

Which electronic structure method? An introduction to Density Functional Theory (part 3)

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Recap of Previous lecture

Kohn-Sham equations

The Local-Density Approximation

Spin Density Functional Theory

Local Spin Density Approximation

LSD performance

Self Interaction Error

Perdew-Zunger SIC

more SIC

Kohn-Sham equations

Now the very clever idea by Kohn and Sham was to rewrite

$$E_v[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho]$$

as

$$E_v[\rho] = T_s[\rho] + V_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \quad (1)$$

where

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \quad (2)$$

The quantity $E_{xc}[\rho]$ is the *exchange-correlation energy*, which contains the difference between $T[\rho]$ and $T_s[\rho]$ and the non-classical part of $V_{ee}[\rho]$.

$$\begin{aligned}
 E[\rho] &= T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int v(r)\rho(r)dr = \\
 &= \sum_i^N \sum_s \int \psi_i^*(x_i) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(x_i) dr + J[\rho] + E_{xc}[\rho] + \int v(r)\rho(r)dr
 \end{aligned}$$

and the electron density

$$\rho(r) = \sum_i^N \sum_s |\psi_i(r, s)|^2 \quad (3)$$

The variational search for the minimum of $E[\rho]$ can be equivalently effected in the space of orbitals ψ_i , constraining the orbitals to be orthonormal:

$$\int \psi_i^*(x) \psi_j(x) dx = \delta_{ij}. \quad (4)$$

Kohn-Sham equations

We derived the *Kohn-Sham equations* in their canonical form:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}} \right] \psi_i = \epsilon_i \psi_i \quad (5)$$

$$v_{\text{eff}}(r) = v(r) + \int \frac{\rho(r')}{|r-r'|} dr' + v_{\text{xc}}(r) \quad (6)$$

$$\rho(r) = \sum_i^N \sum_s |\psi_i(r, s)|^2 \quad (7)$$

These equations are non-linear and must be solved iteratively.

Local-density

An explicit form of $E_{xc}[\rho]$ is needed!

$$E_{xc}^{LDA}[\rho] = \int \rho(r) \epsilon_{xc}(\rho) dr \quad (8)$$

where $\epsilon_{xc}(\rho)$ is the exchange and correlation energy per particle of a uniform electron gas of density ρ . the corresponding xc potential is

$$v_{xc}^{LDA}(r) = \frac{\delta E_{xc}^{LDA}}{\delta \rho(r)} = \epsilon_{xc}(\rho(r)) + \rho(r) \frac{\partial \epsilon_{xc}(\rho)}{\partial \rho} \quad (9)$$

and the KS orbitals read:

$$\left[-\frac{1}{2} \nabla^2 + v(r) + \int \frac{\rho(r')}{|r-r'|} dr' + v_{xc}^{LDA}(r) \right] \psi_i = \epsilon_i \psi_i \quad (10)$$

Local-density

$\epsilon_{xc}(\rho)$ can be divided into exchange and correlation contributions:

$$\epsilon_{xc}(\rho) = \epsilon_x(\rho) + \epsilon_c(\rho) \quad (11)$$

- ▶ The exchange part is give by the **Dirac (1930) exchange-energy functional**

$$\epsilon_x(\rho) = -C_x \rho(r)^{1/3}, \quad C_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \quad (12)$$

- ▶ accurate values of $\epsilon_c(\rho)$ are available thanks to quantum-MC calculations (Ceperly, Alder 1980), and have been interpolated to provide an analytical form for $\epsilon_c(\rho)$.

Gradient expansion

Among limitations of LDA there the fact that inhomogeneities in the density are not taken into account. This can be introduced semi-locally by expanding $E_{xc}[\rho]$ in terms of density and its gradient.

$$E_{xc}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}[\rho(\mathbf{r})] F_{xc}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \dots] d\mathbf{r} \quad (13)$$

the second order gradient expansion corresponds to:

$$E_{xc}[\rho] = \int A_{xc}[\rho] \rho(\mathbf{r})^{4/3} d\mathbf{r} + \int C_{xc}[\rho] |\nabla[\rho]|^2 / \rho(\mathbf{r})^{4/3} d\mathbf{r} \quad (14)$$

Gradient expansion

GGAs have been obtained following two different approaches:

- ▶ Theoretical derivation of an appropriate expression with coefficients chosen so that number of formal conditions are fulfilled: namely sum rules, long range decay etc...
- ▶ Fit the parameters of the functional in order to reproduce a number of experimental results in a molecular database (structural parameters, formation energies, thermochemical data (possible issue: transferability)).

BLYP functional

An example from the second category is the BLYP functional. The exchange functional has been proposed by Becke in 1988¹, fitting the parameters to experimental molecular data.

$$\epsilon_x = \epsilon_x^{LDA} \left(1 - \frac{\beta}{2^{1/3} A_x} \frac{x^2}{1 + 6\beta x \sinh^{-1}(x)} \right) \quad (15)$$

where $x = 2^{1/3} |\nabla \rho(\mathbf{r})| / \rho(\mathbf{r})$, $A_x = (3/4)(3/\pi)^{1/3}$, and $\beta = 0.0042$. this was complemented by a correlation derived by Lee, Yang and Parr².

$$\epsilon_c = -\frac{a}{1 + d\rho^{-1/3}} \left\{ \rho + b\rho^{-2/3} \left[C_F \rho^{5/3} - 2t_w + \frac{1}{9} \left(t_w + \frac{1}{2} \nabla^2 \rho \right) \right] e^{-c\rho^{-1/3}} \right\} \quad (16)$$

where $t_w = \frac{1}{8} \left(\frac{|\nabla \rho|^2}{\rho} - \nabla^2 \rho \right)$, $C_F = 3/10(3\pi^2)^{2/3}$, $a=0.04918$, $b=0.132$, $c=0.2533$ and $d=0.349$.

