

Quantum Chemistry

Lecture 22

Density Functional Theory
Thomas-Fermi Exchange
Correlation Functionals

NC State University

Density Functional Theory (DFT) provides an alternative to Hartree-Fock and post-Hartree-Fock theory. As the name implies, the central feature of the theory is the use of the electron density, rather than molecular orbitals, as the important quantity to be computed. The use of a theory based on the electron density is appealing because of the connection with experiment. For example, electron diffraction can be used to measure the shape electron density. The density is related to the number of electrons.

$$\int \rho(\vec{r})d^3r = N$$

Here, we have used a representation of the 3-dimensional volume element as d^3r because we will consider the individual integrals over each of the electrons in the following. This is equivalent to the $d\tau$, which is the volume element used previously in this text.

DFT methods are based on the Born-Oppenheimer approximation. The nuclei are treated a fixed set of charges, which comprises an external potential, V_{ext} . A stationary electron state can be described by a wave function $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$, which satisfies the Schrodinger equation.

$$\begin{aligned}\hat{H}\Psi &= [\hat{T} + \hat{V} + \hat{U}]\Psi \\ &= \left[\sum_{i=1}^N \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 \right) + \sum_{i=1}^N V(\vec{r}_i) + \sum_{i<j}^N U(\vec{r}_i, \vec{r}_j) \right] \Psi = E\Psi\end{aligned}$$

where, for the N-electron system,

\hat{H} is the Hamiltonian, E is the total energy,

\hat{T} is the kinetic energy,

\hat{V} is the external potential due to the positively charged nuclei

\hat{U} is the electron-electron interaction energy.

From 3N variables to 3 variables

DFT provides an alternative method to post-Hartree-Fock that can include both exchange and correlation in a single method. DFT does this by mapping the many-body problem that includes electron repulsion, onto a single-body problem that lacks the complexity of electron exchange integrals.

The key variable is the electron density $\rho(\vec{r})$, which is given by:

$$\rho(\vec{r}) = N \int d^3 r_2 \int d^3 r_3 \dots \int d^3 r_N \Psi^*(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

This relation can be reversed. Instead of calculating the density from the square of the wave function, it is possible to calculate the ground state wave function, $\Psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ from the density, $\rho_0(\vec{r})$.

DFT assumes the uniqueness of the electron density for a given nuclear conformation

Stated another way, Ψ_0 is a unique functional of ρ_0 .

$$\Psi_0 = \Psi[\rho_0]$$

Therefore, the ground-state expectation value of an observable O is also a functional of ρ_0 . $O[\rho_0] = \langle \Psi[\rho_0] | \hat{O} | \Psi[\rho_0] \rangle$

In particular, the ground-state energy is a functional of ρ_0 .

$$E_0 = E[\rho_0] = \langle \Psi[\rho_0] | \hat{T} + \hat{V} + \hat{U} | \Psi[\rho_0] \rangle$$

where the contribution of the external potential $\langle \Psi[\rho_0] | \hat{V} | \Psi[\rho_0] \rangle$ can be written explicitly in terms of the ground-state density ρ_0 .

DFT uses the variational principle

The variational theorem applies to DFT methods. The energy functional $E[\rho]$ can be solved by application of the Lagrangian method of undetermined multipliers. Initially, one can consider an energy functional that lacks an electron-electron interaction energy term,

$$E_s[\rho_0] = \langle \Psi_s[\rho] | \hat{T} + \hat{V}_s | \Psi_s[\rho] \rangle$$

One can solve the so-called Kohn–Sham equations of this auxiliary non-interacting system,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_s(\vec{r}) \right] \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})$$

which yields the orbitals that reproduce the density of the original many-body system.

