

# **CHEM 6353: Density-Functional Theory**

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# Chapter 1

## Theory Fundamentals

### 1.1 Review of Wavefunction Theory

For a general chemical system, the Hamiltonian (in atomic units) is

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_A \frac{Z_A}{r_{iA}} + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

where  $Z_A$  is the nuclear charge,  $r_{iA}$  is the electron-nuclear distance, and  $r_{ij}$  is the electron-electron distance,  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ . This is often re-written as

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i V_i + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

where

$$V_i = - \sum_A \frac{Z_A}{r_{iA}}$$

is the attractive potential for interaction between the nuclei and electron  $i$ .

We generally assume that the wavefunction is a single Slater determinant,

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1 & \phi_2 & \cdots & \phi_N \end{vmatrix}$$

formed from the occupied, real orbitals. A Slater determinant is the simplest possible form that ensures antisymmetry. Then, the (Hartree-Fock) energy is

$$E_{\text{HF}} = \langle \psi | \hat{H} | \psi \rangle = -\frac{1}{2} \sum_i \langle \phi_i | \nabla_i^2 | \phi_i \rangle + \sum_i \langle \phi_i | V_i | \phi_i \rangle + \frac{1}{2} \sum_{i \neq j} \left\langle \psi \left| \frac{1}{r_{ij}} \right| \psi \right\rangle$$

The first two terms are easy to evaluate as they are only 1- $e^-$  integrals, but the last term, consisting of 2- $e^-$  integrals, is more difficult. It is typically split up into the classical Coulomb integrals, describing electron-electron repulsion, and the purely quantum-mechanical exchange integrals, which serve to lower the repulsion energy.

$$E_{\text{HF}} = -\frac{1}{2} \sum_i \langle \phi_i | \nabla_i^2 | \phi_i \rangle + \sum_i \langle \phi_i | V_i | \phi_i \rangle + \frac{1}{2} \sum_{i \neq j} \left\langle \phi_i \phi_j \left| \frac{1}{r_{12}} \right| \phi_i \phi_j \right\rangle - \frac{1}{2} \sum_{i \neq j} \left\langle \phi_i \phi_j \left| \frac{1}{r_{12}} \right| \phi_j \phi_i \right\rangle$$

Recall that the notation for the 2- $e^-$  integrals is:

Coulomb integrals: 
$$J = \left\langle \phi_i \phi_j \left| \frac{1}{r_{12}} \right| \phi_i \phi_j \right\rangle = \iint \frac{\phi_i^2(\mathbf{r}_1) \phi_j^2(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

Exchange integrals: 
$$K = \left\langle \phi_i \phi_j \left| \frac{1}{r_{12}} \right| \phi_j \phi_i \right\rangle = \iint \frac{\phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \phi_j(\mathbf{r}_1) \phi_i(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

The problem with this Hartree-Fock theory is the assumption of a single Slater-determinant wavefunction, which neglects the effects of electron correlation. This causes prediction of electronic energies that are much too high and also results in poor thermochemistry.

To improve on HF theory, electron correlation can be modeled using the virtual orbitals, as in MP, CC, or CI theories. While more accurate, these methods scale very poorly with system size.

Density-functional theory can improve on HF using the occupied orbitals. In DFT, the fundamental variable is the electron density,

$$\rho = \rho(\mathbf{r}_1) = \int \cdots \int \psi^2(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N = \sum_i |\phi_i|^2.$$

## 1.2 Hohenberg-Kohn Theory

In conventional wavefunction theory, the potential determines the wavefunction, which determines the density, as well as the energy and other properties of interest,  $V \rightarrow \rho$ .

Hohenberg and Kohn proved that this mapping is unique and one-to-one, so the mapping is reversible and  $\rho \rightarrow V$ .

This means that all properties are unique functionals of the density. It is easy to write the

electron-nuclear energy,  $V_{\text{nuc}}$ , as a functional of the density.

$$\begin{aligned} V_{\text{nuc}}(\rho) &= \langle \psi | V | \psi \rangle \\ &= \int \cdots \int \psi^2 V d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N \\ &= \int \rho(\mathbf{r}_1) V d\mathbf{r}_1 \end{aligned}$$

In principle, we can also write the total kinetic energy,  $T$ , and the electron-electron repulsion energy,  $V_{\text{ee}}$ , as functionals of the density.

$$\begin{aligned} T(\rho) &= \left\langle \psi \left| -\frac{1}{2} \sum_i \nabla_i^2 \right| \psi \right\rangle \\ V_{\text{ee}}(\rho) &= \left\langle \psi \left| \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \right| \psi \right\rangle \end{aligned}$$

but we do not have simple  $\rho$ -dependent expressions for them. If we did, then the total energy would be

$$E(\rho) = T(\rho) + V_{\text{nuc}}(\rho) + V_{\text{ee}}(\rho)$$

and would be a unique functional of the density.

## 1.3 Kohn-Sham Theory

To get around the problem of not having expressions for  $T(\rho)$  and  $V_{\text{ee}}(\rho)$ , Kohn and Sham considered a system of so-called “non-interacting” electrons (although they still obey the Pauli exclusion principle) that has the same electron density as the real chemical system. The electron density is determined from the set of real orbitals that satisfy the Schrödinger equation

$$-\frac{1}{2} \nabla^2 \psi_i + V_o \psi_i = \varepsilon_i \psi_i$$

where  $\varepsilon_i$  is the energy of orbital  $i$  and  $V_o$  is an effective 1- $e^-$  potential. The density is

$$\rho = \sum_i \psi_i^2$$

The kinetic energy of the electrons,  $T_o$ , is

$$T_o = -\frac{1}{2} \sum_i \langle \psi_i | \nabla^2 | \psi_i \rangle = -\frac{1}{2} \sum_i \int \psi_i \nabla^2 \psi_i d\mathbf{r}$$

also, the classical Coulomb repulsion energy between the electrons is

$$J(\rho) = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

The Kohn-Sham energy is then written as

$$E(\rho) = T_{\circ} + V_{\text{nuc}}(\rho) + J(\rho) + E_{\text{XC}}(\rho)$$

Here,  $E_{\text{XC}}$  is called the exchange-correlation energy, which is the difference between this and the exact energy expression involving  $T$  and  $V_{\text{ee}}$ .

$$E_{\text{XC}}(\rho) = [T(\rho) - T_{\circ}] + [V_{\text{ee}}(\rho) - J(\rho)]$$

The benefit of KS theory is that we no longer need to approximate  $T(\rho)$  and  $V_{\text{ee}}(\rho)$ . Instead, we have exact formulae for  $T_{\circ}$  and  $J(\rho)$  and only need to approximate  $E_{\text{XC}}$ , which is a much smaller contribution to the total energy.

