Appendix 2.

Theoretical background of computational methods

2.1 Quantum chemistry[1]

The starting point of the following overview is the Schrödinger equation in its time dependent and time independent forms (2.1.1) and (2.1.2) respecively

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} \hat{H} \Psi \tag{2.1.1}$$

$$\hat{H}\psi = E\psi \tag{2.1.2}$$

where the wave functions Ψ and ψ are functions of all coordinates of the relevant system and Ψ is also a function of time. In our case of a molecular Hamiltonian $\hat{H}$ is given by

$$\hat{H} = -\frac{\hbar^2}{2}\sum_I \frac{1}{m_I}\nabla_I^2 - \frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_I\sum_{J>I}\frac{Z_I Z_J e^2}{r_{IJ}} - \sum_I\sum_i\frac{Z_I e^2}{r_{iI}} + \sum_j\sum_{i>j}\frac{e^2}{r_{ij}} \tag{2.1.3}$$

where I and J refer to the nuclei i and j refer to electrons. The first term in (2.1.3) is the operator of the kinetic energy[2] of the nuclei. The second term is the operator of the kinetic energy of the electrons. The third term is the potential energy of repulsions between the nuclei, r_{IJ} is the distance between the nuclei I and J with atomic numbers Z_I and Z_J. The fourth term is the potential energy of the attractions between the electrons and the nuclei and r_{iI} is the distance between electron i and nucleus I. The last term is the potential energy of the repulsions between the electrons, r_{ij} is the distance between electrons i and j.

The **_Born-Oppenheimer approximation_** simplifies the general molecular problem by separating nuclear and electronic motions. This approximation is reasonable since the mass of a typical nucleus is thousands of times greater than that of an electron. The nuclei move really slowly with respect to the electrons. Thus, the electronic motion can be described as occurring in a field of fixed nuclei.

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[1] This section in the theoretical background is based on references [1-4].

[2] $\nabla_i = \dfrac{\partial^2}{\partial x_i^2} + \dfrac{\partial^2}{\partial y_i^2} + \dfrac{\partial^2}{\partial z_i^2}$

We can use the Born-Oppenheimer approximation to construct an electronic Hamiltonian, which neglects the kinetic energy term of the nuclei,

$$\hat{H}^{elec} = -\frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_I\sum_{J>I}\frac{Z_IZ_Je^2}{r_{IJ}} - \sum_I\sum_i\frac{Z_Ie^2}{r_{iI}} + \sum_j\sum_{i>j}\frac{e^2}{r_{ij}} \qquad (2.1.4)$$

This Hamiltonian is used in the Schrödinger equation describing the motion of the electrons in the field of the fixed nuclei:

$$\hat{H}^{elec}\psi^{elec} = E^{eff}\psi^{elec} \qquad (2.1.5)$$

Solving this equation for the electronic wave function will produce the effective-nuclear potential function E^{eff} that depends on the nuclear coordinates and describes the potential energy surface of the system. For bond electronic problem, ψ should satisfy two requirements: antisymmetricity and normalization. ψ should change sign when two electrons of the molecule interchange and the integral of ψ over all space should be equal to the number of electrons of the molecule.

In what follows, we briefly review some technical details concerning the numerical solution of the time independent Schrödinger equation for molecular systems.

2.1.1 Molecular orbital theory

Electrons can have spin up $+1/2$ or down $-1/2$. Most calculations are closed shell calculations, using doubly occupied orbitals, holding two electrons of opposite spins. We define two functions, α and β as follows:

$$\begin{aligned}\alpha(\uparrow) &= 1, \ \alpha(\downarrow) = 0\\ \beta(\uparrow) &= 0, \ \beta(\downarrow) = 1\end{aligned} \qquad (2.1.6)$$

Molecular orbital theory approximates ψ the molecular wave function as a antisymmetrized product of orthonormal spatial one-electron functions (or "molecular orbitals")

$$\psi = \hat{A}(f_1, f_2, ...) \qquad (2.1.7)$$

where $\hat{A}$ is the antisymmetrization operator and

$$f_i = \phi_i(x_i, y_i, z_i)\sigma_k \qquad (2.1.8)$$

where $k = \pm 1/2$, $\sigma_{1/2} = \alpha$, $\sigma_{-1/2} = \beta$ and ϕ_i satisfies (2.1.9).

