

Hybrid functionals in DFT

Lecture notes for DST School
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Hartree-Fock Method

HF approximation is a variational approach to solving interacting problem many-body

$$H = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i v(\vec{r}_i) + \frac{1}{2} \sum_{i < j} \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (1)$$

Approximation is to assume a single determinant form for the many-body wave function

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \dots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \dots & \chi_N(x_2) \\ \dots & \dots & \dots & \dots \\ \chi_1(x_N) & \chi_2(x_N) & \dots & \chi_N(x_N) \end{vmatrix} \quad (2)$$

χ 's are the spin-orbitals, and $x = (\vec{r}, s)$ is space and spin coordinates of an electron.

- Variational freedom is in choice of χ_i 's.
- Tasks
 1. Calculate expectation value of the Hamiltonian in the state Ψ .
 2. Vary the spin-orbitals χ 's to minimize it
 3. Subject to the constraint that they are orthonormal : $\langle \chi_i | \chi_j \rangle = \delta_{ij}$.
- Expectation value of H in the state Ψ is

$$E_{\Psi} = \sum_i H_i + \frac{1}{2} \sum_{ij} (J_{ij} - K_{ij}) \quad (3)$$

Where

$$H_i = \int \chi_i^*(x) \left[-\frac{1}{2} \nabla^2 + v(\vec{r}) \right] \chi_i(x) dx \quad (4)$$

$$J_{ij} = \int \int \chi_i^*(x_1) \chi_j^*(x_2) \frac{1}{r_{12}} \chi_i(x_1) \chi_j(x_2) dx_1 dx_2 \quad (5)$$

and

$$K_{ij} = \int \int \chi_i^*(x_1) \chi_j^*(x_2) \frac{1}{r_{12}} \chi_i(x_2) \chi_j(x_1) dx_1 dx_2 \quad (6)$$

J_{ij} : Hartree term; K_{ij} : Exchange term Note: $J_{ii} = K_{ii}$, no self-interaction.

E_ψ in Eqn. 3 has to be minimized subject to the constraints

$$\int \chi_i^*(x) \chi_j(x) dx = \delta_{ij} \quad (7)$$

Optimality condition is

$$\delta \left(E_\psi + \epsilon_{ij} \left(\int \chi_i^*(x) \chi_j(x) dx - \delta_{ij} \right) \right) = 0 \quad (8)$$

Differentiating this w.r.t. χ_i^* we get the HF equation

$$\left[-\frac{1}{2} \nabla^2 + v(\vec{r}) + \sum_{j \neq i} (\hat{J}_j(x) - \hat{K}_j(x)) \right] \chi_i(x) = \sum_j \epsilon_{ij} \chi_j(x) \quad (9)$$

where \hat{J} is the Coulomb operator

$$\hat{J}_j(x_1) \chi_i(x_1) = \left[\int \chi_j^*(x_2) \frac{1}{r_{12}} \chi_j(x_2) dx_2 \right] \chi_i(x_1) \quad (10)$$

and \hat{K} is the exchange operator

$$\hat{K}_j(x_1) \chi_i(x_1) = \left[\int \chi_j^*(x_2) \frac{1}{r_{12}} \chi_i(x_2) dx_2 \right] \chi_j(x_1) \quad (11)$$

HF exchange operator is non-local.

Through a unitary transform of the spin orbitals, one gets the canonical HF equations

$$\left[-\frac{1}{2}\nabla^2 + v(\vec{r}) + \sum_{j \neq i} (\hat{J}_j(x) - \hat{K}_j(x)) \right] \chi_i(x) = \epsilon_i \chi_i(x)$$

Ref: [Modern Quantum Chemistry, Szabo and Ostlund.](#)

We integrate out the spin degrees. For simplicity we consider spatial parts of up and down spin orbitals are identical: Restricted Hartree-Fock.

N electrons: $N/2$ spin-up, $N/2$ spin-down.

For spin up $\chi_i(x) = \psi_i(\vec{r})\alpha(s)$, for spin down $\chi_i(x) = \psi_i(\vec{r})\beta(s)$.

Now,

$$\begin{aligned} H_i &= \int \psi_i(\vec{r})\alpha^*(s) \left[-\frac{1}{2}\nabla^2 + v(\vec{r}) \right] \psi_i(\vec{r})\alpha(s) d^3r ds \\ &= \int \psi_i(\vec{r}) \left[-\frac{1}{2}\nabla^2 + v(\vec{r}) \right] \psi_i(\vec{r}) d^3r. \end{aligned} \quad (12)$$

If χ_i and χ_j have the same spin part (either α or β)

$$\begin{aligned}
 J_{ij} &= \int \int \psi_i^*(\vec{r}_1)\alpha^*(s_1)\psi_j^*(\vec{r}_2)\alpha^*(s_2) \\
 &\quad \frac{1}{r_{12}}\psi_i(\vec{r}_1)\alpha(s_1)\psi_j(\vec{r}_2)\alpha(s_2)d\vec{r}_1ds_1d\vec{r}_2ds_2 \\
 &= \int |\psi_i(\vec{r}_1)|^2 \frac{1}{r_{12}} |\psi_j(\vec{r}_2)|^2 d^3r_1 d^3r_2.
 \end{aligned}$$

