

4. QUANTUM CHEMISTRY METHODS: II DENSITY FUNCTIONAL THEORY

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The **Density Functional Theory** (DFT) (Parr, 1989) represents an alternative to the conventional *ab initio* methods of introducing the effects of electron correlation into the solution to the electronic Schrödinger equation. According to the DFT, the energy of the ground state of a many-electron system can be expressed through the electron density, and in fact, the use of the electron density in place of the wave function to calculate the energy is the foundation of the DFT. Unfortunately, the precise mathematical formula relating energy to **electron density** is not known, so it is necessary to resort to approximate expressions. These expressions usually provide surprisingly good results if one takes into consideration the approximations upon which they are based on. The greatest disadvantage of these methods lies in the fact that, in systems in which the DFT gives erroneous results, there is no systematic way to improve them. Nevertheless, during the last decade methods to calculate systems of medium to large size using DFT methods have become very popular, especially for transition metal complexes. It is nowadays routinely applied to analyze chemical problems concerning, among other matters, molecular structure and chemical reactivity in organic, organometallic, and inorganic chemistry. The results obtained when using non-local exchange-correlation functionals are comparable or superior to those obtained by the MP2 method. In the following sections the fundamental principles and the functional formulation of the DFT are discussed.

4.1. Preliminary concepts: density functions and matrices

4.1.1. Density functions

Let us consider a system of N electrons described by a wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$. The product $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N$ gives us the probability of finding electron 1 between \mathbf{x}_1 and $\mathbf{x}_1+d\mathbf{x}_1$, electron 2 between \mathbf{x}_2 and $\mathbf{x}_2+d\mathbf{x}_2$, ..., and electron N between \mathbf{x}_N and $\mathbf{x}_N+d\mathbf{x}_N$. The probability of finding electron 1 between \mathbf{x}_1 and $\mathbf{x}_1+d\mathbf{x}_1$, independently of where the others are found, is given by:

$$d\bar{x}_1 \int \Psi(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) \Psi^*(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) d\bar{x}_2 \dots d\bar{x}_N \quad (4.1)$$

and given that the electrons are indistinguishable:

$$\rho(\bar{x}_1) d\bar{x}_1 = N d\bar{x}_1 \int \Psi(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) \Psi^*(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) d\bar{x}_2 \dots d\bar{x}_N \quad (4.2)$$

gives us the probability of finding an electron between \mathbf{x}_1 and $\mathbf{x}_1+d\mathbf{x}_1$, independently of where the others are found. $\rho(\mathbf{x})$ is the so-called **density function**. The **electron density** $\rho(\mathbf{r})$, which can also be obtained experimentally through the X-ray technique, is obtained integrating with respect to the spin coordinate.

$$\rho(\bar{r}_1) = \int \rho(\bar{x}_1) ds_1 = N \int \Psi(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) \Psi^*(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) ds_1 d\bar{x}_2 \dots d\bar{x}_N \quad (4.3)$$

Given that Ψ is normalised:

$$\int \rho(\bar{r}) d\bar{r} = N \quad (4.4)$$

In a system with N electrons, N_α electrons have α spin and the remaining N_β electrons have β spin. It is possible to define the electron densities corresponding to the α and β electrons separately, $\rho^\alpha(\mathbf{r})$ and $\rho^\beta(\mathbf{r})$. For the particular case of $\rho^\alpha(\mathbf{r})$ we have that:

$$\rho^\alpha(\bar{r}_1) = N_\alpha \int \Psi(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) \Psi^*(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) ds_1 d\bar{x}_2 \dots d\bar{x}_N \quad (4.5)$$

gives us the probability of finding an α electron between \mathbf{r}_1 and $\mathbf{r}_1+d\mathbf{r}_1$.

The difference $\rho^S(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})$ constitutes the so-called **spin density**. A value of $\rho^S(\mathbf{r}) \geq 0$ indicates an α density excess at point \mathbf{r} . The spin density on an atom can be used to theoretically determine the **Fermi contact couplings** which can be compared with experimental values obtained through the electron spin resonance (ESR) technique.

On the other hand, the integral:

$$d\bar{x}_1 d\bar{x}_2 \int \Psi(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) \Psi^*(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N) d\bar{x}_3 \dots d\bar{x}_N \quad (4.6)$$

gives us the probability of finding electron 1 between \mathbf{x}_1 and $\mathbf{x}_1+d\mathbf{x}_1$ and electron 2 between \mathbf{x}_2 and $\mathbf{x}_2+d\mathbf{x}_2$, independently of where the others are found. The **second order density**, $\gamma_2(\mathbf{x}_1, \mathbf{x}_2)$, is defined according to:

$$\gamma_2(\vec{x}_1, \vec{x}_2) = N(N-1) \int \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \Psi^*(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) d\vec{x}_3 \dots d\vec{x}_N \quad (4.7)$$

where $N(N-1)$ are the possible electron pairs that can be formed, and given that the electrons are indistinguishable, $\gamma_2(\mathbf{x}_1, \mathbf{x}_2)d\mathbf{x}_1d\mathbf{x}_2$ consequently gives us the probability of finding any electron between \mathbf{x}_1 and $\mathbf{x}_1+d\mathbf{x}_1$ and another between \mathbf{x}_2 and $\mathbf{x}_2+d\mathbf{x}_2$. Integrating with respect to the spin variables, we obtain the **two-electron density** or **pair function**:

$$\gamma_2(\vec{r}_1, \vec{r}_2) = \int \gamma_2(\vec{x}_1, \vec{x}_2) ds_1 ds_2 \quad (4.8)$$

which gives us the probability of finding any two electrons, one between \mathbf{r}_1 and $\mathbf{r}_1 + d\mathbf{r}_1$ and the other between \mathbf{r}_2 and $\mathbf{r}_2 + d\mathbf{r}_2$, under any spin combination ($\alpha\alpha, \alpha\beta, \beta\alpha, \beta\beta$). Just as the total electron density is the sum of densities α and β , it is also possible to separate the pair function in the following four contributions:

$$\gamma_2(\vec{r}_1, \vec{r}_2) = \gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) + \gamma_2^{\alpha\beta}(\vec{r}_1, \vec{r}_2) + \gamma_2^{\beta\alpha}(\vec{r}_1, \vec{r}_2) + \gamma_2^{\beta\beta}(\vec{r}_1, \vec{r}_2) \quad (4.9)$$

where:

$$\gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) = N_\alpha(N_\alpha - 1) \int \Psi(\vec{r}_1 s_1, \vec{r}_2 s_2, \vec{x}_3 \dots \vec{x}_N) \Psi^*(\vec{r}_1 s_1, \vec{r}_2 s_2, \vec{x}_3 \dots \vec{x}_N) ds_1 ds_2 d\vec{x}_3 \dots d\vec{x}_N \quad (4.10)$$

is the probability density of finding two α electrons in positions defined by vectors \mathbf{r}_1 and $\mathbf{r}_1 + d\mathbf{r}_1$ and \mathbf{r}_2 and $\mathbf{r}_2 + d\mathbf{r}_2$. Likewise, $\gamma_2^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$ is:

$$\gamma_2^{\alpha\beta}(\vec{r}_1, \vec{r}_2) = N_\alpha N_\beta \int \Psi(\vec{r}_1 s_1, \vec{r}_2 s_2, \vec{x}_3 \dots \vec{x}_N) \Psi^*(\vec{r}_1 s_1, \vec{r}_2 s_2, \vec{x}_3 \dots \vec{x}_N) ds_1 ds_2 d\vec{x}_3 \dots d\vec{x}_N \quad (4.11)$$

With the definitions given by the equations (4.7), (4.10) and (4.11) and taking into account:

$$N(N-1) = (N_\alpha + N_\beta)(N_\alpha + N_\beta - 1) = N_\alpha(N_\alpha - 1) + N_\alpha N_\beta + N_\beta N_\alpha + N_\beta(N_\beta - 1) \quad (4.12)$$

it can be demonstrated by simple substitution that equation (4.9) holds.

4.1.2. Density matrices

For certain applications it is appropriate to work with the so-called **first-order** or **Fock-Dirac density matrix** defined by:

$$\rho_1(\vec{x}_1, \vec{x}'_1) = N \int \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \Psi^*(\vec{x}'_1, \vec{x}_2, \dots, \vec{x}_N) d\vec{x}_2 \dots d\vec{x}_N \quad (4.13)$$

Integrating with respect to the spin coordinate, the **first-order reduced density matrix** is obtained:

$$\rho_1(\vec{r}_1, \vec{r}'_1) = \int \rho_1(\vec{x}_1, \vec{x}'_1) ds_1 ds'_1 \quad (4.14)$$

Unlike the density functions, the elements of the density matrices do not have physical meaning, except the diagonal elements, which coincide with the **electron density** in the case of the first-order reduced density matrix.

$$\rho_1(\vec{r}_1, \vec{r}_1) = \rho(\vec{r}_1) \geq 0 \quad (4.15)$$

It is noteworthy that the sum of the first-order reduced density matrix elements, which is an integral due to the continuous character of the matrix indices, gives us the total number of electrons:

$$\text{tr } \rho_1 = \int \rho_1(\vec{r}_1, \vec{r}_1) d\vec{r}_1 = \int \rho(\vec{r}_1) d\vec{r}_1 = N \quad (4.16)$$

As we will see shortly, many properties of the many-electron systems, energy in particular, can be expressed as functions of the first-order density matrix and from the two-electron density.

The density matrices of an order higher than one can be defined in the exact same way. The most interesting is the **second-order density matrix** defined from the expression:

$$\gamma_2(\vec{x}_1, \vec{x}_2; \vec{x}'_1, \vec{x}'_2) = N(N-1) \int \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \Psi^*(\vec{x}'_1, \vec{x}'_2, \dots, \vec{x}_N) d\vec{x}_3 \dots d\vec{x}_N \quad (4.17)$$

Integrating with respect to the spin coordinates, the **reduced second-order density matrix** is obtained:

$$\gamma_2(\vec{r}_1, \vec{r}_2; \vec{r}'_1, \vec{r}'_2) = \int \gamma_2(\vec{x}_1, \vec{x}_2; \vec{x}'_1, \vec{x}'_2) ds_1 ds'_1 ds_2 ds'_2 \quad (4.18)$$

As in the previous case, on the one hand, only the diagonal elements have physical meaning and, on the other, the trace of the matrix gives us the total number of electron pairs:

$$\gamma_2(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) = \gamma_2(\vec{r}_1, \vec{r}_2) \quad (4.19)$$

$$\text{tr } \gamma_2 = \int \gamma_2(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = \int \gamma_2(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = N(N-1) \quad (4.20)$$

4.1.3. Single determinant wave functions

In this section we develop the expressions obtained for the first- and second-order density functions and matrices for a system of N electrons described by wave functions consisting of only one **Slater determinant**. We will distinguish between the cases of a determinant for a restricted closed-shell system, in which:

$$\psi = \frac{1}{\sqrt{N!}} \left| \chi_1(1) \bar{\chi}_1(2) \chi_2(3) \dots \bar{\chi}_{\frac{N}{2}}(N) \right| \quad (4.21)$$

and for an unrestricted system, for which:

$$\psi = \frac{1}{\sqrt{(N_\alpha + N_\beta)!}} \left| \chi_1(1)\chi_2(2)\cdots\chi_{N_\alpha}(N_\alpha)\chi_{N_\alpha+1}(N_\alpha+1)\cdots\chi_{N_\alpha+N_\beta}(N_\alpha+N_\beta) \right| \quad (4.22)$$

4.1.3.1. Restricted closed-shell Slater determinant

For the **electron density** we proceed from definition (4.3) and with the wave function (4.21) developing the Slater determinant according to (3.7), we obtain:

$$\rho(\vec{r}_1) = N \frac{1}{N!} \int \sum_{P_i} \sum_{P_j} (-1)^{P_i} (-1)^{P_j} P_i \left\{ \chi_1(1)\bar{\chi}_1(2)\cdots\bar{\chi}_N(N) \right\} P_j \left\{ \chi_1(1)\bar{\chi}_1(2)\cdots\bar{\chi}_N(N) \right\} d\vec{x}_1 d\vec{x}_2 \cdots d\vec{x}_N \quad (4.23)$$

and therefore:

$$\rho(\vec{r}_1) = N \frac{1}{N!} (N-1)! \cdot 2 \sum_{i=1}^{\frac{N}{2}} |\chi_i(\vec{r}_1)|^2 = 2 \sum_{i=1}^{\frac{N}{2}} |\chi_i(\vec{r}_1)|^2 \quad (4.24)$$

In the same way, for the first-order density matrix we have that:

$$\rho_1(\vec{r}_1, \vec{r}'_1) = 2 \sum_{i=1}^{\frac{N}{2}} \chi_i(\vec{r}_1) \chi_i^*(\vec{r}'_1) \quad (4.25)$$

Within the LCAO approximation, introduced in Section 3.2.2, substituting (3.34) in equation (4.24) leads to:

$$\rho(\vec{r}_1) = 2 \sum_{i=1}^{\frac{N}{2}} \sum_{\mu} \sum_{\nu} c_{\mu i}^* c_{\nu i} \phi_{\mu}^*(\vec{r}_1) \phi_{\nu}(\vec{r}_1) = \sum_{\mu} \sum_{\nu} P_{\nu\mu} \phi_{\mu}^*(\vec{r}_1) \phi_{\nu}(\vec{r}_1) \quad (4.26)$$

where $\mathbf{P}_{\nu\mu}$ are elements of the density matrix, defined in Section 3.2.2.1.1.

With regard to the **pair function** proceeding from (4.7) and (4.8) and following the same procedure, we obtain the expression:

$$\gamma_2(\vec{r}_1, \vec{r}_2) = 4 \sum_{i=1}^{\frac{N}{2}} \sum_{j=1}^{\frac{N}{2}} \left(\chi_i^*(\vec{r}_1) \chi_j^*(\vec{r}_2) \chi_i(\vec{r}_1) \chi_j(\vec{r}_2) - \frac{1}{2} \chi_i^*(\vec{r}_1) \chi_j^*(\vec{r}_2) \chi_j(\vec{r}_1) \chi_i(\vec{r}_2) \right) \quad (4.27)$$

which, within the LCAO scheme, is converted into:

$$\gamma_2(\vec{r}_1, \vec{r}_2) = 4 \sum_{i=1}^{\frac{N}{2}} \sum_{j=1}^{\frac{N}{2}} \sum_{\mu} \sum_{\nu} \sum_{\sigma} \sum_{\lambda} \left[c_{\mu i}^* c_{\nu j}^* c_{\sigma i} c_{\lambda j} - \frac{1}{2} c_{\mu i}^* c_{\nu j}^* c_{\sigma j} c_{\lambda i} \right] \phi_{\mu}^*(\vec{r}_1) \phi_{\nu}^*(\vec{r}_2) \phi_{\sigma}(\vec{r}_1) \phi_{\lambda}(\vec{r}_2) \quad (4.28)$$

Defining the second-order density matrix, Γ , according to:

$$\Gamma_{\mu\nu\sigma\lambda} = 4 \sum_{i=1}^{\frac{N}{2}} \sum_{j=1}^{\frac{N}{2}} \left[c_{\mu i}^* c_{\nu j}^* c_{\sigma i} c_{\lambda j} - \frac{1}{2} c_{\mu i}^* c_{\nu j}^* c_{\sigma j} c_{\lambda i} \right] = P_{\sigma\mu} P_{\lambda\nu} - \frac{1}{2} P_{\lambda\mu} P_{\sigma\nu} \quad (4.29)$$

finally results in:

$$\gamma_2(\vec{r}_1, \vec{r}_2) = \sum_{\mu} \sum_{\nu} \sum_{\sigma} \sum_{\lambda} \Gamma_{\mu\nu\sigma\lambda} \phi_{\mu}^*(\vec{r}_1) \phi_{\nu}^*(\vec{r}_2) \phi_{\sigma}(\vec{r}_1) \phi_{\lambda}(\vec{r}_2) \quad (4.30)$$

4.1.3.2. Unrestricted closed-shell Slater determinant

For a system of $N=N_{\alpha}+N_{\beta}$ electrons described by an unrestricted **Slater determinant**, such as the one in equation (4.22), the **electron density** is expressed:

$$\rho(\vec{r}_1) = N \frac{1}{M} (N-1)! \left[\sum_{i=1}^{N_{\alpha}} |\chi_i(\vec{r}_1)|^2 + \sum_{i=1+N_{\alpha}}^{N_{\alpha}+N_{\beta}} |\chi_i(\vec{r}_1)|^2 \right] = \rho^{\alpha}(\vec{r}_1) + \rho^{\beta}(\vec{r}_1) = \sum_{i=1}^{N_{\alpha}+N_{\beta}} |\chi_i(\vec{r}_1)|^2 \quad (4.31)$$

Within the LCAO approximation, equation (4.31) is transformed into:

$$\rho(\vec{r}_1) = \sum_{\mu} \sum_{\nu} P_{\nu\mu}^{\alpha} \phi_{\mu}^*(\vec{r}_1) \phi_{\nu}(\vec{r}_1) + \sum_{\mu} \sum_{\nu} P_{\nu\mu}^{\beta} \phi_{\mu}^*(\vec{r}_1) \phi_{\nu}(\vec{r}_1) = \sum_{\mu} \sum_{\nu} P_{\nu\mu}^T \phi_{\mu}^*(\vec{r}_1) \phi_{\nu}(\vec{r}_1) \quad (4.32)$$

with:

$$P_{\nu\mu}^{\alpha} = \sum_{i=1}^{N_{\alpha}} c_{\mu i}^* c_{\nu i} \quad ; \quad P_{\nu\mu}^{\beta} = \sum_{i=1+N_{\alpha}}^{N_{\alpha}+N_{\beta}} c_{\mu i}^* c_{\nu i} \quad ; \quad P_{\nu\mu}^T = P_{\nu\mu}^{\alpha} + P_{\nu\mu}^{\beta} \quad (4.33)$$