$$\int \phi_i^* \phi_i d\tau = 1$$

$$\int \phi_i^* \phi_j d\tau = 0; \quad i \neq j \qquad (2.1.9)$$

The antisymmetrization operator is defined as the operator that antisymmetrizes a product of n one-electron functions and multiplies them by $(n!)^{-1/2}$. This can be represented as the determinant

$$\Psi = (n!)^{-1/2} \begin{vmatrix} \phi_1(\vec{x}_1)\alpha(1) & \phi_1(\vec{x}_1)\beta(1) & \phi_2(\vec{x}_1)\alpha(1) & \phi_2(\vec{x}_1)\beta(1) & ... & \phi_{n/2}(\vec{x}_1)\beta(1) \\ \phi_1(\vec{x}_2)\alpha(2) & \phi_1(\vec{x}_2)\beta(2) & \phi_2(\vec{x}_2)\alpha(2) & \phi_2(\vec{x}_2)\beta(2) & ... & \phi_{n/2}(\vec{x}_2)\beta(2) \\ ... & & & & & ... \\ \phi_1(\vec{x}_n)\alpha(n) & \phi_1(\vec{x}_n)\beta(n) & \phi_2(\vec{x}_n)\alpha(n) & \phi_2(\vec{x}_n)\beta(n) & ... & \phi_{n/2}(\vec{x}_n)\beta(n) \end{vmatrix}$$

$$(2.1.10)$$

The molecular orbitals themselves are approximated as linear combinations of a pre-defined set of one-electron functions centered on the atomic nuclei and so bear some resemblance to atomic orbitals. A particular molecular orbital is then written in the form

$$\phi_i = \sum_{s=1}^{b} c_{si} \chi_s \qquad (2.1.11)$$

where c_{si} are the ***molecular orbital-expansion coefficients*** that are to be found and the basis functions $\chi_1,...,\chi_b$ are chosen to be normalized.

2.1.2 <u>The variational principle</u>

The variational principle states that given a system whose Hamiltonian operator $\hat{H}$ is time independent and whose lowest energy eigenvalue is E_0, if ϕ is any normalized well-behaved function of the coordinates of the system's particles that satisfies the boundary conditions of the problem, then

$$\int \phi^* \hat{H} \phi d\tau \geq E_0$$

Thus, the problem becomes one of finding the set of the coefficients c_{si} of Eq. (2.1.11) that minimize the energy of the resultant wave function.

2.1.3 The Hartree-Fock method

We shall restrict ourselves to closed shell configurations, for such cases, a single Slater determinant is sufficient to describe the molecular wave function. Using the variational principle within this framework lead to the restricted HF theory. The Hartree-Fock energy for molecules with only closed shells is

$$E_{HF} = 2\sum_{i=1}^{n/2} H_{ii}^{core} + \sum_{i=1}^{n/2}\sum_{j=1}^{n/2}(2J_{ij} - K_{ij}) + V_{NN} \qquad (2.1.12)$$

$$H_{ii}^{core} \equiv \left\langle \phi_i(1)\left|\hat{H}^{core}(1)\right|\phi_i(1)\right\rangle = \left\langle \phi_i(1)\left|-\frac{1}{2}\nabla_1^2 - \sum_I Z_I / r_{1I}\right|\phi_i(1)\right\rangle \qquad (2.1.13)$$

$$J_{ij} \equiv \left\langle \phi_i(1)\phi_j(2)\left|1/r_{12}\right|\phi_i(1)\phi_j(2)\right\rangle, \quad K_{ij} \equiv \left\langle \phi_i(1)\phi_j(2)\left|1/r_{12}\right|\phi_j(1)\phi_i(2)\right\rangle \qquad (2.1.14)$$

where

$$V_{NN} = \sum_I \sum_{J>I} \frac{Z_I Z_J e^2}{r_{IJ}} \qquad (2.1.15)$$

and where

$$\hat{H}^{core}(1) \equiv -\frac{1}{2}\nabla_1^2 - \sum_I \frac{Z_I}{r_{1I}} \qquad (2.1.16)$$

$\hat{H}^{core}(1)$ is the ***one-electron core Hamiltonian***, which is the sum of the kinetic-energy operator for electron 1 and the potential-energy operator for the attractions between electron 1 and the nuclei. The sums over i and j are over the $n/2$ occupied spatial orbitals ϕ_i of the n-electron molecule. The ***Coulomb integrals*** J_{ij} and the ***exchange integrals*** K_{ij} are associated with electron-electron interaction and involve integrals over the coordinates of two electrons.