DFT uses orbitals to define the density

Just as one can calculate the electron density from the molecular orbitals in HF theory, one can define Kohn-Sham orbitals that comprise the density in DFT. These have the property that

$$\rho(\vec{r}) \equiv \rho_s(\vec{r}) = \sum_i^N |\phi_i(\vec{r})|^2$$

The effective single-particle potential can be written in more detail as

$$V_s(\vec{r}) = V(\vec{r}) + e^2 \int \frac{\rho_s(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' + V_{xc}[\rho_s(\vec{r})]$$

where the second term denotes the so-called Hartree term describing the electron-electron Coulomb repulsion, while the last term V_{xc} is called the exchange-correlation potential.

The Kohn-Sham method for connecting the real and virtual systems

The Kohn-Sham approach is to turn on the interactions using a parameter λ , which can vary from 0 to 1. When $\lambda = 0$ the system consists of non-interacting electrons. On the other hand, when $\lambda = 1$ the system is the real system with the full set of interactions, including exchange and correlation. The Kohn-Sham scheme is summarized in the equation:

$$F_\lambda[\rho] = \langle \Psi_\rho^{min,\lambda} | \hat{T} + \lambda \hat{U} | \Psi_\rho^{min,\lambda} \rangle$$

where $\Psi_\rho^{min,\lambda}$ is the wave function that minimizes the value of the $F_\lambda[\rho]$.

The Kohn-Sham energy partitioning

Now, the assumption is that for any real system with density $\rho(r)$, the non-interacting system has the same ground state density. Thus,

$$F[\rho] = T_s[\rho] + \hat{V}_{coul}[\rho] + E_{xc}[\rho]$$

Application of the variational principle in this case means taking the derivative

$$\frac{\delta E}{\delta \rho(r)} = 0$$

This results in the equation

$$E[\rho] = \int v(r)\rho(r)d^3r + T_s[\rho] + \hat{V}_{coul}[\rho] + E_{xc}[\rho]$$

The Kohn-Sham equations

Using these expressions we can express the Kohn-Sham equations as:

$$\left[-\frac{1}{2} \nabla^2 + v(r) + \int \frac{\rho(r')}{|r - r'|} d^3r' + v_{xc}(r) \right] \phi_i(r) = \varepsilon_i \phi_i(r)$$

It is evident that the exchange-correlation potential, $v_{xc}(r)$ is the crucial term. The essence of DFT is the search for an appropriate form for the exchange-correlation functional that will provide as close as possible to an exact solution. But, the great weakness of the theory is that there is no road map for how to find such a functional.

DFT uses a SCF Approach

V_{xc} includes all the many-particle interactions. Since the Hartree term and V_{xc} depend on $\rho(r)$, which depends on the $\phi_i(r)$, which in turn depend on V_s , the problem of solving the Kohn–Sham equation resembles the self-consistent field method seen HF. Usually one starts with an initial guess for $\rho(r)$ then calculates the corresponding V_s , and solves the Kohn-Sham equations for the $\phi_i(r)$.

From these one calculates a new density and starts again. This procedure is then repeated until convergence is reached.

Adiabatic integration

The major obstacle to implementation of DFT is that the exact functionals for exchange and correlation are not known except for the free electron gas. However, approximations exist which permit the calculation of certain physical quantities quite accurately. We can begin with application of Feynman-Hellman theorem to the system:

$$\frac{\delta F_\lambda[\rho]}{\delta \lambda} = \langle \Psi_\rho^{min,\lambda} | \hat{U} | \Psi_\rho^{min,\lambda} \rangle$$

We can integrate this expression from $\lambda = 0$ to $\lambda = 1$. This is known as adiabatic integration.

