Theoretical Chemistry

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Summary

- The Hartree-Fock-Roothaan method
- Pople and Dunning basis sets
- Semiempirical models
- Configuration interaction
- Möller-Plesset perturbation theory
- **Density functional theory**
- Time-dependent DFT

THE DENSITY FUNCTIONAL THEORY

TIME-INDEPENDENT SCHRÖDINGER EQUATION

$$\hat{H}\Psi = E\Psi$$

Electronic hamiltonian $\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_0$

T = Kinetic energy; W = Coulomb interaction; V_0 = External potential

H is fully defined by the number of electrons N and the external potential V_0

For a molecule with N electrons and P nuclei:

$$\hat{T} = -\sum_{\mu=1}^{N} \frac{1}{2}\Delta_\mu$$ *Kinetic energy*

$$\hat{V}_{ee} = \sum_{\mu=1}^{N}\sum_{\upsilon>1}^{N} \frac{1}{r_{\mu\upsilon}}$$ *2-electron Coulomb interactions*

$$\hat{V}_0 = \hat{V}_{ne} = -\sum_{\mu=1}^{N}\sum_{p=1}^{P} \frac{Z_p}{r_{\mu p}}$$ *External potential = static nuclear field*

THE DENSITY FUNCTIONAL THEORY

Basic idea of DFT

It is not necessary to determine the N-electron wavefunction $\Psi(\mathbf{r}_1 \ldots \mathbf{r}_N)$
to compute the ground-state energy and the ground-state properties

DFT allows to replace the complicated N-electron wavefunction by the much simpler electron density

THE ELECTRON DENSITY

Definition

Electron density : integral over the spin coordinates (s_1, s_2, … , s_N) of all electrons and over all but one of the spatial variables ($\mathbf{r_1}$, $\mathbf{r_2}$, … , $\mathbf{r_N}$).

$$\rho(\vec{r}) = N \int \dots \int |\Psi(\vec{r}_1, s_1, \vec{r}_2, s_2, \dots, \vec{r}_N, s_N)|^2 ds_1 d\vec{r}_2 ds_2 \dots d\vec{r}_N ds_N$$

Probability "density" of finding any of the N electron in a volume element $d\vec{r}_1$
(with arbitrary spin and arbitrary positions and spins of the other N-1 electrons)

Properties

$\rho(\vec{r})$ is a function of only 3 spatial variables !!!

$$\lim_{(\vec{r}\to\infty)} \rho(\vec{r}) = 0$$

$$\int_{\text{space}} \rho(\mathbf{r}) d\mathbf{r} = N$$

THE ELECTRON PAIR DENSITY

Definition

Pair density = probability of finding a pair of two electrons with spins s_1 et s_2 simultaneously in two volume elements $d\mathbf{r_1}$ and $d\mathbf{r_2}$ *(with arbitrary positions and spin of the other N-2 electrons).*

$$\rho_2(\vec{r}_1, s_1, \vec{r}_2, s_2) = N(N-1) \int \dots \int |\Psi(\vec{r}_1, s_1, \vec{r}_2, s_2, \dots, \vec{r}_N, s_N)|^2 d\vec{r}_3 ds_3 \dots d\vec{r}_N ds_N$$

This quantity contains all information about electron correlation !!!

Discussion

If electrons were *identical and not distinguishable particles with no interaction*

$$\rho_2(\vec{r}_1, s_1, \vec{r}_2, s_2) = \frac{N-1}{N} \rho(\vec{r}_1, s_1) \rho(\vec{r}_2, s_2)$$

Problem: electrons are *fermions* (antisymmetric wave-function) and negatively charged particles that *interact through Coulomb repulsion*

THE ELECTRON PAIR DENSITY

Required constraints

Exchange correlation or "Fermi correlation" = the probability of finding two electrons with the same spin at the same point in space should be zero

$$\rho_2(\vec{r}_1, s_1, \vec{r}_1, s_1) = 0$$

This correlation is not connected to the charge of the electrons but to the Pauli principle

Electron correlation or "Coulomb correlation" = electrostatic repulsion which prevents the electrons from coming too close to each other.

This is a consequence of the charge of electrons on the pair density.