For the first-order density matrix we have:

$$\rho_1(\vec{r}_1, \vec{r}'_1) = \sum_{i=1}^{N_{\alpha}+N_{\beta}} \chi_i(\vec{r}_1) \chi_i^*(\vec{r}'_1) \quad ; \quad \rho_1^{\alpha}(\vec{r}_1, \vec{r}'_1) = \sum_{i=1}^{N_{\alpha}} \chi_i(\vec{r}_1) \chi_i^*(\vec{r}'_1) \quad (4.34)$$

Finally and in accordance with equation (4.9), we basically have two possibilities for the **pair function**, depending on whether the two electrons located in \mathbf{r}_1 and \mathbf{r}_2 have the same or different spin. For the first case, supposing that the two electrons are α -type electrons, we are left with:

$$\gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) = \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\alpha}} \left(\chi_i^*(\vec{r}_1) \chi_j^*(\vec{r}_2) \chi_i(\vec{r}_1) \chi_j(\vec{r}_2) - \chi_i^*(\vec{r}_1) \chi_j^*(\vec{r}_2) \chi_j(\vec{r}_1) \chi_i(\vec{r}_2) \right) \quad (4.35)$$

which, taking into account (4.31) and (4.34), is translated into:

$$\gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) = \rho^{\alpha}(\vec{r}_1) \rho^{\alpha}(\vec{r}_2) - \rho_1^{\alpha}(\vec{r}_1, \vec{r}_2) \rho_1^{\alpha}(\vec{r}_2, \vec{r}_1) \quad (4.36)$$

and, within the LCAO approximation:

$$\gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) = \sum_{\mu\nu\sigma\lambda} \Gamma_{\mu\nu\sigma\lambda}^{\alpha\alpha} \phi_{\mu}^*(\vec{r}_1) \phi_{\nu}^*(\vec{r}_2) \phi_{\sigma}(\vec{r}_1) \phi_{\lambda}(\vec{r}_2) \quad (4.37)$$

$$\Gamma_{\mu\nu\sigma\lambda}^{\alpha\alpha} = P_{\sigma\mu}^{\alpha} P_{\lambda\nu}^{\alpha} - P_{\lambda\mu}^{\alpha} P_{\sigma\nu}^{\alpha} \quad (4.38)$$

Obviously we have identical expressions for the case of two β electrons simply by changing α for β in equations (4.35) to (4.38). For the case of an α -type electron in \mathbf{r}_1 and another β -type in \mathbf{r}_2 we are left with:

$$\gamma_2^{\alpha\beta}(\vec{r}_1, \vec{r}_2) = \sum_{i=1}^{N_\alpha} \sum_{j=N_\alpha+1}^{N_\alpha+N_\beta} \chi_i^*(\vec{r}_1) \chi_j^*(\vec{r}_2) \chi_i(\vec{r}_1) \chi_j(\vec{r}_2) = \rho^\alpha(\vec{r}_1) \rho^\beta(\vec{r}_2) \quad (4.39)$$

$$\gamma_2^{\alpha\beta}(\vec{r}_1, \vec{r}_2) = \sum_{\mu\nu\sigma\lambda} \Gamma_{\mu\nu\sigma\lambda}^{\alpha\beta} \phi_\mu^*(\vec{r}_1) \phi_\nu^*(\vec{r}_2) \phi_\sigma(\vec{r}_1) \phi_\lambda(\vec{r}_2) \quad (4.40)$$

$$\Gamma_{\mu\nu\sigma\lambda}^{\alpha\beta} = P_{\sigma\mu}^\alpha P_{\lambda\nu}^\beta \quad (4.41)$$

4.1.4. Exchange-correlation hole

Two-electron density, $\gamma_2(\mathbf{r}_1, \mathbf{r}_2)$, gives us the probability density of simultaneously finding two electrons, one in \mathbf{r}_1 and the other in \mathbf{r}_2 . In other words, the two-electron density contains information about the correlated motion of two electrons. The same information about the electron correlation is contained in the exchange-correlation density, the conditional probability density, and the exchange-correlation holes described below.

The **exchange-correlation density**, $\Gamma_{XC}(\mathbf{r}_1, \mathbf{r}_2)$, is defined from the expression:

$$\gamma_2(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1) \rho(\vec{r}_2) + \Gamma_{XC}(\vec{r}_1, \vec{r}_2) \quad (4.42)$$

In this equation $\gamma_2(\mathbf{r}_1, \mathbf{r}_2)$ represents the probability density of finding an electron in \mathbf{r}_1 and another in \mathbf{r}_2 . Considering electrons as uncorrelated independent particles, the term $\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)$ is the probability density of finding an electron in \mathbf{r}_1 and another in \mathbf{r}_2 . Consequently, the exchange-correlation density, $\Gamma_{XC}(\mathbf{r}_1, \mathbf{r}_2)$, represents the difference between the probability density of finding two electrons, one in \mathbf{r}_1 and the other in \mathbf{r}_2 , correlated or uncorrelated.

Dividing $\gamma_2(\mathbf{r}_1, \mathbf{r}_2)$ by $\rho(\mathbf{r}_1)$:

$$\frac{\gamma_2(\vec{r}_1, \vec{r}_2)}{\rho(\vec{r}_1)} = P(\vec{r}_1, \vec{r}_2) \quad (4.43)$$

results in the **conditional probability density**, $P(\mathbf{r}_1, \mathbf{r}_2)$, which gives us the probability density of finding an electron in \mathbf{r}_2 when there is already another one in \mathbf{r}_1 . This is seen much more clearly when (4.43) is rearranged to produce:

$$\gamma_2(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1) P(\vec{r}_1, \vec{r}_2) \quad (4.44)$$

which has the same form as the probability that events A and B will occur, $P(A \cup B) = P(A) P_A(B)$, in which $P(A)$ is the probability that A happens, and $P_A(B)$ is the probability that B will take place after A has happened.

Dividing (4.42) by $\rho(\mathbf{r}_1)$ leads to:

$$P(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_2) + \rho_{XC}(\vec{r}_1, \vec{r}_2) \quad (4.45)$$

with:

$$\rho_{XC}(\vec{r}_1, \vec{r}_2) = \frac{\Gamma_{XC}(\vec{r}_1, \vec{r}_2)}{\rho(\vec{r}_1)} \quad (4.46)$$

$\rho_{XC}(\mathbf{r}_1, \mathbf{r}_2)$ is given the name **exchange-correlation or Fermi-Coulomb hole**. According to (4.45), the exchange-correlation hole is the correction term which must be added to the unconditional probability in order to obtain the conditional probability. It is the region around the electron in which the presence of other electrons is excluded to a greater or lesser degree. Substituting (4.45) into (4.44) we have that:

$$\gamma_2(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2) + \rho(\vec{r}_1)\rho_{XC}(\vec{r}_1, \vec{r}_2) \quad (4.47)$$

In the same way that equation (4.9) separates the two-electron density for each pair of points into four contributions, it is also possible to separate the contributions into $\rho_{XC}(\mathbf{r}_1, \mathbf{r}_2)$. Thus:

$$\gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) = \rho^\alpha(\vec{r}_1)\rho^\alpha(\vec{r}_2) + \Gamma_{XC}^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) \quad (4.48)$$

$$\frac{\gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_2)}{\rho^\alpha(\vec{r}_1)} = P^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) = \rho^\alpha(\vec{r}_2) + \frac{\Gamma_{XC}^{\alpha\alpha}(\vec{r}_1, \vec{r}_2)}{\rho^\alpha(\vec{r}_1)} = \rho^\alpha(\vec{r}_2) + \rho_{XC}^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) \quad (4.49)$$

where $\rho_{XC}^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)$ is the so-called **Fermi hole** and represents a specific reference electron with α spin located in \mathbf{r}_1 , the region of the space from which the presence of another electron of the same spin is excluded to a greater or lesser extent. The probability of finding an electron in \mathbf{r}_2 when there is another of the same spin in \mathbf{r}_1 is reduced, especially for small $|\mathbf{r}_1 - \mathbf{r}_2|$. In addition:

$$\frac{\gamma_2^{\alpha\beta}(\vec{r}_1, \vec{r}_2)}{\rho^\alpha(\vec{r}_1)} = P^{\alpha\beta}(\vec{r}_1, \vec{r}_2) = \rho^\beta(\vec{r}_2) + \frac{\Gamma_{XC}^{\alpha\beta}(\vec{r}_1, \vec{r}_2)}{\rho^\alpha(\vec{r}_1)} = \rho^\beta(\vec{r}_2) + \rho_{XC}^{\alpha\beta}(\vec{r}_1, \vec{r}_2) \quad (4.50)$$

$\rho_{XC}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$ is the so-called **Coulomb hole** and would give us the zone where the presence of a β electron is excluded or favoured in the case in which we have a reference electron with α spin located in \mathbf{r}_1 .

The functions $\rho_{XC}(\mathbf{r}_1, \mathbf{r}_2)$ are obviously complicated, although it is possible to determine some of their properties based on general considerations. Therefore, by the **Pauli exclusion principle**:

$$\gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_1) = \gamma_2^{\beta\beta}(\vec{r}_1, \vec{r}_1) = 0 \quad (4.51)$$

which, taking into account (4.49), leads to:

$$\rho_{XC}^{\alpha\alpha}(\vec{r}_1, \vec{r}_1) = -\rho^\alpha(\vec{r}_1) \quad (4.52)$$

From (4.10) and (4.5) it is easily demonstrated that:

$$\int \gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 = (N_\alpha - 1)\rho^\alpha(\vec{r}_1) \quad (4.53)$$

and from (4.11) and (4.5) it is likewise found that:

$$\int \gamma_2^{\alpha\beta}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 = N_\beta \rho^\alpha(\vec{r}_1) \quad (4.54)$$

Based on (4.50) and using (4.54) the following equation holds:

$$\int \rho_{xc}^{\alpha\beta}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 = \int \rho_{xc}^{\beta\alpha}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 = 0 \quad (4.55)$$

In a similar way, starting from (4.49) and using (4.53) leads to:

$$\int \rho_{xc}^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 = -1 \quad (4.56)$$

Given that for any α electron:

$$\rho_{xc}(\vec{r}_1, \vec{r}_2) = \rho_{xc}^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) + \rho_{xc}^{\alpha\beta}(\vec{r}_1, \vec{r}_2) \quad (4.57)$$

leads by substitution to:

$$\int \rho_{xc}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 = -1 \quad (4.58)$$

which constitutes the so-called **sum rule**. Thus, an electron located in \mathbf{r} creates around itself a hole, a charge deficit, with the displaced charge being exactly equal to that of a positive electron. This hole follows the motion of the electron.

4.1.4.1. Exchange-correlation hole in single determinant wave functions

At the Hartree-Fock (HF) level, at which the wave function is described using a single Slater determinant, and based on (4.39) and (4.50), it can easily be proven that:

$$\rho_{xc}^{\alpha\beta}(\vec{r}_1, \vec{r}_2) = \rho_{xc}^{\beta\alpha}(\vec{r}_1, \vec{r}_2) = 0 \quad (4.59)$$

which demonstrates that at this level there is no electron correlation between two electrons of different spin. The **Coulomb hole** is not well described at this level. On the other hand, it is also possible to work with expressions (4.49), (4.36) and (4.34) to demonstrate that at the HF level:

$$\rho_{xc}^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) = - \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\alpha} \frac{\chi_i^*(\vec{r}_1) \chi_i(\vec{r}_2) \chi_j(\vec{r}_1) \chi_j^*(\vec{r}_2)}{\rho^\alpha(\vec{r}_1)} \neq 0 \quad (4.60)$$

that is, the parallel spin electrons are correlated, which is not surprising since the wave function described by a Slater determinant fulfils the Pauli exclusion principle.

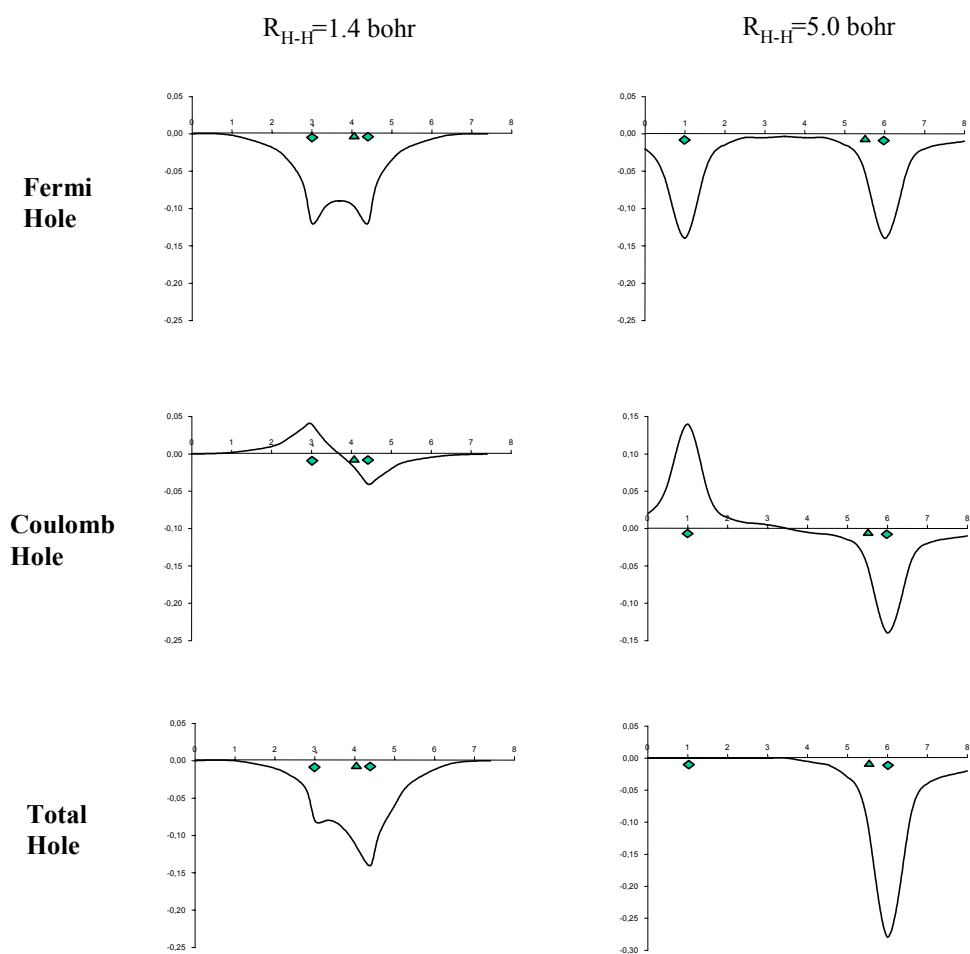


FIGURE 4.1. Fermi hole, Coulomb hole, and total hole in the hydrogen molecule for two values of the internuclear distance. The rhombuses indicate the locations of the nuclei and the triangle the position of the reference electron.

Figure 4.1 provides a schematic picture of the **Fermi hole**, the **Coulomb hole**, and the sum of both for a hydrogen molecule with internuclear distances of 1.4 and 5.0 bohrs (Baerends, 1997). The Fermi hole displays a very similar shape to that of the orbital of the reference electron, in this case the $1\sigma_g$ bonding orbital of the hydrogen molecule, and the shape does not vary with the change in the position of the reference electron, which is why the Fermi hole is said to have a static nature. This hole comprises an electron which prevents another electron of the same spin from

occupying the same orbital. It should be mentioned that the **electron density** moved away from around the nucleus containing the reference electron only corresponds to half an electron. On the other hand, the **Coulomb hole** has a dynamic nature because its shape depends to a great extent on the position of the reference electron. It gives a zero charge by integration, with which the Coulomb correlation, on the one hand, reduces the probability of finding an electron of a different spin from that of the reference electron in the region near the reference electron, but on the other hand, the probability of finding it increases in regions further away from the reference electron. The total hole, considering that it is the sum of the two previous holes, gives an electron by integration. While the Fermi hole and the total hole have similar shapes at equilibrium distances, at greater distances the difference between the two holes is substantial. HF only includes the Fermi hole and, as a consequence, it is understood that HF gives an acceptable result for the equilibrium distance, but that it is clearly inadequate to study bond dissociation, as has been commented on in Section 3.2.3.

Other consequences resulting from the HF only incorporating the **Fermi hole** which, as has been mentioned, is static and weak around the reference electron are: a) it is easier to place an electron in the same atom, and therefore, HF gives excessive weight to the ionic structures; b) the orbitals (and the electronic density) are usually too diffuse given that the electron does not experience the attraction of its nucleus with enough strength (due to the excessive screening of the nuclear charge by the electron fraction which should not be found in the same atom); c) the weakness of the Fermi hole and its static nature cause poor results at the HF level in systems with weak bonds and multiple bonds; and finally d) on average two electrons are closer in the HF level than in correlated methods, and consequently, HF overestimates the interelectronic repulsion.

4.2. Expected value expression of an operator as a function of density

It is possible to express the expected value of any one- or two-electron operator using the first- and second-order density functions and density matrices. In the particular case of a one-electron system, the expected value of an operator \hat{F} is given by:

$$\langle F \rangle = \int \Psi^*(\vec{x}) \hat{F} \Psi(\vec{x}) d\vec{x} \quad (4.61)$$

In the case of operators \hat{F} that contain only products or divisions, the expression resulting as a function of the electron density is:

$$\langle F \rangle = \int \hat{F} \rho(\vec{x}) d\vec{x} \quad (4.62)$$

In the case of operators that contain derivatives and other functions that impede the

two functions Ψ from being multiplied before applying the operator \hat{F} , we have:

$$\langle F \rangle = \int_{\vec{x}'=\vec{x}} \hat{F} \psi(\vec{x}) \psi^*(\vec{x}') d\vec{x} = \int_{\vec{x}'=\vec{x}} \hat{F} \rho_1(\vec{x}, \vec{x}') d\vec{x} \quad (4.63)$$

where, first of all, \hat{F} acts on the variable \mathbf{x} and then, before proceeding onto the integration, the variable \mathbf{x}' is transformed into \mathbf{x} , which is indicated with $\mathbf{x}'=\mathbf{x}$ below the integration sign.