If χ_i and χ_j have different spin parts (α and β), then also

$$\begin{aligned}
 J_{ij} &= \int \int \psi_i^*(\vec{r}_1)\alpha^*(s_1)\psi_j^*(\vec{r}_2)\beta^*(s_2) \\
 &\quad \frac{1}{r_{12}}\psi_i(\vec{r}_1)\alpha(s_1)\psi_j(\vec{r}_2)\beta(s_2)d\vec{r}_1ds_1d\vec{r}_2ds_2 \\
 &= \int |\psi_i(\vec{r}_1)|^2 \frac{1}{r_{12}} |\psi_j(\vec{r}_2)|^2 d^3r_1 d^3r_2
 \end{aligned}$$

Classical density-density interactions: $J[\rho] = \frac{1}{2} \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d^3r_1 d^3r_2$

If χ_i and χ_j have different spin parts (α and β)

$$\begin{aligned}
 K_{ij} &= \int \int \psi_i^*(\vec{r}_1) \alpha^*(s_1) \psi_j^*(\vec{r}_2) \beta^*(s_2) \\
 &\quad \frac{1}{r_{12}} \psi_i(\vec{r}_2) \alpha(s_2) \psi_j(\vec{r}_1) \beta(s_1) d^3 r_1 ds_1 d^3 r_2 ds_2 \\
 &= 0.
 \end{aligned}$$

If χ_i and χ_j have the same spin part (either α or β)

$$\begin{aligned}
 K_{ij} &= \int \int \psi_i^*(\vec{r}_1) \alpha^*(s_1) \psi_j^*(\vec{r}_2) \alpha^*(s_2) \\
 &\quad \frac{1}{r_{12}} \psi_i(\vec{r}_2) \alpha(s_2) \psi_j(\vec{r}_1) \alpha(s_1) d^3 r_1 ds_1 d^3 r_2 ds_2 \\
 &= \int \psi_i(\vec{r}_1)^* \psi_j^*(\vec{r}_2) \frac{1}{r_{12}} \psi_i(\vec{r}_2) \psi_j(\vec{r}_1) d^3 r_1 d^3 r_2.
 \end{aligned}$$

Thus

$$K_{ij} = \int \psi_i^*(\vec{r}_1) \psi_j^*(\vec{r}_2) \frac{1}{r_{12}} \psi_i(\vec{r}_2) \psi_j(\vec{r}_1) d^3 r_1 d^3 r_2 \delta_{s_1 s_2}. \quad (13)$$

Important Lessons

- There are non-classical terms in the electron-electron interaction energy.
- Exchange operates only between electrons of same spin.
- Is of purely quantum origin.
- Is always negative.

Density matrices

Let $\Psi(x_1 x_2 \cdots x_N)$ be a normalized N -electron wave function.

$$\gamma_N(x'_1 x'_2 \cdots x'_N, x_1 x_2 \cdots x_N) = \Psi(x'_1, x'_2, \cdots, x'_N) \Psi^*(x_1, x_2, \cdots, x_N)$$

is called the density matrix.

Coordinate representation of the *density operator* $|\Psi\rangle\langle\Psi| \equiv \hat{\gamma}_N$.

$$\begin{aligned} \langle x'_1 x'_2 \cdots x'_N | \hat{\gamma}_N | x_1 x_2 \cdots x_N \rangle &= \\ \langle x'_1 x'_2 \cdots x'_N | \Psi \rangle \langle \Psi | x_1 x_2 \cdots x_N \rangle &= \\ \gamma_N(x'_1 x'_2 \cdots x'_N, x_1 x_2 \cdots x_N) &= \\ \Psi(x'_1, x'_2, \cdots, x'_N) \Psi^*(x_1, x_2, \cdots, x_N) & \end{aligned}$$

$\hat{\gamma}_N$ is a projection operator.

$$\text{tr}(\hat{\gamma}_N) = \int \gamma_N(x_1 x_2 \cdots x_N, x_1 x_2 \cdots x_N) dx^N = 1. \quad (14)$$

Expectation value of an operator \hat{A}

$$\begin{aligned} \langle A \rangle &= \int \Psi^*(x_1, x_2, \cdots, x_N) \hat{A} \Psi(x_1, x_2, \cdots, x_N) dx^N \\ &= \int \langle x_1 x_2 \cdots x_N | \Psi \rangle \hat{A} \langle \Psi | x_1 x_2 \cdots x_N \rangle dx^N = \text{tr}(\gamma_N A). \end{aligned}$$

We only have one- and two-body operators in the Hamiltonian.

Useful to define *reduced density matrices*.