Adiabatic integration as a tool

The adiabatic integral represents a method to connect the ideal non-interacting particles assumed by Hohenberg and Kohn with real particles.

$$\int_0^1 \frac{\delta F_\lambda[\rho]}{\delta \lambda} d\lambda = F_1[\rho] - F_0[\rho] = \hat{V}_{coul}[\rho] + E_{xc}[\rho]$$

We can use adiabatic integration to obtain a general prescription for the calculation of the exchange-correlation energy.

$$E_{xc}[\rho] = \langle \Psi_\rho^{min,\lambda} | \hat{U} | \Psi_\rho^{min,\lambda} \rangle - \hat{V}_{coul}[\rho] = \int_0^1 \frac{\delta E_{xc}^\lambda[\rho]}{\delta \lambda} d\lambda$$

Ultimately, this energy depends on the density times a hole functional $h_{xc}(\vec{r}_1, \vec{r}_2)$. The essential feature of the hole functional is to describe the shape and dynamics of the region of repulsion around any electron in the system. After all, correlation is really the detailed description of how electrons do their dance to avoid each other as they move in a pattern dictated by the nuclear charge (i.e. the external potential).

$$E_{xc}[\rho] = \frac{1}{2} \int_0^1 d\lambda \int \int \frac{\rho(\vec{r}_1) h_{xc}^\lambda(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3\vec{r}_1 d^3\vec{r}_2$$

The hole functional can also be treated using adiabatic integration.

$$\bar{h}_{xc}(\vec{r}_1, \vec{r}_2) = \int_0^1 h_{xc}^\lambda(\vec{r}_1, \vec{r}_2) d\lambda$$

Formal treatment of the hole

The hole functional can also be treated using adiabatic integration.

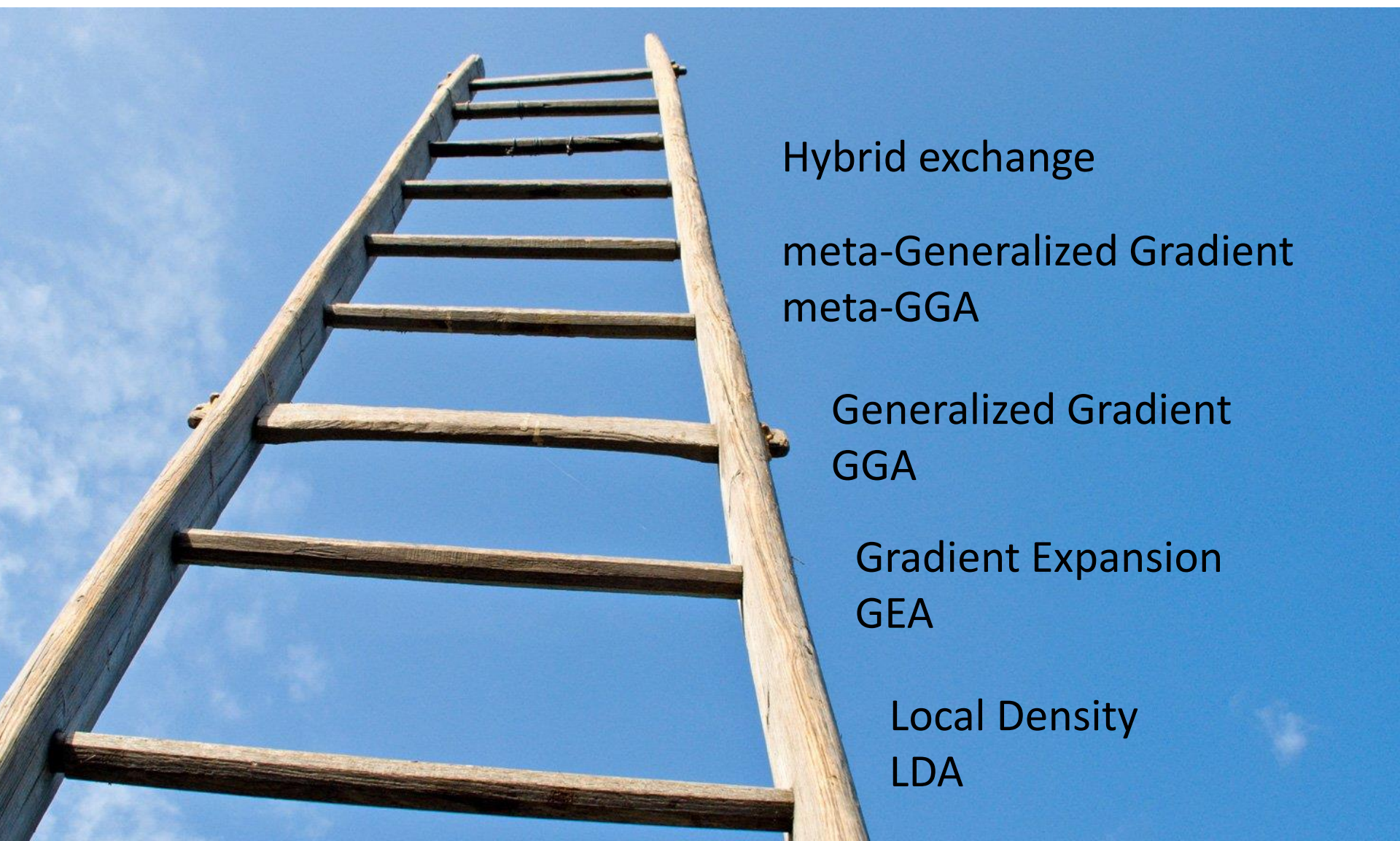
$$\bar{h}_{xc}(\vec{r}_1, \vec{r}_2) = \int_0^1 h^\lambda_{xc}(\vec{r}_1, \vec{r}_2) d\lambda$$