Similarly, in the most general of cases, a many-electron system, we find that for a one-electron operator of the type:

$$\hat{\mathcal{G}}_1 = \sum_i \hat{h}(i) \quad (4.64)$$

the expected value of this operator can be established as a function of the **first-order density matrix** according to:

$$\langle \Psi | \hat{\mathcal{G}}_1 | \Psi \rangle = \int_{\vec{r}'_1=\vec{r}_1} \hat{h}(\vec{r}_1) \rho_1(\vec{r}_1, \vec{r}'_1) d\vec{r}_1 \quad (4.65)$$

and that for a two-electron operator such as:

$$\hat{\mathcal{G}}_2 = \sum_i \sum_{j>i} \hat{g}(i, j) \quad (4.66)$$

it is possible to obtain the expected value from the **two-electron density**:

$$\langle \Psi | \hat{\mathcal{G}}_2 | \Psi \rangle = \frac{1}{2} \iint \hat{g}(1,2) \gamma_2(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (4.67)$$

Using (4.65) and (4.67), the expected value of the electron energy can be expressed for a system of n electrons and N nuclei for a given nuclear configuration as a function of the first-order density matrix and of the two-electron density. The operator which must be taken into consideration is the Hamiltonian:

$$\hat{H}_{el} = \sum_{i=1}^n \left(-\frac{1}{2} \nabla^2(i) + \hat{v}(i) \right) + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (4.68)$$

by which:

$$E_{el} = \langle \Psi | \hat{H}_{el} | \Psi \rangle = \int_{\vec{r}'_1=\vec{r}_1} \left(-\frac{1}{2} \nabla^2(1) + \hat{v}(1) \right) \rho_1(\vec{r}_1, \vec{r}'_1) d\vec{r}_1 + \frac{1}{2} \iint \frac{\gamma_2(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \quad (4.69)$$

Substituting (4.47) in the previous equation we are left with:

$$\begin{aligned}
E_{el} = & \int_{r'_1=r_1} \left(-\frac{1}{2} \nabla^2 (1) \right) \rho_1(\vec{r}_1, \vec{r}'_1) d\vec{r}_1 + \int \hat{v}(1) \rho(\vec{r}_1) d\vec{r}_1 + \\
& \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho_{xc}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2
\end{aligned} \quad (4.70)$$

The different terms appearing in (4.70) are, respectively, the kinetic energy of the electrons, the electron-nuclear potential energy, the Coulomb electron repulsion, and the electronic exchange-correlation energy. For this last term it is possible to write:

$$W_{xc}[\rho] = \frac{1}{2} \int \rho(\vec{r}_1) d\vec{r}_1 \int \frac{\rho_{xc}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 = \int \rho(\vec{r}_1) v_{xc}^{hole}(\vec{r}_1) d\vec{r}_1 \quad (4.71)$$

W_{xc} represents the interaction of $\rho(\mathbf{r}_1)$ with its **exchange-correlation hole** $\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)$. The electron interacts with an effective charge distribution corresponding to a positive electron, as follows from the sum rule.

In short, equation (4.70) shows that it is possible to express the energy from the first- and second-order density functions and matrices, and the energy is consequently said to be a functional of the density.

By **functional** we understand a mathematical expression associating a number to a function, i.e., a functional is a function whose argument is also a function. It is usually written between square brackets. A classic example is the variational integral,

$$W[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (4.72)$$

Given a function ψ , the result of applying (4.72) is the energy and therefore the energy is a functional of the wave function. The functionals can be differentiated and derived.

A functional differential of $F[f]$ has the form:

$$\delta F = \int \frac{\delta F}{\delta f(x)} \delta f(x) dx \quad (4.73)$$

In order to determine the derivative of a functional, $\frac{\delta F}{\delta f(x)}$, (4.73) is used evaluating δF as $F[f+\delta f]-F[f]$:

$$\delta F = F[f + \delta f] - F[f] = \int \frac{\delta F}{\delta f(x)} \delta f(x) dx \quad (4.74)$$

For example, considering the electron-nucleus interaction potential as a functional of the electron density:

$$V_{Ne}[\rho] = \int \hat{v}(\vec{r})\rho(\vec{r}) d\vec{r} \quad (4.75)$$

the derivative of this functional with respect to density would be obtained from the following equations:

$$V_{Ne}[\rho + \delta\rho] = \int \hat{v}(\vec{r})[\rho + \delta\rho] d\vec{r} \quad (4.76)$$

$$\delta V_{Ne} = V_{Ne}[\rho + \delta\rho] - V_{Ne}[\rho] = \int \hat{v}(\vec{r})\delta\rho d\vec{r} = \int \frac{\delta V_{Ne}}{\delta\rho} \delta\rho d\vec{r} \quad (4.77)$$

by which:

$$\frac{\delta V_{Ne}}{\delta\rho} = \hat{v}(\vec{r}) \quad (4.78)$$

4.3. The Hohenberg-Kohn theorems

4.3.1. The first theorem

Equation (4.70) shows us that it is possible to express the electron energy of a system as a functional of first- and second-order density functions and matrices. The first **Hohenberg-Kohn theorem** (Hohenberg, 1964), which is considered to have given rise to the rigorous DFT, goes further to demonstrate that:

Any observable of a stationary non-degenerate ground state can be calculated, exactly in theory, from the electron density of the ground state. In other words, any observable can be written as a functional of the electron density of the ground state.

To prove this theorem, we will first of all demonstrate that given a density $\rho(\mathbf{r})$, the external potential is determined except in an additive constant. We will demonstrate this via *reductio ad absurdum*, supposing that what this theorem states is not true and leading to a contradiction.

Let us consider that we have the exact density of a ground state $\rho(\mathbf{r})$ and also suppose that it is a non-degenerate state (there is only one wave function with the energy of this state). We assume that the same density $\rho(\mathbf{r})$ can be obtained from two different external potentials (electron-nucleus) ($v_1(\mathbf{r})$ and $v_2(\mathbf{r})$) that logically generate two different Hamiltonians \hat{H}_1 and \hat{H}_2 . These Hamiltonians produce two

different wave functions for the ground state, ψ_1 and ψ_2 , which correspond, in turn, to two distinct energies $E_1 = \langle \psi_1 | \hat{H}_1 | \psi_1 \rangle$ and $E_2 = \langle \psi_2 | \hat{H}_2 | \psi_2 \rangle$. In these conditions we calculate the expected value of the energy of ψ_2 with the \hat{H}_1 Hamiltonian and, from the variational principle, we have:

$$E_1 < \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle = \langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle = E_2 + \int \rho(\vec{r}) [v_1(\vec{r}) - v_2(\vec{r})] d\vec{r} \quad (4.79)$$

In the same way, we calculate the expected value of the energy of ψ_1 with the \hat{H}_2 Hamiltonian and based on the variational principle we obtain:

$$E_2 < \langle \Psi_1 | \hat{H}_2 | \Psi_1 \rangle = \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle + \langle \Psi_1 | \hat{H}_2 - \hat{H}_1 | \Psi_1 \rangle = E_1 + \int \rho(\vec{r}) [v_2(\vec{r}) - v_1(\vec{r})] d\vec{r} \quad (4.80)$$

Finally, summing up equations (4.79) and (4.80) the following inequality is obtained:

$$E_1 + E_2 < E_2 + E_1 \quad (4.81)$$

This result is inconsistent and proves that our initial assumption was incorrect. Thus, the ground state electron density $\rho(\mathbf{r})$ associated with $v(\mathbf{r})$ cannot be reproduced by a different potential, and therefore the external potential is entirely determined by the density (except in an additive constant).

Given that $\rho(\mathbf{r})$ determines the total number of electrons of the system from (4.4) and also establishes $v(\mathbf{r})$ according to the first Hohenberg-Kohn theorem, it is concluded that $\rho(\mathbf{r})$ determines the Hamiltonian (except in an additive constant given that the sum of a constant in the \hat{H} operator leaves the eigenfunctions, and therefore the density, unaltered) and the wave function of the ground state and, by extension, the expectation value of any observable of the ground state, including the kinetic energy of the electrons, the Coulomb repulsion, etc., and $E = E[\rho]$ in particular. Therefore, there is a direct relationship between the density and the wave function through the external potential:

$$\rho(\vec{r}) \rightarrow v(\vec{r}) \rightarrow \hat{H} \rightarrow \psi \quad (4.82)$$

$$\rho(\vec{r}) \Leftrightarrow \psi \quad (4.83)$$

Note moreover that the Hamiltonian determines not only the ground state, but also all excited states wave functions, so there is an incredible amount of information coded in the ground state density.

It is important to point out that the first Hohenberg-Kohn theorem is only valid for non-degenerate ground states and always when $\rho(\mathbf{r})$ is N-representable and v-representable. That is N-representable refers basically to $\rho(\mathbf{r})$ having to be a

positive function defined in the entire space and that its integral must be equal to the total number of electrons of the system:

$$\rho(\vec{r}) \geq 0 \quad \text{and} \quad \int \rho(\vec{r}) d\vec{r} = N \quad (4.84)$$

That it is v -representable means there is an external potential from which density $\rho(\mathbf{r})$ can be derived. This condition is more difficult to prove and, in fact, it has been demonstrated that there are reasonable trial densities that cannot be derived from any external potential. In the remaining cases (degenerate ground states and excited states) inequalities (4.79) and (4.80) do not have to be fulfilled. For the cases where this theorem is valid we have that:

$$E[\rho] = T[\rho] + V_{Ne}[\rho] + V_{ee}[\rho] \quad (+V_{NN}) \quad (4.85)$$

$T[\rho]$ and $V_{ee}[\rho]$ are universal functionals, given that they do not depend on the external potential. They are usually encompassed within the Hohenberg-Kohn functional $F_{HK}[\rho]$, with which:

$$E_v[\rho] = \int \rho(\vec{r}) v(\vec{r}) d\vec{r} + F_{HK}[\rho] \quad (4.86)$$

where $E_v[\rho]$ indicates that, for a specific external potential $v(\mathbf{r})$, the energy is a functional of density.

4.3.2. The second theorem

The second **Hohenberg-Kohn theorem** provides the variational principle for $E[\rho]$. It can be expressed in the following way:

The electron density of a non-degenerate ground state can be calculated, exactly in theory, determining the density that minimizes the energy of the ground state.

Or what is the same, for a trial density, $\tilde{\rho}(\vec{r})$, that is v -representable and N -representable it is fulfilled that:

$$E_o \leq E_v[\tilde{\rho}(\vec{r})] \quad (4.87)$$

To demonstrate (4.87) we will apply the first Hohenberg-Kohn theorem to the trial density and to the exact density. According to this, each one of the two densities defines a different Hamiltonian and therefore a corresponding wave function.

$$\text{Trial density:} \quad \tilde{\rho}(\vec{r}) \rightarrow \tilde{v}_n(\vec{r}) \rightarrow \tilde{H} \rightarrow \tilde{\psi} \quad (4.88)$$

$$\text{Exact density:} \quad \rho(\vec{r}) \rightarrow v_n(\vec{r}) \rightarrow \hat{H} \rightarrow \psi \quad (4.89)$$

If we calculate the energy for the trial density with the exact Hamiltonian we are left with:

$$E_v[\tilde{\rho}(\vec{r})] = \langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle \geq \langle \psi | \hat{H} | \psi \rangle = E_o \quad (4.90)$$

where E_o is the exact energy of the considered ground state and the inequality that appears in (4.90) is a consequence of the variational principle. So we have demonstrated (4.87), with which we have obtained a variational principle for the energy in the framework of the DFT. This principle assures that any trial density results in an energy greater or equal to the exact energy of the ground state. Therefore, to obtain the exact density of the ground state, we will have to find the density that minimises the energy:

$$\left[\frac{\delta E_v[\rho]}{\delta \rho} \right] = 0 \quad (4.91)$$

4.3.3. Levy's constrained-search formulation

Levy's constrained-search formulation (Levy, 1982) is one more proof that a one-to-one mapping exists between the density and the wave function of the ground state. The principal advantage over the first Hohenberg-Kohn theorem is that in this formulation the density is not required to be v -representable. In addition, the demonstration is also extended for degenerate ground states. To do that, we proceed from the set of functions, $\{\psi_{\rho_o}\}$ that integrate to ρ_o , which is the exact density of the ground state, Ψ_o . By the variational principle:

$$\langle \psi_{\rho_o} | \hat{H} | \psi_{\rho_o} \rangle > \langle \Psi_o | \hat{H} | \Psi_o \rangle = E_o \quad (4.92)$$

by which:

$$\langle \psi_{\rho_o} | \hat{T} + \hat{V}_{ee} | \psi_{\rho_o} \rangle + \int \rho_o(\vec{r}) v_n(\vec{r}) d\vec{r} > \langle \Psi_o | \hat{T} + \hat{V}_{ee} | \Psi_o \rangle + \int \rho_o(\vec{r}) v_n(\vec{r}) d\vec{r} \quad (4.93)$$

Given that Ψ_o and Ψ_{ρ_o} lead by integration to the same density ρ_o , the terms of the electron-nucleus interaction at each side of the inequality are identical, and therefore:

$$\langle \psi_{\rho_o} | \hat{T} + \hat{V}_{ee} | \psi_{\rho_o} \rangle > \langle \Psi_o | \hat{T} + \hat{V}_{ee} | \Psi_o \rangle \quad (4.94)$$

Thus, from the set of wave functions which by integration give ρ_o , $\{\psi_{\rho_o}\}$, the Ψ_o is the one that minimises the expected value of $\hat{T} + \hat{V}_{ee}$. It is, therefore, possible to determine Ψ_o only from the knowledge of ρ_o , through *constrained* minimisation within the set $\{\psi_{\rho_o}\}$ of the expected value of $\hat{T} + \hat{V}_{ee}$:

$$F_{HK}[\rho] = \underset{\psi \rightarrow \rho_0}{\text{Min}} \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle \quad (4.95)$$

Consequently, it is demonstrated that there is a one-to-one mapping between ρ_0 and Ψ_0 , without the need to pass through $v(\mathbf{r})$, which represents another proof of the first **Hohenberg-Kohn theorem**, but without the restriction that ρ_0 be v -representable. The only condition is that ρ_0 must be N -representable, but this condition is easier to fulfil given that we know in which conditions a density is N -representable.

On the other hand, the degenerate states are no longer a problem given that the restricted search is limited to one of the degenerate functions, that which corresponds to the density that interests us. For two degenerate states with Ψ_1 and Ψ_2 we would have:

$$\rho_1(\vec{r}) \rightarrow v_n(\vec{r}) \rightarrow \hat{H} \rightarrow \psi_1 \quad (4.96)$$

$$\rho_2(\vec{r}) \rightarrow v_n(\vec{r}) \rightarrow \hat{H} \rightarrow \psi_2 \quad (4.97)$$

In the Hohenberg-Kohn formulation, the one-to-one mapping cannot be directly established between ρ_1 and Ψ_1 , given that passing through an identical potential, the connection is lost. In Levy's constrained-search formulation, however, this is possible because we restrict the minimisation to the set of functions Ψ which, by integration, gives ρ_1 (precisely between which Ψ_2 is not found given that by integration it gives ρ_2), and therefore, this formulation allows the first Hohenberg-Kohn theorem to be generalised to degenerate ground states.

It is worth noting that the variational principle given by equation (4.94) applies to the exact functional only. Indeed, in some particular cases it is possible to obtain an energy lower than the exact energy using standard functionals present in the literature.

4.3.4. Extension to excited states

The demonstration of the validity of the DFT for the study of the *lowest-energy excited state of a given symmetry and/or spin*, is similar to the previous case (Parr, 1989). It is only necessary to restrict the set of trial functions used in the variational procedure to suitable symmetry and spin multiplicity functions. Energy minimisation leads to the lowest-energy state of that symmetry and multiplicity. Using the same arguments as in the previous case and proceeding from the set of symmetry functions λ that by integration gives ρ_λ , $\{\psi_{\rho_\lambda}^\lambda\}$, obtaining the wave function associated with the

density ρ_λ requires the constrained minimisation of:

$$F_{HK}^\lambda[\rho] = \underset{\psi \rightarrow \psi_{\rho_\lambda}^\lambda}{\text{Min}} \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle \quad (4.98)$$

However, it is worth noticing that it has recently been demonstrated (Gaudoin, 2004) that, in general, for a given excited state there might exist more than one external potential which yields the electron density of that state. Consequently, the excited state energy is not a functional of the excited state density, in the Hohenberg-Kohn sense. This lack of Hohenberg-Kohn theorem for excited states carries serious difficulties for the extension of formal DFT constructions to excited states, a problem which remain unsolved nowadays.

4.3.5. Fundamental equation

The minimisation of the energy functional with respect to the electron density, $\delta E_v[\rho] = 0$, must be carried out assuring the conservation of the N-representability during the optimisation process. This is done by introducing the restriction $\int \rho(\vec{r}) d\vec{r} - N = 0$ by means of **Lagrange undetermined multipliers method**. For that the following function is constructed:

$$E_v[\rho] - \mu \left[\int \rho(\vec{r}) d\vec{r} - N \right] \quad (4.99)$$

where μ is the undetermined Lagrange multiplier and has the meaning of a **chemical potential** as we will see further on. Next it is minimised:

$$\delta \left[E_v[\rho] - \mu \left(\int \rho(\vec{r}) d\vec{r} - N \right) \right] = 0 \quad (4.100)$$

and proceeding from the definition of a functional differential given in (4.73) we are left with:

$$\int \frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} \delta \rho(\vec{r}) d\vec{r} - \mu \int \delta \rho(\vec{r}) d\vec{r} = 0 \quad (4.101)$$

and rearranging:

$$\int \left\{ \frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} - \mu \right\} \delta \rho(\vec{r}) d\vec{r} = 0 \quad (4.102)$$

which provides the condition of constrained minimisation and allows the minimum value of μ to be obtained:

$$\mu = \frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} = v_n(\vec{r}) + \frac{\delta F_{HK}[\rho]}{\delta \rho(\vec{r})} \quad (4.103)$$

Equation (4.103) is given the name *fundamental equation of density functional theory*. The right-hand-side of this equation is derived taking $E_v[\rho]$ from equation (4.86).