To evaluate the KS energy, we need to obtain the orbitals, so we need an expression for  $V_{\circ}$ , the Kohn-Sham potential. We seek to minimize the KS energy

$$E(\rho) = T_{\circ} + V_{\text{nuc}}(\rho) + J(\rho) + E_{\text{XC}}(\rho)$$

wrt variations  $\delta\psi_i$  in each orbital, so that  $\delta E/\delta\psi_i = 0$ . Considering the terms individually,

$$\frac{\delta\rho}{\delta\psi_i} = \frac{\delta}{\delta\psi_i} \left( \sum_j \psi_j^2 \right) = \sum_j \left( \frac{\delta}{\delta\psi_i} \psi_j^2 \right) = 2\psi_i$$

$$\begin{aligned} \frac{\delta T_{\circ}}{\delta\psi_i} &= -\frac{1}{2} \int \frac{\delta}{\delta\psi_i} (\psi_i \nabla_i^2 \psi_i) d\mathbf{r} \\ &= -\frac{1}{2} \int \left( \frac{\delta\psi_i}{\delta\psi_i} \nabla_i^2 \psi_i + \psi_i \nabla_i^2 \frac{\delta\psi_i}{\delta\psi_i} \right) d\mathbf{r} \\ &= - \int \nabla_i^2 \psi_i d\mathbf{r} \end{aligned}$$

$$\frac{\delta V_{\text{nuc}}}{\delta\psi_i} = \int V \frac{\delta\rho}{\delta\psi_i} d\mathbf{r} = 2 \int V \psi_i d\mathbf{r}$$

$$\begin{aligned} \frac{\delta J}{\delta\psi_i} &= \frac{1}{2} \iint \frac{\delta\rho(\mathbf{r}_1)}{\delta\psi_i} \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + \frac{1}{2} \iint \frac{\delta\rho(\mathbf{r}_2)}{\delta\psi_i} \frac{\rho(\mathbf{r}_1)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \iint \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \frac{\delta\rho(\mathbf{r}_1)}{\delta\psi_i} d\mathbf{r}_1 \\ &= 2 \int V_{\text{el}} \psi_i d\mathbf{r}_1 \end{aligned}$$

where  $V_{\text{el}}$  is the classical Coulomb potential is defined as

$$V_{\text{el}} = \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2$$

$$\frac{\delta E_{\text{XC}}}{\delta \psi_i} = \int \frac{\delta E_{\text{XC}}}{\delta \rho} \frac{\delta \rho}{\delta \psi_i} d\mathbf{r} = 2 \int \frac{\delta E_{\text{XC}}}{\delta \rho} \psi_i d\mathbf{r}$$

where  $\frac{\delta E_{\text{XC}}}{\delta \rho}$  is the functional derivative of  $E_{\text{XC}}$ .

Lastly, we need to enforce orbital normalization:  $\int \psi_i^2 d\mathbf{r} = 1$ , so we add a Langrange multiplier term,  $L$ .

$$L = - \sum_i \varepsilon_i \int \psi_i^2 d\mathbf{r}$$

$$\frac{\delta L}{\delta \psi_i} = -2\varepsilon_i \int \psi_i d\mathbf{r}$$

Then, setting  $\delta E / \delta \psi_i = 0$ , we have

$$- \int \nabla^2 \psi_i d\mathbf{r} + 2 \int V \psi_i d\mathbf{r} + 2 \int V_{\text{el}} \psi_i d\mathbf{r} + 2 \int \frac{\delta E_{\text{XC}}}{\delta \rho} \psi_i d\mathbf{r} - 2\varepsilon_i \int \psi_i d\mathbf{r} = 0$$

Dividing by 2 and equating the integrands,

$$-\frac{1}{2} \nabla^2 \psi_i + V \psi_i + V_{\text{el}} \psi_i + \frac{\delta E_{\text{XC}}}{\delta \rho} \psi_i = \varepsilon_i \psi_i$$

which has the same form as the KS equations, so the effective KS potential,  $V_o$  is

$$V_o = V + V_{\text{el}} + \frac{\delta E_{\text{XC}}}{\delta \rho}$$

and the set of KS equations can be solved self-consistently (as in HF theory) to obtain the orbitals that minimize the energy.

## 1.4 The Adiabatic Connection

Understanding of the form of  $E_{\text{XC}}$  is needed to develop approximations. We can obtain a useful expression for  $E_{\text{XC}}$  in terms of the “exchange-correlation hole” by a coupling-strength integration approach called the adiabatic connection.

First, we define the pair density,  $\Pi(\mathbf{r}_1, \mathbf{r}_2)$ . If  $\rho(\mathbf{r}_1)$  is the probability of finding an electron in volume element  $d\mathbf{r}_1$ , then the pair density is the probability of finding a pair of electrons simultaneously in  $d\mathbf{r}_1$  and  $d\mathbf{r}_2$ . Note that

$$\int \Pi(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = (N - 1) \rho(\mathbf{r}_1)$$

also, the electron-electron repulsion energy (or the expectation value of any other  $2-e^-$  operator) can be determined from the pair density.

$$\left\langle \psi \left| \frac{1}{r_{12}} \right| \psi \right\rangle = \iint \frac{\Pi(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

For a Slater-determinant wavefunction, the pair density is

$$\Pi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ij} \psi_i^2(\mathbf{r}_1) \psi_j^2(\mathbf{r}_2) - \sum_{ij} \psi_i(\mathbf{r}_1) \psi_j(\mathbf{r}_2) \psi_j(\mathbf{r}_1) \psi_i(\mathbf{r}_2) \delta_{\sigma_i \sigma_j}$$

and this integration gives the usual Coulomb and exchange integrals. The  $\delta_{\sigma_i \sigma_j}$  ensures that the exchange integral vanishes for opposite spins.