The Hartree-Fock method uses the variational principle and looks for those orbitals ϕ_i that minimize E_{HF}. Each molecular orbital is taken to be normalized:

$$\left\langle \phi_i(1) \,|\, \phi_i(1)\right\rangle = 1. \qquad (2.1.17)$$

Moreover, for computational convenience the molecular orbitals are taken to be orthogonal:

$$\left\langle \phi_i(1) \,|\, \phi_j(1)\right\rangle = 0 \qquad \text{for } i \neq j \qquad (2.1.18)$$

One finds that the closed-shell orthogonal Hartree-Fock molecular orbitals satisfy

$$\hat{F}(1)\phi_i(1) = \varepsilon_i\phi_i(1) \tag{2.1.19}$$

where ε_i is the orbital energy and where the **(Hartree-) Fock operator** $\hat{F}$ is

$$\hat{F}(1) = \hat{H}^{core}(1) + \sum_{j=1}^{n/2}\left[2\hat{J}_j(1) - \hat{K}_j(1)\right] \tag{2.1.20}$$

The **Coulomb operator** $\hat{J}_j$ and the **exchange operator** $\hat{K}_j$ are defined by

$$\hat{J}_j(1)f(1) = f(1)\int\left|\phi_j(2)\right|^2\frac{1}{r_{12}}dv_2$$

$$\hat{K}_j(1)f(1) = \phi_j(1)\int\frac{\phi_j^*(2)f(2)}{r_{12}}dv_2 \tag{2.1.21}$$

where f is an arbitrary function, the integrals are definite integrals over all space, $\hat{J}_j(1)$ is the potential energy of interaction between electron 1 and a *smeared-out electron* with electronic density $-\left|\phi_j(2)\right|^2$; the factor 2 in (2.1.20) occurs because there are two electrons in each spatial orbital. The exchange operator has no simple physical interpretation but arises from the requirement that the wave function must be antisymmetric with respect to electron exchange.

To obtain expression for the orbital energies ε_i, we multiply (2.1.19) by $\phi_i^*(1)$ and integrate over all space. Using the fact that ϕ_i is normalized and using the fact that the Coulomb and exchange integrals can be written as

$$J_{ij} = \left\langle\phi_i(1)\,|\,\hat{J}_j(1)\,|\,\phi_i(1)\right\rangle \tag{2.1.22}$$

and

$$K_{ij} = \left\langle\phi_i(1)\,|\,\hat{K}_j(1)\,|\,\phi_i(1)\right\rangle \tag{2.1.23}$$

we obtain

$$\varepsilon_i = \int\phi_i^*(1)\hat{F}(1)\phi_i(1)dv_1 = H_{ii}^{core} + \sum_{j=1}^{n/2}\left[2J_{ij} - K_{ij}\right] \tag{2.1.24}$$

The spatial molecular orbitals are expanded as linear combinations of a set of local one-electron basis functions χ_s

$$\phi_i = \sum_{s=1}^{b} c_{si} \chi_s \qquad (2.1.25)$$

To avoid confusion, we shall use the letters r, s, t, u to label the basis functions χ and the letters i, j, k, l to label molecular orbitals ϕ_i. Substitution of the expansion (2.1.25) into the Hartree-Fock equations (2.1.19) gives

$$\sum_s c_{si} \hat{F} \chi_s = \varepsilon_i \sum_s c_{si} \chi_s \qquad (2.1.26)$$

Multiplication by χ_r^* and integration gives

$$\sum_{s=1}^{b} c_{si}(F_{rs} - \varepsilon_i S_{rs}) = 0, \qquad r = 1, 2, ..., b \qquad (2.1.27)$$

$$\text{and} \qquad F_{rs} \equiv \left\langle \chi_r \left| \hat{F} \right| \chi_s \right\rangle, \qquad S_{rs} \equiv \left\langle \chi_r | \chi_s \right\rangle \qquad (2.1.28)$$

For a nontrivial solution, we must have

$$\det(F_{rs} - \varepsilon_i S_{rs}) = 0 \qquad (2.1.29)$$

Since the F_{rs} integrals depend on the orbitals ϕ_i (throughout the dependence of $\hat{F}$ on the $\phi_i's$), which in turn depend on the unknown coefficients c_{si}, the *(Hartree-Fock) Roothaan equations* (2.1.27) must be solved by an iterative process. One starts with guesses for the occupied molecular orbitals expressions as linear combinations of basis functions. This initial set of molecular orbitals is used to compute the Fock operator $\hat{F}$ from (2.1.20) and (2.1.21). The matrix elements (2.1.28) are computed and the secular equation (2.1.29) is solved to give an initial set of ε_i's. These ε_i's are used to solve (2.1.27) for an improved set of coefficients, giving an improved set of molecular orbitals, which are then used to compute an improved $\hat{F}$ and so on. One continues until no further improvement in molecular orbitals coefficients and energies occurs from one cycle to the next.