Reduced density matrix of order p

$$\gamma_p(x'_1 x'_2 \cdots x'_p, x_1 x_2 \cdots x_p) = C_p^N \int \gamma_p(x'_1 x'_2 \cdots x'_p x_{p+1} \cdots x_N, x_1 x_2 \cdots x_p x_{p+1} \cdots x_N) dx_{p+1} \cdots dx_N.$$

Second order density matrix

$$\gamma_2(x'_1 x'_2, x_1 x_2) = \frac{N(N-1)}{2} \int \gamma_N(x'_1 x'_2 x_3 \cdots x_N, x_1 x_2 x_3 \cdots x_N) dx_3 \cdots dx_N.$$

First order density matrix

$$\gamma_1(x'_1, x_1) = N \int \gamma_N(x'_1 x_2 \cdots x_N, x_1 x_2 \cdots x_N) dx_2 \cdots dx_N.$$

Normalization of γ_2

$$\begin{aligned} \int \gamma_2(x_1x_2, x_1x_2) dx_1 dx_2 &= \\ \int \left[\frac{N(N-1)}{2} \int \gamma_N(x_1x_2 \cdots x_3 \cdots x_N, x_1x_2x_3 \cdots x_N) dx_3 \cdots dx_N \right] dx_1 dx_2 &= \\ &= N(N-1)/2. \end{aligned}$$

Normalization of γ_1

$$\begin{aligned} \int \gamma_1(x_1, x_1) dx_1 &= \\ \int \left[N \int \gamma_N(x_1x_2 \cdots x_3 \cdots x_N, x_1x_2x_3 \cdots x_N) dx_2 \cdots dx_N \right] dx_1 &= \\ &= N \end{aligned}$$

Question:

$$\frac{2}{N-1} \int \gamma_2(x'_1x_2, x_1x_2) dx_2 = ?.$$

One-electron local operators $\hat{O}_1 = \sum_i O_1(x_i)$.

$$\begin{aligned}\langle O_1 \rangle &= \int \Psi^* \sum_i O_1(x_i) \Psi dx^N \\ &= N \int \Psi^* O_1(x_1) \Psi dx^N \\ &= \int O_1(x_1) \gamma_1(x_1, x_1) dx_1.\end{aligned}$$

Two-electron local operators $\hat{O}_2 = \sum_{i < j} O_2(x_i, x_j)$.

$$\langle O_2 \rangle = \int O_2(x_1, x_2) \gamma_2(x_1 x_2, x_1 x_2) dx_1 dx_2.$$

Energy

$$\begin{aligned}E = \text{tr}(H\gamma_N) &= \int \left[\left(-\frac{1}{2} \nabla_1^2 + v(\vec{r}_1) \right) \gamma_1(x_1, x_2) \right]_{x_1=x_2} dx_1 \\ &\quad + \int \frac{1}{r_{12}} \gamma_2(x_1 x_2, x_1 x_2) dx_1 dx_2.\end{aligned}$$

Spinless density matrices

First order spinless density matrix

$$\rho_1(\vec{r}_1, \vec{r}'_1) = \int \gamma_1(\vec{r}_1 s_1, \vec{r}'_1 s_1) ds_1 \quad (15)$$

Second order spinless density matrix

$$\rho(\vec{r}_1 \vec{r}_2, \vec{r}'_1 \vec{r}'_2) = \int \gamma_2(\vec{r}_1 s_1 \vec{r}_2 s_2, \vec{r}'_1 s_1 \vec{r}'_2 s_2) ds_1 ds_2. \quad (16)$$

Diagonal elements

$$\begin{aligned} \rho_2(\vec{r}_1, \vec{r}_2) &\equiv \rho_2(\vec{r}_1 \vec{r}_2, \vec{r}_1 \vec{r}_2) \\ \rho(\vec{r}_1) &\equiv \rho_1(\vec{r}_1, \vec{r}_1). \end{aligned}$$

Since our Hamiltonian is spin-independent, we integrate spin degrees of freedom and obtain

$$\begin{aligned} E = \int \left[\left(-\frac{1}{2} \nabla^2 \rho(\vec{r}, \vec{r}') \right) \right]_{\vec{r}=\vec{r}'} d^3 r + \int v(\vec{r}) \rho(\vec{r}) d^3 r \\ + \int \frac{1}{r_{12}} \rho_2(\vec{r}_1, \vec{r}_2) d^3 r_1 d^3 r_2. \end{aligned}$$

Idea of exchange-correlation hole

Classical e-e interaction energy

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d^3r_1 d^3r_2. \quad (17)$$

Full e-e interaction energy

$$E_{ee} = \int \int \frac{1}{r_{12}} \rho_2(\vec{r}_1, \vec{r}_2) d^3r_1 d^3r_2. \quad (18)$$

Let us write

$$\rho_2(\vec{r}_1, \vec{r}_2) = \frac{1}{2} \rho(\vec{r}_1)\rho(\vec{r}_2) [1 + h(\vec{r}_1, \vec{r}_2)]. \quad (19)$$

h called pair-correlation function.