Now, we consider a series of partially interacting systems, all having the same density, where we gradually turn on the electron-electron repulsion so that

$$\hat{H} = \sum_i \left( -\frac{1}{2} \nabla_i^2 + V_i \right) + \frac{\lambda}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

Here,  $\lambda = 0$  gives the non-interacting KS system and  $\lambda = 1$  gives the real, fully interacting system. The energy at  $\lambda = 1$  is

$$E_1 = E_0 + \int_0^1 dE_\lambda$$

$$E_1 = T_o + V_{\text{nuc}} + \frac{1}{2} \iint \frac{1}{r_{12}} \left( \int \Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2) d\lambda \right) d\mathbf{r}_1 d\mathbf{r}_2$$

where  $\Pi_\lambda$  is the pair density at coupling strength  $\lambda$ . We can perform the  $\lambda$  integration first, to obtain a coupling-strength average,

$$\Pi_{\text{avg}} = \int_0^1 \Pi_\lambda d\lambda$$

Then

$$E_1 = T_o + V_{\text{nuc}} + \frac{1}{2} \iint \frac{\Pi_{\text{avg}}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

Adding and subtracting the classical Coulomb repulsion energy

$$E_1 = T_o + V_{\text{nuc}} + J + \frac{1}{2} \iint \frac{1}{r_{12}} \left[ \Pi_{\text{avg}}(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2$$

and comparing with the total KS energy,

$$E_{\text{XC}} = \frac{1}{2} \iint \frac{1}{r_{12}} \left[ \Pi_{\text{avg}}(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2$$

Multiplying and dividing the integrand by  $\rho(\mathbf{r}_1)$ ,

$$E_{\text{XC}} = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)}{r_{12}} \left[ \frac{\Pi_{\text{avg}}(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} - \rho(\mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2$$

$\frac{\Pi_{\text{avg}}(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)}$  is called the conditional pair density and is the probability of finding an electron at  $\mathbf{r}_2$  if another electron is known to be at  $\mathbf{r}_1$ . The quantity in square brackets is the difference



between the conditional probability of finding an electron at  $\mathbf{r}_2$  for the  $\lambda$ -averaged system and the classical probability. This is called the exchange-correlation hole.

$$h_{\text{XC}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\Pi_{\text{avg}}(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} - \rho(\mathbf{r}_2)$$

$E_{\text{XC}}$  can be determined from the exchange-correlation hole by

$$E_{\text{XC}} = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)}{r_{12}} h_{\text{XC}}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

## 1.5 Properties of Exchange-Correlation Holes

The exchange-correlation hole contains one electron at any reference point,  $\mathbf{r}_1$  in a chemical system.

$$\begin{aligned} \int h_{\text{XC}}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 &= \int \frac{\Pi_{\text{avg}}(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} d\mathbf{r}_2 - \int \rho(\mathbf{r}_2) d\mathbf{r}_2 \\ &= \frac{1}{\rho(\mathbf{r}_1)} [(N-1)\rho(\mathbf{r}_1)] - N \\ &= (N-1) - N \\ &= -1 \end{aligned}$$

Also, as  $E_{\text{XC}}$  depends on  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ , we need only consider the spherical average of the hole around  $\mathbf{r}_1$ , so spherically symmetric hole models can be used.

The hole is usually decomposed into various spin components through the pair density.

$$\Pi_{\text{avg}} = \Pi_{\text{avg}}^{\alpha\alpha} + \Pi_{\text{avg}}^{\beta\beta} + \Pi_{\text{avg}}^{\alpha\beta} + \Pi_{\text{avg}}^{\beta\alpha}$$

So, the spin-dependent holes are

$$h_{\text{XC}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\Pi_{\text{avg}}^{\sigma\sigma'}}{\rho_{\sigma}(\mathbf{r}_1)} - \rho_{\sigma'}(\mathbf{r}_2)$$

and the exchange-correlation energy is a sum over spins.

$$E_{\text{XC}} = \frac{1}{2} \sum_{\sigma, \sigma'} \iint \frac{\rho_{\sigma}(\mathbf{r}_1)}{r_{12}} h_{\text{XC}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

The spin-dependent hole is the difference in conditional probability of finding a  $\sigma'$ -spin electron at  $\mathbf{r}_2$  if a  $\sigma$ -spin electron is at  $\mathbf{r}_1$ . The opposite-spin ( $\sigma \neq \sigma'$ ) and parallel-spin ( $\sigma = \sigma'$ ) holes have differing behaviours.

The Pauli exclusion principle tells us that there is zero probability of finding two parallel-spin electrons at the same point in space, so

$$\Pi_{\text{avg}}^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_1) = 0$$

This means that the value of the parallel-spin holes at  $\mathbf{r}_1 = \mathbf{r}_2$  is

$$h_{\text{XC}}^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_1) = -\rho_{\sigma}(\mathbf{r}_1)$$

Like the total XC hole, the parallel-spin hole integrates to  $-1$  electron.

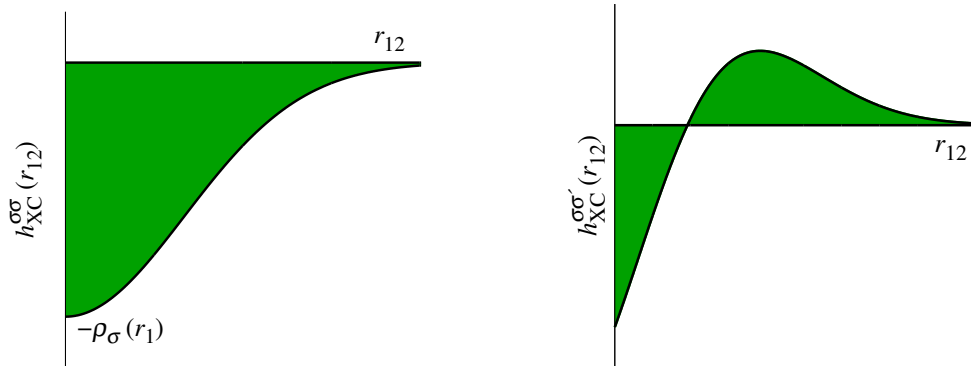
$$\begin{aligned} \int h_{\text{XC}}^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 &= \int \frac{\Pi_{\text{avg}}^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_{\sigma}(\mathbf{r}_1)} d\mathbf{r}_2 - \int \rho_{\sigma}(\mathbf{r}_2) d\mathbf{r}_2 \\ &= \frac{1}{\rho_{\sigma}(\mathbf{r}_1)} [(N_{\sigma} - 1)\rho_{\sigma}(\mathbf{r}_1)] - N_{\sigma} \\ &= (N_{\sigma} - 1) - N_{\sigma} \\ &= -1 \end{aligned}$$