¹Phys Rev A **38**, 3098, number of citations from ISI 18,596

²Phys Rev B **37**, 785, number of citations from ISI 30,166

Spin Density Functional Theory

So far we have only considered many-electron system with only one scalar external potential $v(\mathbf{r})$ (usually the electrostatic potential due to the nuclei).

Let's consider a system with a more generalized potential, for example a magnetic potential in addition to usual scalar potential.

What we need to describe the system are:

- ▶ $\rho^\alpha(\mathbf{r})$ and $\rho^\beta(\mathbf{r})$
- ▶ or $\rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r})$ and $\rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})$

Also in the absence of magnetic field it allows one to built in more physics in the xc pot through its spin dependence.

In the presence of a magnetic field $\mathbf{B}(\mathbf{r})$, the Hamiltonian of the system becomes:

$$\hat{H} = \sum_{i=1,}^N \left(-\frac{1}{2} \nabla_i^2\right) + \sum_{i=1,}^N v(r_i) + \sum_{i < j}^N \frac{1}{r_{ij}} + 2\beta_e \sum_i^N \mathbf{B}(\mathbf{r}_i) \cdot \mathbf{S}_i \quad (17)$$

where $\beta_e = e\hbar/2mc$ is the Bohr magneton and \mathbf{S}_i is the electron spin (and spin-orbit and spin-spin interactions are neglected).

- The magnetic interaction is still a one-electron operator.

We can combine terms as:

$$\hat{V} = \sum_i^N v(\mathbf{r}_i) + 2\beta_e \sum_i^N \mathbf{B}(\mathbf{r}) \cdot \mathbf{S}_i \quad (18)$$

$$= \int v(\mathbf{r}) \hat{\rho}(\mathbf{r}) - \int \mathbf{B}(\mathbf{r}) \cdot \hat{\mathbf{m}}(\mathbf{r}) d\mathbf{r} \quad (19)$$

$\hat{\rho}(\mathbf{r})$ is the operator for the electron density

$$\hat{\rho}(\mathbf{r}) = \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (20)$$

and $\hat{\mathbf{m}}(\mathbf{r})$ is the operator for the electron magnetization density

$$\hat{\mathbf{m}}(\mathbf{r}) = -2\beta_e \sum_i^N \mathbf{S}_i \delta(\mathbf{r} - \mathbf{r}_i). \quad (21)$$

The expectation value for \hat{V} for the state $|\Psi\rangle$ is:

$$\langle \Psi | \hat{V} | \Psi \rangle = \int v(\mathbf{r}) \rho(\mathbf{r}) - \int \mathbf{B}(\mathbf{r}) \cdot \mathbf{m}(\mathbf{r}) d\mathbf{r} \quad (22)$$

where the electron density is given by:

$$\rho(\mathbf{r}) = \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle \quad (23)$$

and the magnetization density is given by:

$$\mathbf{m}(\mathbf{r}) = \langle \Psi | \hat{\mathbf{m}}(\mathbf{r}) | \Psi \rangle. \quad (24)$$

If we now consider the simple case of $\mathbf{B}(\mathbf{r})$ directed along the z direction, namely $\mathbf{B}(\mathbf{r}) = b(\mathbf{r})\mathbf{z}$, we have

$$\langle \Psi | \hat{V} | \Psi \rangle = \int v(\mathbf{r})\rho(\mathbf{r}) - \int b(\mathbf{r})m(\mathbf{r})d\mathbf{r} \quad (25)$$

$$\text{where } m(\mathbf{r}) = -2\beta_e \langle \Psi | \sum_i^N s_z(i)\delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle \quad (26)$$

$$= -2\beta_e \int s_z\delta(\mathbf{r} - \mathbf{r}')\gamma_1(\mathbf{x}', \mathbf{x}')d\mathbf{x}' \quad (27)$$

$$= -2\beta_e \sum_{s=\alpha,\beta} s_z\gamma_1(\mathbf{r}s, \mathbf{r}s) \quad (28)$$

$$= -2\beta_e \left[\frac{1}{2}\gamma_1(\mathbf{r}\alpha, \mathbf{r}\alpha) + \left(-\frac{1}{2}\right)\gamma_1(\mathbf{r}\beta, \mathbf{r}\beta) \right] \quad (29)$$

$$= [\rho^\beta(\mathbf{r}) - \rho^\alpha(\mathbf{r})] \quad (30)$$

$$\gamma_1(\mathbf{x}'_1, \mathbf{x}_1) = N \int \dots \int \Psi(\mathbf{x}'_1, \mathbf{x}_2 \dots \mathbf{x}_N)\Psi^*(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_N)d\mathbf{x}_2 \dots d\mathbf{x}_N \quad (31)$$

Spin Density Functional Theory

$$E_0 = \text{Min}_{\rho^\alpha, \rho^\beta} \{ F[\rho^\alpha, \rho^\beta] + \int d\mathbf{r} [(v(\mathbf{r}) + \beta_e b(\mathbf{r}))\rho^\alpha(\mathbf{r}) + (v(\mathbf{r}) - \beta_e b(\mathbf{r}))\rho^\beta(\mathbf{r})] \} \quad (32)$$