Comment: It can be easily be shown that HF does include the "Fermi-correlation" but completely neglects the Coulomb part.

$$\rho_2^{HF}(\vec{r}_1, s_1, \vec{r}_2, s_2) = [det\{\phi_1(\vec{r}_1)\sigma_1(s_1)\phi_2(\vec{r}_2)\sigma_2(s_2)\}]^2$$
$$= \rho(\vec{r}_1, s_1)\rho(\vec{r}_2, s_2)$$

Uncorrelated situation

THE ELECTRON PAIR DENSITY

New expression for the pair density

$$\rho_2(\vec{r}_1, s_1, \vec{r}_2, s_2) = \rho(\vec{r}_1, s_1)\rho(\vec{r}_2, s_2)\{1 + f(\vec{r}_1, \vec{r}_2)\}$$

Correlation factor

Probability of finding any electron at position $\mathbf{r_2}$ with the spin s_2 if there is already one electron at position $\mathbf{r_1}$ with the spin s_1:

$$\Omega(\vec{r}_1, s_1, \vec{r}_2, s_2) = \frac{\rho_2(\vec{r}_1, s_1, \vec{r}_2, s_2)}{\rho(\vec{r}_1, s_1)}$$

This is a conditional probability which integrates to N-1 electrons and prevents from the *unphysical self-interaction* problem:

$$\int \Omega(\vec{r}_1, s_1, \vec{r}_2, s_2)\, d\vec{r}_2 ds_2 = N - 1$$

THE EXCHANGE-CORRELATION HOLE

Fermi and Coulomb correlation leads to a depletion of the electron density at ($\mathbf{r_2}$, s_2) as compared to the independent particle model.

$h_{XC}(\vec{r}_1, s_1, \vec{r}_2, s_2)$ is called the ***exchange-correlation hole***

$$h_{XC}(\vec{r}_1, s_1, \vec{r}_2, s_2) = \Omega(\vec{r}_1, s_1, \vec{r}_2, s_2) - \rho(\vec{r}_2, s_2) = \rho(\vec{r}_2, s_2) f(\vec{r}_1, \vec{r}_2)$$

h_{XC} as a negative sign, in particular in the vicinity of the reference electron.

The exchange-correlation hole contains exactly the charge of one electron:

$$\int h_{XC}(\vec{r}_1, s_1, \vec{r}_2, s_2) d\vec{r}_2 ds_2 = -1$$

The concept of exchange-correlation hole is used in density functional theory !!!

THE EXCHANGE-CORRELATION HOLE

Using the exchange-correlation hole definition, one can rewrite the expectation value V_{ee} of the electron-electron repulsion hamiltonian term :

$$V_{ee} = \left\langle \Psi \middle| \hat{V}_{ee} \middle| \Psi \right\rangle = \left\langle \Psi \middle| \sum_{\mu=1}^{N} \sum_{\upsilon>1}^{N} \frac{1}{r_{\mu\upsilon}} \middle| \Psi \right\rangle = \frac{1}{2} \int\int \frac{\rho_2(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

and

$$V_{ee} = \underbrace{\frac{1}{2} \int\int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2}_{\text{Coulomb repulsion energy, } J_{ee}(r)} + \underbrace{\frac{1}{2} \int\int \frac{\rho(\vec{r}_1) h_{XC}(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2}_{\text{Correction term for the exchange-correlation effects and the self-interaction problem}}$$

In calculations, the better we can approximate the exchange-correlation hole, the more accurate are the results !!!

HOHENBERG-KOHN THEOREM 1

The external potential V_{ne} is determined, within a trivial additive constant, by the electron density $\rho(r)$

Consequence:

The hamiltonian H, and thus the ground-state energy, are completely defined by the electron density $\rho(\mathbf{r})$. Therefore, the total electronic energy can be expressed as a functional of $\rho(\mathbf{r})$:

$$E\left[\rho(\mathbf{r})\right] = T\left[\rho(\mathbf{r})\right] + V_{ne}\left[\rho(\mathbf{r})\right] + V_{ee}\left[\rho(\mathbf{r})\right]$$

This holds true for every quantum mechanical observable

HOHENBERG-KOHN THEOREM 2

The electron density $\rho(r)$ obeys a variational principle

Consequence:

Among different densities $\rho(\mathbf{r})$, those that provide lower energies are closer to the exact one.