The opposite-spin holes integrate to zero electrons.

$$\begin{aligned} \int h_{\text{XC}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 &= \int \frac{\Pi_{\text{avg}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_{\sigma}(\mathbf{r}_1)} d\mathbf{r}_2 - \int \rho_{\sigma'}(\mathbf{r}_2) d\mathbf{r}_2 \\ &= \frac{1}{\rho_{\sigma}(\mathbf{r}_1)} [N_{\sigma'}\rho_{\sigma}(\mathbf{r}_1)] - N_{\sigma'} \\ &= N_{\sigma'} - N_{\sigma'} \\ &= 0 \end{aligned}$$

The first integral here is  $N_{\sigma'}$ . We don't have to subtract 1 since the reference electron has a different spin,  $\sigma$ .

Sketches of the rough shapes of parallel- and opposite-spin holes are:



The XC energies and holes can be further decomposed into exchange and correlation components.

$$E_{XC} = E_X + E_C$$

$$h_{XC}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) = h_X^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) + h_C^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2)$$

There is no exchange between opposite spins, so

$$h_X^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = h_X^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) = 0$$

The same properties for the parallel-spin XC hole are satisfied by the exchange hole.

$$h_X^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_1) = -\rho_\sigma(\mathbf{r}_1)$$

$$\int h_X^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1$$

Exchange is a purely QM effect for fermions and does not depend on electron-electron repulsion, so the exchange hole is  $\lambda$  independent and the full XC hole reduces to the exchange hole in the  $\lambda = 0$  limit.

$$\lim_{\lambda \rightarrow 0} h_{XC}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) = h_X^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2)$$

Conversely, the correlation holes are  $\lambda$  dependent.

Both the opposite- and parallel-spin correlation holes have zero normalization.

$$\int h_C^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0$$

Because the correlation holes integrate to zero while the exchange hole integrates to  $-1$ ,  $E_X$  contributes much more than  $E_C$  to  $E_{XC}$ . Our primary focus going forward will be to model  $E_X$ .

## 1.6 Connection with Hartree-Fock Theory

In HF theory, the parallel-spin pair density for a Slater determinant is

$$\Pi^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) = \rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2) - \sum_{ij} \psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)$$

and the exchange hole is

$$h_X^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{\rho_\sigma(\mathbf{r}_1)} \sum_{ij} \psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)$$

so the exchange energy is

$$\begin{aligned}
 E_X &= -\frac{1}{2} \sum_{\sigma} \sum_{i,j} \iint \frac{1}{r_{12}} \psi_{i\sigma}(\mathbf{r}_1) \psi_{j\sigma}(\mathbf{r}_2) \psi_{j\sigma}(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\
 &= -\frac{1}{2} \sum_{\sigma} \iint \frac{1}{r_{12}} \left| \sum_i \psi_{i\sigma}(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_2) \right|^2 d\mathbf{r}_1 d\mathbf{r}_2
 \end{aligned}$$

and this is the exact exchange energy written in terms of the KS orbitals.

# Chapter 2

## Density Functionals: the LSDA, GGAs, and Hybrids

### 2.1 The Uniform Electron Gas

The first and simplest DFT exchange functional was developed using the uniform electron gas as a model system. Consider a cube of side length  $L$  containing  $N$  electrons. The potential is zero within the cube and infinite without.

Inside the cube, the S.E. is

$$-\frac{1}{2}\nabla^2\psi = E\psi$$

The solutions are products of the 1D particle-in-a-box wavefunctions.

$$\psi_k = \frac{1}{\sqrt{L^3}}e^{i(kx+ky+kz)} = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}}$$

with  $k_i = \frac{2\pi}{L}n_i$ , where  $n_i = 0, \pm 1, \pm 2, \dots$  for  $i = x, y, z$ . For this wavefunction, we can show that

$$\sum_i \psi_{i\sigma}^*(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2) = \frac{3\rho_\sigma}{k_F s} j_1(k_F s)$$

where  $j_1(x)$  is a spherical Bessel function,  $s = |\mathbf{r}_2 - \mathbf{r}_1|$  and

$$k_F = (3\pi^2\rho)^{1/3} = (6\pi^2\rho_\sigma)^{1/3}$$

as  $\rho = 2\rho_\sigma$  for paired electrons.

Returning to the exchange-energy expression,

$$E_X = \sum_\sigma \frac{1}{2} \iint \frac{\rho_\sigma(\mathbf{r}_1)}{r_{12}} h_X^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

This is often written as

$$E_X = \sum_{\sigma} \int \varepsilon_X^{\sigma}(\mathbf{r}_1) d\mathbf{r}_1$$

where

$$\varepsilon_X^{\sigma}(\mathbf{r}_1) = \frac{\rho_{\sigma}}{2} \int \frac{1}{r_{12}} h_X^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2$$

is the exchange-energy density. We seek the exchange-energy density for the uniform electron gas.

Recall that the exchange hole is

$$\begin{aligned} h_X^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) &= -\frac{1}{\rho_{\sigma}} \left| \sum_i \psi_{i\sigma}^*(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_2) \right|^2 \\ &= -\frac{1}{\rho_{\sigma}} \left[ \frac{3\rho_{\sigma}}{k_F s} j_1(k_F s) \right]^2 \\ &= -\frac{9\rho_{\sigma}}{k_F^2 s^2} j_1^2(k_F s) \end{aligned}$$