Integrating over \vec{r}_2

$$\frac{N-1}{2}\rho(\vec{r}_1) = \frac{1}{2}\rho(\vec{r}_1) \left[N + \int \rho(\vec{r}_2)h(\vec{r}_1, \vec{r}_2)d^3r_2 \right]. \quad (20)$$

Hence

$$\int \rho(\vec{r}_2)h(\vec{r}_1, \vec{r}_2)d^3r_2 = -1. \quad (21)$$

$\rho_{xc}(\vec{r}_1, \vec{r}_2) \equiv \rho(\vec{r}_2)h(\vec{r}_1, \vec{r}_2)$ called exchange-correlation hole for an electron at \vec{r}_1 .

Exchange-correlation hole obeys the sum rule

$$\int \rho_{xc}(\vec{r}_1, \vec{r}_2)d^3r_2 = -1 \quad (22)$$

e-e interaction energy now is

$$E_{ee} = J[\rho] + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho_{xc}(\vec{r}_1, \vec{r}_2)}{r_{12}} d^3r_1 d^3r_2. \quad (23)$$

Discussion on density matrices were general, true for any N -electron wave function which is, of course, anti-symmetric.

Show for a single determinant wave function

$$\gamma_2(x'_1 x'_2, x_1 x_2) \frac{1}{2} [\gamma_1(x'_1, x_1) \gamma_1(x'_2, x_2) - \gamma_1(x'_1, x_2) \gamma_1(x'_2, x_1)].$$

From this it follows

$$\frac{1}{2} \int \int \frac{1}{r_{12}} [\gamma_1(x_1, x_1) \gamma_1(x_2, x_2) - \gamma_1(x_1, x_2) \gamma_1(x_2, x_1)] dx_1 dx_2$$

Since

$$\gamma_1(x_1, x_2) = \gamma_1^*(x_2, x_1)$$

exchange is always negative.

Ref: Density Functional Theory of Atoms and Molecules, R. G. Parr and W. Yang

HF for uniform electron gas

The model: Interacting electrons.

Positive charge is uniformly spread as a background.

Electron charge density is exactly compensated by the background charge density.

Only the exchange energy contribution survives in the interaction part.

Plane wave states are solutions for this problem. So one-electron spin orbitals are

$$\chi_i(x) = \frac{1}{\sqrt{V}} e^{(i\vec{k}_i \cdot \vec{r})} \times \alpha \text{ or } \beta.$$

Each \vec{k}_i state doubly occupied: for α and β .

Let us recall the canonical HF equation

$$\left[-\frac{1}{2}\nabla^2 + v(\vec{r}) + \sum_{j \neq i} (\hat{J}_j(x) - \hat{K}_j(x)) \right] \chi_i(x) = \epsilon_i \chi_i(x)$$

Which, after integrating out the spin degrees of freedom, becomes

$$\begin{aligned} & -\frac{1}{2}\nabla^2 \psi_i(\vec{r}) + v(\vec{r})\psi_i(\vec{r}) + v_{ee,cl}\psi_i(\vec{r}) \\ & - \sum_j \int d^3r' \frac{1}{|\vec{r} - \vec{r}'|} \psi_j^*(\vec{r}')\psi_i(\vec{r}')\psi_j(\vec{r})\delta_{s_i s_j} = \epsilon_i \psi_i(\vec{r}) \end{aligned}$$

The second and third terms on LHS cancel in a uniform electron gas.

Using the Fourier transform of the Coulomb potential

$$\frac{1}{|\vec{r} - \vec{r}'|} \rightarrow 4\pi \int \frac{d^3q}{(2\pi)^3} \frac{e^{i\vec{q}\cdot(\vec{r}-\vec{r}')}}{q^2}$$

we get

$$\left(\frac{k_i^2}{2} - \int_{k' < k_F} \frac{d^3k'}{(2\pi)^3} \frac{4\pi}{|\vec{k}_i - \vec{k}'|} \right) \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}).$$

k_F is the Fermi wave vector. Energy of a state of wave vector \vec{k} is

$$\epsilon(\vec{k}) = \frac{k^2}{2} - \frac{2}{\pi} k_F F \left(\frac{k}{k_F} \right)$$

with

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

Total energy of the electron gas is (with proper units)

$$E = 2 \sum_{k < k_F} \frac{k^2}{2} - \frac{e^2 k_F}{\pi} \sum_{k < k_F} \left[1 + \frac{k_F^2 - k^2}{2kk_F} \ln \left| \frac{k_F + k}{k_F - k} \right| \right]$$

The first term is the energy of a free-electron gas (kinetic energy only). The second term can be evaluated by converting the sums into integrals,

$$E = N \left[\frac{3}{5} \epsilon_F - \frac{3e^2 k_F}{4\pi} \right].$$

ϵ_F is the Fermi energy.

