

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,

$$\psi = \frac{1}{\sqrt{N!}} |\phi_1 \ \phi_2 \ \cdots \ \phi_N|$$

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:

$$J = \iint \frac{\phi_i^2(\mathbf{r}_1) \phi_j^2(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

Exchange integrals:

$$K = \iint \frac{\phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \phi_j(\mathbf{r}_1) \phi_i(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

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,

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

which integrates to the total number of electrons.

$$\int \rho(\mathbf{r}_1) d\mathbf{r}_1 = N$$

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_{nuc} , as a functional of the density.

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

In principle, we can also write the total kinetic energy, T , and the electron-electron repulsion energy, V_{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 ρ -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 non-interacting electrons (meaning no electron-electron repulsion) 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 ε_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 non-interacting system, $T_o(\rho)$, 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

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

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

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

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 $T_o(\rho)$ and $J(\rho)$ and only need to approximate E_{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_o , the Kohn-Sham potential. We seek to minimize the KS energy

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

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

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

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

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

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

where V_{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_{XC} .

Lastly, we need to enforce orbital normalization: $\int \psi_i^2 d\mathbf{r} = 1$, so we add a Lagrange 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_{\circ} is

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

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_{XC} is needed to develop approximations. We can obtain a useful expression for E_{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 Π_λ is the pair density at coupling strength λ . We can perform the λ 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

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

and comparing with the total KS energy,

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

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 λ -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_{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_{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 σ' -spin electron at \mathbf{r}_2 if a σ -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.

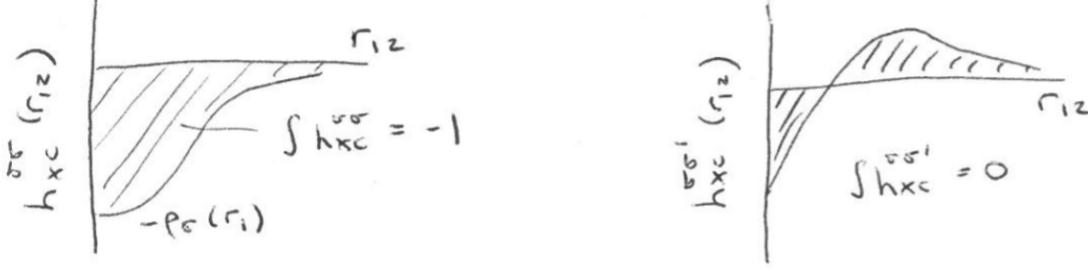
$$\begin{aligned} \int h_{\text{XC}}^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 &= \int \frac{\Pi_{\text{avg}}^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_{\sigma}(\mathbf{r}_1)} d\mathbf{r}_2 - \int \rho_{\sigma}(\mathbf{r}_2) d\mathbf{r}_2 \\ &= \frac{1}{\rho_{\sigma}(\mathbf{r}_1)}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

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, σ .

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.

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

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 λ independent and the full XC hole reduces to the exchange hole in the $\lambda = 0$ limit. Conversely, the correlation holes are λ dependent.

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

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 and GGAs

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 $i = x, y, z$.

The values of n for the occupied states depend on N and lie within a sphere of radius n_{\max} . If all orbitals are doubly occupied,

$$2\frac{4}{3}\pi n_{\max}^3 = N \quad \Rightarrow \quad n_{\max}^3 = \frac{3N}{8\pi}$$

or in terms of the wave vector, \mathbf{k} , the values lie within a ‘‘Fermi sphere’’ of radius k_F ,

$$k_F^3 = \left(\frac{2\pi}{L}\right)^3 \left(\frac{3N}{8\pi}\right) = 3\pi^2 \frac{N}{V}$$

and using the electron density, $\rho = N/V$, then

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

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.

We first consider one component of the hole – the one-body spin density matrix

$$\sum_i \psi_{i\sigma}^*(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_2) = \frac{1}{V} \sum_{\substack{\text{fermi} \\ \text{sphere}}} e^{i\mathbf{k}\cdot(\mathbf{r}_2-\mathbf{r}_1)}$$

we let $\mathbf{s} = \mathbf{r}_2 - \mathbf{r}_1$ and, in the limit of a very large sphere, the sum becomes an integral, I :

$$I = \frac{1}{V} \iiint e^{i\mathbf{k}\cdot\mathbf{s}} d\mathbf{n}$$

but

$$d\mathbf{k} = \left(\frac{2\pi}{L}\right)^3 d\mathbf{n}$$

so

$$I = \frac{1}{L^3} \left(\frac{L}{2\pi}\right)^3 \iiint e^{i\mathbf{k}\cdot\mathbf{s}} d\mathbf{k}$$