A Hartree-Fock wave function takes into account the interactions between electrons only in an average way. Actually, we must consider the instantaneous interactions between electrons. Since electrons repel each other they tend to keep out of each other's way. The motions of electrons are correlated with each other, and we speak about *electron correlation*. One way to include correlation is by using the density functional theory.

2.1.4 Density Functional theory (DFT)

2.1.4.1 Electron probability density

The electronic wave function ψ of an n-electron molecule is a function of the spatial and spin coordinates of the electrons of the molecule. We know that

$$\left| \psi\left(x_1,...,z_n, m_{s1},..., m_{sn}\right)\right|^2 dx_1 dy_1 dz_1....dx_n dy_n dz_n \qquad (2.1.30)$$

is the probability of simultaneously finding electron 1 with spin m_{s1} in the volume $dx_1 dy_1 dz_1$ at (x_1, y_1, z_1), electron 2 with spin m_{s2} in the volume $dx_2 dy_2 dz_2$ at (x_2, y_2, z_2) and so on. The probability density ρ of finding an electron in the point (x, y, z) is

$$\rho(x, y, z) = n \sum_{all\ m_s} \int...\int \left|\psi(x, y, z, x_2,..., z_n, m_{s1},..., m_{sn})\right|^2 dx_2...dz_n \qquad (2.1.31)$$

Let $B(\vec{r}_i)$ be a function of the spatial coordinates (x_i, y_i, z_i) of electron i. For an n-electron molecule, consider the average value

$$\left\langle \psi \left| \sum_{i=1}^{n} B(\vec{r}_i) \right| \psi \right\rangle = \int \psi * \sum_{i=1}^{n} B(\vec{r}_i) \psi d\tau = \sum_{i=1}^{n} \int |\psi|^2 B(\vec{r}_i) d\tau \qquad (2.1.32)$$

Since the electrons are indistinguishable, each term in the sum $\sum_i \int |\psi|^2 B d\tau$ must have the same value. Hence,

$$\left\langle \psi \left| \sum_{i=1}^{n} B(\vec{r}_i) \right| \psi \right\rangle = \int n |\psi|^2 B(\vec{r}_1) d\tau \qquad (2.1.33)$$

Since $B(\vec{r}_1)$ depends only on x_1, y_1, z_1, we can integrate over the spatial coordinates of electrons 2 to n and sum over all spin coordinates. From (2.1.31), this produces the electron probability density $\rho(\vec{r}_1)$. Therefore,

$$\left\langle \psi \left| \sum_{i=1}^{n} B(\vec{r}_i) \right| \psi \right\rangle = \int \rho(\vec{r}_1) B(\vec{r}_1) d\vec{r}_1 \qquad (2.1.34)$$

The subscript 1 on the integration variables is not needed, and the final result is

$$\int \psi^* \sum_{i=1}^{n} B(\vec{r}_i) \psi d\tau = \int \rho(\vec{r}) B(\vec{r}) d\vec{r} \qquad (2.1.35)$$

where the integration is over the three spatial coordinates x, y, z.

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2.1.4.2 The Hohenberg-Kohn theorem

In 1964, Hohenberg and Kohn[3] proved that for molecules with a nondegenerate ground state, all the ground-state molecular electronic properties are uniquely determined by the ground state probability density $\rho_0(\vec{r})$ where

$$\rho_0(\vec{r}) = n \sum_{all\ m_s} \int...\int \left| \psi_0(\vec{r}, \vec{r}_2,...,\vec{r}_n, m_{s1},...,m_{sn}) \right|^2 d\vec{r}_2 \cdots d\vec{r}_n \qquad (2.1.36)$$

and ψ_0 is the ground state electronic wave function of an n-electron molecule. One says that the ground state electronic energy E_0 is a functional of ρ_0 and writes $E_0 = E_0[\rho_0]$, where the square brackets denote a functional relation. ***Density Functional Theory*** (DFT) attempts to calculate E_0 and other molecular properties from the ground state electron density ρ_0.

2.1.4.3 The Hohenberg-Kohn variational theorem

E_0 and ψ_0 are the ground state eigenvalue and eigenfunction of the electronic Hamiltonian defined for a given nuclear configuration