4.4. Chemical concepts

DFT not only offers a road to accurate calculation and prediction, but also allows interpretation and understanding of chemical phenomena. Using the language of the DFT it is possible to rigorously define and quantify classic concepts very closely connected with chemical structure and reactivity such as the *chemical potential*, the *hardness*, and the *Fukui functions*, in what is called the conceptual DFT (Parr, 1989) (Geerlings, 2003). As we will see next, this has been possible due to the central role played by the electron density and the number of electrons in this theory.

Given that the Hamiltonian of a system depends only on the number of electrons and on the external potential, we have that $E=E[N,v]$. Differentiating, we obtain:

$$dE = \left(\frac{\partial E}{\partial N} \right)_v dN + \int \left(\frac{\delta E}{\delta v(\vec{r})} \right)_N \delta v(\vec{r}) d\vec{r} \quad (4.104)$$

In turn, we have demonstrated in Section 4.3 that $E=E_v[\rho]$. The energy differential can then be written:

$$dE = \int \left(\frac{\delta E}{\delta \rho(\vec{r})} \right)_v \delta \rho(\vec{r}) d\vec{r} + \int \left(\frac{\delta E}{\delta v(\vec{r})} \right)_\rho \delta v(\vec{r}) d\vec{r} \quad (4.105)$$

It is worth noting that Eq. (4.105) is approximate, because it assumes that $\rho(\mathbf{r})$ and $v(\mathbf{r})$ are independent functions, while the Hohenberg-Kohn theorems demonstrate that $v(\mathbf{r})$ completely determines $\rho(\mathbf{r})$ for the ground state. Then, from the fundamental equation of the DFT, we have that:

$$\frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} = \mu = \text{constant} \quad (4.106)$$

and differentiating (4.4) we obtain:

$$dN = \int \delta \rho(\vec{r}) d\vec{r} \quad (4.107)$$

Substituting (4.106) and (4.107) into (4.105) we arrive at:

$$dE = \mu dN + \int \left(\frac{\delta E}{\delta v(\vec{r})} \right)_\rho \delta v(\vec{r}) d\vec{r} \quad (4.108)$$

Comparison of (4.108) and (4.104) leads us to a new definition for μ :

$$\left(\frac{\delta E}{\delta \rho(\vec{r})} \right)_v = \left(\frac{\partial E}{\partial N} \right)_v = \mu \quad (4.109)$$

Equation (4.109) tells us that $\mu = \mu[N, v]$ is the derivative of the energy with respect to the total number of electrons at a constant external potential. It indicates how the energy changes when the number of electrons varies, and thus it is given the name of chemical potential, considering that this definition is analogous to the definition of chemical potential in classic thermodynamics.

If we take equation (4.86) and we analyse how the energy is modified when the external potential varies and $\rho(\mathbf{r})$ is maintained constant, we are left with:

$$dE = \int \rho(\vec{r}) \delta v(\vec{r}) d\vec{r} \quad (4.110)$$

If we do the same proceeding from (4.105) we will have:

$$dE = \int \left(\frac{\delta E}{\delta v(\vec{r})} \right)_\rho \delta v(\vec{r}) d\vec{r} \quad (4.111)$$

Comparing (4.110) and (4.111) we see that:

$$\rho(\vec{r}) = \left(\frac{\delta E}{\delta v(\vec{r})} \right)_\rho \quad (4.112)$$

This equation, introduced in (4.108), leads us to the so-called **fundamental equation of chemical change**:

$$dE = \mu \cdot dN + \int \rho(\vec{r}) \cdot \delta v(\vec{r}) \cdot d\vec{r} \quad (4.113)$$

This equation provides the framework for the precise formulation of concepts related to chemical reactivity. Differentiating $\mu[N, v]$ we have:

$$d\mu = \left(\frac{\partial \mu}{\partial N} \right)_v dN + \int \left(\frac{\delta \mu}{\delta v(\vec{r})} \right)_N \delta v(\vec{r}) d\vec{r} \quad (4.114)$$

Defining the following functions:

$$\eta = \left(\frac{\partial \mu}{\partial N} \right)_v \quad (4.115)$$

$$f(\vec{r}) = \left(\frac{\delta \mu}{\delta v(\vec{r})} \right)_N = \left(\frac{\delta^2 E}{\delta v(\vec{r}) \partial N} \right) = \left(\frac{\delta^2 E}{\partial N \delta v(\vec{r})} \right) = \left(\frac{\partial \rho(\vec{r})}{\partial N} \right)_v \quad (4.116)$$

leads to:

$$d\mu = \eta dN + \int f(\vec{r}) \delta v(\vec{r}) d\vec{r} \quad (4.117)$$

which indicates how the chemical potential varies when there is a change in the

number of electrons and in the external potential. Function η is the so-called hardness and $f(\mathbf{r})$ is the Fukui function. As we shall see next, the chemical potential, the hardness, and the Fukui function are very useful tools for the analysis of chemical reactivity.

4.4.1. Chemical potential

Starting from equation (4.109) and deriving at constant external potential by finite differences, it is found that:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_v \cong \frac{\Delta E}{\Delta N} = \frac{E(N+1) - E(N-1)}{(N+1) - (N-1)} = \frac{(E(N) - A) - (E(N) + I)}{2} \quad (4.118)$$

$$\mu = -\frac{(A+I)}{2} = -\chi_M \quad (4.119)$$

where A is the electron affinity and I the ionization potential of our system. This **chemical potential**, with the sign reversed, is simply Mulliken's original definition for **electronegativity**. In **Koopmans' approximation** (Koopmans, 1933):

$$-\mu = \chi_M = \frac{(A+I)}{2} \cong -\frac{\varepsilon_{HOMO} + \varepsilon_{LUMO}}{2} \quad (4.120)$$

For any reaction between a system i and another system j , assuming that the external potential remains constant and for small charge transfers, ΔN , the fundamental equation of the chemical change leads to:

$$\Delta E \cong \mu \Delta N \quad (4.121)$$

for each system. Given that in a reaction $\Delta E = \Delta E_i + \Delta E_j$, assuming that $\Delta N_i = -\Delta N_j = \Delta N > 0$ we have that:

$$\Delta E = (\mu_i^o - \mu_j^o) \Delta N \quad (4.122)$$

In these conditions the reaction is exothermic if the chemical potential μ_j^o is greater than μ_i^o , and therefore, if the electronegativity of i is greater than that of j . In short, from an energetic point of view, a charge transfer from the system of greater chemical potential or lesser electronegativity to the one of lesser chemical potential or greater electronegativity is beneficial. Chemical potential is thus a measure of the tendency of the electrons to escape from the system. A large chemical potential difference between two systems helps electron transfer. According to the **Sanderson's Electronegativity Equalization Principle** the charge transfer will occur until the chemical potential of the two initial fragments become identical in the final system. This principle states that when two or more atoms, initially possessing different electronegativities, link to form a molecule, their electronegativities become adjusted to a same intermediate value within the molecule.

The ΔN term in this particular process ($v(\mathbf{r})$ constant and $\Delta N_i = -\Delta N_j = \Delta N > 0$) can be calculated taking into account equation (4.117) for the i and j systems:

$$\mu_i = \mu_i^o + \eta_i^o \Delta N \quad (4.123)$$

$$\mu_j = \mu_j^o - \eta_j^o \Delta N \quad (4.124)$$

Because, once the molecule is formed, $\mu_i = \mu_j$, then we have:

$$\Delta N = \frac{\mu_j^o - \mu_i^o}{\eta_j^o + \eta_i^o} \quad (4.125)$$

Substituting this result into equation (4.122) we arrive at:

$$\Delta E = -\frac{(\mu_j^o - \mu_i^o)^2}{\eta_j^o + \eta_i^o} \quad (4.126)$$

This equation suggests that the difference in electronegativity (or chemical potential) drives the reaction, and the sum of the hardness parameters acts as a resistance. However, this equation is only approximate since when the fragments come to bonding distance, there will be large changes in energy due to variations of the external potential that are not considered in equations (4.125) and (4.126).

4.4.2. Hardness

Equations (4.115) and (4.109) lead to the operational definition of **hardness** (Pearson, 1993) as the second derivative of the energy with respect to the number of electrons at a constant external potential:

$$\eta = \left(\frac{\partial \mu}{\partial N} \right)_v = \left(\frac{\partial^2 E}{\partial N^2} \right)_v \quad (4.127)$$

The graph of the energy with respect to the total number of electrons for any system is a concave function. At a constant external potential, the chemical potential is the slope at point N and the hardness is the curvature at this point. As equation (4.125) tells us, hardness can be considered a measure of the charge-transfer resistance. Varying the number of electrons in a hard system (high curvature of E versus N) is going to be energetically costly and therefore this system will have little tendency to give or accept electrons. The finite-differences approximation applied in this case leads to:

$$\eta = I - A \cong \varepsilon_{LUMO} - \varepsilon_{HOMO} \quad (4.128)$$

Equation (4.128) shows us that the hardness is simply the energy difference between the HOMO and LUMO energies. It is generally foreseeable that a large energy difference (large η) will correspond to stable and not very reactive systems,

while a small HOMO-LUMO gap supposes an unstable and highly reactive system. Experimentally, the hardness is the reaction energy for the following disproportionation reaction:



The softness, S , is simply the inverse of the hardness:

$$S = \frac{1}{\eta} = \left(\frac{\partial N}{\partial \mu} \right)_v \quad (4.130)$$

Connected with hardness are two very important reactivity principles. The first is the *Hard-Soft Acid-Base (HSAB) principle* which says that hard acids prefer hard bases and soft acids prefer soft bases. The second is the *maximum hardness principle (MHP)* which states that a system with constant chemical potential, temperature and external potential tends towards a state of maximum hardness. There is no single chemical process that satisfies these two severe constraints (chemical and external potentials unchanged). However, relaxation of these restrictions has been found to be permissible in many internal rotations, vibrational motions, and chemical reactions. Based on the MHP and the empirical inverse relationship between hardness and polarizability (α), Chattaraj and Sengupta (Chattaraj, 1996) have introduced the *minimum polarizability principle (MPP)*. This principle states that any system evolves naturally towards a state of minimum polarizability. These two principles, the MHP and the MPP, have been applied to a number of different chemical processes with many successes, but also some reported failures. In many cases it is found that, as expected from the MHP (MPP), the profile of the hardness (polarizability) of a chemical species along the reaction path goes through a minimum (maximum) at the transition state and through maxima (minima) for reactants and products.

4.4.3. Fukui functions

The definition given in equation (4.116) of the *Fukui function* indicates that it can be interpreted either as a measurement of the sensitivity of the chemical potential of a system to a change in the external potential, or as a measurement of the local changes in the electron density of the system due to the perturbation in the global number of electrons. In this sense, it reflects the behaviour of a molecule when accepting (donating) electrons from (to) another system. This last definition:

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N} \right)_v \quad (4.131)$$

provides an easy demonstration through use of equation (4.107) that the Fukui

function is normalized:

$$\int f(\vec{r}) d\vec{r} = 1 \quad (4.132)$$

Proceeding from (4.131) and once again using the finite-differences approximation, three types of Fukui functions can be defined. The $f^+(\mathbf{r})$ is defined according to:

$$f^+(\vec{r}) \cong \frac{\rho_{N+1}(\vec{r}) - \rho_N(\vec{r})}{N+1-N} = \rho_{N+1}(\vec{r}) - \rho_N(\vec{r}) \cong \rho_{LUMO}(\vec{r}) \quad (4.133)$$

giving us the region of the space in which the charge is located when the system acquires an electron. It is a good measurement of the reactivity of our system in front of a nucleophile and in the first approximation it is the electron density of the LUMO. For its part, the $f^-(\mathbf{r})$ is a measurement of the reactivity in front of an electrophile:

$$f^-(\vec{r}) \cong \frac{\rho_N(\vec{r}) - \rho_{N-1}(\vec{r})}{N-N+1} = \rho_N(\vec{r}) - \rho_{N-1}(\vec{r}) \cong \rho_{HOMO}(\vec{r}) \quad (4.134)$$

Finally, $f^0(\mathbf{r})$ is the average of the two previous measurements and gives us the reactivity to a radical attack:

$$f^0(\vec{r}) = \frac{1}{2} [f^+(\vec{r}) + f^-(\vec{r})] \cong \frac{1}{2} [\rho_{N+1}(\vec{r}) - \rho_{N-1}(\vec{r})] \cong \frac{1}{2} [\rho_{LUMO}(\vec{r}) + \rho_{HOMO}(\vec{r})] \quad (4.135)$$

The name Fukui function is suitable for $f(\mathbf{r})$ given that it obviously deals with a reactivity index closely related to the **frontier molecular orbital** (FMO) theory. The advantage of the Fukui function over the FMO theory is that the former can be obtained from any method used to solve the Schrödinger equation that yields an electron density. In contrast, the FMO theory can only be applied in methods that provide molecular orbitals. Figure 4.2 represents the functions $f^+(\mathbf{r})$ and $f(\mathbf{r})$ for formaldehyde. The shape of $f^+(\mathbf{r})$ recalls the shape of the antibonding π -LUMO orbital. Against a nucleophile, such as the hydroxyl group, the attack will occur most likely on the carbon atom because the Fukui function $f^+(\mathbf{r})$ has greater density over this atom.

Condensed Fukui functions are numbers obtained by approximate integrations of the Fukui functions over atomic regions. As an example, the nucleophilic condensed Fukui function for atom A is obtained as:

$$f_A^+(A) = q_{N+1}(A) - q_N(A) \quad (4.136)$$

where $q_N(A)$ denotes the electronic population of atom A of the reference system with N electrons. These values can be used to discuss the regioselectivity of the chemical reactions. The charges in equation (4.136) can be obtained from any charge partitioning scheme, such as the atoms-in-molecules, Mulliken, or the natural orbital population analysis, among others.

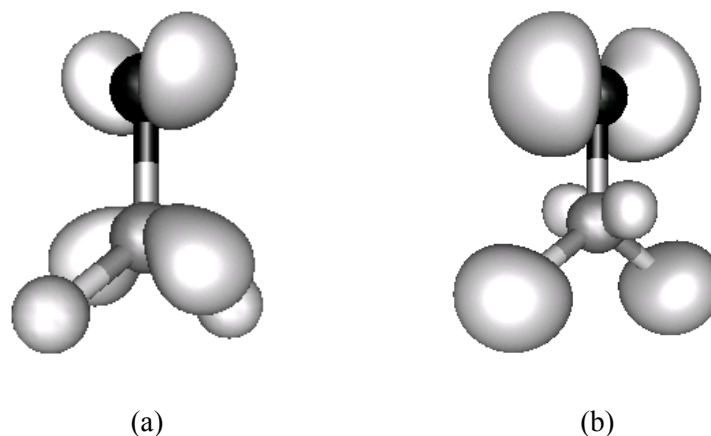


FIGURE 4.2. Drawing of the 0.01 a.u. contour of the Fukui functions (a) f^+ and (b) f^- for the formaldehyde molecule.

The local softness, $s(\vec{r})$, was introduced in 1985 by Yang and Parr as (Parr, 1989):

$$s(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial \mu} \right)_v \quad (4.137)$$

Using the definition of the global softness in equation (4.130) we have:

$$S = \int s(\vec{r}) d\vec{r} \quad (4.138)$$

and:

$$s(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial \mu} \right)_v = \left(\frac{\partial \rho(\vec{r})}{\partial N} \right)_v \left(\frac{\partial N}{\partial \mu} \right)_v = f(\vec{r})S \quad (4.139)$$

From this relation, one can infer that local softness and Fukui function are closely related and both should play an important role in the field of chemical reactivity. The local softness can be considered a distribution of the global softness, S , weighted by the Fukui function over the molecule. Remarkably, the local softness function can be measured experimentally using the scanning tunnel microscopy technique (Chermette, 1999). While the chemical potential, the hardness, and the softness are global functions and have a unique value for the whole system, the Fukui and the local softness functions are local functions and possess different values among the different sites in a molecule. In this sense, these latter functions are especially suitable to discuss regioselectivity in chemical processes.

4.4.4. Other DFT descriptors of chemical reactivity

The energy expansion in equation (4.104) may not be limited to first order. First and second order derivatives with respect to the total number of electrons and the external potential are given in Figure 4.3. Arrows toward the left represent partial derivatives with respect to the number of electrons N , while arrows toward the right are partial derivatives with respect to $v(\mathbf{r})$ (Chermette, 1999). Taken into account these derivatives, the following functional Taylor expansion series of the electronic energy ($E=E[N, v(\mathbf{r})]$) emerges:

$$\begin{aligned} \Delta E = & \left(\frac{\partial E}{\partial N} \right)_v \Delta N + \int \left(\frac{\delta E}{\delta v(\vec{r})} \right)_N \Delta v(\vec{r}) d\vec{r} + \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_v \Delta N^2 \\ & + \frac{1}{2} \iint \left(\frac{\delta^2 E}{\delta v(\vec{r}) \delta v(\vec{r}')} \right)_N \Delta v(\vec{r}) \Delta v(\vec{r}') d\vec{r} d\vec{r}' + \int \left(\frac{\delta^2 E}{\delta v(\vec{r}) \partial N} \right) \Delta N \Delta v(\vec{r}) d\vec{r} \end{aligned} \quad (4.140)$$

The chemical reactivity can be explored in DFT through the above functional Taylor expansion. Taken into account the derivatives of Figure 4.3, one gets:

$$\begin{aligned} \Delta E = & \mu \Delta N + \int \rho(\vec{r}) \Delta v(\vec{r}) d\vec{r} + \frac{1}{2} \eta \Delta N^2 \\ & + \frac{1}{2} \iint \chi(\vec{r}, \vec{r}') \Delta v(\vec{r}) \Delta v(\vec{r}') d\vec{r} d\vec{r}' + \Delta N \int f(\vec{r}) \Delta v(\vec{r}) d\vec{r} \end{aligned} \quad (4.141)$$

Equation (4.141) gives the electronic energy change due to a variation in the external potential and the number of electrons of the system up to the second order.