Assuming that \mathbf{s} is aligned along the z axis and converting to spherical coordinates,

$$\begin{aligned}
I &= \frac{1}{(2\pi)^3} \int_0^{k_F} \int_0^\pi \int_0^{2\pi} e^{iks \cos \theta} k^2 \sin(\theta) dk d\theta d\phi \\
&= \frac{2\pi}{(2\pi)^3} \int_0^{k_F} k^2 \left(\int_0^\pi e^{iks \cos \theta} \sin(\theta) d\theta \right) dk \\
&= \frac{1}{4\pi^2} \int_0^{k_F} k^2 \left(\frac{2}{ks} \sin(ks) \right) dk \\
&= \frac{1}{2\pi^2} \int_0^{k_F} \frac{k}{s} \sin(ks) dk \\
&= \frac{1}{2\pi^2 s^3} [\sin(k_F s) - k_F s \cos(k_F s)]
\end{aligned}$$

multiplying and dividing by k_F^3 ,

$$\begin{aligned}
I &= \frac{6\pi^2 \rho_\sigma}{2\pi^2 k_F^3 s^3} [\sin(k_F s) - k_F s \cos(k_F s)] \\
&= \frac{3\rho_\sigma}{k_F s} j_1(k_F s)
\end{aligned}$$

where $j_1(x)$ is a spherical Bessel function.

Recall that the exchange hole is

$$h_X^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{\rho_\sigma} \left| \sum_i \psi_{i\sigma}^*(\mathbf{r}_1) \psi_{i\sigma}(\mathbf{r}_2) \right|^2$$

so, replacing the term on the right with our integral, I , the spherically averaged hole is

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

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.

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

2.2 Beyond the Local Spin-Density Approximation

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.

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

To motivate the form of the gradient correction, consider dimensional analysis. The dimensions of ρ 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_{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

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

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 exchange potential (i.e. the functional derivative) diverges asymptotically in the density tails, far from an atomic or molecular system.

2.3 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 ρ 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 ρ 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,

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

Functional derivatives of GGAs are more complicated to evaluate, as derivative operations on $\delta\rho$ must be removed using integration by parts, Green's theorems, etc. For our simple, proposed GGA, it can be shown that

$$\frac{\delta E_X}{\delta\rho_\sigma} = \frac{4}{3} \rho_\sigma^{1/3} - \frac{4}{3} \beta \frac{(\nabla\rho_\sigma)^2}{\rho_\sigma^{7/3}} + 2\beta \frac{\nabla^2\rho_\sigma}{\rho_\sigma^{4/3}}$$

Recall that the Laplacian operator, in spherical coordinates is

$$\begin{aligned} \nabla^2 f &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial f}{\partial\theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 f}{\partial\phi^2} \\ &= \frac{1}{r} \frac{\partial^2}{\partial r^2} (rf) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial f}{\partial\theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 f}{\partial\phi^2} \end{aligned}$$

Assuming an exponential spin density, $\rho_\sigma = Ae^{-ar}$, as is usually seen in chemistry, the density gradient is

$$\nabla\rho_\sigma = \frac{\partial}{\partial r} \rho_\sigma = -Aae^{-ar}$$

and the Laplacian of the density is

$$\nabla^2\rho_\sigma = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial\rho_\sigma}{\partial r} \right) = \frac{1}{r^2} \left(2r \frac{\partial\rho_\sigma}{\partial r} + r^2 \frac{\partial^2\rho_\sigma}{\partial r^2} \right) = \frac{\partial^2\rho_\sigma}{\partial r^2} + \frac{2}{r} \frac{\partial\rho_\sigma}{\partial r}$$

The last two terms in the functional derivative are then

$$\frac{(\nabla\rho_\sigma)^2}{\rho_\sigma^{7/3}} = \frac{A^2 a^2 e^{-2ar}}{A^{7/3} e^{-7ar/3}} = \frac{a^2}{A^{1/3}} e^{ar/3}$$

$$\frac{\nabla^2 \rho_\sigma}{\rho_\sigma^{4/3}} = \frac{\frac{\partial^2 \rho_\sigma}{\partial r^2} + \frac{2}{r} \frac{\partial \rho_\sigma}{\partial r}}{\rho_\sigma^{4/3}} = \frac{Aa^2 e^{-ar} + \frac{2}{r} A(-a)e^{-ar}}{A^{4/3} e^{-4ar/3}} = A^{-1/3} \left(a^2 - \frac{2a}{r} \right) e^{ar/3}$$

In the exponential asymptote, consider the behaviour as $r \rightarrow \infty$,

$$\lim_{r \rightarrow \infty} e^{ar/3} = \infty$$

so the functional derivative diverges exponentially. We need an alternative form for a GGA that is still dimensionally correct, but prevents this divergence.

2.4 The PBE (or B86a) Functional

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 χ_σ , 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 β and γ 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.

