$\langle H \rangle = \frac{\int \Phi^* H \Phi}{\int \Phi^* \Phi} = \frac{\sum_{nm} c_m^* c_n \int \Psi_m^* H \Psi_n}{\sum_{nm} c_m^* c_n \int \Psi_m^* \Psi_n} = \frac{\sum_{nm} c_m^* c_n E_n \delta_{nm}}{\sum_{nm} c_m^* c_n \delta_{nm}} = \frac{\sum_n E_n |c_n|^2}{\sum_n |c_n|^2} = E_0 + \frac{\sum_n (E_n - E_0) |c_n|^2}{\sum_n |c_n|^2}$$

Since $E_n \geq E_0$, we have $(E_n - E_0) \geq 0$. Therefore:

$$\langle H \rangle = \frac{\int \Phi^* H \Phi}{\int \Phi^* \Phi} \geq E_0$$

Any function Φ yields for the expectation value of the energy an upper estimate of the ground-state energy. If the ground-state is unknown, an approximation can be found by varying Ψ inside a given set of functions and look for the one which minimizes $\langle H \rangle$.

Take-home messages:

- the eigenstates of the many-body hamiltonian are stationary points of $\langle H \rangle$;
- the ground-state wavefunction Ψ_0 is the state with lowest energy and can be determined (in principle) by minimizing the total energy with respect to all parameters in $\Psi(\{r_i\})$, with the constraint that Ψ must obey particle-hole symmetry and any conservation law;

The Hellmann-Feynman theorem

The following theorem allows for the computation of forces at a given atomic configuration when only the atomic positions are known. In the following, the nuclei of the atoms are to be held fixed as point charges and the force required to be applied to the nuclei to hold them is to be calculated.

Let λ be one of any number of parameters which specify nuclear positions (i.e. x component of the position of one of the nuclei). In a steady state of energy E the force is defined as:

$$f_\lambda = -\frac{\partial E}{\partial \lambda} \quad (55)$$

Now:

$$E = \langle H \rangle = \int dr \Psi^* H \Psi$$

$$\frac{\partial E}{\partial \lambda} = \frac{\partial}{\partial \lambda} \int dr \Psi^* H \Psi = \int dr \frac{\partial \Psi^*}{\partial \lambda} H \Psi + \int dr \Psi^* \frac{\partial H}{\partial \lambda} \Psi + \int dr \Psi^* H \frac{\partial \Psi}{\partial \lambda}$$

Consider the first and the last term:

$$\int dr \frac{\partial \Psi^*}{\partial \lambda} H \Psi + \int dr \Psi^* H \frac{\partial \Psi}{\partial \lambda} = E \left\{ \int dr \frac{\partial \Psi^*}{\partial \lambda} \Psi + \int dr \Psi^* \frac{\partial \Psi}{\partial \lambda} \right\} = E \frac{\partial}{\partial \lambda} \left\{ \int dr \Psi^* \Psi \right\} = 0$$

Therefore, in the end we have:

$$f_\lambda = - \int dr \Psi^* \frac{\partial H}{\partial \lambda} \Psi = - \langle \frac{\partial H}{\partial \lambda} \rangle \quad (56)$$

In the case of solids:

$$\frac{\partial H}{\partial \mathbf{R}_I} = \frac{\partial}{\partial \mathbf{R}_I} \{T + V_{ext} + V_{int} + E_{II}\} = \frac{\partial V_{ext}}{\partial \mathbf{R}_I} + \frac{\partial E_{II}}{\partial \mathbf{R}_I}$$

since T and V_{int} depends only on electrons' coordinates. Then:

$$\mathbf{F}_I = - \frac{\partial E}{\partial \mathbf{R}_I} = - \int d^3r n(\mathbf{r}) \times \frac{\partial V_{ext}}{\partial \mathbf{R}_I} - \frac{\partial E_{II}}{\partial \mathbf{R}_I} \quad (57)$$

where $n(\mathbf{r})$ is the unperturbed electronic density. The force depends upon only the density of the electrons and the other nuclei. It can be shown [R. P. Feynman, "Forces in molecules", Phys. Rev. 56, 15 (1939)] that the force on any nucleus (considered fixed) is the charge on that nucleus times the electric field due to all the electrons, plus the fields from the other nuclei.