The $\chi(\vec{r}, \vec{r}') = \left(\frac{\delta \rho(\vec{r})}{\delta v(\vec{r}')} \right)_N$ term is the so-called **linear response function**. This

derivative measures the variation of the electron density at point \mathbf{r} when the external potential is locally perturbed at \mathbf{r}' . As seen in Figure 4.3, the response of the system to variations in N for a fixed potential is measured by global properties such as μ or η , while the local properties such as $\rho(\mathbf{r})$ or $f(\mathbf{r})$ describe the response of the system to perturbations of $v(\mathbf{r})$ at a constant number of electrons.

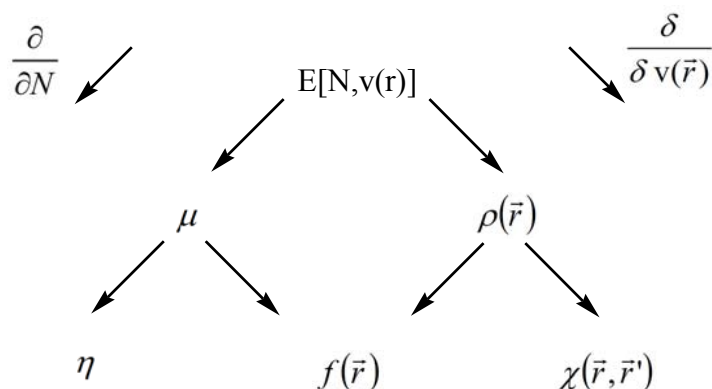


FIGURE 4.3. Derivatives of the electronic energy. Left derivatives are partial derivatives with respect to the number of electrons, N , while right derivatives are against the external potential, $v(\mathbf{r})$.

Upon the course of a chemical reaction, molecules adjust their number of electrons and their external potential. This implies changes in both the electronic structure, characterized by the electron density $\rho(\vec{r})$, and the geometric structure defined by the position vectors $\{\mathbf{R}_\alpha\}$ of the nuclei. To describe the electronic changes, one can use the Fukui function, the hardness, and the linear response function. These are electronic indexes that measure the electron density and electronic chemical potential responses to a change in N or $v(\mathbf{r})$. To describe the geometrical changes, a set of nuclear reactivity indexes that characterize the response of the nuclei due to changes in N or $v(\mathbf{r})$ of the system have been recently defined (Geerlings, 2003). These indices try to answer the question of what will be the response of the nuclei to a perturbation in the number of electrons or the external potential. This is an important aspect of the reactivity of the systems since all chemical reactions involve changes in nuclear positions. In particular, the **nuclear Fukui function** (NFF) has been defined by Cohen and coworkers (Cohen, 1994) as the electronic force \mathbf{F} acting on the nuclei due to the perturbation in N at a constant $v(\mathbf{r})$:

$$\phi_\alpha = \left(\frac{\partial \bar{F}_\alpha}{\partial N} \right)_v . \quad (4.142)$$

This NFF measures the force inducing the displacement of the nucleus α due to a change in the number of electrons. In analogy with the electronic Fukui function, it is possible to define three NFFs corresponding to nucleophilic, electrophilic, and radical attacks as:

$$\phi_{\alpha}^{+} = \left(\frac{\partial \bar{F}_{\alpha}}{\partial N} \right)_{\nu}^{+} = \bar{F}_{\alpha}(N+1) - \bar{F}_{\alpha}(N) \quad (4.143)$$

$$\phi_{\alpha}^{-} = \left(\frac{\partial \bar{F}_{\alpha}}{\partial N} \right)_{\nu}^{-} = \bar{F}_{\alpha}(N) - \bar{F}_{\alpha}(N-1) \quad (4.144)$$

$$\phi_{\alpha}^o = \left(\frac{\partial \bar{F}_{\alpha}}{\partial N} \right)_{\nu}^o = \frac{1}{2} (\bar{F}_{\alpha}(N+1) - \bar{F}_{\alpha}(N-1)) \quad (4.145)$$

Baekelandt (Baekelandt, 1996) via a Maxwell relation has shown that this NFF can be interpreted as the conformational contribution to the change in the electronic chemical potential:

$$\phi_{\alpha} = \left(\frac{\partial \bar{F}_{\alpha}}{\partial N} \right)_{\nu} = - \left(\frac{\partial^2 E}{\partial N \partial \bar{R}_{\alpha}} \right) = - \left(\frac{\partial \mu}{\partial \bar{R}_{\alpha}} \right)_{N} . \quad (4.146)$$

It is remarkable the similarity between equations (4.116) and (4.146). Because of the coupling between the electronic and nuclear responses to external perturbations, one can expect that relationships between nuclear and reactivity indexes exist. Indeed, it can be demonstrated (Torrent-Sucarrat, 2003) the following relation between the electronic and nuclear Fukui functions:

$$\int f(\bar{r}) \Delta v(\bar{r}) d\bar{r} = - \sum_{\alpha} \phi_{\alpha} \Delta \bar{R}_{\alpha} . \quad (4.147)$$

Only a relative small number of studies have been devoted to the NFF until now. These studies, however, have reinforced the idea that a complete representation of the total chemical response to a given perturbation must involve the analysis of both electronic and nuclear reactivity descriptors.

4.5. The Kohn and Sham method

The equation (4.103) gives us a formula to minimise the energy and thereby determine the density of the ground state. The complexity of this equation is apparently tremendously reduced as compared to the conventional wave function approach. The problem that arises is that the exact expression relating F_{HK} with the density is unknown. In particular, the exact form of $T[\rho]$ is not known precisely enough. On the other hand, the kinetic energy is easily calculated if ψ is known. Proceeding from the expression of $T[\psi]$ for a single determinant function, Kohn and Sham (Kohn, 1965) proposed an ingenious method to calculate the energy

from ρ .

For that they used as a *reference system* a system of N electrons that do not interact among themselves and that move under external potential $v_s(\mathbf{r})$. This potential, when applied to the system, provides a wave function, ψ_s , which has the same density as the real system. In this system the electrons do not interact among themselves although there are Coulomb interactions with the nuclei. For such an ideal system, the HF method is exact considering that without electron-electron interactions the orbital approximation leading to the HF equations provides the exact result. The Hamiltonian of this system only contains the single-electron terms:

$$\hat{H}_s = \sum_{i=1}^N \hat{h}(i) = \sum_{i=1}^N -\frac{1}{2} \nabla^2(i) + \sum_{i=1}^N \hat{v}_s(i) \quad (4.148)$$

The exact wave function of this system is the Slater determinant:

$$\psi_s = \frac{1}{\sqrt{N!}} |\chi_1(1)\chi_2(2)\chi_3(3)\cdots\chi_N(N)| \quad (4.149)$$

The molecular orbitals of this determinant are obtained by solving the HF equations:

$$\left[-\frac{1}{2} \nabla^2 + v_s(\vec{r}) \right] \chi_i = \varepsilon_i \chi_i \quad ; \quad \langle \chi_i | \chi_j \rangle = \delta_{ij} \quad (4.150)$$

The exact density and the exact kinetic energy for this system are, respectively:

$$\rho(\vec{r}) = \sum_{i=1}^{N_{occ}} |\chi_i(\vec{r})|^2 \quad (4.151)$$

$$T_s[\rho] = \sum_{i=1}^{N_{occ}} \left\langle \chi_i \left| -\frac{1}{2} \nabla^2 \right| \chi_i \right\rangle \quad (4.152)$$

For this system, the fundamental equation of the DFT, equation (4.103), which once solved would give the density (4.151), is:

$$\frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\vec{r})} + v_s(\vec{r}) = \mu \quad (4.153)$$

with:

$$E_v[\rho] = \sum_{i=1}^{N_{occ}} \varepsilon_i = T_s[\rho] + \int \rho(\vec{r}) v_s(\vec{r}) d\vec{r} \quad (4.154)$$

Let us now move on to the real system in which the N electrons interact. In this case, the equation of energy $E_v[\rho]$ has the form:

$$E_v[\rho] = T[\rho] + \int \rho(\vec{r}) v_n(\vec{r}) d\vec{r} + V_{ee}[\rho] \quad (4.155)$$

The exact kinetic energy for the real system $T[\rho]$ and that corresponding to the reference system $T_s[\rho]$ are different. The exact kinetic energy is reduced to (4.152) only in the case in which the HF solution is exact. We are now going to carry out the energy partition given by (4.155) in the following way:

$$E_v[\rho] = T_s[\rho] + \int \rho(\vec{r})v_n(\vec{r})d\vec{r} + J[\rho] + (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - J[\rho]) \quad (4.156)$$

In this equation, $T_s[\rho]$ is the kinetic energy of the electrons in a system that has the same density as that of the real system, but in which the electron-electron interactions are switched off. $J[\rho]$ is the Coulomb repulsion energy and is given by:

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \quad (4.157)$$

The term $T_C[\rho] = T[\rho] - T_s[\rho]$ is the difference between the kinetic energy of the real system and that of the reference system and is called correlation kinetic energy. Lastly, the term $W_{XC}[\rho] = V_{ee}[\rho] - J[\rho]$ is the **exchange-correlation energy** of the electronic part. These last two contributions are usually grouped in one single term, $E_{XC}[\rho]$, which is the so-called total exchange-correlation energy:

$$E_{XC}[\rho] = (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - J[\rho]) = T_C[\rho] + W_{XC}[\rho] \quad (4.158)$$

$E_{XC}[\rho]$ contains all the contributions to the energy for which we do not have a simple expression as a function of the electron density. In particular, in $E_{XC}[\rho]$ we find the exchange energy, the correlation energy, the portion of kinetic energy necessary to correct $T_s[\rho]$, and the correction made to the self-interaction introduced into the calculation of the electron repulsion based on expression (4.157). In exactly the same way we had expressed $W_{XC}[\rho]$ in (4.71), for $E_{XC}[\rho]$ we have that:

$$E_{XC}[\rho] = \int \rho(\vec{r})v_{XC}(\vec{r})d\vec{r} \quad (4.159)$$

Taking this into consideration, the resulting energy equation (4.155) is:

$$E_v[\rho] = T_s[\rho] + \int \rho(\vec{r})v_n(\vec{r})d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 + E_{XC}[\rho] \quad (4.160)$$

Applying the fundamental equation of the DFT to (4.160) leads to:

$$\frac{\delta E_v[\rho]}{\delta \rho(\vec{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\vec{r})} + v_n(\vec{r}) + \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 + \frac{\delta E_{XC}[\rho]}{\delta \rho(\vec{r})} = \mu \quad (4.161)$$

Defining the Coulomb potential as:

$$v_n(\vec{r}) + \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 = \phi(\vec{r}) \quad (4.162)$$

and the exchange-correlation potential following:

$$v_{XC}(\vec{r}) = \frac{\delta E_{XC}[\rho]}{\delta \rho(\vec{r})} \quad (4.163)$$

we get:

$$\frac{\delta T_s[\rho]}{\delta \rho(\vec{r})} + (\phi(\vec{r}) + v_{XC}(\vec{r})) = \mu \quad (4.164)$$

or else:

$$\frac{\delta T_s[\rho]}{\delta \rho(\vec{r})} + v_{eff}(\vec{r}) = \mu \quad (4.165)$$

Comparing (4.165) with (4.153) we can conclude that the equation to solve for a system of interacting electrons is the same as for a system of electrons without interactions subjected to a potential $v_{eff}(\mathbf{r})$. Consequently, the solution to equation (4.165) is the same for (4.153), changing $v_s(\mathbf{r})$ for $v_{eff}(\mathbf{r})$. The equations to solve with:

$$v_{eff}(\vec{r}) = v_n(\vec{r}) + \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 + v_{XC}(\vec{r}) \quad (4.166)$$

will therefore be:

$$\hat{h}_{KS} \chi_i = \epsilon_i \chi_i \quad (4.167)$$

$$\hat{h}_{KS} = -\frac{1}{2} \nabla^2 + v_{eff}(\vec{r}) \quad ; \quad \langle \chi_i | \chi_j \rangle = \delta_{ij} \quad (4.168)$$

These equations are very similar to the HF equations in (3.33). The orbitals that appear in (4.167), called **Kohn-Sham orbitals**, allow the immediate calculation of the electron density proceeding from:

$$\rho(\vec{r}) = \sum_{i=1}^{N_{oc}} |\chi_i(\vec{r})|^2 \quad (4.169)$$

Like the HF method, the resolution procedure proceeds from a set of trial molecular orbitals, $\{\chi_i(\vec{r})\}$, with which the electron density is determined using (4.169). This density in turn serves to obtain $v_{eff}(\mathbf{r})$ proceeding from (4.166), and to subsequently solve its equation of values and eigenfunctions (4.167). This process must be repeated until convergence is obtained.

Let us briefly analyse some of the consequences that can be derived from the previous expressions. First of all, it is important to point out that in $v_{eff}(\mathbf{r})$ everything is known except $v_{XC}(\mathbf{r})$. It is expected that the electron density $\rho(\mathbf{r})$ will approach the exact density as $v_{XC}(\mathbf{r})$ approaches the exact exchange-correlation potential. In this way, DFT has the potential capacity to incorporate all the correlation energy, unlike HF. Despite the different starting approach, the

similarity between the HF and DFT methods is noteworthy, and in fact substituting $E_{XC}[\rho]$ in equation (4.160) with the HF exchange expression, the same energy expression is obtained in the two methods. There are, nevertheless, fundamental differences between the two methods. Although in DFT an approximate Hamiltonian is used, the final electron density is potentially exact (in other words, the only source of error in the theory is the use of an approximate $v_{XC}(\mathbf{r})$), while in HF it is just the opposite. The Hamiltonian used is exact, but a Slater determinant used as a wave function for a many-electron system is always an approximate solution. Finally it is interesting that if the Slater determinant constructed from the Kohn-Sham orbitals is used to calculate the energy with the exact Hamiltonian, by the variational principle, the energy obtained (E^{KS}) is always more positive than that obtained at the HF level (Baerends, 1997). The correlation energy in DFT defined as $E_C = E_{\text{exact}} - E^{KS}$ is always more negative (greater in absolute value) than the correlation energy at the HF level defined by (3.56), as can be seen schematically in Figure 4.4.

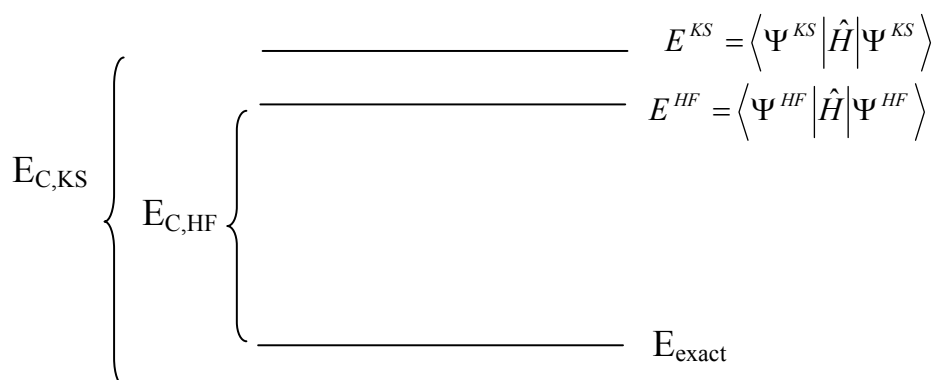


FIGURE 4.4. The correlation energy is greater in absolute value in DFT than in HF.

In practice, the algebraic solving of the Kohn-Sham equations is reached using the LCAO approximation. Equations (3.34) to (3.46) continue being applicable with the only difference being that the Fock operator has to be substituted by the Kohn-Sham operator.

There is another important difference between the HF and DFT methods. In HF the energy with respect to the LCAO expansion coefficients is minimized maintaining the orbitals orthonormalised with the Lagrange undetermined multipliers ϵ_i . In this process the molecular orbitals and the energies ϵ_i of these orbitals have physical meaning. In DFT the energy functional is minimized with respect to the density with the restriction that the density integral is the total number of electrons. In this case only the electron density and μ , which is the Lagrange undetermined multiplier used in the constrained

minimisation, have physical meaning. Neither the Kohn-Sham molecular orbitals used to expand the density, nor the ε_i associated with these orbitals have strict physical meaning. Likewise, neither the wave function Ψ^{KS} nor its square has strict physical meaning, and in fact, Ψ^{KS} , being a Slater determinant, can never be the exact function of a many-electron system. Ψ^{KS} is a wave function that belongs to the set $\{\Psi_\rho\}$ of functions whose integral is ρ . Nonetheless, even in the case in which $v_{\text{xc}}(\mathbf{r})$ was exact and the solution $\rho(\mathbf{r})$ was also exact, Ψ^{KS} would only be an approximation, and not a very good one, of the exact wave function. For this reason, it is not totally justified to use this Ψ^{KS} to calculate values of observables, although it is often used to estimate \hat{S}^2 . There is only one case in which the ε_i associated with the Kohn-Sham orbitals has physical meaning, and it is in the case of the HOMO energy that, as proven by the **Janak theorem** (Janak, 1978), is the exact ionization potential with the opposite sign. Despite what has been said, the Kohn-Sham orbitals do not have to be rejected for reactivity studies, given that the shape, symmetry and energetic order of these orbitals have been proven to coincide with those of the HF orbitals (Strowasser, 1999).

4.6. Approximations to the exchange-correlation potential

As has been seen in Section 4.5, a good **exchange-correlation potential** is a basic aspect of the DFT. Equations (4.159) and (4.163) present the relationship existing between the exchange-correlation potential and the **exchange-correlation energy**. For their part, the equations:

$$E_{\text{xc}}[\rho] = \int \rho(\vec{r}) \varepsilon_{\text{xc}}[\rho] d\vec{r} = \int e_{\text{xc}}[\rho] d\vec{r} \quad (4.170)$$

$$v_{\text{xc}}(\vec{r}) = \frac{\delta(\rho(\vec{r}) \varepsilon_{\text{xc}}[\rho])}{\delta \rho(\vec{r})} = \frac{\delta e_{\text{xc}}[\rho]}{\delta \rho(\vec{r})} \quad (4.171)$$

relate the total exchange-correlation energy and potential with the exchange-correlation energy per particle, ε_{xc} , and with the exchange-correlation energy per unit volume, e_{xc} .