2.5 The PW86 and B86b Functionals

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.

2.6 The B88 Functional

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

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

In the $r \rightarrow \infty$ limit, the gradient term of the exchange-energy density is

$$\begin{aligned} \lim_{r \rightarrow \infty} F^{\text{B88}}(\chi_\sigma) &= \lim_{r \rightarrow \infty} \left[-\beta\rho_\sigma^{4/3} \frac{\chi_\sigma^2}{1 + 6\beta\chi_\sigma \operatorname{arcsinh}(\chi_\sigma)} \right] \\ &= \lim_{r \rightarrow \infty} \left[-\beta\rho_\sigma^{4/3} \frac{\chi_\sigma^2}{\beta\chi_\sigma \ln(2\chi_\sigma)} \right] \end{aligned}$$

since $\operatorname{arcsinh}(x) = \ln(x + \sqrt{x^2 + 1})$ and $\lim_{x \rightarrow \infty} \operatorname{arcsinh}(x) = \lim_{x \rightarrow \infty} \ln(2x) = \ln x$.

For an exponential density,

$$\rho_\sigma = Ae^{-ar} \quad \nabla\rho_\sigma = -Aae^{-ar} \quad \chi_\sigma = aA^{-1/3}e^{ar/3}$$

$$\begin{aligned} \lim_{r \rightarrow \infty} F^{\text{B88}}(\chi_\sigma) &= \lim_{r \rightarrow \infty} \left[-\beta\rho_\sigma^{4/3} \frac{a^2 A^{-2/3} e^{2ar/3}}{6\beta a A^{-1/3} e^{ar/3} \ln(e^a r/3)} \right] \\ &= \lim_{r \rightarrow \infty} \left[-\rho_\sigma^{4/3} \frac{a A^{-1/3} e^{ar/3}}{6(ar/3)} \right] \\ &= \lim_{r \rightarrow \infty} \left[-\rho_\sigma^{4/3} \frac{\rho_\sigma^{-1/3}}{2r} \right] \\ &= -\frac{\rho_\sigma}{2r} \end{aligned}$$

So this functional has the correct limit.

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.

There is still room to improve further on GGAs if the desirable limiting properties of B88 and B86b could be combined. However, GGAs are limited as they use local models of the exchange hole, depending only on ρ_σ and $\nabla\rho_\sigma$. For significantly greater accuracy, we need to go beyond GGAs.

2.7 The PBE Correlation Functional

Correlation functionals tend to have more complicated forms than exchange functionals. However, they still follow the same hierarchy, with the simplest being LSDA correlation, obtained from parameterization of the UEG correlation energy.

Several GGA correlation functionals have been developed to improve on the LSDA, with the most popular being LYP and PBE.

Like GGA exchange functionals, GGA correlation functionals are based on the uniform electron gas limit, multiplied by an enhancement factor:

$$E_C^{\text{GGA}} = \int \varepsilon_C^{\text{LSDA}}(\rho_\alpha, \rho_\beta) F_C(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta) d\mathbf{r}$$

The popular PBE correlation functional uses the total electron density,

$$\rho = \rho_\alpha + \rho_\beta,$$

the total density gradient,

$$\nabla\rho = \nabla\rho_\alpha + \nabla\rho_\beta,$$

and the relative spin polarization,

$$\zeta = \frac{\rho_\alpha - \rho_\beta}{\rho_\alpha + \rho_\beta},$$

as central ingredients. The relative spin polarization is then used to define a spin-scaling factor:

$$\phi = \frac{1}{2} [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}]$$

The correlation energy is

$$E_C^{\text{PBE}} = \int [\varepsilon_C^{\text{LSDA}} + H(\rho, \nabla\rho, \phi)\rho] d\mathbf{r}$$

where

$$H = \gamma\phi^3 \ln \left[1 + \frac{\beta}{\gamma} t^2 \left(\frac{1 + At^2}{1 + At^2 + A^2 t^4} \right) \right],$$

$$A = \frac{\beta}{\gamma} \left[\exp \left(-\frac{\varepsilon_C^{\text{LSDA}}}{\gamma\phi^3\rho} \right) - 1 \right]^{-1}$$

β and γ are constants and

$$t = \frac{\nabla\rho}{2(3\pi^2)^{1/3}\phi\rho^{4/3}}$$

is a reduced density gradient (although a different one from χ). This PBE form was constructed to obey three known limits: $t \rightarrow 0$, $t \rightarrow \infty$, and the high-density limit.