Independent electron approximation

In the non-interacting approximation we assume that electrons are uncorrelated except for the exclusion principle. There is some effective potential that incorporates some effect of the real interaction, however there is no interaction term explicitly included in the effective Hamiltonian:

$$H_{eff} \Psi_i^\sigma(\mathbf{r}) = \left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{eff}^\sigma(\mathbf{r}) \right] \Psi_i^\sigma(\mathbf{r}) = \epsilon_i^\sigma \Psi_i^\sigma(\mathbf{r}) \quad (58)$$

where $V_{eff}^\sigma(\mathbf{r})$ is an effective potential that acts on each electron of spin σ at point \mathbf{r} .

For non interacting particles; in a grand-canonical framework:

$$H_G = \sum_i (\epsilon_i - \mu) c_i^\dagger c_i = \sum_i (\epsilon_i - \mu) \hat{n}_i \quad (59)$$

The partition function is then:

$$Z_G = e^{-\beta \Omega} = Tr \{ e^{-\beta H_G} \} = \sum_i \langle \Psi_i | e^{-\beta H_G} | \Psi_i \rangle$$

Using the fact that:

$$\sum_i |\Psi_i\rangle = \sum_{n_i=0}^1 |n_i\rangle_1 |n_i\rangle_2 \cdots$$

We obtain:

$$Z_G = \prod_i \sum_{n_i=0}^1 e^{-\beta(\varepsilon_i - \mu)n_i} = \prod_i (1 + e^{-\beta(\varepsilon_i - \mu)})$$

Therefore, the average number of particle is given by:

$$\langle \hat{N} \rangle = -\frac{\partial \Omega_G}{\partial \mu} = \frac{1}{\beta} \sum_i \frac{\partial}{\partial \mu} \ln(1 + e^{-\beta(\varepsilon_i - \mu)}) = \sum_i \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1} = \sum_i f_i$$

where f_i is the Fermi-Dirac distribution which tends to $\theta(\varepsilon_F - \varepsilon_i)$ as $T \rightarrow 0$.

The expectation value of an operator can then be written as:

$$\langle \hat{O} \rangle = \text{Tr}\{\hat{\rho}_G \hat{O}\} = \frac{1}{Z} \text{Tr}\{e^{-\beta \hat{H}_G} \hat{O}\} = \sum_{i,\sigma} f_i^\sigma \langle \psi_i^\sigma | \hat{O} | \psi_i^\sigma \rangle$$

where now we have explicitly taken into account also spin σ . Therefore, in the independent electron picture:

$$E(T) = \sum_{i,\sigma} f_i^\sigma \varepsilon_i^\sigma$$

i.e. it is the weighted sum of non-interacting particle energies ε_i^σ . Finally, the electron density can be written as:

$$n^\sigma(\mathbf{r}) = \sum_i f_i^\sigma |\psi_i^\sigma(\mathbf{r})|^2$$

Two-body correlation

The key problem of electronic structure is that electrons give rise to an interacting many-body system:

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

Since interactions mostly involve pairs of electrons, we are interested in two-body correlation functions.

The density can be defined as the probability of finding an electron at position \mathbf{r} :

$$\begin{aligned}
n(\mathbf{r}) &= \langle \psi | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) | \psi \rangle = \sum_{i=1}^N \int d\mathbf{r}_1 \cdots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \cdots d\mathbf{r}_N |\psi(\mathbf{r}_1, \dots, \mathbf{r}_{i-1}, \mathbf{r}, \mathbf{r}_{i+1}, \dots, \mathbf{r}_N)|^2 = \\
&= N \int d\mathbf{r}_2 \cdots d\mathbf{r}_N |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2
\end{aligned}$$

The joint probability is defined as the probability of finding an electron at position \mathbf{r} and another one at position \mathbf{r}' :

$$n(\mathbf{r}, \mathbf{r}') = \langle \psi | \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) | \psi \rangle = \cdots = N(N-1) \int d\mathbf{r}_3 \cdots d\mathbf{r}_N |\psi(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N)|^2$$

For uncorrelated particles, the joint density is just the product of the single probabilities:

$$n(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})n(\mathbf{r}')$$

Therefore we can link the joint density and the single-electron density by:

$$n(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})n(\mathbf{r}') + \Delta n(\mathbf{r}, \mathbf{r}')$$

where $\Delta n(\mathbf{r}, \mathbf{r}')$ is the measure of electron correlations and is null for an independent particle picture.