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 + \sum_{i=1}^{n} v(\vec{r}_i) + \sum_j \sum_{i>j} \frac{1}{r_{ij}} = \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee} \qquad (2.1.37)$$

where

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2, \quad \hat{V}_{Ne} = \sum_{i=1}^{n} v(\vec{r}_i), \quad \hat{V}_{ee} = \sum_j \sum_{i>j} \frac{1}{r_{ij}} \qquad (2.1.38)$$

and where

$$v(\vec{r}_i) = -\sum_I \frac{Z_I}{r_{iI}} \qquad (2.1.39)$$

Taking the average of the purely electronic Hamiltonian for the ground state, we have

$$E_0 = \left\langle \psi_0 \left| \hat{T} \right| \psi_0 \right\rangle + \left\langle \psi_0 \left| \hat{V}_{Ne} \right| \psi_0 \right\rangle + \left\langle \psi_0 \left| \hat{V}_{ee} \right| \psi_0 \right\rangle = \bar{T} + \bar{V}_{Ne} + \bar{V}_{ee} \qquad (2.1.40)$$

According to the first theorem of Hohenberg and Kohn, each of the average values of this equation is a molecular property determined by the ground state electronic wave

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[3] See Ref. [5].

function, which, in turn, is determined by $\rho_0(\vec{r})$. Therefore, each of these averages is a functional of ρ_0:

$$E_0 = E_v\left[\rho_0\right] = \overline{T}\left[\rho_0\right] + \overline{V}_{Ne}\left[\rho_0\right] + \overline{V}_{ee}\left[\rho_0\right] \qquad (2.1.41)$$

where

$$E_v = E_v[\rho] \equiv \overline{T}[\rho] + \overline{V}_{Ne}[\rho] + \overline{V}_{ee}[\rho] \qquad (2.1.42)$$

Now, we can use (2.1.35) to get

$$\overline{V}_{Ne} = \left\langle \psi_0 \left| \sum_{i=1}^{n} v(\vec{r}_i) \right| \psi_0 \right\rangle = \int \rho_0(\vec{r}) v(\vec{r}) d\vec{r} \qquad (2.1.43)$$

where $v(\vec{r})$ is the nuclear attraction potential energy function for an electron located at point $\vec{r}$. Thus $\overline{V}_{Ne}[\rho_0]$ is known but the functionals $\overline{T}[\rho_0]$ and $\overline{V}_{ee}[\rho_0]$ are unknown. We have

$$E_0 = E_v\left[\rho_0\right] = \int \rho_0(\vec{r}) v(\vec{r}) d\vec{r} + \overline{T}\left[\rho_0\right] + \overline{V}_{ee}\left[\rho_0\right] = \int \rho_0(\vec{r}) v(\vec{r}) d\vec{r} + F\left[\rho_0\right]$$

$$(2.1.44)$$

where

$$F\left[\rho_0\right] \equiv \overline{T}\left[\rho_0\right] + \overline{V}_{ee}\left[\rho_0\right] \qquad (2.1.45)$$

To turn (2.1.44) from a formal relation to a practical tool, we need a second theorem proven by Hohenberg and Kohn, and an approach developed by Kohn and Sham.

Hohenberg and Kohn proved that for every density function $\rho(\vec{r})$ that satisfies

$$\int \rho(\vec{r}) d\vec{r} = n \qquad (2.1.46)$$

and

$$\rho(\vec{r}) \geq 0 \qquad \text{for all } \vec{r} \qquad (2.1.47)$$

the following inequality holds:

$$E_0 \leq E_v\left[\rho\right] \qquad (2.1.48)$$

where E_v is the energy functional in (2.1.44). Since $E_0 = E_v[\rho_0]$, where ρ_0 is the true ground state electron density, *the true ground state electron density minimizes the energy functional* $E_v[\rho]$.

2.1.4.4 The Kohn-Sham method

In 1965, Kohn and Sham[4] devised a practical method for finding ρ_0 and for finding E_0 from ρ_0. Kohn and Sham considered a fictitious reference system (denoted by subscript s) of n noninteracting electrons, which experience the same external potential energy function $v_s(\vec{r}_i)$, where $v_s(\vec{r}_i)$ is such as to make the ground state electron probability density $\rho_s(\vec{r})$ of the reference system equal to the exact ground state electron probability density $\rho_0(\vec{r})$ of the molecule we are interested in;

$$\rho_s(\vec{r}) = \rho_0(\vec{r}) \tag{2.1.49}$$

Since Hohenberg and Kohn proved that the ground state probability density function determines the external potential, once $\rho_s(\vec{r})$ is defined, $v_s(\vec{r}_i)$ is uniquely determined.