ρ^α and ρ^β are all you need to describe the ground state of a many-electron system in the presence of a magnetic field $b(\mathbf{r})$. However $F[\rho^\alpha, \rho^\beta]$ is unknown, and approximation is necessary for the theory to be implemented.

the Kohn-Sham method can be introduced as for the *simple* DFT:

$$F[\rho^\alpha, \rho^\beta] = T_s[\rho^\alpha, \rho^\beta] + J[\rho^\alpha + \rho^\beta] + E_{xc}[\rho^\alpha, \rho^\beta] \quad (33)$$

where $T_s[\rho^\alpha, \rho^\beta]$ is the Kohn-Sham kinetic energy functional corresponding to a system of non-interacting electrons with densities ρ^α and ρ^β , and $E_{xc}[\rho^\alpha, \rho^\beta]$ is the exchange correlation energy functional.

$$\begin{aligned} E[\rho^\alpha, \rho^\beta] &= \sum_{i\sigma} n_{i\sigma} \int d\mathbf{r} \phi_{i\sigma}^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \phi_{i\sigma}(\mathbf{r}) \\ &+ J[\rho^\alpha + \rho^\beta] + E_{xc}[\rho^\alpha, \rho^\beta] \\ &+ \int d\mathbf{r} [(v(\mathbf{r}) + \beta_e b(\mathbf{r}))\rho^\alpha(\mathbf{r}) + (v(\mathbf{r}) - \beta_e b(\mathbf{r}))\rho^\beta(\mathbf{r})] \end{aligned} \quad (34)$$

The variational search of the minimum of $E[\rho^\alpha, \rho^\beta]$ can be carried out on the space of orbitals $\phi_{i\sigma}$, subject to normalization constraints:

$$\int \phi_{i\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}) = 1. \quad (35)$$

the resulting Kohn-Sham equations are:

$$\hat{h}_{eff}^\alpha \phi_{i\alpha}(\mathbf{r}) = \left[-\frac{1}{2}\nabla^2 + v_{eff}^\alpha(\mathbf{r}) \right] \phi_{i\alpha}(\mathbf{r}) \quad (36)$$

$$= \frac{\epsilon'_{i\alpha}}{n_{i\alpha}} \phi_{i\alpha}(\mathbf{r}) = \epsilon_{i\alpha} \phi_{i\alpha}(\mathbf{r}) \quad i = 1, 2, \dots, N^\alpha \quad (37)$$

$$\hat{h}_{eff}^\beta \phi_{j\beta}(\mathbf{r}) = \left[-\frac{1}{2}\nabla^2 + v_{eff}^\beta(\mathbf{r}) \right] \phi_{j\beta}(\mathbf{r}) \quad (38)$$

$$= \frac{\epsilon'_{j\beta}}{n_{j\beta}} \phi_{j\beta}(\mathbf{r}) = \epsilon_{j\beta} \phi_{j\beta}(\mathbf{r}) \quad j = 1, 2, \dots, N^\beta \quad (39)$$

The spin-dependent effective potentials are:

$$v_{eff}^{\alpha} = v(\mathbf{r}) + \beta_e b(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc} [\rho^{\alpha}, \rho^{\beta}]}{\delta \rho^{\alpha}(\mathbf{r})} \quad (40)$$

$$v_{eff}^{\beta} = v(\mathbf{r}) - \beta_e b(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc} [\rho^{\alpha}, \rho^{\beta}]}{\delta \rho^{\beta}(\mathbf{r})} \quad (41)$$

$\epsilon_{i\sigma}$ are the Lagrange multiplier for the constraint $\int \phi_{i\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}) = 1$.

And

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

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

$$N = N^{\alpha} + N^{\beta}.$$

The kinetic energy term $T_s [\rho^{\alpha}, \rho^{\beta}]$ is treated exactly here, and the exact exchange-correlation functional $E_{xc} [\rho^{\alpha}, \rho^{\beta}]$ exists, even though is unknown.

Advantages of spin-polarized Kohn-Sham Theory:

- ▶ describe many electron system in the presence of a magnetic field (Also spin-orbit and relativistic effects can be included.
- ▶ can be applied also in the absence of a magnetic field.

If $b(\mathbf{r}) = 0$ do SDFT and DFT give the same results?

YES if the exact form of $E_{xc} [\rho^\alpha, \rho^\beta]$ and $E_{xc} [\rho]$ are used.

NO in practice with approximate E_{xc} .

An approximate form for $E_{xc} [\rho^\alpha, \rho^\beta]$ can be (usually is) a better description of the real system than the approximate form of $E_{xc} [\rho]$.
(e.g. open shell systems, system with spontaneous magnetization)

Connection between Spin-DFT and spin-compensated DFT

$$T_s [\rho^\alpha, \rho^\beta] = T_s [\rho^\alpha, 0] + T_s [0, \rho^\beta] \quad (42)$$

where

$$T_s [\rho^\alpha, 0] = \sum_{i\alpha} n_{i,\alpha} \int d\mathbf{r} \phi_{i\alpha}^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \phi_{i\alpha}(\mathbf{r}) \quad (43)$$