2.8 Numerical Integration in DFT

In practise, performing a DFT calculation follows a similar procedure as a HF calculation. An initial guess for the KS orbitals is obtained from linear combinations of atomic orbitals using Generalized Hückel theory, or some similar semi-empirical approach. From this initial guess, we can solve self-consistently for the optimum KS orbitals that minimize the energy using the KS equations.

$$-\frac{1}{2}\nabla^2\psi_i + \left(V_{\text{nuc}} + V_{\text{el}} + \frac{\delta E_{\text{XC}}}{\delta\rho} \right) \psi_i = \varepsilon_i\psi_i$$

This is done in the same way as the Roothan-Hall scheme, using repeated matrix diagonalization. All of the integrals that form the matrix elements can be evaluated easily using Gaussian basis functions, except for integrals involving the XC functional or potential, which require 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

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

In DFT calculations, the weights (“Becke weights”) are obtained from smoothed Voronoi polyhedra. However, in analysis of properties of the electron density, other definitions are common, such as Hirshfeld partitioning, which uses free atomic densities, and Bader partitioning, which uses density gradients.

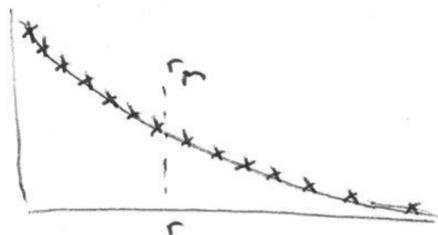
For each single-center integral, I_n , we use spherical coordinates

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

where the angular integration is carried out using Lebedev quadratures. The radial integration requires mapping the interval $-1 < x < 1$ used in standard Gaussian quadratures to $0 < r < \infty$, which is done using the transform

$$r = r_m \frac{1+x}{1-x}$$

where r_m is a parameter corresponding to the midpoint of the integration interval.



To ensure we have a balance of points near the nuclei and points in the bonding regions or density tails, r_m is taken as half the Bragg-Slater radius (obtained from internuclear distances in crystals), except for H, where the 1/2 factor is not applied.

Increasing the size of the radial and angular meshes increases numerical precision in evaluating the integrals, but also increases the computational time. Standard grids are (75,302), meaning 75 radial points and 302 angular points per atom. Finer grids, such as (99,590) or larger, are needed for many meta-GGA functionals, where the enhancement factors are not well-behaved numerically.

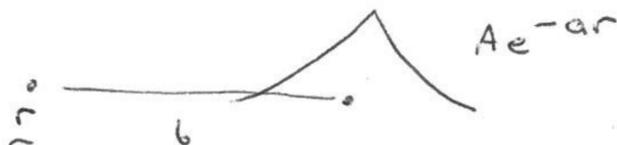
Chapter 3

Density Functionals: Meta-GGAs and Hybrids

3.1 The BR Exchange Meta-GGA

Functionals that contain τ_σ , and possibly $\nabla^2\rho_\sigma$, are called meta-GGAs. The first exchange meta-GGA was the Becke-Roussel (BR) functional.

In the BR model, we consider a different reference system from the UEG. For a hydrogen atom, we know that the exchange hole is an exponential function that remains centered on the nucleus, away from the reference point.



This model of the hole can be used for other systems if we impose known constraints to fit the parameters (A, a, b) . The first imposed constraint is that the hole must be normalized to -1 electron so $A = a^3/8\pi$.

The exchange energy depends only on the spherical average of the hole about the reference point

$$h_{X\sigma}(\mathbf{r}, s) = \frac{a}{16\pi bs} [(a|b - s| + 1)e^{-a|b-s|} - (a|b + s| + 1)e^{-a|b+s|}]$$

The Taylor expansion of this hole about the reference point is

$$h_{X\sigma}(\mathbf{r}, s) = -Ae^{-x} - \frac{Aa^2}{6} \left(1 - \frac{2}{x}\right) e^{-x} s^2 + \dots$$

where $x = ab$. At the reference point ($s = 0$), the hole must obey

$$h_{X\sigma}(\mathbf{r}, 0) = -\rho_\sigma(\mathbf{r})$$

so from the first term in the expansion,

$$-Ae^{-x} = -\rho_\sigma$$

$$a^3e^{-x} = 8\pi\rho_\sigma$$

The last constraint is that the second term (the curvature) in the Taylor expansion of the model hole must equal the curvature of the exact exchange hole:

$$h_{X\sigma}(\mathbf{r}, s) = -\rho_\sigma - Q_\sigma s^2 + \dots$$

where

$$Q_\sigma = \frac{1}{6} (\nabla^2 \rho_\sigma - 2D_\sigma),$$

and

$$D_\sigma = \tau_\sigma - \tau_\sigma^W$$

is the difference between the exact kinetic-energy density, $\tau_\sigma = \sum_i |\nabla\psi_i|^2$, and the von Weizsäcker approximation:

$$\tau_\sigma^W = \frac{1}{4} \frac{(\nabla\rho_\sigma)^2}{\rho_\sigma}$$

Thus,

$$\frac{Aa^2}{6} \left(1 - \frac{2}{x}\right) e^{-x} = Q_\sigma$$

Replacing A ,

$$\frac{a^2\rho_\sigma}{6} \left(1 - \frac{2}{x}\right) = Q_\sigma$$

multiplying both sides by $xe^{-2x/3}$,

$$(a^2e^{-2x/3}) \cdot \frac{\rho_\sigma}{6} (x - 2) = Q_\sigma xe^{-2x/3}$$

using the density constraint,

$$(8\pi\rho_\sigma)^{2/3} \cdot \frac{\rho_\sigma}{6} (x - 2) = Q_\sigma xe^{-2x/3}$$

$$\frac{2}{3}\pi^{2/3}(x - 2)\rho_\sigma^{5/3} = Q_\sigma xe^{-2x/3}$$

$$\frac{2}{3}\pi^{2/3}\frac{\rho_\sigma^{5/3}}{Q_\sigma} = \frac{x}{x - 2}e^{-2x/3}$$

This 1D non-linear equation can be solved for x . Then, from the density constraint,

$$a^3 e^{-x} = 8\pi\rho_\sigma$$

$$x^3 e^{-x} = 8\pi\rho_\sigma b^3$$

$$b^3 = \frac{x^3 e^{-x}}{8\pi\rho_\sigma}$$

and so the values of x , b , and a can be obtained for each reference point.

Lastly, the exchange energy is

$$E_X = -\frac{1}{2} \sum_\sigma \iint \frac{\rho(\mathbf{r})}{s} h_{X\sigma}(\mathbf{r}, s) d\mathbf{r} ds$$

and performing the integration of the spherically averaged hole over \mathbf{s} ,

$$E_X^{\text{BR}} = -\frac{1}{2} \sum_\sigma \int \frac{\rho_\sigma}{b} \left(1 - e^{-x} - \frac{1}{2} x e^{-x} \right) d\mathbf{r}$$

This functional is much more complex than a GGA as it contains the additional ingredients of τ_σ and $\nabla^2\rho_\sigma$ (as well as the non-linear equation).

3.2 The B88 Correlation Meta-GGA

Real-space models of correlation holes can also be used to develop opposite- and parallel-spin meta-GGA correlation functionals.

Returning to the adiabatic connection, we can Taylor expand the spherically averaged λ -dependent holes around the reference point.

For opposite spins:

$$h_{C\lambda}^{\alpha\beta}(\mathbf{r}, s) = (B_{\alpha\beta} - \rho_\beta) + \lambda B_{\alpha\beta} s + \dots$$

and for parallel spins:

$$h_{XC\lambda}^{\sigma\sigma}(\mathbf{r}, s) = -\rho_\sigma + \left(B_{\sigma\sigma} - \frac{1}{6} \nabla^2 \rho_\sigma \right) s^2 + \frac{\lambda}{2} B_{\sigma\sigma} s^3 + \dots$$

where the B 's are position-dependent coefficients.

We also know the Taylor expansion of the exchange hole:

$$h_X(\mathbf{r}, s) = -\rho_\sigma - \frac{1}{6} (\nabla^2 \rho_\sigma - 2D_\sigma) s^2 + \dots$$

which is λ independent. Subtracting this from the XC hole gives the expansion of the parallel-spin correlation hole:

$$h_{C\lambda}^{\sigma\sigma}(\mathbf{r}, s) = \left(B_{\sigma\sigma} - \frac{1}{3}D_{\sigma} \right) s^2 + \frac{\lambda}{2}B_{\sigma\sigma}s^3 + \dots$$

To develop a real-space model, we use functions that recover these expansions for the cusp conditions, and change sign when s is equal to some correlation length $z_{\sigma\sigma}$ or $z_{\alpha\beta}$:

$$h_{C\lambda}^{\alpha\beta}(\mathbf{r}, s) = \frac{\lambda(s - z_{\alpha\beta})\rho_{\beta}}{1 - \lambda z_{\alpha\beta}} F(\gamma_{\alpha\beta}s)$$

$$h_{C\lambda}^{\sigma\sigma}(\mathbf{r}, s) = \frac{\lambda s^2(s - z_{\sigma\sigma})D_{\sigma}}{6(1 - \lambda z_{\sigma\sigma}/2)} F(\gamma_{\sigma\sigma}s)$$

where $F(\gamma s)$ is a suitable damping function, required to damp the hole to zero at large s , with quadratic behaviour at small s :

$$\lim_{s \rightarrow 0} F(\gamma s) = 1 - a\gamma^2 s^2 + \dots$$

Possible functions considered were $F(x) = \text{sech}(x)$, $F(x) = (1+x)e^{-x}$, and $F(x) = e^{-x^2}$.