The Hamiltonian of the reference system is

$$\hat{H}_s = \sum_{i=1}^{n} \left[-\frac{1}{2} \nabla_i^2 + v_s(\vec{r}_i) \right] \equiv \sum_{i=1}^{n} \hat{h}_i^{KS} \tag{2.1.50}$$

where

$$\hat{h}_i^{KS} \equiv -\frac{1}{2} \nabla_i^2 + v_s(\vec{r}_i) \tag{2.1.51}$$

$\hat{h}_i^{KS}$ is the **one electron Kohn-Sham Hamiltonian**. The ground state wave function $\psi_{s,0}$ of the reference system is the antisymmetrized product (Slater determinant) of the lowest energy **Kohn-Sham spin orbitals** u_i^{KS} of the reference system, where the spatial part $\theta_i^{KS}(\vec{r}_i)$ of each spin-orbital is an eigenfunction of $\hat{h}_i^{KS}$, that is

$$\psi_{s,0} = \left| u_1 u_2 \cdots u_n \right|, \qquad u_i = \theta_i^{KS}(\vec{r}_i)\sigma_i \tag{2.1.52}$$

$$\hat{h}_i^{KS}\theta_i^{KS} = \varepsilon_i^{KS}\theta_i^{KS} \tag{2.1.53}$$

and σ_i is a spin function (either α or β) and ε_i^{KS}'s are the **Kohn-Sham orbital energies**.

Let $\Delta\overline{T}$ be defined by

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[4] See Ref. [6]

$$\Delta \overline{T}[\rho] \equiv \overline{T}[\rho] - \overline{T}_s[\rho] \qquad (2.1.54)$$

where, for convenience, the zero subscript on ρ is omitted. $\Delta \overline{T}$ is the difference in the average ground state electronic kinetic energy between the molecule and the reference system. Let

$$\Delta \overline{V}_{ee}[\rho] \equiv \overline{V}_{ee}[\rho] - \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \qquad (2.1.55)$$

where r_{12} is the distance between points (x_1, y_1, z_1) and (x_2, y_2, z_3). The quantity $\frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$ is the classical expression for the electrostatic interelectronic repulsion energy if the electrons where smeared out in a continuous distribution of charge with electron density ρ.

With the definitions (2.154) and (2.1.55), (2.1.44) becomes

$$E_v[\rho] = \int \rho(\vec{r})v(\vec{r})d\vec{r} + \overline{T}_s[\rho] + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + \Delta \overline{T}[\rho] + \Delta \overline{V}_{ee}[\rho]$$

$$(2.1.56)$$

The functionals $\Delta \overline{T}$ and $\Delta \overline{V}_{ee}$ are unknown. Defining the **exchange-correlation energy functional** $E_{xc}[\rho]$ by

$$E_{xc}[\rho] \equiv \Delta \overline{T}[\rho] + \Delta \overline{V}_{ee}[\rho] \qquad (2.1.57)$$

we have

$$E_0 = E_v[\rho] = \int \rho(\vec{r})v(\vec{r})d\vec{r} + \overline{T}_s[\rho] + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho] \quad (2.1.58)$$

Since the wave function of the reference system is a Slater determinant of u_i^{KS}, we have

$$\rho = \rho_s = \sum_{i=1}^{n} \left| \theta_i^{KS} \right|^2 \qquad (2.1.59)$$

Thus, (2.1.58) becomes

$$E_0 = -\sum_\alpha Z_\alpha \int \frac{\rho(\vec{r}_1)}{r_{1\alpha}} d\vec{r}_1 - \frac{1}{2}\sum_{i=1}^{n} \left\langle \theta_i^{KS}(1) \left| \nabla_1^2 \right| \theta_i^{KS}(1) \right\rangle + \frac{1}{2}\int\int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho]$$

$$(2.1.60)$$

Now, we need to find θ_i^{KS} and $E_{xc}[\rho]$. The Hohenberg-Kohn variational theorem tells us that we can find the ground state energy by varying ρ so as to minimize $E_v[\rho]$. Equivalently, instead of varying ρ, we can vary θ_i^{KS}. It is convenient to constrain θ_i^{KS}'s to be orthonormal. Kohn and Sham orbitals that minimize the expression (2.1.60) satisfy:

$$\left[-\frac{1}{2}\nabla_1^2 - \sum_\alpha \frac{Z_\alpha}{r_{1\alpha}} + \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + v_{xc}(1) \right] \theta_i^{KS}(1) = \varepsilon_i^{KS}\theta_i^{KS}(1) \qquad (2.1.61)$$

where $v_{xc}(1)$ is defined by (2.1.62) and the **exchange-correlation potential** v_{xc} is the **functional derivative**[5] of the exchange potential energy E_{xc}:

$$v_{xc}(\vec{r}) \equiv \frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})} \qquad (2.1.62)$$

Eq. (2.1.61) is a single one-electron eigenvalue problem that is easily solved in principle, however, both E_{xc} in the expression (2.1.60) and v_{xc} in (2.1.61) and (2.1.62) are unknown. Several approximations to E_{xc} are discussed below.