Stationarity condition:

$$\frac{\delta E\left[\rho\left(\mathbf{r}\right)\right]}{\delta\rho\left(\mathbf{r}\right)} = 0$$

The ground-state density correspond to the minimum of the $E[\rho(r)]$ functional

Note: a functional is a composite function f(g(x)) : the output of g is the argument of f
Chain rule for a derivative of a functional f:

$$\left.\frac{\delta f}{\delta x}\right|_{x=x_0} = \frac{\delta f}{\delta g} \times \frac{\delta g}{\delta x} \qquad \frac{\delta f}{\delta g} = \left.\frac{\delta f}{\delta g}\right|_{g(x)=g(x_0)} \qquad \frac{\delta g}{\delta x} = \left.\frac{\delta g}{\delta x}\right|_{x=x_0}$$

THE KOHN-SHAM EQUATIONS

Practically, ρ is determined by solving the Kohn-Sham equations

The Kohn-Sham formalism transforms the stationarity equation into a system of eigenvalue equations whose solutions are the *Khon-Sham orbitals*

The density is then calculated using the KS orbitals :

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} n_i \left|\psi_i(\mathbf{r})\right|^2$$

Starting point:

We consider a ***fictitious*** system of non-interacting electrons that have for their overall ground-state density $\rho(\mathbf{r})$ the same density as some ***real*** system of interest where the electrons do interact

THE KOHN-SHAM EQUATIONS

	***real* system** (interacting electrons)	***fictitious* system** (non-interacting electrons)
Kinetic energy	$T[\rho]$	$T_S[\rho] = -\frac{1}{2}\sum_{i=1}^{N}\int \psi_i(\mathbf{r})\Delta\psi_i(\mathbf{r})d\mathbf{r}$
Electron-electron interactions	$V_{ee}[\rho]$	$J_{ee}[\rho] = \frac{1}{2}\int\frac{\rho(\mathbf{r_1})\rho(\mathbf{r_2})}{\lvert\mathbf{r_2}-\mathbf{r_1}\rvert}d\mathbf{r_1}\,d\mathbf{r_2}$

KS Energy functional for the real system:

$$E[\rho] = T_S[\rho] + V_{ne}[\rho] + J_{ee}[\rho] + E_{XC}[\rho]$$

Exchange-Correlation (XC) functional:

$$E_{XC}[\rho] = \left(T[\rho] - T_S[\rho]\right) + \left(V_{ee}[\rho] - J_{ee}[\rho]\right)$$

$$\frac{1}{2}\int\int\frac{\rho(\vec{r}_1)h_{XC}(\vec{r}_1,\vec{r}_2)}{r_{12}}d\vec{r}_1 d\vec{r}_2$$

E_{XC} corrects the error made in using the non-interacting kinetic energy and in treating the electron-electron interactions classically

THE KOHN-SHAM EQUATIONS

Applying the variational theorem

The orbitals that minimize the energy satisfy the Khon-Sham equations, which have the same structure as the HF equations

$$\left\{-\frac{1}{2}\Delta + \underbrace{\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \upsilon_{XC}(\mathbf{r}) + V_0(\mathbf{r})}_{\upsilon_{KS}(\mathbf{r})}\right\}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

The non-interacting electrons move in an effective KS potential depending on $\rho(\mathbf{r})$

$$\upsilon_{KS}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \upsilon_{XC}(\mathbf{r}) + V_0(\mathbf{r})$$

Local exchange-correlation potential

$$\upsilon_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[\rho]}{\delta\rho}$$

The main difficulty of DFT is to find an appropriate description of E_{XC} as a function of $\rho(\mathbf{r})$ → ***Many XC functionals***

CLASSES OF XC FUNCTIONALS

Local Density Approximation (LDA)

Assumes that the density $\rho(\mathbf{r})$ *is uniform*

$$E_{xc}\left[\rho(\mathbf{r})\right] = \int \rho(\mathbf{r})\varepsilon_{xc}\left[\rho(\mathbf{r})\right]d\mathbf{r}$$