Integrating these correlation-hole expressions gives forms for the correlation energies:

$$E_C^{\alpha\beta+\beta\alpha} = -I_1 \int \rho_{\alpha}\rho_{\beta}z_{\alpha\beta}^2 \left[1 - \frac{\ln(1 - z_{\alpha\beta})}{z_{\alpha\beta}} \right] d\mathbf{r}$$

$$E_C^{\sigma\sigma} = I_2 \int \rho_{\sigma}D_{\sigma}z_{\sigma\sigma}^4 \left[1 - \frac{2}{z_{\sigma\sigma}} \ln \left(1 + \frac{z_{\sigma\sigma}}{2} \right) \right] d\mathbf{r}$$

The particular values of the integrals I_1 and I_2 depend on the functional form chosen for $F(\gamma s)$ and were assigned final values of -0.8 and -0.01, respectively.

The remaining term is the correlation length, z . This taken to be proportional to the sum of exchange-hole (or Fermi) radii (R_F), since this should be a good measure of the length scale for electron-electron interactions:

$$z_{\sigma\sigma'} = c_{\sigma\sigma'}(R_F^{\sigma} + R_F^{\sigma'})$$

The mean inverse radius of the exchange hole is given by the exchange potential:

$$U_X^{\sigma} = \int \frac{1}{s} |h_X^{\sigma\sigma}(\mathbf{r}, s)| d\mathbf{r} = \langle s^{-1} \rangle$$

Thus, the correlation length is taken to be

$$z_{\sigma\sigma'} = c_{\sigma\sigma'}(|U_X^{\sigma}|^{-1} + |U_X^{\sigma'}|^{-1})$$

The exchange potential is determined from the particular exchange functional as

$$E_X^\sigma = -\frac{1}{2} \int \rho_\sigma U_X^\sigma d\mathbf{r}$$

which shows a connection between the exchange and correlation terms.

If we take our exchange functional as the LSDA, then

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

so our mean Fermi hole radius is

$$R_F^\sigma = -\frac{1}{3} \left(\frac{3}{4\pi\rho_\sigma} \right)^{-1/3}$$

The parameters $c_{\sigma\sigma'}$ were then fit to minimize errors in LSDA correlation energies. The resulting values of $c_{\alpha\beta} = 0.62$ and $c_{\sigma\sigma} = 1.11$ indicate the opposite-spin correlation is shorter in range than parallel-spin correlation. This is reasonable since exchange already serves to separate parallel-spin electrons.

This correlation model has been paired with both the B88 and BR exchange functionals, using those particular exchange potentials to determine the correlation lengths.

3.3 Chemical Bonding Descriptors: ELF and LOL

Two functions involving the kinetic-energy density have been successfully used to visualize electron localization.

The first is the electron localization function (ELF):

$$\text{ELF} = \left[1 + \left(\frac{D_\sigma}{D_\sigma^{\text{UEG}}} \right)^2 \right]^{-1}$$

where

$$D_\sigma^{\text{UEG}} = \tau_\sigma^{\text{UEG}} = \frac{3}{5} (6\pi^2)^{2/3} \rho_\sigma^{5/3}$$

is the uniform electron gas kinetic-energy density.

It can be shown that D_σ is the leading-order term in the Taylor expansion of the spherically averaged conditional pair density:

$$\frac{\Pi(\mathbf{r}, s)}{\rho_\sigma(\mathbf{r})} = \frac{1}{3} D_\sigma s^2 + \dots$$

So smaller D_σ means that there is a small probability of finding a second same-spin electron near the reference point, \mathbf{r} .

Thus, there is an inverse relationship between D_σ and electron localization – small D_σ means that the reference electron is highly localized, while large D_σ means that the reference electron is delocalized.

The ratio $D_\sigma/D_\sigma^{\text{UEG}}$ is used to give a dimensionless quantity and to express the extent of electron localization relative to the uniform electron gas.

Because $0 \leq D_\sigma/D_\sigma^{\text{UEG}} < \infty$, the inverse form is used to map the ELF values onto the interval $0 \leq \text{ELF} \leq 1$.

Values of ELF near 1 correspond to highly localized electrons, while values of 0.5 correspond to a UEG-like electron distribution. Typically ELF isosurfaces of 0.8 are used to visualize chemical bonding and electron lone pairs.

An alternative chemical bonding descriptor is the localized orbital locator (LOL):

$$\text{LOL} = \frac{t_\sigma}{1 + t_\sigma}$$

where

$$t_\sigma = \tau_\sigma^{\text{UEG}}/\tau_\sigma$$

Ideally, the ratio of exact to UEG exchange-energy densities would be used instead to describe electron localization, but the exact exchange-energy density is expensive to compute for large molecules and solids, so the ratio of exact to UEG kinetic-energy densities is used to approximate it.