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[5] The following formula allows one to find the functional derivative of most functionals occur in DFT. For functionals defined by

$$F[\rho] = \int_e^f \int_c^d \int_a^b g(x, y, z, \rho, \rho_x, \rho_y, \rho_z) dx\, dy\, dz$$

where ρ is a functional of x, y and z that vanishes at the limits of the integral, and where $\rho_x \equiv (\partial\rho/\partial x)_{y,z}$ etc., the functional derivative can be shown to be given by

$$\frac{\delta F}{\delta\rho} = \frac{\partial g}{\partial\rho} - \frac{\partial}{\partial x}\frac{\partial g}{\partial\rho_x} - \frac{\partial}{\partial y}\frac{\partial g}{\partial\rho_y} - \frac{\partial}{\partial z}\frac{\partial g}{\partial\rho_z}$$

2.1.4.5 The exchange and correlation energy functionals

It is a common practice to write E_{xc} as the sum of an ***exchange-energy functional*** E_x and a ***correlation-energy functional*** E_c:

$$E_{xc} = E_x + E_c \qquad (2.1.63)$$

and to look for approximations for each of these contributions. For example, for closed-shell molecules E_x may be defined by formula

$$E_x \equiv -\frac{1}{4}\sum_{i=1}^{n}\sum_{j=1}^{n}\left\langle \theta_i^{Ks}(1)\theta_j^{KS}(2)\middle|1/r_{12}\middle|\theta_j^{Ks}(1)\theta_i^{KS}(2)\right\rangle \qquad (2.1.64)$$

and the correlation-energy functional, defined by

$$E_c \equiv E_{xc} - E_x \qquad (2.1.65)$$

is evaluated by one of the currently available models (such as the VWN[6]). This procedure usually gives poor results for molecular properties. Thus, in practice, it is better to model both E_x and E_c because this leads to cancellation of errors and better results. The simplest example is the ***Local density Approximation*** (LDA)**.**

2.1.4.6 The local density approximation (LDA)

Hohenberg and Kohn showed that if ρ varies extremely slowly with position, then $E_{xc}[\rho]$ is accurately given by

$$E_{xc}^{LDA}[\rho] = \int \rho(\vec{r})\varepsilon_{xc}(\rho)d\vec{r} \qquad (2.1.66)$$

where the integral is all over space and $\varepsilon_{xc}(\rho)$ is the exchange plus correlation energy per electron in a homogeneous electron gas with electron density ρ. Good approximation for ε_{xc} are available. In particular, separating it to its exchange and correlation components

$$\varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho) \qquad (2.1.67)$$

the exchange contribution is known explicitly

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[6] See below.

$$\varepsilon_x(\rho) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\left(\rho(\vec{r})\right)^{1/3} \tag{2.1.68}$$

and the correlation part can be readily calculated as was done by Vosko, Wilk and Nusair[7]. We will not reproduce their result here, and simply write

$$\varepsilon_c(\rho) = \varepsilon_c^{VWN}(\rho) \tag{2.1.69}$$

where ε_c^{VWN} is a known function.

Taking the functional derivative of E_{xc}^{LDA}, one finds

$$v_{xc}^{LDA} = \frac{\delta E_{xc}^{LDA}}{\delta \rho} = \varepsilon_{xc}(\rho(\vec{r})) + \rho(\vec{r})\frac{\partial \varepsilon_{xc}(\rho)}{\partial \rho} \tag{2.1.70}$$

Kohn and Sham suggested the use of (2.1.66) and (2.1.70) as approximations to E_{xc} and v_{xc} in (2.1.60) and (2.1.57). This procedure is called the local density approximation. To summarize, in this approximation

$$v_{xc}^{LDA} = v_x^{LDA} + v_c^{LDA}, \qquad v_x^{LDA} = -\left[(3/\pi)\rho(\vec{r})\right]^{1/3}, \quad v_c^{LDA} = v_c^{VWN} \tag{2.1.71}$$

$$E_x^{LDA} \equiv \int \rho \varepsilon_x d\vec{r} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int\left[\rho(\vec{r})\right]^{4/3}d\vec{r} \tag{2.1.72}$$

For open-shell molecules and molecular geometries near dissociation, *__the Local-Spin-Density Approximation__* (LSDA) gives better results than the LDA. Whereas in the LDA, electrons with opposite spins paired with each other have the same KS orbital, the LSDA allows such electrons to have different spatial KS orbitals $\theta_{i\alpha}^{KS}$ and $\theta_{i\beta}^{KS}$. Thus, in LSDA, one deals separately with the electron density $\rho^{\alpha}(\vec{r})$ due to spin-α electrons and density $\rho^{\beta}(\vec{r})$ due to spin-β electrons. The LDA and LSDA are based on uniform electron gas model, which is appropriate for a system where ρ varies slowly with position.