Finally, we end up with a general form of an exchange-correlation functional. The problem is now to find the appropriate hole functional.

$$E_{xc}[\rho] = \frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \bar{h}_{xc}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3\vec{r}_1 d^3\vec{r}_2$$

This form of the equation provides a starting point for the construction of exchange-correlation functionals. The form is that of a function that multiplies the density.

The ladder of density functional approximations



Hybrid exchange

meta-Generalized Gradient
meta-GGA

Generalized Gradient
GGA

Gradient Expansion
GEA

Local Density
LDA

The Local Density Approximation (LDA)

The most widely used approximation is the local density approximation (LDA), where the functional depends only on the density at the coordinate where the functional is evaluated:

$$E_{\text{xc}}^{\text{LDA}}[\rho] = \int \epsilon_{\text{xc}}(\rho) \rho(\vec{r}) d^3r$$

In the LDA the energy and other properties at a point in space are determined by the value of the density at that point in space.

Perdew and Wang LDA

Perdew and Wang define “the exchange-correlation energy E_{XC} as the electrostatic interaction of the electron at r with the density $\rho_{xc}(r, r + u) = \rho_x + \rho_c$ at $r + u$ of the exchange correlation hole that surrounds it.” {Perdew, 1996 #1} In atomic units they give the functional form as

$$E_{xc}[\rho] = \frac{1}{2} \int \rho(\vec{r}) d^3r \int \frac{\rho_{xc}(\vec{r} + \vec{u})}{u} d^3u$$

This functional provides relatively accurate energies, but suffers from relatively poor agreement with molecular structures. As a general rule the LDA is valid for slowly varying density. However, in molecules the density changes are not slowly varying.

Gradient Expansion Approximation (GEA)

The next higher level of theory is the second-order gradient expansion approximation (GEA).

$$E_{xc}^{\text{GEA}}[\rho] = E_{xc}^{\text{LDA}}[\rho] + \sum_{\sigma, \sigma'} \int C_{xc}^{\sigma, \sigma'} \frac{\nabla \rho_{\sigma} \cdot \nabla \rho_{\sigma'}}{\rho_{\sigma}^{2/3} \rho_{\sigma'}^{2/3}} d^3r$$

The GEA is less accurate than the LDA despite the fact that it includes a term containing the gradient. The GEA is no longer a local functional since the second term in Eqn. 11.2.10 depends on the product of gradients at two different locations in space indicated by the indices σ and σ' .