For the spin-compensated case we have

$$\rho^\alpha(\mathbf{r}) = \rho^\beta(\mathbf{r}) = \frac{1}{2} \rho(\mathbf{r}) \quad (44)$$

$$T_s \left[\frac{1}{2} \rho, \frac{1}{2} \rho \right] = T_s \left[\frac{1}{2} \rho, 0 \right] + T_s \left[0, \frac{1}{2} \rho \right] \quad (45)$$

$$= 2 T_s \left[\frac{1}{2} \rho, 0 \right] \quad (46)$$

Local Spin Density Approximation

$$T_s [\rho^\alpha, \rho^\beta] = T_s [\rho^\alpha, 0] + T_s [0, \rho^\beta] \quad (47)$$

$$= \frac{1}{2} T_s [\rho^\alpha, \rho^\alpha] + \frac{1}{2} T_s [\rho^\beta, \rho^\beta] \quad (48)$$

$$= \frac{1}{2} T_s^0 [2\rho^\alpha] + \frac{1}{2} T_s^0 [2\rho^\beta] \quad (49)$$

For non-even number of paired electron

$$T_s [\rho] \neq T_s \left[\frac{1}{2}\rho, \frac{1}{2}\rho \right] = T_s^0 [\rho] \quad (50)$$

Using eq.49 the TF model for the spin polarized case:

$$T_{TF} [\rho^\alpha, \rho^\beta] = 2^{2/3} C_F \int \left[(\rho^\alpha)^{5/3} + (\rho^\beta)^{5/3} \right] d\mathbf{r} \quad (51)$$

and its gradient corrections:

$$T_W [\rho^\alpha, \rho^\beta] = \frac{1}{8} \int \frac{|\nabla\rho^\alpha|^2}{\rho^\alpha} d\mathbf{r} + \frac{1}{8} \int \frac{|\nabla\rho^\beta|^2}{\rho^\beta} d\mathbf{r} \quad (52)$$

In the case of the hydrogen atom $T=0.5$ a.u. (exact solution).

$$T_{TF} [\rho_{1s}] = C_F \int \rho^{5/3} = 0.2891 \quad (53)$$

while the spin polarized result is:

$$T_{TF} [\rho_{1s}, 0] = 2^{2/3} C_F \int \rho^{5/3} = 0.4590 \quad (54)$$

Also adding the gradient correction, we obtain:

$$T_{TF} [\rho_{1s}, 0] + \frac{1}{9} T_w [\rho_{1s}] = 0.5146 \quad (55)$$

For spin-polarized system the use of spin-density functional is mandatory!

How to treat the exchange and correlation potential in spin-DFT?

$$E_{xc} [\rho^\alpha, \rho^\beta] = E_x [\rho^\alpha, \rho^\beta] + E_c [\rho^\alpha, \rho^\beta] \quad (56)$$

For the exchange part

$$E_x [\rho^\alpha, \rho^\beta] = -\frac{1}{2} \iint \frac{1}{r_{12}} \left[|\rho_1^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\rho_1^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2)|^2 \right] d\mathbf{r}_1 d\mathbf{r}_2 \quad (57)$$

with

$$\rho_1^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) = \sum_i n_{i\alpha} \phi_{i\alpha}(\mathbf{r}_1) \phi_{i\alpha}^*(\mathbf{r}_2) \quad (58)$$

$$\rho_1^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) = \sum_i n_{i\beta} \phi_{i\beta}(\mathbf{r}_1) \phi_{i\beta}^*(\mathbf{r}_2) \quad (59)$$

The same formalism we used to compare the spin-polarized T_s and the spin-compensated T_s can be used for the exchange functional E_x :

$$E_x [\rho^\alpha, \rho^\beta] = \frac{1}{2} E_x [\rho^\alpha, \rho^\alpha] + \frac{1}{2} E_x [\rho^\beta, \rho^\beta] \quad (60)$$

$$= \frac{1}{2} E_x^0 [2\rho^\alpha] + \frac{1}{2} E_x^0 [2\rho^\beta] \quad (61)$$

where

$$E_x^0 [\rho] = E_x \left[\frac{1}{2}\rho, \frac{1}{2}\rho \right] \quad (62)$$

Using the Dirac local density approximation, we obtain the *local spin density approximation*(LSD).

$$E_x^{LSD} [\rho^\alpha, \rho^\beta] = 2^{1/3} C_x \int \left[(\rho^\alpha)^{4/3} + (\rho^\beta)^{4/3} \right] d\mathbf{r} \quad (63)$$

We can define a spin-polarization parameter:

$$\zeta = \frac{\rho^\alpha - \rho^\beta}{\rho} = \frac{\rho^\alpha - \rho^\beta}{\rho^\alpha + \rho^\beta} \quad (64)$$

Then $\rho^\alpha = \frac{1}{2}\rho(1 + \zeta)$, $\rho^\beta = \frac{1}{2}\rho(1 - \zeta)$ and

$$E_x^{LSD} [\rho^\alpha, \rho^\beta] = \frac{1}{2} C_x \int \rho^{4/3} \left[(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} \right] d\mathbf{r} \quad (65)$$

$$= \int \rho \epsilon_x(\rho, \zeta) d\mathbf{r} \quad (66)$$

where

$$\epsilon_x(\rho, \zeta) = \epsilon_x^0(\rho) + [\epsilon_x^1(\rho) - \epsilon_x^0(\rho)] f(\zeta) \quad (67)$$

where $\epsilon_x^0(\rho)$ is the exchange density for the compensated (paramagnetic) homogeneous electron gas given by

$$\epsilon_x^0(\rho) = \epsilon_x^0(\rho, 0) = C_x \rho^{1/3} \quad (68)$$

$\epsilon_x^1(\rho)$ is the exchange density for the spin-polarized homogeneous electron gas give by

$$(69)$$

$$\epsilon_x^1(\rho) = \epsilon_x(\rho, 1) = 2^{1/3} C_x \rho^{1/3} \quad (70)$$

and

$$f(\zeta) = \frac{1}{2} (2^{1/3} - 1)^{-1} \left[(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2 \right] \quad (71)$$