Finally, the exchange-energy density is

$$\begin{aligned} \varepsilon_X(\mathbf{r}_1) &= \frac{\rho_{\sigma}}{2} \iiint \frac{1}{s} h_X^{\sigma\sigma}(\mathbf{r}_1, s) s^2 \sin(\theta) ds d\theta d\phi \\ &= 2\pi\rho_{\sigma} \int_0^{\infty} h_X^{\sigma\sigma}(\mathbf{r}_1, s) s ds \\ &= -\frac{18\pi\rho_{\sigma}^2}{k_F^2} \int_0^{\infty} \frac{j_1^2(k_F s)}{s} ds \\ &= -\frac{18\pi\rho_{\sigma}^2}{k_F^2} \int_0^{\infty} \frac{j_1^2(x)}{x} dx \end{aligned}$$

where  $x = k_F s$ . From a table of definite integrals, this is  $1/4$ , so

$$\varepsilon_X(\mathbf{r}_1) = -\frac{9\pi\rho_{\sigma}^2}{2k_F^2} = -\frac{3}{2} \left( \frac{3}{4\pi} \right)^{1/3} \rho_{\sigma}^{4/3}$$

and the exchange energy is

$$E_X^{\text{LSDA}} = -\frac{3}{2} \left( \frac{3}{4\pi} \right)^{1/3} \sum_{\sigma} \int \rho_{\sigma}^{4/3}(\mathbf{r}) d\mathbf{r}$$

The approximation of using the uniform-electron-gas exchange hole to evaluate the exchange energy is called the local spin-density approximation. It is much simpler than HF theory as

it uses only the value of the electron density at each point in space to evaluate the exchange energy.

Uniform-electron-gas correlation holes can also be used to obtain the correlation energy, but no closed-form expression exists – parameterizations to Quantum Monte Carlo results for UEG correlation energies are used instead.

## 2.2 Functional Derivatives

To perform KS DFT calculations in practise, we need to evaluate the functional derivative of the XC energy in order to optimize the KS orbitals.

For a functional

$$F(\rho) = \int f(\rho, \nabla\rho, \dots) d\mathbf{r}$$

if  $\rho$  is changed by an infinitesimal variation,  $\delta\rho$ , then the first-order change in  $F$  is

$$dF = \int \frac{\delta F}{\delta\rho} \delta\rho$$

where  $\frac{\delta F}{\delta\rho}$  is the functional derivative.

To obtain  $\frac{\delta F}{\delta\rho}$ , replace  $\rho$  everywhere in the integrand,  $f(\rho, \nabla\rho, \dots)$  by  $\rho + \delta\rho$  and expand to first order in  $\delta\rho$ . Then manipulate the result until  $\delta\rho$  is factored out of the integral for  $dF$ . The function multiplying  $\delta\rho$  in the integral is the functional derivative.

For the LSDA,

$$E_X^{\text{LSDA}}(\rho_\sigma) = \int c_x \rho_\sigma^{4/3} d\mathbf{r}$$

$$E_X^{\text{LSDA}}(\rho_\sigma + \delta\rho_\sigma) = \int c_x (\rho_\sigma + \delta\rho_\sigma)^{4/3} d\mathbf{r}$$

To first order in  $\delta\rho$ ,

$$(\rho_\sigma + \delta\rho_\sigma)^{4/3} = \rho_\sigma^{4/3} + \frac{4}{3} \rho_\sigma^{1/3} \delta\rho_\sigma + \dots$$

$$\begin{aligned} E_X^{\text{LSDA}}(\rho_\sigma + \delta\rho_\sigma) &= \int c_x \left( \rho_\sigma^{4/3} + \frac{4}{3} \rho_\sigma^{1/3} \delta\rho_\sigma \right) d\mathbf{r} \\ &= E_X^{\text{LSDA}}(\rho_\sigma) + \int c_x \frac{4}{3} \rho_\sigma^{1/3} \delta\rho_\sigma d\mathbf{r} \end{aligned}$$

So, examining the integrand,

$$\frac{\delta E_X^{\text{LSDA}}}{\delta\rho_\sigma} = \frac{4}{3} \rho_\sigma^{1/3}$$

## 2.3 Beyond the Local Spin-Density Approximation

The LSDA typically underestimates exchange energies and overestimates both correlation energies and bond energies – more sophisticated models are needed.

In real chemical systems, the density is not uniform, so the first improvement on the LSDA was to add a gradient term. The exchange energy density now depends on both the density and density gradient,  $\nabla\rho$ . These types of functionals are called generalized gradient approximations.

$$E_X^{\text{GGA}} = \sum_{\sigma} \int \varepsilon_X(\rho_{\sigma}, \nabla\rho_{\sigma}) d\mathbf{r}$$

Functionals that also contain  $\tau_{\sigma}$ , and possibly  $\nabla^2\rho_{\sigma}$ , are called meta-GGAs. There is an extensive literature on meta-GGA functionals but due to time constraints, these will not be discussed further here.

To motivate the form of the gradient correction, consider dimensional analysis. The dimensions of  $\rho$  are  $\frac{1}{\text{volume}} = \frac{1}{\text{distance}^3}$  and of  $\nabla\rho$  are  $\frac{1}{\text{distance}^4}$ . All of the KS energy terms should have dimensions of  $\frac{1}{\text{distance}}$ . This is most easily seen from the  $V_{\text{nuc}}$  and  $E_X$  terms:

$$\begin{aligned} \int \rho(\mathbf{r}) V_{\text{nuc}} d\mathbf{r} : & \quad \left( \frac{1}{\text{distance}^3} \right) \left( \frac{1}{\text{distance}} \right) \text{distance}^3 = \frac{1}{\text{distance}} \\ \sum_{\sigma} C_x \int \rho_{\sigma}^{4/3} d\mathbf{r} : & \quad \left( \frac{1}{\text{distance}^3} \right)^{4/3} \text{distance}^3 = \frac{1}{\text{distance}} \end{aligned}$$

So, the simplest gradient correction is

$$E_X = E_X^{\text{LSDA}} - \beta \sum_{\sigma} \int \frac{(\nabla\rho_{\sigma})^2}{\rho_{\sigma}^{4/3}} d\mathbf{r}$$

as the dimensions of the last term are

$$\left( \frac{1}{\text{distance}^4} \right)^2 (\text{distance}^3)^{4/3} \text{distance}^3 = \frac{1}{\text{distance}}$$

However, there are significant problems with this expression as the functional derivative diverges asymptotically in the density tails, far from an atomic or molecular system. We need an alternative form for a GGA that is still dimensionally correct, but prevents this divergence.