Generalized Gradient Approximation (GGA)

The generalized gradient approximation (GGA) is still local but also takes into account the gradient of the density at the same coordinate:

$$E_{xc}^{GGA}[\rho] = \int \rho(\vec{r}) \epsilon_{xc}(\rho, \nabla\rho) d^3r$$

Good results for molecular geometries and ground-state energies have been achieved using the GGA. Well known functionals that include this level of theory include PBE and BLYP. The GGA approach provides good agreement with molecular structure, but is often criticized for poor agreement with thermochemistry.

meta-Generalized Gradient Approximation (meta-GGA)

To move beyond the GGA functional one can include the second derivative with respect to the density. The second derivative is the Laplacian and this is also the function that gives the kinetic energy. The gradient is still included in these functionals. We will return to these various rungs of the ladder of DFT functionals that increase in complexity. However, first we consider the historical starting point for DFT in order to understand how simple the initial assumptions were. In particular, the notion of a density of a free electron gas used in the late 1920s is a remarkable theoretical innovation. It seems too simple. And yet, it worked quite well for a number of systems.

History of DFT

Thomas-Fermi model

Slater $X\alpha$

Hohenberg-Kohn
Theorems

Kohn-Sham
equations

The Thomas-Fermi Model

The earliest approach to DFT can be found in the Thomas-Fermi model, which was developed independently by both Thomas and Fermi in 1927. They used a statistical model to approximate the distribution of electrons in an atom. The mathematical basis for the theory is based on a model, in which electrons are distributed uniformly in phase space with two electrons in every h^3 of volume. This is the so-called free electron gas. For each element of coordinate space volume d^3r we can fill out a sphere of momentum space up to the Fermi momentum p_f .

$$\frac{4}{3} \pi p_f^3(\vec{r})$$

The Thomas-Fermi Model

The electron density is defined as the number of electrons in coordinate space to that in phase space. This is obtained by multiplying the momentum space by $2/h^3$. The electrons are spin paired, which gives rise to the factor of 2 and the phase space volume element is $1/h^3$. We can understand this definition from the DeBroglie relation, $p = h/\lambda$, which tells us that the previous equation has units of number of electrons per unit volume.

$$\rho(\vec{r}) = \frac{8\pi}{3h^3} p_f^3(\vec{r})$$

The Thomas-Fermi Model

Solving for P_f and substituting into the classical kinetic energy formula then leads directly to a kinetic energy represented as a functional of the electron density:

$$T_{\text{TF}}[\rho] = C_{\text{F}} \int \rho(\vec{r}) \rho^{\frac{2}{3}}(\vec{r}) d^3r = C_{\text{F}} \int \rho^{5/3}(\vec{r}) d^3r$$

and

$$C_{\text{F}} = \frac{3h^2}{10m_e} \left(\frac{3}{8\pi} \right)^{2/3}$$

Limitations of Thomas-Fermi Model

Molecular Bonding Requires Correlation

One can calculate the energy of an atom using this kinetic energy functional combined with the classical expressions for the nuclear-electron and electron-electron interactions (which can both also be represented in terms of the electron density).

Although this was an important first step, the Thomas-Fermi equation's accuracy is limited because the resulting kinetic energy functional is only approximate, and because the method does not attempt to represent the exchange energy. An exchange energy functional was added by Dirac in 1928. However, these functionals do not account for electron correlation.

Weizsacker correction

In 1962, Teller showed that the Thomas-Fermi model cannot describe molecular bonding. This deficiency can be overcome by using an improved kinetic energy function.

An example is the Weizsacker correction:

$$T_W[\rho] = \frac{\hbar^2}{8m_e} \int \frac{|\nabla\rho(\vec{r})|^2}{\rho(\vec{r})} d^3r$$

This correction is a first step in the direction of a gradient approach.