Good approximations to the exchange-correlation energy are required to put this theory into practice. The simplest but at the same time a tremendously useful approximation is the **local density approximation** (LDA). At the following level the so-called non-local or generalized gradient approximations (GGA) are found. These two types of approximations together with the meta-GGA and hybrid functionals are discussed below.

4.6.1. Local density approximation (LDA)

In this approximation $\varepsilon_{XC}[\rho]$ is a functional that depends exclusively on the density. Contributions to the correlation and to the exchange are usually treated separately:

$$\varepsilon_{XC}^{LDA}[\rho] = \varepsilon_X^{LDA}[\rho] + \varepsilon_C^{LDA}[\rho] \quad (4.172)$$

The homogeneous electron gas of constant density $\rho(\mathbf{r})$ is taken as a model for the part corresponding to the exchange. Equation (4.173) with $\alpha=2/3$ gives us the exchange energy per particle (Slater, 1974) for this model:

$$\varepsilon_X^{LDA}[\rho] = -\frac{9}{4}\alpha\left(\frac{3}{8\pi}\right)^{\frac{1}{3}}\rho^{\frac{1}{3}} \quad (4.173)$$

with:

$$E_X^{LDA}[\rho] = -\frac{9}{4}\alpha\left(\frac{3}{8\pi}\right)^{\frac{1}{3}}\int\rho^{\frac{4}{3}}d\vec{r} \quad (4.174)$$

and:

$$v_X^{LDA}(\vec{r}) = \frac{\delta(\rho(\vec{r})\varepsilon_X[\rho])}{\delta\rho(\vec{r})} = -\frac{3}{2}\alpha\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\rho^{\frac{1}{3}} \quad (4.175)$$

Various possibilities exist for the correlation energy per particle. The method known as X_α takes $\varepsilon_C[\rho]=0$ and $\alpha=2/3$. More sophisticated is the analytic expression of Vosko, Wilk and Nusair (Vosko, 1980) developed from the interpolation of a set of correlation energy values obtained by Ceperley and Alder based on Monte Carlo calculations.

The LDA approximation works very well in systems in which the density is maintained approximately constant. For atoms and molecules where the density variations are important, uniform electron gas approximation in infinitesimal volumes is applied (Figure 4.5). Nonetheless, and for well-known reasons, the LDA approximation works reasonably well in these cases.

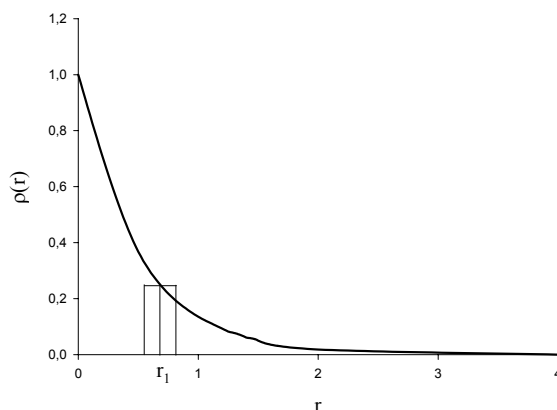


FIGURE 4.5. The LDA approximation applied to a volume differential at point r_1 .

4.6.2. Local spin density approximation (LSDA)

In closed-shell systems the α density and the β density coincide so it is not necessary to minimize the two densities separately. Nevertheless, the two densities are different for open-shell systems. In this case the correct method to treat these systems consists in solving the equations for α and β densities separately. This method is equivalent to the UHF method developed in Section 3.2.2.2, and is, in fact, also known as the *unrestricted Kohn-Sham (UKS) method*. The resulting equation for the energy corresponding to the α density is:

$$E_v[\rho^\alpha] = T_s[\rho^\alpha] + \int \rho^\alpha(\vec{r}) v_n(\vec{r}) d\vec{r} + J[\rho^\alpha, \rho^\beta] + E_{xc}[\rho^\alpha, \rho^\beta] \quad (4.176)$$

where the kinetic energy and the exchange energy depend exclusively on the type α Kohn-Sham orbitals, while the Coulomb repulsion energy and the correlation energy are dependent on the α density and on the β density according to:

$$T_s[\rho^\alpha] = \sum_{i=1}^{N_\alpha} \left\langle \chi_i \left| -\frac{1}{2} \nabla^2 \right| \chi_i \right\rangle \quad (4.177)$$

$$J[\rho^\alpha, \rho^\beta] = \frac{1}{2} \iint \frac{\rho^\alpha(\vec{r}_1) \rho^\alpha(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \iint \frac{\rho^\alpha(\vec{r}_1) \rho^\beta(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \quad (4.178)$$

$$E_{xc}^{LSDA}[\rho^\alpha] = E_x^{LSDA}[\rho^\alpha] + E_c^{LSDA}[\rho^\alpha, \rho^\beta] \quad (4.179)$$

$$E_X^{LSDA}[\rho^\alpha] = -\frac{9}{4}\alpha\left(\frac{3}{8\pi}\right)^{\frac{1}{3}}\int(\rho^\alpha)^{\frac{4}{3}}d\vec{r} \quad (4.180)$$

$$E_C^{LSDA}[\rho^\alpha, \rho^\beta] = \int \rho^\alpha(\vec{r})\varepsilon_c[\rho^\alpha, \rho^\beta]d\vec{r} \quad (4.181)$$

Equivalent equations can be developed for the β part. The energy of the α electrons and the energy of the β electrons are minimized separately, although not independently, given that in the equations corresponding to the energy of the α electrons we need the β density, and the other way round. The equations to solve are:

$$\delta\left[E_v[\rho^\alpha] - \mu^\alpha\left(\int\rho^\alpha(\vec{r})d\vec{r} - N_\alpha\right)\right] = 0 \quad (4.182)$$

$$\delta\left[E_v[\rho^\beta] - \mu^\beta\left(\int\rho^\beta(\vec{r})d\vec{r} - N_\beta\right)\right] = 0 \quad (4.183)$$

Although formally the descriptions provided by the UDFT and UHF methods are quite similar, the background of the **spin-symmetry breaking** is different. Take for instance the case of a biradical with a singlet open-shell ground state (like p-benzyne). In HF, the UHF solution given by a Slater determinant such as that in by Eq. (4.22) is a mixture of singlet and triplet states and the resulting spin contaminated wave function can never be the exact solution for the singlet open-shell ground state. On the other hand, in DFT, one would get the exact density and energy of the singlet open-shell ground state if one had the exact functional available. Thus, in DFT, spin-symmetry breaking simply reflects the limitations of the approximate functionals used and potentially the restricted version of the method can provide the exact solution (Gräfenstein, 2000).

4.6.3. Non-local corrections or Generalized Gradient Approximations (GGA) to the exchange-correlation energy

In the LDA approximation it is assumed that the exchange-correlation effects are local and depend only on the value of electron density at each point. Generally, the LDA methods provide surprisingly good results, especially if one considers the simplicity of the model upon which they are based. The LDA methods yield good geometries, although the bond distances appear somewhat underestimated, good vibrational frequencies, and reasonable charge densities, except in the regions close to nuclei. Nevertheless, they are not suitable for systems with weak bonds or for making reliable thermochemical predictions. These two methods have a general tendency to exaggerate the strength of the bonds, overestimating the bond energy by approximately 30%.

The following step consists in introducing density gradients into the description of exchange and correlation effects. This takes into account the value of the density at each point and how it varies around each point. It should be referred to as a semi-local correction rather than a non-local one, in the sense that the exchange-correlation energy per unit volume continues to only depend on the density and on the density derivative at each point. This approximation results in:

$$E_{XC}^{GGA}[\rho] = \int f(\rho, \nabla\rho) d\vec{r} \quad (4.184)$$

These methods attempt to modify the LDA exchange-correlation energy to have suitable asymptotic behaviour as well as correct scaling properties. With regard to the asymptotic behaviour, from the comparison of equations:

$$E_X[\rho] = \int \rho(\vec{r}) \varepsilon_X[\rho] d\vec{r} \quad (4.185)$$

and

$$E_X[\rho] = \frac{1}{2} \int \rho(\vec{r}_1) d\vec{r}_1 \int \frac{\rho_{XC}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 \quad (4.186)$$

we obtain:

$$\varepsilon_X[\rho] = \frac{1}{2} \int \frac{\rho_{XC}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2 \quad (4.187)$$

Taking as the limit when $r=|\mathbf{r}_1-\mathbf{r}_2|$ tends to infinity, where the denominator of (4.187) can be considered to be maintained constant in a first approximation, and using the sum rule (4.58), it can be seen that the exact asymptotic behaviour of the exchange energy is:

$$\lim_{r \rightarrow \infty} \varepsilon_X[\rho] = -\frac{1}{2r} \quad (4.188)$$

Becke's non-local correction (Becke, 1988) to the exchange energy presents an interesting example to analyse. It must be said that the main source of error of the LDA methods is found in the exchange energy which is usually underestimated by approximately 10-15%. Becke's proposal consists in adding a term to the LDA expression given by equations (4.173)-(4.175) for the exchange. Thus:

$$E_X^{GGA}[\rho] = E_X^{LDA}[\rho] + E_X^{NLDA}[\rho] \quad (4.189)$$

The following equation is chosen for the **non-local density approximation** (NLDA):

$$E_X^{NLDA}[\rho] = \int \rho^{\frac{4}{3}}(\vec{r}) f^{NLDA}(x) d\vec{r} \quad (4.190)$$

x being, on the one hand, a dimensionless parameter assuring that the integral in (4.190) has energy units and, on the other, a parameter which is dependent on the density gradient to be able to introduce the gradient effects:

$$x = \frac{|\nabla\rho|}{\rho^{\frac{4}{3}}} \quad (4.191)$$

Comparing equations (4.190) and (4.170) we have that:

$$\varepsilon_X^{NLDA}[\rho] = \rho^{\frac{1}{3}}(\vec{r})f^{NLDA}(x) \quad (4.192)$$

Taking into account the asymptotic behaviour of the density:

$$\lim_{r \rightarrow \infty} \rho(r) = e^{-ar} \quad (4.193)$$

it is easily demonstrated that the exchange energy defined by (4.173) at the limit is:

$$\lim_{r \rightarrow \infty} \varepsilon_X^{LDA} = 0 \quad (4.194)$$

As has already been mentioned, this is not the exact asymptotic behaviour for the exchange energy. This behaviour can be corrected with (4.189) and (4.190) taking any of the following functions:

$$f^{NLDA}(x) = -\frac{x}{6 \ln x}; f^{NLDA}(x) = -\frac{\beta x^2}{1 + 6\beta x \ln x}; f^{NLDA}(x) = -\frac{\beta x^2}{1 + 6\beta x \sinh^{-1} x} \quad (4.195)$$

For any of these three functions it can be demonstrated from (4.192) and taking into account (4.193) that they have the correct asymptotic behaviour given by (4.188). However, Becke showed that the latter with $\beta=0.0042$ is the one which fits best to the exact exchange densities for a series of atoms.

In addition to Becke's correction to the exchange there are many other non-local corrections for both the exchange part and the correlation part. The most often used correction for the exchange is Becke's. For the correlation part perhaps the most applied are those of Perdew (Perdew, 1986) and those of Lee, Yang and Parr (Lee, 1988).

The geometries, the frequencies, and the LDA charge densities improve with the non-local corrections. Average errors of 6 kcal/mol are obtained on thermochemical tests that function reasonably well for systems with hydrogen bonds, although they still fail to describe van der Waals complexes.

4.6.4. Meta-GGA functionals

Meta-GGA functionals represent the next step in the development of DFT functionals. Thus, while the LDA and GGA approximations correspond to the first two rungs of the so-called Jacob's ladder of DFT (Perdew, 2001), the meta-GGA functionals are considered the next rung of the ladder. In meta-GGA functionals,

the exchange-correlation energy functional contains not only the density and its gradient, but also the kinetic energy density $\tau(\mathbf{r})$:

$$\tau(\vec{r}) = \frac{1}{2} \sum_{i=1}^{N_{occ}} |\nabla \chi_i(\vec{r})|^2 \quad (4.196)$$

and/or the Laplacian of the density, $\nabla^2 \rho(\mathbf{r})$,

$$E_{XC}^{meta-GGA}[\rho] = \int f(\rho, \nabla \rho, \tau, \nabla^2 \rho) d\vec{r} \quad (4.197)$$

As can be seen in equation (4.196), in meta-GGA functionals there is a specific dependence on the occupied Kohn-Sham orbitals. These orbitals are functionals of the density and hence the energy can be written as a functional of the density. On the other hand, the presence of $\nabla^2 \rho(\mathbf{r})$ means that is necessary to calculate second derivatives of the basis functions and, consequently, a larger quadrature grid must be used in the calculations. Among these functionals we can list the BB95, mPWB95, PBEKCIS, Becke00, TPSS, and VSXC.

4.6.5. The adiabatic connection. Hybrid methods.

The fourth rung of the Jacob's ladder to improved functionals corresponds to the **hybrid methods**, which include exact exchange from a HF calculation. The existence of hybrid methods can be justified by the so-called **adiabatic connection formula** for the exchange-correlation energy. For that, a system with a two-electron interaction λ/r_{12} is considered. For this system an external potential $v_s^\lambda(\mathbf{r})$ is adjusted so that for any value of λ , the density $\rho(\mathbf{r})$ corresponding to $\lambda=1$ is obtained. λ is given the so-called coupling constant. $\lambda=0$ corresponds to a system without electron-electron interactions, while $\lambda=1$ corresponds to a system with electrons that interact with a Coulomb potential. The parameter λ continuously connects the model system without electron-electron interactions with the real system. The Hamiltonian and the energy for the system with two-electron interaction λ/r_{12} can be expressed according to:

$$\hat{H}^\lambda = \sum_{i=1}^N -\frac{1}{2} \nabla^2(i) + \sum_{i=1}^N \hat{v}_s^\lambda(i) + \sum_{i=1}^N \sum_{j>i}^N \frac{\lambda}{r_{ij}} \quad (4.198)$$

$$E^\lambda = \langle \psi^\lambda | \hat{H}^\lambda | \psi^\lambda \rangle \quad (4.199)$$

The energy for the system with $\lambda=0$ is given by:

$$E(0) = T_s[\rho] + \int \rho(\vec{r}) v_s(\vec{r}) d\vec{r} \quad (4.200)$$

and for $\lambda=1$ by:

$$E(1) = T_s[\rho] + \int \rho(\vec{r}) v_n(\vec{r}) d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho] \quad (4.201)$$

Subtracting these last two equations results in:

$$E_{xc}[\rho] = E(1) - E(0) + \int \rho(\vec{r})(v_s(\vec{r}) - v_n(\vec{r})) d\vec{r} - \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \quad (4.202)$$

On the other hand, the **Hellmann-Feynman theorem** allows us to write:

$$\frac{dE^\lambda}{d\lambda} = \int \psi^\lambda * \frac{d\hat{H}^\lambda}{d\lambda} \psi^\lambda d\vec{r} \quad (4.203)$$

by using the derivative with respect to λ of (4.199):

$$\frac{dE^\lambda}{d\lambda} = \left\langle \psi^\lambda \left| \frac{d\hat{H}^\lambda}{d\lambda} \right| \psi^\lambda \right\rangle = \left\langle \psi^\lambda \left| \sum_i^N \frac{dv_s^\lambda}{d\lambda} + \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}} \right| \psi^\lambda \right\rangle \quad (4.204)$$

Given that:

$$\int_0^1 \frac{dE^\lambda}{d\lambda} d\lambda = E(1) - E(0) \quad (4.205)$$

and substituting (4.203) in (4.205), and making use of (4.67) which gives us the expected value of a two-electron operator as a function of the two-electron density leads to:

$$E(1) - E(0) = \int_0^1 \frac{dE^\lambda}{d\lambda} d\lambda = \int_0^1 \left\langle \psi^\lambda \left| \sum_i^N \frac{dv_s^\lambda}{d\lambda} \right| \psi^\lambda \right\rangle d\lambda + \frac{1}{2} \iint \int_0^1 \frac{\gamma_2^\lambda(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 d\lambda \quad (4.206)$$

Substituting (4.47) in the previous equation we have:

$$E(1) - E(0) = \int_0^1 \int \rho(\vec{r}) \frac{dv_s^\lambda}{d\lambda} d\vec{r} d\lambda + \frac{1}{2} \iint \int_0^1 \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 d\lambda + \frac{1}{2} \iint \int_0^1 \frac{\rho(\vec{r}_1)\rho_{xc}^\lambda(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 d\lambda \quad (4.207)$$

Integrating with respect to λ :

$$E(1) - E(0) = \int \rho(\vec{r})(v_n(\vec{r}) - v_s(\vec{r})) d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \iint \int_0^1 \frac{\rho(\vec{r}_1)\rho_{xc}^\lambda(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 d\lambda \quad (4.208)$$

Finally, substituting (4.208) in (4.202) leads to:

$$E_{xc}[\rho] = \frac{1}{2} \iint \int_0^1 \frac{\rho(\vec{r}_1)\rho_{xc}^\lambda(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 d\lambda = \frac{1}{2} \iint \int_0^1 \rho(\vec{r}) v_{xc}^\lambda(\vec{r}) d\vec{r} d\lambda \quad (4.209)$$

which, using (4.71), can be written as:

$$E_{XC}[\rho] = \int_0^1 W_{XC}^{\lambda}[\rho] d\lambda \quad (4.210)$$

This expression makes up the **adiabatic connection formula** for the exchange-correlation energy, where, $W_{XC}^{\lambda}[\rho]$ is the exchange-correlation energy of the electronic part for a system with two-electron interaction λ/r_{12} . The total exchange-interaction energy $E_{XC}[\rho]$ can be generated by integration from $W_{XC}^{\lambda}[\rho]$. In this way, $W_{XC}^{\lambda}[\rho]$ for $\lambda=0$ in the expression of $E_{XC}[\rho]$ is justified and so is, therefore, the existence of hybrid methods.