## 2.4 Generalized Gradient Approximations

To prevent the asymptotic divergence, a dimensionless factor can be introduced

$$E_X^{\text{B86a}} = E_X^{\text{LSDA}} - \sum_{\sigma} \beta \int \frac{(\nabla \rho_{\sigma})^2}{\rho_{\sigma}^{4/3}} \left( 1 + \gamma \frac{(\nabla \rho_{\sigma})^2}{\rho_{\sigma}^{8/3}} \right)^{-1} d\mathbf{r}$$

where  $\frac{(\nabla \rho_{\sigma})^2}{\rho_{\sigma}^{8/3}}$  is dimensionless, but will become large in the exponential density tails to prevent asymptotic divergence.

This functional is more commonly written in terms of  $\chi_{\sigma}$ , the reduced or dimensionless density gradient:

$$\chi_{\sigma} = \frac{|\nabla \rho_{\sigma}|}{\rho_{\sigma}^{4/3}}$$

$$E_X^{\text{B86a}} = E_X^{\text{LSDA}} - \sum_{\sigma} \beta \int \rho_{\sigma}^{4/3} \frac{\chi_{\sigma}^2}{1 + \gamma \chi_{\sigma}^2} d\mathbf{r}$$

In this form, it is clear that the gradient term is an “enhancement” to the LSDA. GGAs are often rewritten in terms of an enhancement factor,  $F(\chi_{\sigma})$ ,

$$E_X^{\text{GGA}} = - \sum_{\sigma} \int c_x \rho_{\sigma}^{4/3} F(\chi_{\sigma}) d\mathbf{r} = - \sum_{\sigma} \int \varepsilon_X^{\text{LSDA}}(\rho_{\sigma}) F(\chi_{\sigma}) d\mathbf{r}$$

For the case of the B86a functional,

$$F(\chi_{\sigma}) = 1 + \frac{\beta}{c_x} \frac{\chi_{\sigma}^2}{1 + \gamma \chi_{\sigma}^2}$$

This functional has the exact same form as the well-known PBE functional, which was proposed 10 years later based on applying chosen constraints to the enhancement factor, with only slight differences in the values of the  $\beta$  and  $\gamma$  parameters.

This functional recovers the correct behaviour of the enhancement factor in the zero-gradient limit (UEG), but not in the large-gradient limit.

The PBEsol functional also shares this functional form, but with significantly different parameter values, chosen to recover the  $\chi \rightarrow 0$  limit of the enhancement factor for a slowly-varying electron gas:

$$\lim_{\chi_{\sigma} \rightarrow 0} F_X(\chi_{\sigma}) = 1 + \frac{10}{81} \chi_{\sigma}^2 + \dots$$

This worsens the performance relative to PBE for finite atoms and molecules, but improves performance for solids, where there are no regions with large density gradients. PBEsol can be viewed as intermediate between PBE and LSDA. It tends to give good performance for inorganic solids, where the overbinding tendency of the exchange function offsets the lack of London dispersion.

Two additional GGA functionals were proposed with the correct behaviour of the enhancement factor in the large-gradient limit of

$$\lim_{\chi_\sigma \rightarrow \infty} F_X(\chi_\sigma) \sim \chi_\sigma^{2/5}$$

In PW86

$$F(\chi_\sigma) = (1 + a\chi_\sigma^2 + b\chi_\sigma^4 + c\chi_\sigma^6)^{1/15}$$

and in B86b

$$F(\chi_\sigma) = 1 + \frac{\beta}{c_x} \frac{\chi_\sigma^2}{(1 + \gamma\chi_\sigma^2)^{4/5}}$$

Both of these functionals are more accurate for exchange due to the improved large-gradient behaviour. B86b is more robust than PW86, as the  $\frac{1}{15}$  power makes SCF convergence more difficult. These functionals are the most reliable for exchange repulsion in vdW complexes.

Another GGA was developed to satisfy the exact asymptotic behaviour of the exchange-energy density. When an electron is far away from an atom or molecule, the exchange hole remains centered on the system such that the reference electron is interacting with a +1 ion. Thus

$$\lim_{r \rightarrow \infty} \varepsilon_X^\sigma = -\frac{\rho_\sigma}{2r}$$

However, for the LSDA or B86a/PBE functionals, this limit is  $-\rho_\sigma^{4/3}$ .

B88 was designed to recover the exact limit and has

$$F(\chi_\sigma) = 1 + \frac{\beta\chi_\sigma^2}{1 + 6\beta\chi_\sigma \operatorname{arcsinh}(\chi_\sigma)}$$

B88 is the most accurate GGA for atomic exchange energies and has only one parameter,  $\beta = 0.0042$ . It is the most popular in chemistry, while PBE is the most popular in physics.

## 2.5 Numerical Integration in DFT

Evaluating the XC energy requires numerical integration on a grid of points. In numerical integration, the integral can be evaluated approximately as a summation

$$I = \int F(\mathbf{r}) d\mathbf{r} \approx \sum_i A_i F(\mathbf{r}_i)$$

where the  $\mathbf{r}_i$  are the integration grid points and the  $A_i$  are the integration weights.

Because the density changes rapidly near atomic nuclei, we cannot use cubic grids in Cartesian coordinates. Instead, we need to partition the molecule into discrete atomic regions so that numerical integration can be carried out in each region using spherical coordinates, with the nucleus as the origin. This is done by defining weight functions,  $w_n$ , assigned to each nucleus,  $n$ , such that the weights sum to 1 at each grid point:

$$\sum_n w_n(\mathbf{r}_i) = 1$$

Each  $w_n(\mathbf{r}) = 1$  at nucleus  $n$  and decreases smoothly to zero at all other nuclei.

The weights are then used to partition the integrand

$$F(\mathbf{r}) = \sum_n F_n(\mathbf{r}) = \sum_n w_n(\mathbf{r})F(\mathbf{r})$$

and this reduces the integral to a sum of single-center integrals

$$I = \sum_n I_n = \sum_n \left( \int w_n(\mathbf{r})F(\mathbf{r})d\mathbf{r} \right)$$

For each single-center integral,  $I_n$ , we use spherical coordinates

$$I_n = \iiint w_n(\mathbf{r})F(\mathbf{r})r^2 \sin \theta dr d\theta d\phi$$

where the angular integration is carried out using Lebedev quadratures. Increasing the size of the radial and angular meshes increases numerical precision in evaluating the integrals, but also increases the computational time.