Because $0 \leq t_\sigma < \infty$, the form of LOL is chosen to map it onto the interval $0 \leq \text{LOL} \leq 1$. As for ELF, high values of LOL indicate highly localized electrons and isosurfaces can be plotted to visualize chemical bonding and electron lone pairs.

3.4 The B95 Correlation Meta-GGA

Meta-GGA functionals (other than BR and B88C) tend to more closely resemble GGAs, starting from the uniform electron gas, rather than using real-space models of exchange or correlation holes. Ratios involving τ_σ , like $D_\sigma/D_\sigma^{\text{UEG}}$ or t_σ as used in ELF and LOL, are used in the enhancement factors.

The kinetic-energy term can appear in only the correlation functional, or in both exchange and correlation.

One example is the B95 correlation functional, where the UEG correlation energy is decomposed into opposite- and parallel-spin terms:

$$E_{C,\text{opp}}^{\text{LSDA}} = E_C^{\text{LSDA}}(\rho_\alpha, \rho_\beta) - E_C^{\text{LSDA}}(\rho_\alpha, 0) - E_C^{\text{LSDA}}(\rho_\beta, 0)$$

$$E_{C,\text{par}}^{\text{LSDA}} = E_C^{\text{LSDA}}(\rho_\alpha, 0) + E_C^{\text{LSDA}}(\rho_\beta, 0)$$

To add in gradient dependence, we use an enhancement factor, similar to PBE. For opposite spins:

$$E_{C,\text{opp}}^{\text{B95}} = \int \frac{1}{1 + c_{\text{opp}}(\chi_\alpha^2 + \chi_\beta^2)} \varepsilon_{C,\text{opp}}^{\text{LSDA}} d\mathbf{r}$$

For parallel spins:

$$E_{C,\text{par}}^{\text{B95}} = \sum_\sigma \int \frac{1}{(1 + c_{\text{opp}}\chi_\sigma^2)^2} \frac{D_\sigma}{D_\sigma^{\text{UEG}}} \varepsilon_C^{\text{LSDA}} d\mathbf{r}$$

The ratio of $D_\sigma/D_\sigma^{\text{UEG}}$ is used as a self-interaction correction.

$D_\sigma = 0$ in one-electron regions, where the spin density is dominated by a single orbital, ψ :

$$\begin{aligned} D_\sigma &= \tau_\sigma - \frac{1}{4} \frac{(\nabla\rho_\sigma)^2}{\rho_\sigma} \\ &= (\nabla\psi)^2 - \frac{1}{4} \frac{(\nabla\psi^2)^2}{\psi^2} \\ &= (\nabla\psi)^2 - \frac{1}{4} \frac{(2\psi\nabla\psi)^2}{\psi^2} \\ &= (\nabla\psi)^2 - (\nabla\psi)^2 \\ &= 0 \end{aligned}$$

The ratio $D_\sigma/D_\sigma^{\text{UEG}}$ scales the UEG correlation energy to ensure that it vanishes for 1-electron systems, where there should be no correlation.

The drawback with this form is that the parallel-spin correlation energy density will diverge in intermolecular regions of van der Waals dimers. In such regions, both ρ_σ and $\nabla\rho_\sigma \rightarrow 0$ and

$$\lim_{\rho_\sigma, \nabla\rho_\sigma \rightarrow 0} \frac{D_\sigma}{D_\sigma^{\text{UEG}}} \sim \frac{\tau_\sigma}{\rho_\sigma^{5/3}} = \infty$$

This necessitates the use of extremely fine integration grids when using this (or other similar) meta-GGAs to obtain smooth potential energy surfaces and avoid spurious negative vibrational frequencies.

3.5 Other Meta-GGA Functionals

Other meta-GGAs, including the popular TPSS and M06-L functionals, use ratios of $\tau_\sigma^W/\tau_\sigma$, $\tau_\sigma/\tau_\sigma^{\text{UEG}}$, and D_σ/τ_σ to scale both the exchange and correlation terms.

Most meta-GGAs show similar grid sensitivity to B95, although this can be avoided with careful choice of the τ -dependence. Notably, the BMK functional uses the ratio:

$$w_\sigma = \frac{D_\sigma^{\text{UEG}} - \tau_\sigma}{D_\sigma^{\text{UEG}} + \tau_\sigma}$$

which is smoothly varying in intermolecular regions and does not show grid sensitivity.

Meta-GGAs are generally more complicated in form than GGAs, and many (like M06-L) are highly empirical. Fitting can lower errors on common benchmarks, but typically causes larger errors in absolute exchange and correlation energies.