This result is conventionally written in terms of the reduced Wigner-Seitz parameter r_s/a_0 of the electrons gas,

$$\frac{4}{3}\pi r_s^3 = \frac{V}{N}.$$

$$\frac{E}{N} = \frac{e^2}{2a_0} \left[\frac{3}{5}(k_F a_0)^2 - \frac{3}{2\pi}(k_F a_0) \right] = \left[\frac{2.21}{(r_s/a_0)^2} - \frac{0.916}{(r_s/a_0)} \right] \text{Ry}$$

Leading order terms in a high density expansion are

$$\frac{E}{N} = \left[\frac{2.21}{(r_s/a_0)^2} - \frac{0.916}{(r_s/a_0)} + 0.0622 \ln(r_s/a_0) - 0.096 + O(r_s/a_0) \right] \text{Ry}$$

First two terms are HF result, additional terms leading order contribution to *correlation energy*.

HF contains no correlation effect.

$E_{\text{exact}} - E_{HF} = E_c$ is by definition **correlation energy**.

Important points to note in HF results:

1. Exchange energy $E_x = -\frac{3k_F}{4\pi} = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}$.
This is the form of exchange energy density used in LDA.
2. A disturbing feature of $\epsilon(\vec{k})$: $\frac{\partial \epsilon}{\partial k} |_{k=k_F}$ has a logarithmic divergence. Fermi velocity has log divergence.
3. The reason for this is long-range nature of HF exchange interaction. This is a consequence of FT of Coulomb interaction that has the form $4\pi/k^2$, and diverges as $k \rightarrow 0$.
4. Screened Coulomb interaction $v(r) = e^{-k_0 r}/r$ has a FT $4\pi/(k + k_0)^2$. No divergence.

An assessment of DFT calculations for solids:

1. L(S)DA and GGA's are canonical choice for exchange correlation energy functionals.
2. LSDA produces structural properties, lattice constants, bulk moduli, with good accuracy.
3. Band gaps are seriously under-estimated.
4. GGA's improve some aspects: band gaps improve marginally, lattice constants often better with LSDA.
5. Other methods devised for accurate electronic properties such as band gaps: 'Scissor operator', LSDA+U, GW.
6. But these often have to depend on LSDA structure.
7. Need for a universal method which can calculate all properties accurately, for solids, atoms and molecules.

Hybrid functionals:

Hybrid because they incorporate a fraction of exact HF exchange.
Becke half-and-half hybrid (1993)

$$E_{xc} = \frac{1}{2} (E_x + E_{xc}^{\text{DF}})$$

Becke three-parameter hybrid (1993)

$$E_{xc} = E_{xc}^{\text{LDA}} + a_0 (E_x - E_x^{\text{LDA}}) + a_x (E_x^{\text{GGA}} - E_x^{\text{LDA}}) + a_c (E_c^{\text{GGA}} - E_c^{\text{LDA}}).$$

Or a simplification of this (1996) $a_x = 1 - a_0$, $a_c = 1$, leading to

$$E_{xc} = E_{xc}^{\text{DF}} + a_0 (E_x - E_x^{\text{DF}})$$

Others include B3PW91, B3LYP etc.

HF exchange in solids has problems:

For metals log divergence in orbital energies.

For solids exchange interactions decay exponentially with band gap.

Computationally demanding even for small band-gap semiconductors.

Ideas of Heyd, Scuseria and Ernzerhof:

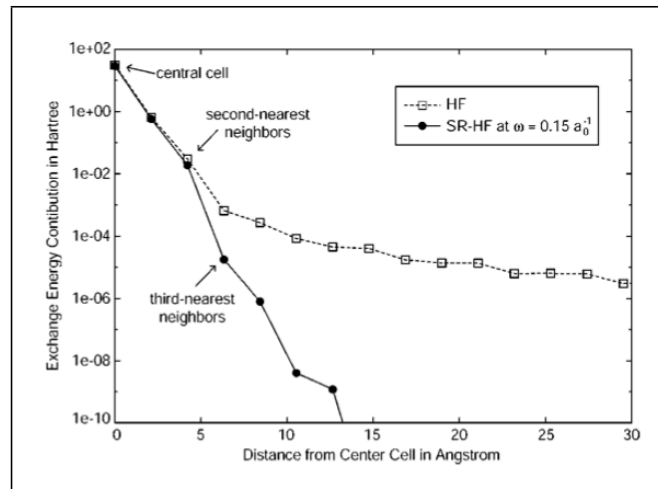
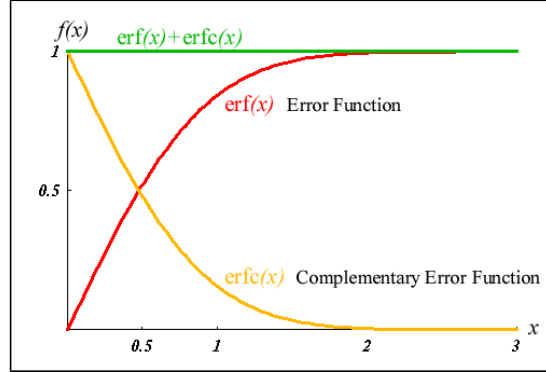
Use screened Coulomb potential for the exchange part only.

$$\frac{1}{r} = \frac{f_1(r)}{r} + \frac{f_2(r)}{r}$$

f_1 should be significant at small r 's, f_2 at large r 's, and $f_1(r) + f_2(r) = 1$.