The correlation energy $E_c [\rho^\alpha, \rho^\beta]$ cannot be decomposed into a sum of two different spin contributions, because correlation energy contains the effect of spin-like electron-electron interaction as well as the unlike-spin electron-electron.

$$V_{ee} = \int \frac{1}{r_{12}} \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (72)$$

with

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho_2^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) + \rho_2^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) + \rho_2^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) + \rho_2^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) \quad (73)$$

So, no closed form for

$$E_c^{LSD} [\rho^\alpha, \rho^\beta] = \int \rho \epsilon_c(\rho, \zeta) d\mathbf{r} \quad (74)$$

Ionization potentials with LSD

Table 8.1 Ionization Potentials in electron volts of Some Light Atoms Calculated in the LSD, LDA, and HF Approximations

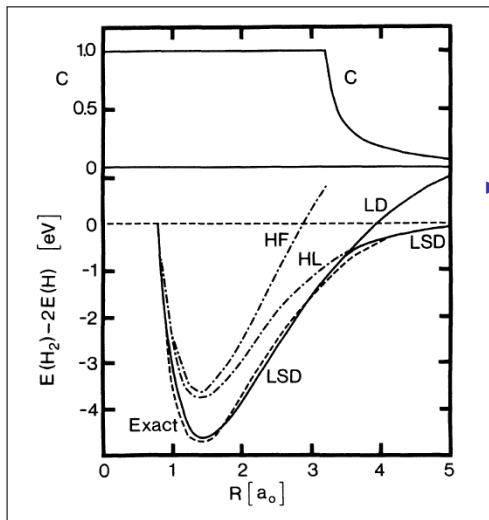
Atom	LSD	LDA	HF	Exptl.
H	13.4	12.0	—	13.6
He	24.5	26.4	—	24.6
Li	5.7	5.4	5.3	5.4
Be	9.1	—	8.0	9.3
B	8.8	—	7.9	8.3
C	12.1	—	10.8	11.3
N	15.3	—	14.0	14.5
O	14.2	16.5	11.9	13.6
F	18.4	—	16.2	17.4
Ne	22.6	22.5	19.8	21.6
Na	5.6	5.3	4.9	5.1
Ar	16.2	16.1	14.8	15.8
K	4.7	4.5	4.0	4.3

Note: LSD = local spin-density method; LDA = local-density approximation; HF = Hartree-Fock.

^a Adapted from Gunnarsson and Lundqvist (1976).

IP = energy difference between neutral species and cations.

The H₂ molecule



▶ LSD gives the proper dissociation limit for the diatomic molecules, while LDA fails, paralleling the performance of UHF vs RHF.

LSD results for diatomic molecules

Table 8.2 LSD Spectroscopic Constants for Diatomic Molecules^a

	r_e (bohrs)		D_e (eV)		ω_e (cm ⁻¹)	
	Expt.	LSD	Expt.	LSD	Expt.	LSD
H ₂	1.40	1.45	4.8	4.9	4400	4190
Li ₂	5.05	5.12	1.1	1.0	350	330
B ₂	3.00	3.03	3.0	3.9	1050	1030
C ₂	2.35	2.35	6.3	7.3	1860	1880
N ₂	2.07	2.07	9.9	11.6	2360	2380
O ₂	2.28	2.27	5.2	7.6	1580	1620
F ₂	2.68	2.61	1.7	3.4	890	1060
Na ₂	5.82	5.67	0.8	0.9	160	160
Al ₂	4.66	4.64	1.8	2.0	350	350
Si ₂	4.24	4.29	3.1	4.0	510	490
P ₂	3.58	3.57	5.1	6.2	780	780
S ₂	3.57	3.57	4.4	5.9	730	720
Cl ₂	3.76	3.74	2.5	3.6	560	570

^a From Becke (1986a).

Bond lengths and freq are good; diss energies overestimated.

Self Interaction Error

Already in 1966 Tong and Sham showed that one shouldn't be over-optimistic about the LSD calculations.

They showed that

- ▶ LSD underestimate E_x by at least 10%
- ▶ LSD overestimate correlation energy by a factor of 2 or more
- ▶ Problem of electron self interaction in approximate functionals

No SIE in the Hartree Fock Approximation!

$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle = \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}) \quad (75)$$

where

$$H_i = \int \psi_i^*(x) \left[-\frac{1}{2} \nabla^2 + v(x) \right] \psi_i(x) dx \quad (76)$$

$$J_{ij} = \iint \psi_i(x_1) \psi_i^*(x_1) \frac{1}{r_{12}} \psi_j^*(x_2) \psi_j(x_2) dx_1 dx_2 \quad (77)$$

$$K_{ij} = \iint \psi_i^*(x_1) \psi_j(x_1) \frac{1}{r_{12}} \psi_i(x_2) \psi_j^*(x_2) dx_1 dx_2 \quad (78)$$

$$J_{ii} = K_{ii} \quad (79)$$

this explain the double sum in (75).