ε_{XC} : Exchange-correlation per electron of the homogeneous electron-gas (HEG) characterized by a density $\rho(\mathbf{r})$

$$\varepsilon_{xc}\left[\rho(\mathbf{r})\right] = \varepsilon_X\left[\rho(\mathbf{r})\right] + \varepsilon_C\left[\rho(\mathbf{r})\right]$$

The exchange-energy density of a HEG is known analytically

$$E_x\left[\rho(\mathbf{r})\right] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho(\mathbf{r})^{4/3}d\mathbf{r}$$

Analytic expressions for the correlation energy of the HEG are not known
→ several LDA's for the correlation functional

The accuracy of the LDA is not outstanding
overestimation of the bond energies, underestimation of the bond lengths
C. S. Wang, B. M. Klein, and H. Krakauer, *Phys. Rev. Lett.*, **54**, 1852 (1985).

CLASSES OF XC FUNCTIONALS

Generalized Gradient Approximation (GGA)

Takes into account the density $\rho(\mathbf{r})$ *and its gradient* $\nabla\rho(\mathbf{r})$ *to better describe the inhomogeneities of the real density*

$$E_{xc}\left[\rho(\mathbf{r})\right] = \int \rho(\mathbf{r})\varepsilon_{xc}\left[\rho(\mathbf{r});\nabla\rho(\mathbf{r})\right]d\mathbf{r}$$

Wrt LDA, gives excellent atomic ground state energies, improves significantly the dissociation energies and bond lengths, reproduces more accurately the cohesive properties of many solids, corrects the vibrational frequencies of molecules built from atoms of the two first rows of the Mendeleev Table …

ε_{XC} *= exchange energy + correlation energy*

$$\varepsilon_{xc}\left[\rho(\mathbf{r})\right] = \varepsilon_X\left[\rho(\mathbf{r})\right] + \varepsilon_C\left[\rho(\mathbf{r})\right]$$

GGA functionals

BLYP, BP86, PBE, PW91…

$$\varepsilon_{XC}^{BLYP} = \varepsilon_X^B + \varepsilon_C^{LYP}$$

Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648.
Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785

CLASSES OF XC FUNCTIONALS

Hybrid Functionals

Contain a given percentage of exact HF exchange, which presents the correct -1/r asymptotic behavior

$$\varepsilon_X^{HYBRID} = a\varepsilon_X^{HF} + (1-a)\varepsilon_X^{GGA}$$

XC functional	% HF exchange (a)
B3LYP	20%
B3P86	20%
B3PW91	20%
PBE0	25%
mPW1PW91	25%
MPW1K	42.8%
BHandHLYP	50%

The most popular Hybrid Functional: B3LYP

$$\varepsilon_{XC}^{B3LYP} = a\varepsilon_X^{HF} + (1-a)\varepsilon_X^{LDA} + b\varepsilon_X^{B} + c\varepsilon_C^{LYP} + (1-c)\varepsilon_C^{LDA}$$

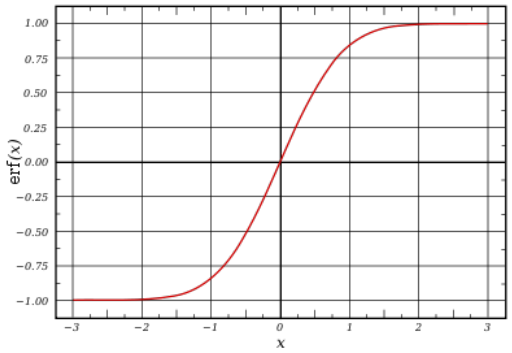
a, *b*, and *c* are semi-empirical coefficients fitted to reproduce experimental atomization and ionization energies.

a = 0.20 ; *b* = 0.72 ; *c* = 0.81

CLASSES OF XC FUNCTIONALS

Long-range corrected Hybrid Functionals

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, \mathrm{d}t.$$



LC-BLYP: the electron repulsion operator $1/r_{12}$ is divided into short- and long-range parts by using a standard error function:

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

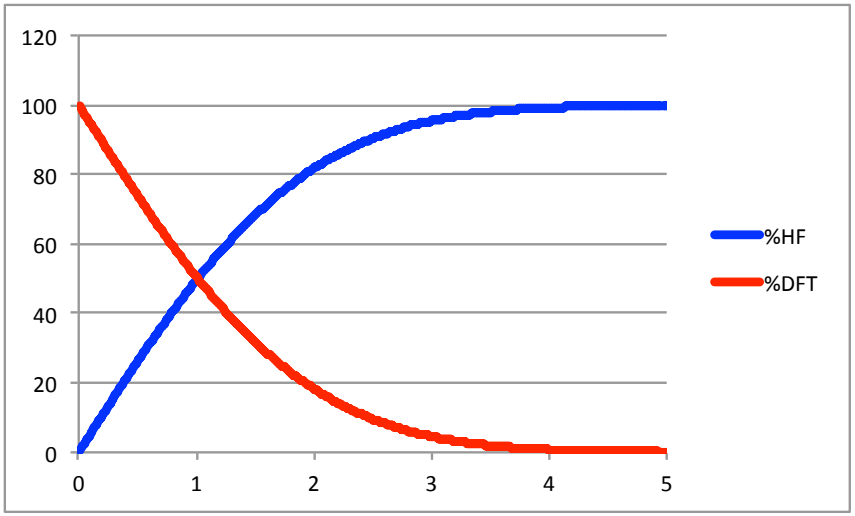
short range part (combined with DFT-LDA exchange)

long-range part (combined with HF exchange)

μ determines the balance of DFT to HF exchange at intermediate r_{12}

μ → 0 pure GGA calculation
μ → inf. pure HF calculation

Standard value in Gaussian09: μ = 0.47



Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K.
J. Chem. Phys., **2001**, *115,* 3540

CLASSES OF XC FUNCTIONALS

Long-range corrected Hybrid Functionals

CAM-B3LYP: adds a long-range correction using the Coulomb-Attenuating Method
19% of HF exchange at short-range and 65% at long-range with μ = 0.33

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

$0 \le \alpha + \beta \le 1;$
$0 \le \alpha \le 1;\ 0 \le \beta \le 1$

short range part (combined with DFT-LDA exchange)

long-range part (combined with HF exchange)

The parameter α allows us to incorporate the HF exchange contribution over the whole range: Yanai, T.; Tew, D.; Handy, N. *Chem. Phys. Lett*. **2004**, *393*, 51.

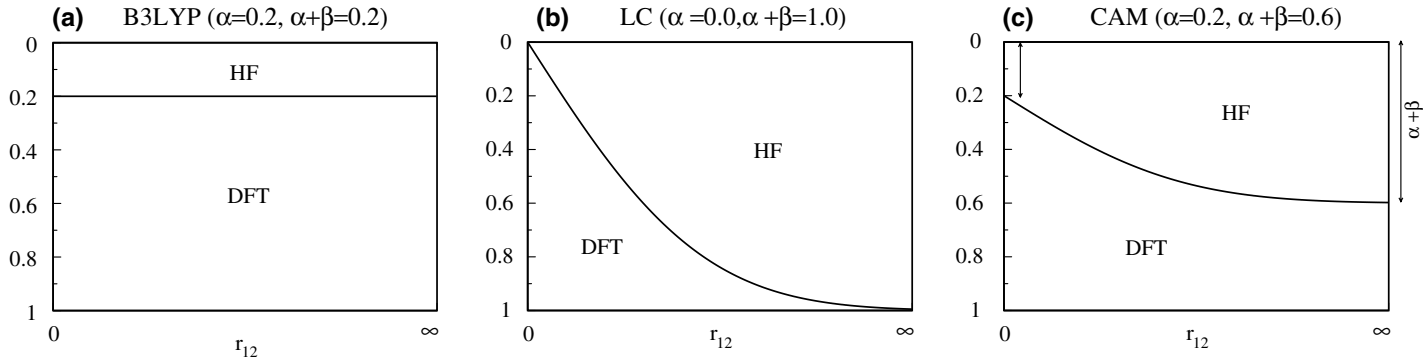


Fig. 2. Schematic plots of the contributions to exchange from r_{12}^{-1}, apportioned into DFT and HF, for: (a) B3LYP, (b) LC, and (c) CAM.