HSE choice:

$$\frac{1}{r} = \frac{\text{erfc}(\omega r)}{r} + \frac{\text{erf}(\omega r)}{r}$$



Contribution of a cell to the exchange energy as a function of its distance from a reference cell in a (6×6) metallic carbon nanotube.

HSE hybrid functional is based on the PBE0 functional.

$$E_{xc}^{\text{PBE0}} = aE_x^{\text{HF}} + (1 - a)E_x^{\text{PBE}} + E_c^{\text{PBE}},$$

$$a = 1/4.$$

HSE modifies only the exchange part of PBE0:

$$E_x^{\text{PBE0}} = aE_x^{\text{HF}} + (1 - a)E_x^{\text{PBE}}.$$

Split these terms into short-range and long-range parts:

$$E_x^{\text{PBE0}} = aE_x^{\text{HF,SR}}(\omega) + aE_x^{\text{HF,LR}}(\omega) + (1 - a)E_x^{\text{PBE,SR}}(\omega) + E_x^{\text{PBE,LR}}(\omega) - aE_x^{\text{PBE,LR}}(\omega).$$

HF and PBE LR contributions are small, tend to cancel.

This leads to the following hybrid functional.

$$E_{xc}^{\text{HSE}} = aE_x^{\text{HF,SR}}(\omega) + (1 - a)E_x^{\text{PBE,SR}}(\omega) + E_x^{\text{PBE,LR}}(\omega) + E_c^{\text{PBE}}.$$

Construction of the screened Coulomb exchange functional.

How E_{xc} is constructed in LDA and PBE, a review.

$$\begin{aligned} E_{xc} &= \frac{1}{2} \int \int d^3r d^3r' \frac{\rho(\vec{r}) \rho_{xc}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} \\ &= \int \int d^3r d^3u \frac{\rho(\vec{r}) \rho_{xc}(\vec{r}, \vec{r} + \vec{u})}{2u} \end{aligned}$$

where $\vec{u} = \vec{r} - \vec{r}'$.

Angle- and system-averaged exchange-correlation hole is defined,

$$\langle \rho_{xc} \rangle(u) = \frac{1}{N} \int d^3r \rho(\vec{r}) \int \frac{d\Omega_{\vec{u}}}{4\pi} \rho_{xc}(\vec{r}, \vec{r} + \vec{u}).$$

E_{xc} in terms of $\langle \rho_{xc} \rangle(u)$:

$$E_{xc} = N \int_0^\infty 4\pi u^2 \frac{\langle \rho_{xc} \rangle(u)}{2u} du.$$

Alternatively, E_{xc} written in terms of the local energy density,

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

thus

$$\epsilon_{xc}(\vec{r}) = \int d^3u \frac{\rho_{xc}(\vec{r}, \vec{r} + \vec{u})}{2u}.$$

For the exchange energy density alone

$$\epsilon_x(\vec{r}) = \int d^3u \frac{\rho_x(\vec{r}, \vec{r} + \vec{u})}{2u}.$$

LDA exchange hole:

$$\rho_x(\vec{r}, \vec{r} + \vec{u}) = \rho_x^{\text{LDA}}[\rho(\vec{r}), u] = \rho(\vec{r}) \tilde{J}(k_F u).$$

$\tilde{J}(k_F u)$ is an oscillating function of its argument:

$$\tilde{J}(y) = -9/2 \left[\frac{\sin y - y \cos y}{y^3} \right]^2,$$

where $y = k_F u$.

Such Friedel-like oscillations are expected in electron gas (metallic systems), but not in every system. Not in finite systems, for example.

System averaged exchange hole

$$\langle \rho_x \rangle(u) = \frac{1}{N} \int d^3 r \rho^2(\vec{r}) \tilde{J}(k_F u)$$

retains some of this oscillation. To eliminate this Perdew and Ernzerhof proposed a modified non-oscillating J : J^{PW92} .

$$J^{\text{PW92}}(y) = -\frac{A}{y^2} \frac{1}{1 + \frac{4}{9} A y^2} + \left(\frac{A}{y^2} + B + C y^2 \right) e^{-D y^2},$$

Some properties of the ρ^{PW92} exchange hole

ρ_x^{PW92} has to satisfy $\int d^3u \rho_x^{\text{PW92}}(\vec{r}, \vec{r} + \vec{u}) = -1$.