2.1.4.7 <u>Performing Kohn-Sham density functional calculations</u>

How does one do a molecular density functional calculation with E_{xc}^{LDA} (or some other functional)?

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[7] See Vosko, S. H., Wilk, L., and Nusair, M. (1980). *Canadian Journal of Physics*. 58, 1200.

1. One starts with initial guess of ρ, which is usually found by superposing calculated electron densities of the individual atoms at the chosen molecular geometry.

2. From the initial guess of $\rho(\vec{r})$, an initial estimate of $v_{xc}(\vec{r})$ is found from (2.1.70) and (2.1.71).

3. This initial $v_{xc}(\vec{r})$ is used in the Kohn-Sham equations (2.1.61), which are solved for the initial estimate of the KS orbitals. In solving (2.1.61), the θ_i^{KS}'s are usually expanded in terms of a set of basis functions χ_r ($\theta_i^{KS} = \sum_{r=1}^{b} c_{ri}\chi_r$), and the equations that are solves are

$$\sum_{s=1}^{b} c_{si}(h_{rs}^{KS} - \varepsilon_i^{KS} S_{rs}) = 0, \qquad r = 1, 2, ..., b \qquad (2.1.73)$$

where

$$h_{rs}^{KS} = \left\langle \chi_r \left| \hat{h}^{KS} \right| \chi_s \right\rangle, \; S_{rs} \equiv \left\langle \chi_r | \chi_s \right\rangle \qquad (2.1.74)$$

and $\hat{h}^{KS}$ is in (2.1.51) and (2.1.53).

4. The initially found θ_i^{KS}'s are used in (2.1.59) to get an improved electronic density, which is then used to find an improved v_{xc}, which is then used in the KS equations (2.1.61) to find improved KS orbitals, and so on.

5. The iterations continue until there is no further significant change in the density and the KS orbitals.

6. Once the calculation has converged, one can find E_0 from (2.1.60) and other electronic molecular properties.

2.1.4.8 <u>Gradient Corrected hybrid functionals</u>

Functionals that go beyond the LSDA aim to correct the LSDA for the variation of electron density with position. They do this by including the gradients of ρ^α and ρ^β in the integrand. Thus,

$$E_{xc}^{GGA}\left[\rho^{\alpha}, \rho^{\beta}\right] = \int f(\rho^{\alpha}(\vec{r}), \rho^{\beta}(\vec{r}), \nabla\rho^{\alpha}(\vec{r}), \nabla\rho^{\beta}(\vec{r}))d\vec{r} \qquad (2.1.75)$$

where f is some function of spin densities and their gradients. The letters GGA stand for **Generalized Gradient Approximation**. The term **gradient correlated functional** is also used. E_{xc}^{GGA} is usually split into exchange and correlation parts, which are modeled separately:

$$E_{xc}^{GGA} = E_{x}^{GGA} + E_{c}^{GGA} \qquad (2.1.76)$$

Hybrid exchange-correlation functionals are widely used. A Hybrid functional mixes together the formula (2.1.64) for E_x with gradient-corrected E_x and E_c formulas. For example, the popular **B3LYP** (or Becke 3 LYP) hybrid functional (where 3 indicates a three parameter functional) is defined by

$$E_{xc}^{B3LYP} = (1 - a_0 - a_x)E_x^{LSDA} + a_0 E_x^{exact} + a_x E_x^{B88} + (1 - a_c)E_c^{VWN} + a_c E_c^{LYP} \quad (2.1.77)$$

where

$$E_x^{LSDA} = -\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3} \int\left[\left(\rho^{\alpha}\right)^{4/3} + \left(\rho^{\beta}\right)^{4/3}\right]d\vec{r} \qquad (2.1.78)$$

E_x^{exact} (which is sometimes denoted E_x^{HF}, since it uses a Hartree-Fock definition of E_x) is given by (2.1.64), E_x^{B88} is the Becke's 1988 gradient-corrected exchange functional[8], E_c^{VWN} is the Vosko-Wilk-Nusair expression for the LSDA correlation functional[9], E_c^{LYP} is the Lee-Yang-Parr gradient-corrected-correlation functional[10] and the parameter values $a_0 = 0.20$, $a_x = 0.72$ and $a_c = 0.81$, were chosen to give good fits to experimental molecular atomization energies.

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[8] See Ref [7].

[9] See Ref [8].

[10] See Ref [9].

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