In Thomas Fermi theory the electron electron interaction is approximated by:

$$V_{ee}^{TF}[\rho] = J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (80)$$

If we consider the one electron system described by $\phi(\mathbf{r})$, we get

$$J[|\phi(\mathbf{r})|^2] \neq 0 \quad (81)$$

while the exact potential energy functional must give 0 for one electron system:

$$V_{ee}[|\phi(\mathbf{r})|^2] = 0 \quad (82)$$

In 1934 Fermi and Amaldi proposed the simple self-interaction corrected formula:

$$V_{ee}^{FA} = \frac{N-1}{2N} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (83)$$

Perdew and Zunger³ Self Interaction Corrections (SIC).

In approximate DFT (including LDA, the exact functional

$$V_{ee} [\rho^\alpha, \rho^\beta] = J [\rho^\alpha, \rho^\beta] + E_{xc} [\rho^\alpha, \rho^\beta] \quad (84)$$

is approximated by the functional:

$$\tilde{V}_{ee} [\rho^\alpha, \rho^\beta] = J [\rho^\alpha, \rho^\beta] + \tilde{E}_{xc} [\rho^\alpha, \rho^\beta] \quad (85)$$


The requirement to exclude the self interaction can be written as

$$V_{ee} [\rho_i^\alpha, 0] = J [\rho_i^\alpha] + E_{xc} [\rho_i^\alpha, 0] = 0 \quad (86)$$

Or in a more detailed form:

$$J [\rho_i^\alpha] + E_x [\rho_i^\alpha, 0] = 0 \quad (87)$$

$$E_c [\rho_i^\alpha, 0] = 0 \quad (88)$$

³Perdew and Zunger (1981) *Phys Rev B* **23**, 5048. 

Perdew-Zunger self interaction corrected (SIC) version of a given approximate exchange and correlation functional is

$$E_{xc}^{SIC} = \tilde{E}_{xc} [\rho^\alpha, \rho^\beta] - \sum_{i\sigma} \left(J[\rho_i^\alpha] + \tilde{E}_x[\rho_i^\alpha, 0] \right) \quad (89)$$

The SIC one-electron equation become

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \beta_e b(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}^{i\alpha, SIC}(\mathbf{r}) \right] \phi_{i\alpha}^{SIC}(\mathbf{r}) = \epsilon_{i\alpha}^{SIC} \phi_{i\alpha}^{SIC}(\mathbf{r})$$

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) - \beta_e b(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}^{j\beta, SIC}(\mathbf{r}) \right] \phi_{j\beta}^{SIC}(\mathbf{r}) = \epsilon_{j\beta}^{SIC} \phi_{j\beta}^{SIC}(\mathbf{r})$$

NOTE: the one electron equation for SIC have different potentials for different orbitals, which causes the orbital to be non-orthogonal.

SIC improves the LSD approximation considerably. For the **exchange energies** we have:

Table 8.3 LSD Calculation of Exchange Energies of Atoms
 (in electron volts)^a

Atom	LSD	LSD-SIC	Hartree-Fock
H	-6.9	-8.5	-8.5
He	-23.2	-27.9	-27.9
Ne	-297.6	-337.8	-329.5
Ar	-755.8	-842.4	-821.3
Kr	-2407.5	-2632.0	-2561.9

^a After Perdew and Zunger (1981).

SIC improves the LSD approximation considerably. For the **correlation energies** we have:

Table 8.4 LSD Calculations of Correlation Energies of Atoms (in electron volts)^a

Atom	LSD	LSD-SIC	Exptl.
H	-0.6	-0.0	-0.0
He	-3.0	-1.5	-1.1
Be	-6.0	-3.1	-2.6
Ne	-19.9	-11.4	-10.4
Mg	-23.9	-13.6	-11.6
Ar	-38.4	-22.3	-19.9

^a After Perdew and Zunger (1981).

Self-Interaction Error for radical water dimers

Self Interaction Error most severe
 for **unpaired delocalized electrons**

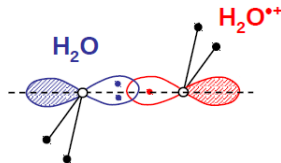
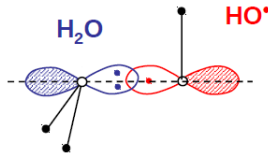
Overestimation hemibond strength

$\text{H}_3\text{O}_2^{\bullet+}$ ~ 8 kcal/mol

$\text{H}_4\text{O}_2^{\bullet+}$ ~19 kcal/mol

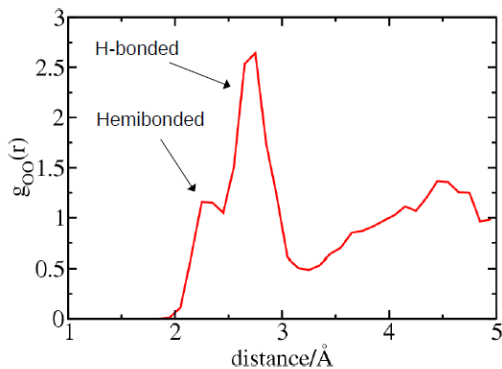
BLYP w.r.t. hydrogen bonded dimer

*Delocalised states favored ->
 hemibonded states stabilized*



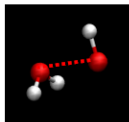
3-electron bonds

$\cdot\text{OH}$ in aqueous solution

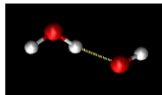


10ps MD of OH+31 H₂O

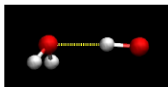
Hemi bonded dimer



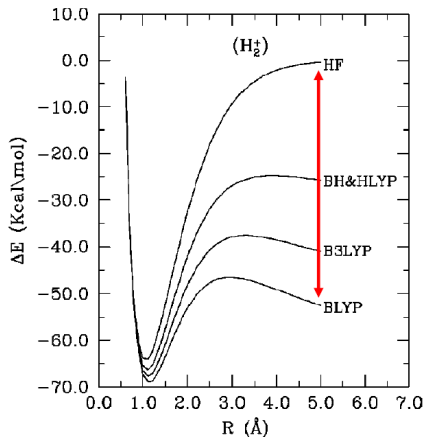
H-bonded (acceptor)