$$\begin{aligned} \int 4\pi u^2 \rho_x^{\text{PW92}}(\rho(\vec{r}), \vec{r} + \vec{u}) du &= \int 4\pi u^2 \rho_x^{\text{PW92}}(\rho(\vec{r}), u) du \\ &= 4\pi \frac{\rho(\vec{r})}{k_F^3} \int_0^\infty y^2 J^{\text{PW92}}(y) dy \\ &= \frac{4}{3\pi} \int_0^\infty y^2 J^{\text{PW92}}(y) dy = -1 \end{aligned}$$

From the relation for LDA energy density,

$$\begin{aligned} \epsilon_x^{\text{LDA}}(\rho(\vec{r})) &= \int_0^\infty 4\pi u^2 \frac{\rho_x(\rho(\vec{r}), u)}{2u} du \\ &= 2\pi \frac{\rho(\vec{r})}{k_F^2} \int_0^\infty y J^{\text{PW92}}(y) dy \end{aligned}$$

Hence

$$\frac{8}{9} \int_0^\infty y J^{\text{PW92}}(y) dy = -1$$

A few other properties

Since $J^{\text{PW92}}(0) = -1/2$, we get

$$\rho_x(\rho(\vec{r}), u = 0) = -\frac{1}{2}\rho(\vec{r}).$$

This LDA on-top value of ρ_x is correct for all spin-unpolarized systems whose N -electron Kohn-Sham wave function is a single determinant.

LDA and GGA approximations for ρ_x and ρ_{xc} usually work well for small e-e separations. Short-range part of ρ_x is transferable to inhomogeneous systems. Second derivatives of J^{PW92} and \tilde{J}^{LDA} matched at $u = 0$.

$$\frac{d^2 \tilde{J}^{\text{LDA}}}{dy^2} \Big|_{y=0} = \frac{d^2 J^{\text{PW92}}}{dy^2} \Big|_{y=0} = \frac{1}{5}.$$

These four conditions determines the four constants $A - D$.

Both \tilde{J}^{LDA} and J^{PW92} have the same asymptote,

$$\lim_{y \rightarrow \infty} \tilde{J}^{\text{LDA}}(y) = \lim_{y \rightarrow \infty} J^{\text{PW92}}(y) = -\frac{9}{4y^2}.$$

To avoid an unwanted shoulder in yJ^{PW92} near $y \approx 6$, and additional term is added in a new function J^{LDA} :

$$J^{\text{LDA}}(y) = -\frac{A}{y^2} \frac{1}{1 + \frac{4}{9}Ay^2} + \left(\frac{A}{y^2} + B + Cy^2 + Ey^4 \right) e^{-Dy^2}.$$

The fifth constant is determined by maximizing the information entropy

$$S[-J^{\text{LDA}}] = 4\pi \int_0^{\infty} y^2 J^{\text{LDA}}(y) \ln [-J^{\text{LDA}}] dy.$$

GGA exchange energy is obtained from

$$E_x^{\text{GGA}} = \int d^3r \rho(\vec{r}) \epsilon_x^{\text{GGA}}(\rho(\vec{r}), s(\vec{r})),$$

where $\epsilon_x^{\text{GGA}}(\rho(\vec{r}), s(\vec{r})) = \epsilon_x^{\text{LDA}}(\rho(\vec{r})) F_x^{\text{GGA}}(s(\vec{r}))$.

$F_x^{\text{GGA}}(s)$ is the GGA (PBE) enhancement factor, is a function of the reduced density gradient

$$s(\vec{r}) = \frac{|\vec{\nabla}\rho(\vec{r})|}{2k_F\rho}.$$

In analogy with the LDA exchange hole,

$$\langle \rho_x^{\text{GGA}} \rangle(u) = \frac{1}{N} \int d^3r \rho^2(\vec{r}) J^{\text{GGA}}(s(\vec{r}), K_F(\vec{r})u)$$

$$2\pi \int_0^\infty \rho J^{\text{GGA}}(s, K_F u) u du = \epsilon_x^{\text{LDA}}(\rho) F_x^{\text{GGA}}(s).$$

And most importantly,

$$\frac{8}{9} \int_0^\infty J^{\text{GGA}}(s, y) y dy = -F_x^{\text{GGA}}(s).$$

Perdew and Ernzerhof gave an ansatz for the function J^{GGA} in [JCP 109, 3313 \(1998\)](#).

SR exchange functional in HSE modifications of the PBE exchange. Instead of J^{GGA} , use

$$J^{\text{PBE,SR}}(\rho, s, y) = J^{\text{GGA}}(s, y) \times \text{erfc}\left(\frac{\omega y}{k_F}\right).$$

Enhancement factor is obtained as

$$F_x^{\text{PBE,SR}}(\rho, s) = -\frac{8}{9} \int_0^\infty y J^{\text{PBE,SR}}(\rho, s, y) dy.$$

Short range exchange energy density is obtained as

$$\epsilon_x^{\text{PBE,SR}}(\rho(\vec{r}), s(\vec{r})) = \epsilon_x^{\text{LDA}}(\rho(\vec{r})) F_x^{\text{PBE,SR}}.$$

The short range PBE exchange energy now is

$$E_x^{\text{PBE,SR}} = \int \rho(\vec{r}) \epsilon_x^{\text{PBE,SR}}(\rho(\vec{r}), s(\vec{r})) d^3r.$$

And the long range part is

$$E_x^{\text{PBE,LR}} = \int \rho(\vec{r}) [\epsilon_x^{\text{PBE}} - \epsilon_x^{\text{PBE,SR}}] d^3r.$$

Lattice constants and band gaps of some semiconductors

Heyd et al.. JCP **123**, 174101 (2005),

Lattice constants in Å.