## 2.6 Hybrid Functionals

GGAs are limited as they use local models of the exchange hole, depending only on  $\rho_\sigma$  and  $\nabla\rho_\sigma$ . For significantly greater accuracy, we need to go beyond GGAs. One way to do this is with hybrid functionals.

Returning to the adiabatic connection, we write

$$E_{X,\sigma} = \int_0^1 U_{X\sigma}^\lambda d\lambda$$

where we are explicitly showing the  $\lambda$  (coupling-strength) dependence of the exchange potential energy,  $U_X$ . Recall that  $\lambda$  switches on the  $1/r_{12}$  Coulomb repulsion between the

electrons, so  $\lambda = 0$  corresponds to the non-interacting KS reference system and  $\lambda = 1$  to the fully interacting real system.

A first approximation to the integral is a linear interpolation

$$E_{X\sigma} = aU_{X\sigma}^{\lambda=0} + (1-a)U_{X\sigma}^{\lambda=1}$$

The  $\lambda = 0$  limit corresponds to the exact exchange energy of the Slater determinant of the KS orbitals,  $E_{X\sigma}^{\text{HF}}$ . At  $\lambda = 1$ , we can use the LSDA or, much more commonly, a GGA functional.

$$E_{X\sigma}^{\text{GGA}} = \int \varepsilon_{X\sigma}(\rho_{\sigma}, \nabla \rho_{\sigma}) d\mathbf{r}$$

Combining these gives a hybrid functional,

$$E_{X\sigma}^{\text{hybrid}} = aE_{X\sigma}^{\text{HF}} + (1-a)E_{X\sigma}^{\text{GGA}}$$

Typically,  $a = 20 - 50\%$  depending on the functional.

These hybrid functionals give an accuracy that far surpasses either HF or GGAs alone and are the most consistently accurate density functionals used in chemistry.

The GGA correlation functionals, in particular LYP and PBE, are used to construct hybrid XC functionals.

Meta-GGA correlation functionals are also possible, but are less commonly used due to their greater complexity and numerical sensitivity.

A simple 1-parameter hybrid functional involving B88 exchange and PBE correlation is

$$E_{\text{XC}} = aE_{\text{X}}^{\text{HF}} + (1-a)E_{\text{X}}^{\text{B88}} + E_{\text{C}}^{\text{PBE}}.$$

3-parameter hybrids are also common, where added empiricism can give better thermochemistry. The original 3-parameter hybrid has the form

$$E_{\text{XC}} = aE_{\text{X}}^{\text{HF}} + (1-a)E_{\text{X}}^{\text{LSDA}} + b\Delta E_{\text{X}}^{\text{GGA}} + E_{\text{C}}^{\text{LSDA}} + c\Delta E_{\text{C}}^{\text{GGA}}$$

B3LYP uses this form with the B88 exchange functional and LYP correlation functional.

## 2.7 B97 and the Limits of Parameterization

How far should one go with introducing empirical fit parameters to density functionals? To assess this, consider a general functional form

$$E_{\text{XC}}^{\text{hybrid}} = aE_{\text{X}}^{\text{HF}} + (1-a)E_{\text{X}}^{\text{GGA}} + E_{\text{C}\sigma\sigma}^{\text{GGA}} + E_{\text{C}\alpha\beta}^{\text{GGA}}$$

with

$$\begin{aligned} E_X^{\text{GGA}} &= \sum_{\sigma} \int \varepsilon_{X\sigma}^{\text{LSDA}} g_{X\sigma}(\chi_{\sigma}^2) d\mathbf{r} \\ E_{C\sigma\sigma}^{\text{GGA}} &= \sum_{\sigma} \int \varepsilon_{C\sigma\sigma}^{\text{LSDA}} g_{C\sigma\sigma}(\chi_{\sigma}^2) d\mathbf{r} \\ E_{C\alpha\beta}^{\text{GGA}} &= \int \varepsilon_{C\alpha\beta}^{\text{LSDA}} g_{C\alpha\beta}(\chi_{\text{avg}}^2) d\mathbf{r} \end{aligned}$$

where  $\chi_{\text{avg}}^2 = \frac{1}{2} (\chi_{\alpha}^2 + \chi_{\beta}^2)$ .

Each of the  $g$ 's takes the form of a polynomial series

$$g = \sum_{i=0}^m c_i U^i$$

where the GGA enhancement factor has the same form as in B86a/PBE

$$\begin{aligned} U_{X\sigma} &= \frac{\gamma_{X\sigma} \chi_{\sigma}^2}{1 + \gamma_{X\sigma} \chi_{\sigma}^2} \\ U_{C\sigma\sigma} &= \frac{\gamma_{C\sigma\sigma} \chi_{\sigma}^2}{1 + \gamma_{C\sigma\sigma} \chi_{\sigma}^2} \\ U_{C\alpha\beta} &= \frac{\gamma_{C\alpha\beta} \chi_{\text{avg}}^2}{1 + \gamma_{C\alpha\beta} \chi_{\text{avg}}^2} \end{aligned}$$

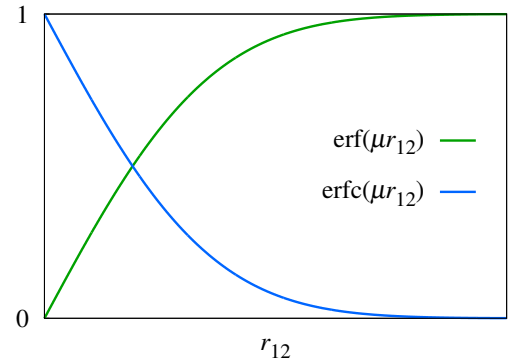
The  $\gamma$ 's are fixed, using reference atomic exchange and correlation energies. The  $c$ 's are linear parameters fit to minimize errors in thermochemical reference data.

No significant improvement occurs from  $m = 2$  to  $m = 3$  (and only minimal improvement from  $m = 1$  to  $m = 2$ ). Also, unphysical oscillatory character in plots of the  $g(\chi)$  enhancement factors occurs starting at  $m = 4$ . This demonstrates that we should stop at first or second order in this expansion, with at most 10 empirical parameters.