For example, the M06-L meta-GGA uses

$$E_X^{\text{M06-L}} = \sum_\sigma \int f(\chi_\sigma, y_\sigma) \varepsilon_X^{\text{LSDA}} d\mathbf{r}$$

$$E_{C,\text{par}}^{\text{M06-L}} = \sum_\sigma \int f(\chi_\sigma, y_\sigma) D_\sigma \varepsilon_{C,\text{par}}^{\text{LSDA}} d\mathbf{r}$$

$$E_{C,\text{opp}}^{\text{M06-L}} = \int f(\chi_{\alpha\beta}, y_{\alpha,\beta}) \varepsilon_{C,\text{opp}}^{\text{LSDA}} d\mathbf{r}$$

with

$$y_\sigma = \frac{3}{5} (6\pi^2)^{2/3} \left(\frac{\tau_\sigma}{\tau_\sigma^{\text{UEG}}} - 1 \right)$$

where $\chi_{\alpha\beta}^2 = \chi_\alpha^2 + \chi_\beta^2$ and $y_{\alpha\beta} = y_\alpha + y_\beta$.

The form of the enhancement factors involves 6 empirical parameters that are fit to distinct values for each of the exchange and correlation terms:

$$f(\chi_\sigma, y_\sigma) = \frac{a_1}{1 + a_6(\chi_\sigma^2 + y_\sigma)} + \frac{a_2\chi_\sigma^2 + a_3y_\sigma}{[1 + a_6(\chi_\sigma^2 + y_\sigma)]^2} + \frac{a_4\chi_\sigma^4 + a_5\chi_\sigma^2 y_\sigma}{[1 + a_6(\chi_\sigma^2 + y_\sigma)]^3}$$

This leads to over fitting, with oscillations in the forms of the enhancement factors.

Overall, meta-GGAs offer only marginal improvements on GGAs, and both suffer from delocalization error. To obtain significantly better accuracy than GGAs, we must include exact (HF) exchange.

3.6 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 λ (coupling-strength) dependence of the exchange potential energy, U_X . Recall that λ 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

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

with $a = 0.2$.

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.

3.7 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

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

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

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

The γ '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.

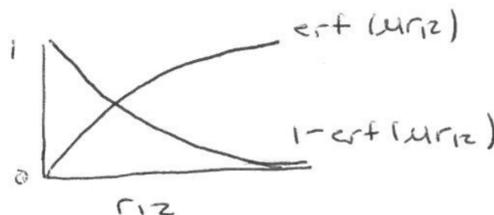
However, since this work, many even more heavily parameterized hybrid meta-GGA functionals (like M06 and M06-2X) have been proposed with > 50 parameters and clear oscillatory behaviour in the enhancement factors, indicating overfitting. The overfitting causes

improved statistical performance for the fit sets, but these functionals do not represent a significant improvement over 1-3 parameter hybrids and cannot be recommended.

3.8 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.

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

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

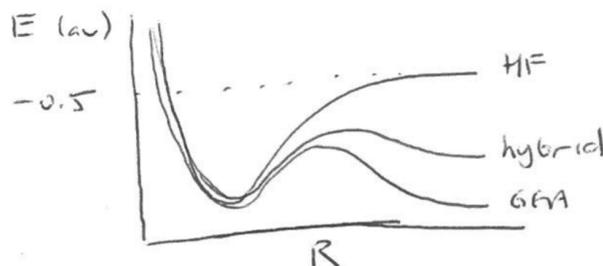
The LC-BLYP functional (the first range-separated hybrid) uses B88 exchange. Subsequent range-separated hybrids, like LC- ω PBE, use GGAs developed specifically for range separation. The base GGA is recovered in the $\mu = 0$ limit.

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 μ 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.

3.9 Delocalization Error

The DFT methods described so far perform quite well for most thermochemistry, with errors in the G3 atomization energies of ~ 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, 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.

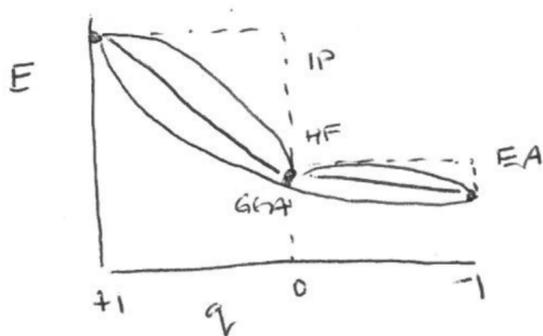
The exact exchange hole in H_2^+ integrates to -1 electron overall, with $-\frac{1}{2}e^-$ around each nucleus, regardless of the reference point.



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, the LSDA/GGAs preferentially stabilize fractional charges due to the incorrect hole normalization. Alternatively, HF destabilizes fractional charges due to neglect of correlation.

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

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

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 μ 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.

Delocalization error is likely the largest outstanding problem in DFT.