Solid	LSDA	PBE	HSE	Expt.
C	3.537	3.579	3.553	3.567
Si	5.410	5.479	5.444	5.430
BN	3.584	3.629	3.603	3.616
MgO	4.178	4.268	4.218	4.207

Band gaps in eV.

Solid	LSDA	PBE	HSE	Expt.
C	4.23	4.17	5.49	5.48
Si	0.59	0.75	1.28	1.17
BN	4.45	4.51	5.98	6.22
MgO	4.92	4.34	6.50	7.22

Average performance for a set of 40 semiconductors/insulators

TABLE VI. Lattice constant error statistics for the SC/40 test set (Å).

Solid	LSDA	PBE	TPSS	HSE
ME ^a	-0.046	0.076	0.063	0.035
MAE ^b	0.047	0.076	0.063	0.037
rms ^c	0.058	0.084	0.071	0.044
Max (+) ^d	0.017	0.158	0.143	0.100
Max (-) ^e	0.139	-0.014

^aMean error.

^bMean absolute error.

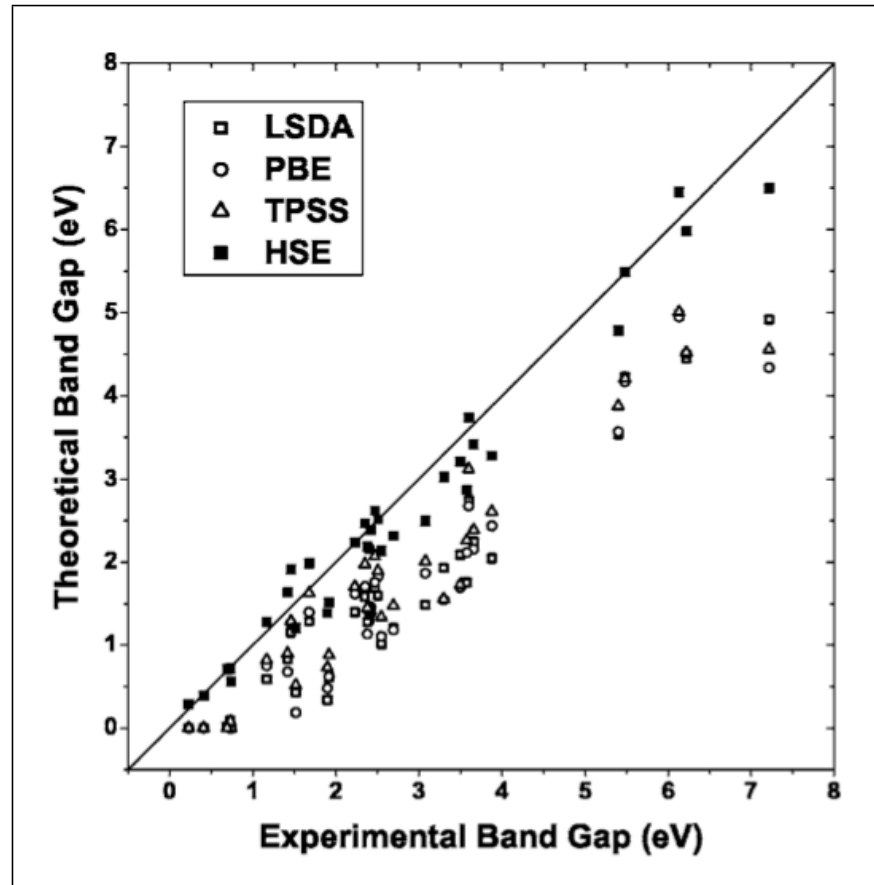
^cRoot-mean-square error.

^dMaximum positive deviation.

^eMaximum negative deviation.

TABLE VII. Band gap error statistics for the SC/40 test set (eV).

Solid	LSDA	PBE	TPSS	HSE
ME ^a	-1.14	-1.13	-0.98	-0.17
MAE ^b	1.14	1.13	0.98	0.26
rms ^c	1.24	1.25	1.12	0.34
Max (+) ^d	0.32
Max (-) ^e	-2.30	-2.88	-2.66	-0.72



References:

1. JCP **118**, 8207.
2. JCP **120**, 7274.
3. JCP **109**, 3313.
4. JCP **105**, 9982.
5. JCP **123**, 174101.
6. PRB **74**, 073101.
7. PRB **46**, 12947.