Slater Exchange Functional

Approximately 20 years later Slater recognized the need to derive theory of exchange based on the density for application to solids. Simply put, the HF exchange was too complicated for a calculation in the solid state. Slater's approach begins with the consideration of a lattice and a consideration of the distance over which exchange is expected to occur. This is defined as:

$$\rho V = \rho \left(\frac{3\pi r_0^3}{4} \right) = e$$

where e is the charge on an electron. This expression gives the relation for the limiting radius of interaction

$$r_0 = \left(\frac{4e}{3\pi\rho} \right)^{\frac{1}{3}}$$

This is the radius of the exchange hole or the Fermi hole. Using this definition the exchange potential energy is

$$v_x = 3 \left(\frac{2}{\pi} \right)^{\frac{2}{3}} \frac{e^2}{4\pi\epsilon_0 r_0} F(\eta)$$

Where the function $F(\eta)$ is:

$$F(\eta) = \frac{1}{2} + \frac{1 - \eta^2}{4\eta} \ln \left(\frac{1 - \eta}{1 + \eta} \right)$$

And $\eta = 1$ in the occupied levels, drops to $\frac{1}{2}$ at the Fermi level and goes to zero above the Fermi level. The average value of $F(\eta)$ is $-3/4$. Therefore,

$$v_x = -\frac{9}{4} \left(\frac{2}{\pi} \right)^{\frac{2}{3}} \frac{e^2}{4\pi\epsilon_0 r_0}$$

Substituting in for r_0 and converting to atomic units ($e^2/4\pi\epsilon_0 = 1/2$) we have the exchange potential in terms of the density:

$$v_x = -\frac{9}{4} \left(\frac{2}{\pi}\right)^{\frac{2}{3}} \left(\frac{1}{2}\right) \left(\frac{3\pi}{4}\right)^{\frac{1}{3}} \rho^{\frac{1}{3}} = -\frac{3}{8} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \rho^{\frac{1}{3}}$$

$$E_x[\rho] = C_x \int \rho(\vec{r}_1) v_x(\vec{r}_1) d^3\vec{r}_1$$

To improve the quality of this approximation an adjustable, semi-empirical parameter a was introduced into the pre-factor in the place C_x . This approach gave rise to the X_α or *Hartree-Fock-Slater* (HFS) method. While this method was used in solid state physics it never had much application in chemistry.

The final form of the Slater X_α functional is:

$$E_{X_\alpha}[\rho] = -\frac{9}{8} \left(\frac{3}{\pi}\right)^{1/3} \alpha \int \rho^{4/3}(\vec{r}_1) d^3\vec{r}_1$$

Typical values of α are between 2/3 and 1. It is important to note that the 4/3 power law for the dependence of the exchange interaction on the electron density was also obtained from a different approach using the concept of the uniform electron gas, by Bloch, 1929, and Dirac, 1930.

This approach replaces the non-local and complicated exchange term of Hartree-Fock theory by a simple approximate expression, which depends only on the *local* value of the electron density. Thus, this expression represents a density functional for the exchange energy. This formula was originally explicitly derived as an approximation to the HF scheme, without any reference to density functional theory.

The Wigner-Seitz Radius

Slater's idea was to assume that the exchange hole is spherically symmetric and centered around the reference electron at r_1 . He further assumed that within the sphere the exchange hole density is constant, having minus the value of $\rho(r_1)$, while outside it is zero. Since the Fermi hole is known to contain exactly one elementary charge, the radius of this sphere is then given by

$$r_s = \left(\frac{3}{4\pi\rho(r_1)} \right)^{1/3}$$

The radius r_s is known as the *Wigner-Seitz* radius. It can be interpreted as the average distance between two electrons in a molecule.

Slater Exchange Functional

Electron exchange provides a second aspect of electron interaction that led to applications in DFT. The approach by Slater, 1951, made the electron density the central quantity. This approach was originally constructed as an approximation to the exchange part of the HF scheme, because of the great computational expense. The original formulation did not have DFT in mind. If we write HF exchange in the form of a functional it has the appearance,

$$E_x = \frac{1}{2} \int \frac{\rho(\vec{r}_1)h(\vec{r}_1; \vec{r}_2)}{r_{12}} d^3\vec{r}_1 d^3\vec{r}_2$$

Hence, if we can construct a simple but reasonable approximation to the functional requirement that electrons avoid each other. This is expressed technically as the Fermi hole.

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