## 2.8 Range-Separated Hybrid Functionals

Hybrid functionals use a global mixing of HF and GGA exchange. Could better accuracy be obtained with a position-dependent mixing? One way to do this is to split the Coulomb operator into short- and long-range components using the error function.

$$\frac{1}{r_{12}} = \underbrace{\frac{1 - \text{erf}(\mu r_{12})}{r_{12}}}_{\text{short range}} + \underbrace{\frac{\text{erf}(\mu r_{12})}{r_{12}}}_{\text{long range}}$$



Then, the individual components replace  $1/r_{12}$  in the HF or GGA exchange-energy integrands.

Usually the long-range component is treated with exact exchange, to ensure the correct limiting behaviour of the exchange hole, and the short-range component is treated with GGA exchange, recovering the UEG limit.

$$E_X^{\text{LR}} = -\frac{1}{2} \sum_{\sigma} \sum_{ij} \iint \frac{\text{erf}(\mu r_{12})}{r_{12}} \psi_{i\sigma}(\mathbf{r}_1) \psi_{j\sigma}(\mathbf{r}_2) \psi_{j\sigma}(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

$$E_X^{\text{SR}} = -\frac{1}{2} \sum_{\sigma} \iint [1 - \text{erf}(\mu s)] \frac{\rho_{\sigma}(\mathbf{r})}{s} h_{X\sigma}^{\text{GGA}}(\mathbf{r}, s) d\mathbf{r} ds$$

The LC-BLYP functional (the first range-separated hybrid) uses B88 exchange. Subsequent range-separated hybrids, like LC- $\omega$ PBE, use GGAs developed specifically for range separation. The base GGA is recovered in the  $\mu = 0$  limit.

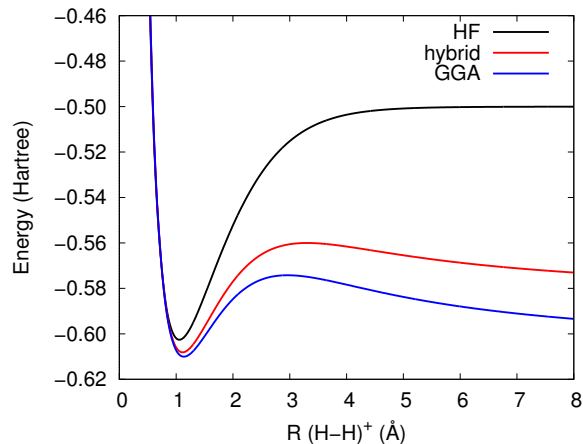
These range-separated functionals are more computationally expensive than GGAs or global hybrids. They typically give improved performance in cases where delocalization error is important, but the optimum  $\mu$  parameter is highly system dependent, preventing consistent accuracy across applications.

Note that the HSE functional, commonly used in solid-state calculations, reverses the typical convention, treating the short-range component with exact exchange and the long-range component with GGA exchange, to reduce the computational cost of performing hybrid DFT calculations with planewave basis sets.

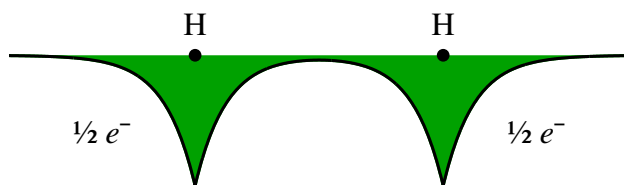
## 2.9 Delocalization Error

The DFT methods described so far perform quite well for most thermochemistry, with errors in the G3 atomization energies of  $\sim 10$  kcal/mol for GGA and 2 – 5 kcal/mol for hybrids. However, they can give very large errors in some cases – the most dramatic is for the simplest chemical system,  $\text{H}_2^+$ .

HF is exact here as it is a 1-electron system, but the LSDA or GGA functionals fail spectacularly in the dissociation limit. To understand why, consider the form of the exchange hole.



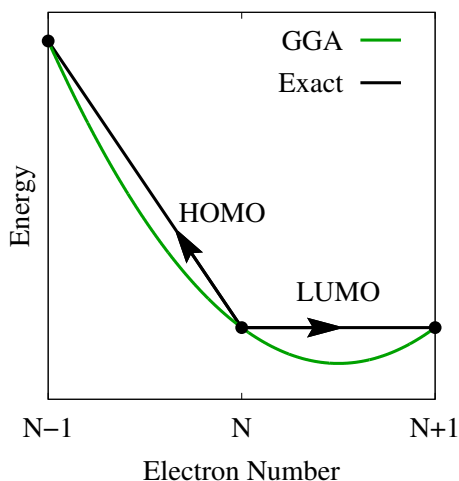
The exact exchange hole in  $\text{H}_2^+$  integrates to  $-1$  electron overall, with  $-\frac{1}{2}e^-$  around each nucleus, regardless of the reference point.



Alternatively, the LSDA or GGA hole is normalized to  $-1$  electron, but is localized about the reference point.



So, we are effectively double-counting the exchange energy when the nuclei are far apart, near the dissociation limit. This problem affects any system with distant, fractional charges. This is often illustrated by plots of the energy versus charge for an atom or molecule.



The exact energy should be piecewise linear, which can be motivated by considering successive ionization of a large ensemble of non-interacting atoms or molecules.

However, GGAs preferentially stabilize fractional charges due to the incorrect hole normalization.

This behaviour explains errors in orbital energies (or band structure) seen with GGAs (or the LSDA).

The HOMO energy is the sided derivative for removing charge:

$$\varepsilon_{\text{HOMO}} = \frac{\partial_- E}{\partial q}$$

With GGAs, this slope is too shallow and the HOMO is too high in energy.

The LUMO energy is the sided derivative for adding charge:

$$\varepsilon_{\text{LUMO}} = \frac{\partial_+ E}{\partial q}$$

With GGAs, this slope is too steep and the LUMO is too low in energy.

This also results in narrowing of the band gap in solids, and incorrect prediction of some semiconductors as metallic.

For some molecular dimers, transfer of electrons from the destabilized HOMO of one molecule to the overstabilized LUMO of the other molecule causes excessive charge transfer and overbinding of the dimer.

Hybrids or range-separated hybrids have intermediate behaviour and consequently reduce delocalization error, but the optimal  $a$  or  $\mu$  needed to recover straight-line behaviour is (a) highly system dependent and (b) very different from the optimal value for accurate thermochemistry in most applications.

Resolving delocalization error is likely the largest outstanding problem in DFT.