Expression (4.210) can be employed to obtain approximations to the exchange-correlation energy. A first approximation proposed by Becke consists in considering that $W_{XC}^{\lambda}[\rho]$ depends linearly on λ . In this case:

$$E_{XC}[\rho] = \frac{1}{2} W_{XC}^{\lambda=1}[\rho] + \frac{1}{2} W_{XC}^{\lambda=0}[\rho] \quad (4.211)$$

For $\lambda=0$, HF is exact, and $W_{XC}^{\lambda=0}[\rho]$ is considered equal to the exchange energy HF. $W_{XC}^{\lambda=1}[\rho]$ is approximated using an already known expression of the exchange-correlation energy, such as BLYP. The method used by equation (4.211) is called the Half & Half method, but there are other methods based on the adiabatic connection. Perhaps the most often used is the **Becke three parameters method** (Becke, 1993) in which:

$$E_{XC} = E_{XC}^{LSDA} + a_o(E_X^{exact} - E_X^{LSDA}) + a_x \Delta E_X^{B88} + a_c \Delta E_C^{PW91} \quad (4.212)$$

with $a_o = 0.20$, $a_x = 0.72$, and $a_c = 0.81$. These values are those which best fit the B3PW91 results to a set of experimental thermochemical data. Other relevant hybrid functionals are PBE0, MPW1K, O3LYP, and X3LYP.

Finally, the fifth and last (till now) rung of the Jacob's ladder correspond to the hybrid meta-GGA functionals that combine meta-GGA functionals and HF exchange. Some functionals belonging to this last category are the MPWB1K, TPSSh, M05, MPBE0KCIS, and PBE1KCIS. Both hybrid GGA and hybrid meta-GGA methods are semiempirical and they have been very successful for the analysis of many problems in chemistry.

The improvement of the exchange-correlation potentials is currently a very active field of research. Various channels are being followed to obtain this objective. One possibility is modifying the exchange-correlation potentials so that they and their derivatives comply with the all the known asymptotic and scaling properties. Also very promising are techniques which, starting from an exact or very precise density, allow the exchange-correlation potential that generates them to be determined. The study of v_{XC} potentials generated in this way can help obtain

improved expressions.

4.6.6. The self-interaction correction (SIC) problem

The sum of the $J[\rho]$ and $E_{xc}[\rho]$ terms in Eqs. (4.157) and (4.159) should be exactly zero in the case of a one-electron system. In this case, the exact exchange-correlation hole is simply the negative of the density and the Coulomb and exchange-correlation terms in (4.70) cancel each other. However, when using approximate functionals, one uses complicated expressions for the exchange-correlation potential and $E_{xc}[\rho]$ is different from $-J[\rho]$ for one-electron systems. This is the origin of the so-called **self-interaction error** (SIE). Basically, the Coulomb term of the DFT energy includes a self-repulsion part that it is only incompletely cancelled by the self-exchange part due to the approximate nature of the exchange functionals used in DFT. It is worth noting that, by construction, the HF theory avoids any self-interaction error and exactly evaluates the exchange energy. In DFT, the $E_{xc}[\rho]$ term must include not only the effects of exchange, correlation, and the difference in kinetic energy between the fictitious non-interacting system and the real one, but also the correction for the classical self-interaction energy. In the last years, many efforts have been devoted to design methods that generate electron density distributions self-interaction corrected (SIC).

4.7. Time dependent density functional theory

Density functional theory, and its implementations as described above, has become very popular among quantum chemists because it provides very reasonable accuracy at an affordable cost. However, molecular applications of regular DFT are limited to the calculations of static properties, since it does not cover the treatment of problems involving time-dependent potentials. This leaves aside many relevant problems found in molecular optics and electronic spectroscopy. This section outlines the extension of DFT to account for the description of the molecular response to time-dependent fields.

Time-dependent density functional theory (TDDFT) provides a formally rigorous extension of Hohenberg-Kohn-Sham density-functional theory to the situation where a system, initially in its ground stationary state, is exposed to a time-dependent perturbation which modifies its external potential (Casida, 1995). This allows for the description of various time-dependent phenomena, such as atoms and solids in time-dependent electric or magnetic fields. In addition, TDDFT provides an efficient way to calculate the dynamic polarizability, a magnitude required to describe the optical

properties of matter.

The first step in the development of the theory is to demonstrate the existence of an unique correspondence between the time dependent one-body density $\rho(\vec{r}, t)$ and the time-dependent potential $v(\vec{r}, t)$. This mapping is proven by the **Runge-Gross theorem** (Runge and Gross, 1984), which can be considered as the time-dependent generalization of the Hohenberg-Kohn theorem. Then, a corresponding Kohn-Sham construction of the theory can be built that yields a set of practical equations for the calculations:

$$i \frac{\partial}{\partial t} \psi_i(\vec{r}, t) = \left[-\frac{\nabla^2}{2} + v_{\text{eff}}(\vec{r}, t) \right] \psi_i(\vec{r}, t) \quad (4.213)$$

The orbitals $\psi_i(\vec{r}, t)$ are the time-dependent Kohn-Sham orbitals which generate the one-body density as:

$$\rho(\vec{r}, t) = \sum_{i=1}^N |\psi_i(\vec{r}, t)|^2 \quad (4.214)$$

As in ordinary Kohn-Sham DFT, here we use an auxiliary system of non-interacting electrons subject to a $v_{\text{eff}}(\vec{r}, t)$ potential which is chosen such that the density built from these Kohn-Sham orbitals is the same as the density of the real interacting system. If the exact time-dependent effective Kohn-Sham potential $v_{\text{eff}}(\vec{r}, t)$ is known, then the equations stated above would lead to the exact one-body density. This $v_{\text{eff}}(\vec{r}, t)$ potential can be divided in various contributions which read as follows,

$$v_{\text{eff}}(\vec{r}, t) = J[\vec{r}, t] + v_{\text{ext}}(\vec{r}, t) + v_{\text{xc}}(\vec{r}, t) \quad (4.215)$$

where $J[\vec{r}, t]$ stands for the classical electrostatic potential of the electron distribution, namely:

$$J[\vec{r}, t] = \int \frac{\rho(\vec{r}', t)}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (4.216)$$

The external potential $v_{\text{ext}}(\vec{r}, t)$ accounts for the interaction of the electrons with the nuclei (whose positions could evolve dynamically) and any other potential that depends on time. For instance, consider the optical absorption of a molecule subject to the effect of a laser radiation of a given frequency, ω . Then, the external potential would be:

$$v_{\text{ext}}(\vec{r}, t) = -\sum_{\alpha=1}^M \frac{Z_{\alpha}}{|\vec{r} - \vec{R}_{\alpha}(t)|} + Ef(t) \cos \omega \left(t - \frac{|\vec{r}|}{c} \right) \quad (4.217)$$

Where c is the velocity of the light and $f(t)$ is a function that controls the laser pulse. The time dependent exchange-correlation potential can be formally defined as the functional derivative of the exchange-correlation action functional,

$$v_{ext}(\vec{r}, t) = \frac{\delta A_{xc}}{\delta \rho(\vec{r}, t)} \quad (4.218)$$

which plays role analogous to the exchange-correlation energy functional in time independent DFT. Opposite to ordinary time-independent DFT, approximations to $v_{xc}(\vec{r}, t)$ are still in their infancy. Most of the existing functionals make use of the adiabatic approximation, which advocates the use of time-independent exchange-correlation functionals. The approximation proceeds as follows: Let us assume that $\tilde{v}[\rho]$ is a reasonable approximate time-independent exchange-correlation potential, then the adiabatic time-dependent exchange-correlation potential is expressed as:

$$v_{xc}^{adiabatic}(\vec{r}, t) = \tilde{v}[\rho(\vec{r})_{\rho=\rho(t)}] \quad (4.219)$$

That is, the adiabatic approximation consists of using the same exchange-correlation potential as in the time-independent theory but evaluated with the electron density at time t , $\rho(\vec{r}, t)$. The functional is local in time. Consequently, it constitutes quite a crude approximation.

Apart from uncertainties associated to approximations of the exchange-correlation potential, the scheme described so far is perfectly general and can be applied to any time-dependent situation. Nevertheless, in practice two different regimes are considered. In the case that the time-dependent potential is weak, linear-response theory can be applied to solve the problem. On the other hand, if the time-dependent potential is strong a full solution of the Kohn-Sham equations is required.

4.7.1. Linear Response Time-dependent density-functional theory

It can be shown that the vertical excitation energies ($\omega_I = E_I - E_0$) from the molecular electronic ground state to the excited state $I(I \leftarrow 0)$ can be obtained from the poles of the mean dynamic polarizability

$$\bar{\alpha}(\omega) = \frac{1}{3} \text{tr} \alpha(\omega) = \sum_I \frac{f_I}{\omega_I^2 - \omega^2} \quad (4.220)$$

The calculation of the dynamical polarizability is difficult. However, TDDFT allows us to calculate the response of the density to a time-dependent perturbing potential at frequency ω . The response function has poles at all the excitation

energies of the system. Therefore, it has the necessary information to calculate all the excitations of the system.

The linear response approximation only takes into account the component that depends linearly on the external potential,

$$\delta\rho(\vec{r}, \omega) = \int d\vec{r}' \chi(\vec{r}, \vec{r}', \omega) \delta v_{ext}(\vec{r}', \omega) \quad (4.221)$$

where $\chi(\vec{r}, \vec{r}', \omega)$ is the density-density response function, which gives the density response of the system to a time dependent perturbation $\delta v_{ext}(\vec{r}', \omega)e^{-i\omega t}$. The exact χ response function which is defined as:

$$\chi^{-1}(\vec{r}, \vec{r}', \omega) = \frac{\delta v_{ext}(\vec{r}, \omega)}{\delta\rho(\vec{r}', \omega)} \quad (4.222)$$

is hard to calculate. Alternatively, TDDFT allows one to express the exact density response $\delta\rho$ via the response function χ_s of the non-interacting Kohn-Sham system.

$$\delta\rho(\vec{r}, \omega) = \int d\vec{r}' \chi_s(\vec{r}, \vec{r}', \omega) \delta v_{eff}(\vec{r}', \omega) \quad (4.223)$$

$\delta v_{eff}(\vec{r}', \omega)$ is the linearized time-dependent Kohn-Sham potential and consists of three contributions,

$$\delta v_{eff}(\vec{r}', \omega) = \delta v_{ext}(\vec{r}', \omega) + \int d\vec{r}'' \frac{\delta\rho(\vec{r}'', \omega)}{|\vec{r}' - \vec{r}''|} + \int d\vec{r}'' f_{xc}(\vec{r}, \vec{r}'', \omega) \delta\rho(\vec{r}'', \omega) \quad (4.224)$$

In the above equation f_{xc} is the exchange correlation kernel, defined as the functional derivative of the exchange-correlation potential with respect to the density, evaluated at the ground state density, and then, Fourier transformed to the ω -space.

$$f_{xc}(\vec{r}, t, \vec{r}', t') = \left[\frac{\delta v_{xc}[\rho](\vec{r}, t)}{\delta\rho(\vec{r}', t')} \right]_{\rho_0} \quad (4.225)$$

The response function of the Kohn-Sham system can be expressed in terms of the time independent Kohn-Sham-orbitals as,

$$\chi_s(\vec{r}, \vec{r}', \omega) = \sum_{j,k} (f_k - f_j) \frac{\psi_j(\vec{r})\psi_k^*(\vec{r})\psi_j^*(\vec{r}')\psi_k(\vec{r}')}{\omega - (\varepsilon_j - \varepsilon_k) + i\eta} \quad (4.226)$$

with f_k being the Fermi occupation number (0 or 1) of the k th Kohn-Sham-orbital. Substituting the expressions for δv_{eff} and χ_s into Equation (4.223) yields:

$$\int d\vec{r}'' \left[\delta(\vec{r} - \vec{r}'') - \int d\vec{r}' \chi_s(\vec{r}, \vec{r}'', \omega) \times \left(\frac{1}{|\vec{r}' - \vec{r}''|} + f_{xc}(\vec{r}', \vec{r}'', \omega) \right) \right] \delta\rho(\vec{r}'', \omega) = \int d\vec{r}' \chi_s(\vec{r}, \vec{r}', \omega) \delta v(\vec{r}', \omega) \quad (4.227)$$

In this equation, $\delta\rho(\vec{r}'', \omega)$ at the left-hand-side shows poles at the exact excitation energies Ω , but the right-hand-side of the equation shows poles at $(\varepsilon_j - \varepsilon_k)$. It is important to notice that the excitation energies will be different to the difference in the Kohn-Sham orbital energies. Therefore, as $\omega \rightarrow \Omega$ the right hand side of the equation has a finite value. The only possibility for the equality to hold when $\omega \rightarrow \Omega$ is that the term within brackets vanishes when $\omega \rightarrow \Omega$. This condition, leads to the following equation,

$$\lambda(\omega) \gamma(\vec{r}, \omega) = \int d\vec{r}' \chi_s(\vec{r}, \vec{r}', \omega) \times \int d\vec{r}'' \left[\frac{1}{|\vec{r}' - \vec{r}''|} + f_{xc}(\vec{r}', \vec{r}'', \omega) \right] \gamma(\vec{r}'', \omega) \quad (4.228)$$

With $\lambda \rightarrow 1$ as $\omega \rightarrow \Omega$. After some algebra this equation can be recast into an eigenvalue problem,

$$\sum_{q'} (M_{qq'}(\Omega) + \omega_q \delta_{qq'}) \beta_{q'} = \Omega \beta_q \quad (4.229)$$

where q denotes a pair of Kohn-Sham orbitals (j, k) , ω_q is the difference in orbital energy of the corresponding pair of Kohn-Sham orbitals: $(\varepsilon_j - \varepsilon_k)$ and $(M_{qq'})$ are elements of the so-called coupling matrix,

$$M_{qq'} = (f_{k'} - f_{j'}) \int d\vec{r} \int d\vec{r}' \psi_k(\vec{r}) \psi_j^*(\vec{r}) \left[\frac{1}{|\vec{r} - \vec{r}'|} + f_{xc}(\vec{r}, \vec{r}', \omega) \right] \psi_{k'}^*(\vec{r}') \psi_{j'}(\vec{r}') \quad (4.230)$$

The solution of the eigenvalue problem gives the true excitation energies Ω , as long as we know the exact exchange-correlation kernel f_{xc} and the Kohn-Sham orbitals that builds up the exact time independent one-body density. The quality of the Kohn-Sham orbitals is dictated by the quality of the static exchange-correlation potential used to solve the time-independent Kohn-Sham equations. As seen in the previous section, the exact static v_{xc} is still not known, but several approximations have been developed that give reasonable results. To get a functional for f_{xc} is a bit more complicated, since it depends, in principle, on the dynamical v_{xc} through the relation (4.225) One can use the adiabatic approximation, Eq. (4.219) and the relation (4.225) to develop an expression for f_{xc} based on the form of the approximate static v_{xc} .

It has been shown, that even considering the LDA approximation (ALDA, **Adiabatic Local Density Approximation**) one can get good results at low frequencies in most cases. In other cases, however, it is mandatory to go beyond these simple functional forms in order to obtain reliable excitation energies.

Another problem with Eq. (4.229) is that has to be truncated to become practical, and this gives rise to different levels of approximations. The most drastic truncation would imply to expand Eq. (4.229) about one particular Kohn-Sham orbital energy difference and calculate only one term of the coupling matrix,

$$\Omega = (\varepsilon_j - \varepsilon_k) + M_{qq} \quad (4.231)$$

where M_{qq} is the element of the coupling matrix that corresponds to the (j,k) excitation ($q=(j,k)$), that is the following integral

$$M_{qq} = \iint d\vec{r}d\vec{r}' \psi_j(\vec{r})\psi_k^*(\vec{r}) \left[\frac{1}{|\vec{r} - \vec{r}'|} + f_{xc}(\vec{r}, \vec{r}', \omega) \right] \psi_j^*(\vec{r}')\psi_k(\vec{r}') \quad (4.232)$$

This truncation is denoted as the **Single-Pole Approximation** (SPA) and already gives a remarkable agreement with the experimental values in many cases. The following Table shows experimental excitation energies for various atoms compared to the difference in the Kohn-Sham orbital energies ($\Delta\varepsilon_{KS}$) and to the SPA excitation energies. The use of ($\Delta\varepsilon_{KS}$) alone to calculate the excitation spectrum is quite poor. However, the SPA correction to ($\Delta\varepsilon_{KS}$) does remarkably well compared to the experimental spectrum, as shown in Table 4.1.

We can also go beyond the Single-Pole approximation and consider more terms of the Eq. (4.229).

Among the highest impact applications of the SPA time dependent density functional response theory to the calculation of vertical excitation energies of molecules stands high. Nuclei are kept fixed and the SPA equations are solved to yield the corresponding optical absorption spectrum of the molecule.

TABLE 4.1. Experimental excitation energies, in eV, for the ($^1S \rightarrow ^1P$) transition compared to the differences in the corresponding Kohn-Sham orbital energies and theoretical excitation energies from Single-Pole Approximation (SPA).