H-bonded (donor)



Self-Interaction Error (SIE) H_2^+



Coulomb + XC energy should be exactly 0 for a 1-electron density

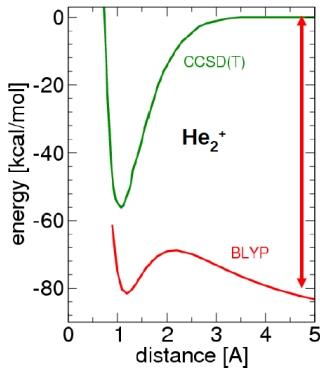
$$E_H[\rho_1] + E_{xc}[\rho_1] = 0$$

Instead XC energy in LDA (GGA) overcorrects for Coulomb energy

$$E_H[\rho_1] + E_{xc}[\rho_1] < 0$$

DFT strongly favours delocalized unpaired electrons (holes) which minimize the Self Interaction

SIE for radical dimer cations



Errors in the order of eV
 Wrong Dissociation !!!

$$E(r) = E_{AB}(r) - E_A - E_B$$

	He	NH ₃	H ₂ O	HF	Ne
CCSD(T)	56.04	36.34	40.75	40.22	30.87
B3LYP	77.38	44.21	52.43	58.50	60.54
BLYP	83.30	48.55	59.93	68.80	75.41

(Gräfenstein et al. PCCP 2004)

Self-interaction correction (SIC)

Original Perdew-Zunger (PRB, 1981) correction

$$E^{\text{SIC}}[\{\rho_{i\sigma}\}] = - \sum_{\sigma=\alpha,\beta} \sum_{i=1}^{N_{\sigma}} (E_{xc}[\rho_{i\sigma}, 0] + J[\rho_{i\sigma}]).$$

Spin only modification by M. d'Avezac, M. Calandra and F. Mauri (2004)

SIC only applied to singly occupied orbital in restricted open shell scheme.

$$E_{sic}^{PZ} = -E_H[m] - E_{xc}[m, 0] \quad \swarrow \text{Proposed by Mauri et al}$$

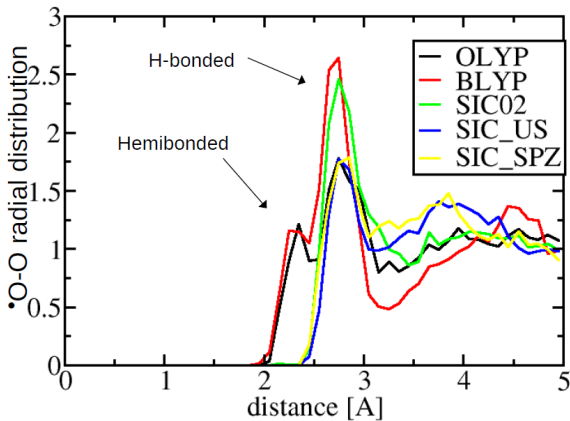
$$E_{sic}^{US} = -E_H[m] - (E_{xc}[\rho_{\alpha}, \rho_{\beta}] - E_{xc}[\rho_{\alpha} - m, \rho_{\beta}])$$

$$E_{sic}^{SS} = -aE_H[m] - bE_{xc}[m, 0]$$

\searrow Scaled SIC

Here $a=0.2$ and $b=0.0$ thus introducing a coulomb only correction

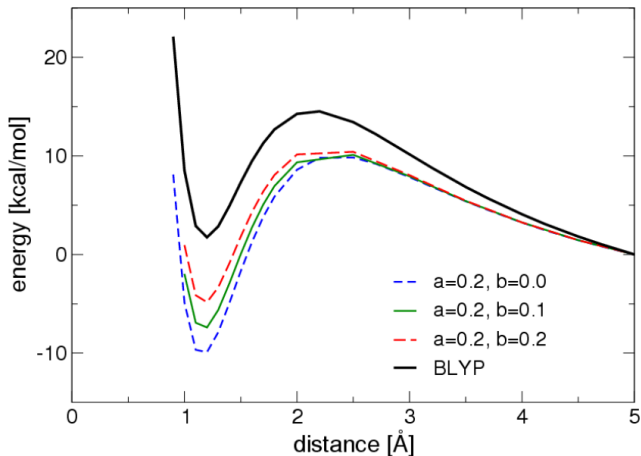
*OH in solution



Each 10ps MD of OH+31 H₂O

(VandeVondele et al. 2005)

He₂²⁺, effect of XC SIC **STILL WRONG DISSOCIATION !!!!**



Some relevant ionization energies

Energies in Ev

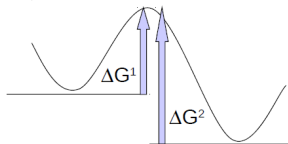
	LiOH	LiF	NaOH	NaCN
CCSD(T)	9.24	12.00	8.1	9.45
BLYP	9.19	11.62	7.91	9.50
SIC(0.2, 0.0)	6.99	9.02	5.72	8.08
SIC(0.2, 0.1)		10.54	7.00	9.06
SIC(0.2, 0.2)		12.01	8.26	9.98
SIC(0.4, 0.0)	4.64	6.26	3.37	6.12
SIC(1.0, 0.0)	-3.05	-2.63	-4.33	-1.35
SIC(1.0, 1.0)	10.73	13.35	9.46	11.34