Atom	Experimental	$(\Delta\varepsilon_{KS})$	$(\Delta\varepsilon_{KS})+M$ (SPA)
Be	0.388	0.259	0.391
Mg	0.319	0.234	0.327
Ca	0.216	0.157	0.234
Zn	0.426	0.315	0.423
Sr	0.198	0.141	0.210
Cd	0.398	0.269	0.391

4.7.2. Full solution of TDDFT Kohn-Sham equations

There are problems for which the linear response time dependent density functional theory is inappropriate. These include the study of non-linear optical properties and the vast majority of chemically relevant photochemical reaction processes. In such cases, one should solve directly the TDDFT Kohn-Sham equations,

$$i \frac{\partial}{\partial t} \psi_i(\vec{r}, t) = \left[-\frac{\nabla^2}{2} + v_{KS}(\vec{r}, t) \right] \psi_i(\vec{r}, t) \quad (4.233)$$

That means that starting from the electron density of an initial state $\rho(\vec{r}, t_0)$ (in most cases, the ground state of the system) generated from the Kohn-Sham-orbitals $\psi_i(\vec{r}, t_0)$, one has to propagate this state in accordance with the changes in the Kohn-Sham orbitals as dictated by Eq. (4.233) until some final time t_f . In order to do it so, it is more convenient to rewrite Eq. (4.233) in its integral form,

$$\psi_i(\vec{r}, t_f) = \hat{U}(t_f, t_0) \psi_i(\vec{r}, t_0) \quad (4.234)$$

where the time-evolution operator \hat{U} is defined by

$$\hat{U}(t', t) = \hat{T} e^{-i \int_t^{t'} d\tau \hat{H}_{KS}(\tau)} \quad (4.235)$$

Notice that \hat{H}_{KS} is explicitly time-dependent because both the Hartree and exchange-correlation potentials are time dependent. The exponential in the expression is clearly too complex to be applied directly and needs to be approximated in some suitable manner. One possibility is to approximate the

exponential in the time-evolution operator as a power series of Δt using schemes specifically designed to enforce time-reversal symmetry, or either, approximate the integral in the exponent by the trapezoidal rule. To reduce errors in the propagation from t_0 to t_f this usually large interval is customarily split into smaller sub-intervals of length Δt . The wave-functions are then propagated as $t_0 \rightarrow t_0 + \Delta t$, then as $t_0 + \Delta t \rightarrow t_0 + 2\Delta t$, and so on. Typical values for the time step are of the order of 0.001 fs. The total simulation time is determined by the accuracy required in the energy. For accuracies in the order of 0.1 eV, one has to go to simulation times of the order of 15 fs.

Additionally, one can couple the electronic degrees of freedom with the nuclear ones, by propagating the nuclei position in time according to the Newton's equations of motion, using the **Verlet algorithm**:

$$\vec{R}_\alpha(t + \Delta t) = 2\vec{R}_\alpha(t) - \vec{R}_\alpha(t - \Delta t) + \vec{a}(t)\Delta t^2 \quad (4.236)$$

The accelerations on the nuclei are estimated by the **Hellman-Feynmann theorem**,

$$\vec{F}_\alpha(\vec{R}, t) = - \left\langle \Psi(t) \left| \frac{\partial}{\partial \vec{R}_\alpha} \right| \Psi(t) \right\rangle \quad (4.237)$$

which describes the forces that electrons exert on the nuclei. Solving the coupled Eqs. (4.233) and (4.236) leads to a combined electron-nuclei dynamics, which can be used to study the dynamics of many interesting phenomena (Marques and Gross, 2004), like photochemical isomerization reactions, laser-induced dissociations, etc.

4.8. Some difficult cases for the density functional theory

The principle advantages offered by this method with respect to HF are: a) the obtainment of high-quality geometries, good dipole moments, excellent vibrational frequencies, and a good estimation of the thermochemistry and of reaction barriers with a cost similar to that of HF, thereby introducing electron correlation at a very reduced cost; b) the spin contamination in unrestricted UKS calculations is normally less than it is in UHF calculations; c) the DFT density has characteristics typical of the densities obtained through high level *ab initio* methods; and d) DFT provides excellent results for molecules traditionally poorly described at the HF level (FOOF, FON, the first series of transition metals...), it being the most frequently used method at present to deal with organometallic and bioinorganic systems.

The main disadvantages include dealing incorrectly, in general, with:

- a) Systems with only one electron given that the resulting exchange-correlation energy is not zero because of SIE (see Section 4.6.6).
- b) Systems with weak bonds such as van der Waals complexes and charge transfer complexes. For van der Waals interactions, new functionals have been developed recently that are explicitly parameterized using experimental data by including damped atom-pairwise dispersion corrections of the form $C_6 \cdot R^{-6}$ (Grimme, 2006). This is an area of current active research.
- c) Electronic excited states and states with clearly many-determinant character as, for example, singlet open-shell species.
- e) Bond dissociation in radical species, in particular those having 2 center-3 electron bonds. Improper dissociation in such systems originates from the fact that the exchange-correlation hole is delocalized over several centres whereas any approximate exchange-correlation functional is centred around the electron.
- e) Many functionals overstabilize systems having more highly delocalized densities over localized alternatives. Such an imbalance can lead to erroneous predictions in, for instance, the electronic states and molecular structure of the ground state of some transition metal complexes (Poater, 2004) and the transition states for cationic [4+3] cycloadditions (Cramer, 1998).

On the other hand, there has not been much experience dealing with excited and clearly many-determinant states. All in all, the main problem with the DFT can be found in the fact that, if the exchange-correlation potential used does not give the expected results, there is no systematic way to improve them. Nevertheless, it must be hoped that, in the future, the current work of many scientists dedicating themselves to improving the existing exchange-correlation potentials will be fruitful and that, finally, computational chemists will have at their disposal a procedure to systematically improve the DFT calculations, using various levels of approximation.

4.9. Exercises

4.1. Consider the He atom in its $1s^1 2s^1$ configuration with the electrons occupying the orthogonal atomic orbitals Φ_{1s} and Φ_{2s} .

The wave function for the singlet state is:

$${}^1\Psi(\vec{x}_1, \vec{x}_2) = \frac{1}{2} [\phi_{1s}(1)\phi_{2s}(2) + \phi_{1s}(2)\phi_{2s}(1)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

and for the triplet there are three possibilities corresponding to the different possible values of M_s :

$${}^3\Psi(\vec{x}_1, \vec{x}_2) = \frac{\sqrt{2}}{2} [\phi_{1s}(1)\phi_{2s}(2) - \phi_{1s}(2)\phi_{2s}(1)] \alpha(1)\alpha(2)$$

$${}^3\Psi(\vec{x}_1, \vec{x}_2) = \frac{\sqrt{2}}{2} [\phi_{1s}(1)\phi_{2s}(2) - \phi_{1s}(2)\phi_{2s}(1)] \beta(1)\beta(2)$$

$${}^3\Psi(\vec{x}_1, \vec{x}_2) = \frac{1}{2} [\phi_{1s}(1)\phi_{2s}(2) - \phi_{1s}(2)\phi_{2s}(1)] [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

Found the expressions for $\rho_1(\mathbf{x}_1)$, $\rho_1(\mathbf{r}_1)$, $\rho_1^\alpha(\mathbf{r}_1)$ and $\rho_1^\beta(\mathbf{r}_1)$ for the above mentioned four electronic states.

4.2. Show that monodeterminantal wave functions the following expressions holds:

$$\int \rho_1(\vec{x}_1; \vec{x}_2) \rho_1(\vec{x}_2; \vec{x}_3) d\vec{x}_2 = \rho_1(\vec{x}_1; \vec{x}_3)$$

4.3. The equation of exercise 4.2 can be generalized to any density. Consider now that

$$\rho_1(\vec{x}_1; \vec{x}_2) = \sum_i \sum_j \rho_{ij} \chi_i(\vec{x}_1) \chi_j^*(\vec{x}_2)$$

and prove from the equation of the latter exercise that $\rho_{ik} = \sum_j \rho_{ij} \rho_{jk}$ and, therefore, $\rho = \rho^2$.

4.4. Prove from the definition of the second-order reduced density matrix that, for closed-shell monodeterminantal wave functions:

$$\gamma_2(\vec{r}_1, \vec{r}_2) = 4 \sum_i^{\frac{N}{2}} \sum_j^{\frac{N}{2}} \left(\chi_i^*(\vec{r}_1) \chi_j^*(\vec{r}_2) \chi_i(\vec{r}_1) \chi_j(\vec{r}_2) - \frac{1}{2} \chi_i^*(\vec{r}_1) \chi_j^*(\vec{r}_2) \chi_j(\vec{r}_1) \chi_i(\vec{r}_2) \right)$$

and that for closed-shell monodeterminantal wave functions with $i, j \in \alpha$:

$$\gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) = \sum_i^{\frac{N_\alpha}{2}} \sum_j^{\frac{N_\alpha}{2}} \left(\chi_i^*(\vec{r}_1) \chi_j^*(\vec{r}_2) \chi_i(\vec{r}_1) \chi_j(\vec{r}_2) - \chi_i^*(\vec{r}_1) \chi_j^*(\vec{r}_2) \chi_j(\vec{r}_1) \chi_i(\vec{r}_2) \right)$$

$$\gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) = \rho_1^\alpha(\vec{r}_1)\rho_1^\alpha(\vec{r}_2) - \rho_1^\alpha(\vec{r}_1, \vec{r}_2)\rho_1^\alpha(\vec{r}_2, \vec{r}_1)$$

$$\begin{aligned}\gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) &= \sum_{\mu\nu\sigma\lambda} \Gamma_{\mu\nu\sigma\lambda}^{\alpha\alpha} \phi_\mu^*(\vec{r}_1)\phi_\nu^*(\vec{r}_2)\phi_\sigma(\vec{r}_1)\phi_\lambda(\vec{r}_2) \\ \Gamma_{\mu\nu\sigma\lambda}^{\alpha\alpha} &= P_{\mu\sigma}^\alpha P_{\nu\lambda}^\alpha - P_{\mu\lambda}^\alpha P_{\nu\sigma}^\alpha\end{aligned}$$

and for $i \in \alpha$ and $j \in \beta$:

$$\gamma_2^{\alpha\beta}(\vec{r}_1, \vec{r}_2) = \sum_{i=1}^{N_\alpha} \sum_{j=N_\alpha+1}^{N_\alpha+N_\beta} \chi_i^*(\vec{r}_1)\chi_j^*(\vec{r}_2)\chi_i(\vec{r}_1)\chi_j(\vec{r}_2) = \rho_1^\alpha(\vec{r}_1)\rho_1^\beta(\vec{r}_2)$$

$$\begin{aligned}\gamma_2^{\alpha\beta}(\vec{r}_1, \vec{r}_2) &= \sum_{\mu\nu\sigma\lambda} \Gamma_{\mu\nu\sigma\lambda}^{\alpha\beta} \phi_\mu^*(\vec{r}_1)\phi_\nu^*(\vec{r}_2)\phi_\sigma(\vec{r}_1)\phi_\lambda(\vec{r}_2) \\ \Gamma_{\mu\nu\sigma\lambda}^{\alpha\beta} &= P_{\mu\sigma}^\alpha P_{\nu\lambda}^\beta\end{aligned}$$

4.5. Prove that for closed-shell systems:

$$\Gamma_{\mu\nu\sigma\lambda} = \Gamma_{\mu\nu\sigma\lambda}^{\alpha\alpha} + \Gamma_{\mu\nu\sigma\lambda}^{\alpha\beta} + \Gamma_{\mu\nu\sigma\lambda}^{\beta\alpha} + \Gamma_{\mu\nu\sigma\lambda}^{\beta\beta} = P_{\mu\sigma} P_{\nu\lambda} - \frac{1}{2} P_{\mu\lambda} P_{\nu\sigma}$$

4.6. Prove the following relationships:

$$\begin{aligned}\int \gamma_2^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 &= (N_\alpha - 1)\rho_1^\alpha(\vec{r}_1) \\ \int \gamma_2^{\alpha\beta}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 &= N_\beta \rho_1^\alpha(\vec{r}_1)\end{aligned}$$

4.7. Prove the sum rule:

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

To this end, it is convenient to demonstrate first that:

$$\begin{aligned}\int \rho_{xc}^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 &= -1 \quad \text{and that} \\ \int \rho_{xc}^{\alpha\beta}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 &= \int \rho_{xc}^{\beta\alpha}(\vec{r}_1, \vec{r}_2) d\vec{r}_2 = 0\end{aligned}$$

4.8. Prove that for monodeterminantal wave functions, the following equation holds:

$$\begin{aligned}\rho_{xc}^{\alpha\beta}(\vec{r}_1, \vec{r}_2) &= \rho_{xc}^{\beta\alpha}(\vec{r}_1, \vec{r}_2) = 0 \\ \rho_{xc}^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) &= -\sum_i^{N_\alpha} \sum_j^{N_\alpha} \frac{\chi_i^*(\vec{r}_1)\chi_i(\vec{r}_2)\chi_j(\vec{r}_1)\chi_j^*(\vec{r}_2)}{\rho_1^\alpha(\vec{r}_1)} \neq 0\end{aligned}$$

4.9. Taking into account the equations derived in the previous exercise prove that:

$$\int \rho_{xc}^{\alpha\alpha}(\vec{r}_1, \vec{r}'_1) d\vec{r}_1 = -N_\alpha$$

4.10. Prove that for a mono-electronic operator like:

$$\mathcal{G}_1 = \sum_i \hat{h}(i)$$

one finds:

$$\langle \Psi | \mathcal{G}_1 | \Psi \rangle = \int \hat{h}(1) \rho_1(\vec{r}_1, \vec{r}'_1) d\vec{r}_1$$

while for a bi-electronic operator:

$$\mathcal{G}_2 = \sum_i \sum_{j>i} \hat{g}(i, j)$$

the following relation holds:

$$\langle \Psi | \mathcal{G}_2 | \Psi \rangle = \frac{1}{2} \iint \hat{g}(1,2) \gamma_2(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

4.11. For mono-electronic systems the kinetic energy is exactly:

$$T_w = \frac{1}{8} \int \frac{|\nabla \rho|^2}{\rho} d\vec{r}$$

Prove the validity of this expression for the ground state of the hydrogen atom

with the wave functions $\Psi_{1s} = \left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-\frac{r}{a_0}}$. The $T_w[\rho]$ functional is the so-called von Weizsäcker kinetic energy functional.

4.12. Prove the following relation:

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 = \sum_i^N \left[\left(\sum_{j>i}^N J_{ij} \right) + \frac{J_{ii}}{2} \right]$$

4.13. The kinetic energy functional in the Thomas-Fermi theory has the expression:

$$T_{TF}[\rho] = c_k \int \rho^{\frac{5}{3}}(\vec{r}) d\vec{r}$$

Find $\frac{\delta T_{TF}}{\delta \rho}$.

- 4.14. The hardness kernel was defined by Parr and Gázquez (J. Phys. Chem. 97 (1993) 3939) as:

$$\eta(\vec{r}, \vec{r}') = \frac{\delta^2 F}{\delta\rho(\vec{r}')\delta\rho(\vec{r})}$$

From the hardness kernel one can obtain the hardness using the formula

$$\eta = \int \frac{\delta^2 F}{\delta\rho(\vec{r}')\delta\rho(\vec{r})} f(\vec{r})f(\vec{r}') d\vec{r} d\vec{r}'. \text{ Find the expression of the hardness}$$

kernel for $F[\rho] = T_{TF}[\rho] + J[\rho] + E_{XC}^{LDA}[\rho]$ with $T_{TF}[\rho] = c_k \int \rho^{\frac{5}{3}}(\vec{r}) d\vec{r}$ and $E_{XC}^{LDA}[\rho] = c_x \int \rho^{\frac{4}{3}}(\vec{r}) d\vec{r}$.

- 4.15. Prove that the Fukui function is normalized:

$$\int f(\vec{r}) d\vec{r} = 1$$

- 4.16. From the definitions of the softness and local softness prove that:

$$S = \int s(\vec{r}) d\vec{r} \text{ and} \\ s(\vec{r}) = f(\vec{r})S$$

- 4.17. Prove the following relationship between the exchange-correlation energy per particle and the exchange-correlation potential:

$$v_{xc} = \frac{\delta(\rho(\vec{r})\varepsilon_{xc}[\rho])}{\delta\rho(\vec{r})}$$

- 4.18. In the Slater functional, the exchange energy is given by:

$$E_X = \int \rho^{\frac{4}{3}} f(x) d\vec{r} \text{ with } x = \frac{|\nabla\rho(\vec{r})|}{\rho^{\frac{4}{3}}(\vec{r})}$$

According to this expression, the exchange-correlation energy per particle is given by:

$$\varepsilon_X = \rho^{\frac{1}{3}}(\vec{r})f(x)$$

In the expression corresponding to the LDA functional:

$$\varepsilon_X^{LDA} = -\frac{3}{4} \left[\frac{3}{\pi} \right]^{\frac{1}{3}} \rho^{\frac{1}{3}}(\vec{r})$$

Taking into account that $\lim_{r \rightarrow \infty} \rho(r) = e^{-ar}$ prove that $\lim_{r \rightarrow \infty} \varepsilon_X^{LDA} = 0$

Consider now the following possibilities for the $f(x)$ function:

$$f^{GGA}(x) = -\frac{x}{6 \ln x}; f^{GGA}(x) = -\frac{\beta x^2}{1 + 6\beta x \ln x};$$

$$f^{GGA}(x) = -\frac{\beta x^2}{1 + 6\beta x \sinh^{-1} x}$$

Show that in these three cases: $\lim_{r \rightarrow \infty} \varepsilon_X^{GGA} = -\frac{1}{2r}$ (correct asymptotic behaviour).

The latter $f(x)$ function is the one used in the Becke-88 exchange potential with $\beta=0.0042$ (A.D. Becke Phys. Rev. A 38 (1988) 3098).

- 4.19. Prove that in an approximate density $\tilde{\rho}(\vec{r})$ obtained from the expansion by means of an auxiliary basis functions $\{f_i\}$:

$$\rho(\vec{r}) \cong \tilde{\rho}(\vec{r}) = \sum_i^{N_f} a_i f_i(\vec{r})$$

the coefficients $\{a_i\}$ that minimize the integral quadratic error

$$\int (\rho(\vec{r}) - \tilde{\rho}(\vec{r}))^2 d\vec{r}$$

with the constraint that the approximated density should integrate to the total number of electrons, $\int \tilde{\rho}(\vec{r}) d\vec{r} = N_e$, are obtained from the equation:

$$a = S^{-1}(t + \lambda n)$$

where:

$$S_{ij} = \int f_i(\vec{r}) f_j(\vec{r}) d\vec{r}$$

$$t_i = \int \rho_i(\vec{r}) f_i(\vec{r}) d\vec{r}$$

$$n_i = \int f_i(\vec{r}) d\vec{r}$$

$$\lambda = \frac{N_e - nS^{-1}t}{nS^{-1}n}$$

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