For this property an XC SIC ($b > 0$) is clearly needed

Barrier Heights for Hydrogen transfer reactions

1	$\text{Cl} + \text{H}_2 \leftrightarrow \text{HCl} + \text{H}$
2	$\text{OH} + \text{H}_2 \leftrightarrow \text{H} + \text{H}_2\text{O}$
3	$\text{CH}_3 + \text{H}_2 \leftrightarrow \text{H} + \text{CH}_4$
4	$\text{CH}_4 + \text{OH} \leftrightarrow \text{CH}_3 + \text{H}_2\text{O}$
5	$\text{CH}_3\text{OH} + \text{H} \leftrightarrow \text{CH}_2\text{OH} + \text{H}_2$
6	$\text{H} + \text{H}_2 \leftrightarrow \text{H}_2 + \text{H}$
7	$\text{NH}_3 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{NH}_2$
8	$\text{HCl} + \text{CH}_3 \leftrightarrow \text{Cl} + \text{CH}_4$
9	$\text{C}_2\text{H}_6 + \text{OH} \leftrightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O}$
10	$\text{F} + \text{H}_2 \leftrightarrow \text{HF} + \text{H}$
11	$\text{PH}_3 + \text{H} \leftrightarrow \text{PH}_2 + \text{H}_2$
12	$\text{HCl} + \text{H} \leftrightarrow \text{H} + \text{HCl}$
13	$\text{H} + \text{N}_2\text{H}_2 \leftrightarrow \text{H}_2 + \text{N}_2\text{H}$
14	$\text{H} + \text{H}_2\text{S} \leftrightarrow \text{H}_2 + \text{SH}$
15	$\text{C}_2\text{H}_6 + \text{NH}_2 \leftrightarrow \text{C}_2\text{H}_5 + \text{NH}_3$
16	$\text{NH}_2 + \text{CH}_4 \leftrightarrow \text{CH}_3 + \text{NH}_3$

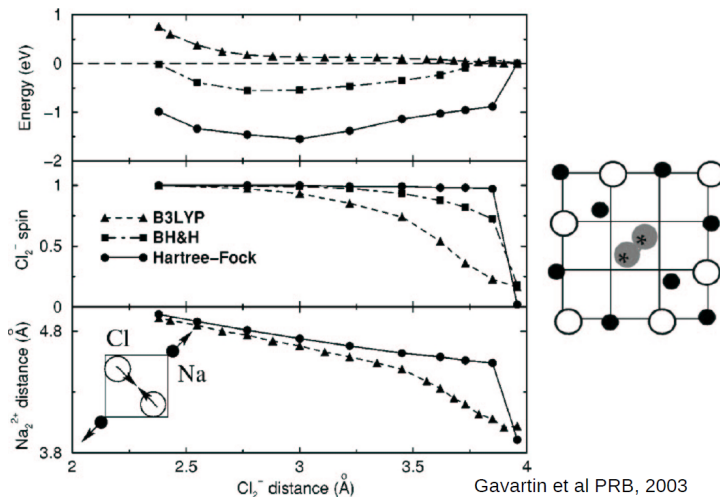
Optimization procedure for a and b on 16 H-transfer reactions.



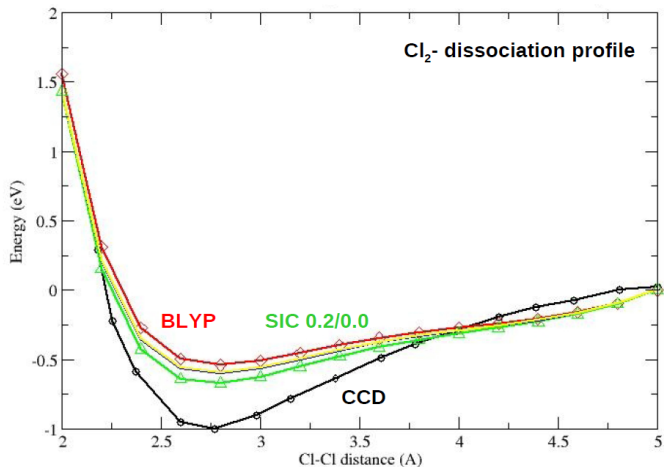
a	b	RMSD	MSE	MUE	MAE
0.2	0.18	2.770	-0.028	2.334	5.70

References structures and energies from Dickson and Becke, JCP 2005

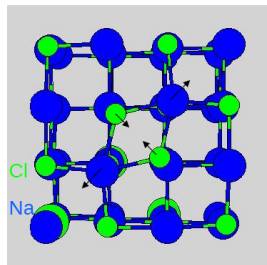
Hole trapping in NaCl



Hole trapping in NaCl



Hole trapping in NaCl



SIC a=0.2 b=0.0		SIC a=0.2 b=0.2	
64 atoms d=2.84 Å	216 atoms d=2.84 Å	64 atoms d=2.84 Å	216 atoms d=2.84 Å
dCl-Cl = 2.90 Å dNa-Na = 4.69 Å dCl-Cl = 4.01 Å dNa-Na = 3.88 Å	dCl-Cl = 2.95 Å dNa-Na = 4.69 Å	No short dist min As in B3LYP	No short dist min As in B3LYP