

Computational Chemistry 2 – Chapter 1

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This course will first focus on solid and surface systems. Many of the concepts has been introduced in the course Computational Chem 1. Almost all calculation in this course will be done with Density Functional Theory (DFT) or with DFT-HF hybrid methods. The higher level methods are usually not implemented with periodic boundaries.

In chemistry, the surfaces are usually more relevant than individual molecules since many chemical processes happen on surfaces. Heterogeneous catalysis is a good example also all growth processes (like ALD) happen at surfaces. Almost all inorganic materials are solids. The periodic simulations can be used to model the solid-liquid interphase.

Density Functional Theory (DFT)

The most important correlated method now is DFT. It is based on a proof that the total energy depend only on the electron density $\rho(r)$. The proof is seemingly simple. The true Schrödingerin equation can be written as $E[\psi] = \langle \psi | G - V(r, R_I) | \psi \rangle = \langle \psi | G | \psi \rangle - \int d^3 r V(r, R_I) \rho(r)$, here the G contain all terms except the interaction between the electrons and nucleus. This term is $V(r, R_I)$ and it is called external potential. The density is $\rho(r) = \int d^3 r_2 d^3 r_3 \dots d^3 r_n \psi^*(r, r_2, \dots, r_n) \psi(r, r_2, \dots, r_n)$

- 1) The external potential V (it depend only on the atomic positions) determine uniquely the wave function and the total energy: $\psi(V) \rightarrow E[V]$ (Proof: Assume two different potentials (V ja V' , they differ more than a constant) produce the same wave function: $(G - V(r, R_I))|\psi\rangle = E|\psi\rangle$ and $(G - V'(r, R_I))|\psi\rangle = E'|\psi\rangle$; subtract them from each other: $(V(r) - V'(r))|\psi\rangle = (E - E')|\psi\rangle$. Because E and E' are constants the equation can be true on if the potentials differ with a constant. This is in contradiction with the assumption, so the potential will determine the wave function.)
- 2) The wave function determine uniquely the density, $\psi \rightarrow \rho$. (Proof: Assume that two different wave function ψ and ψ' will produce the same density ρ . The definition of the density is not convenient. We use here the variational principle: $E[\psi] = \langle \psi | H | \psi \rangle < \langle \psi' | H | \psi' \rangle = \langle \psi' | H' + V - V' | \psi' \rangle = E' + \int d^3 r (V(r) - V'(r))\rho'(r)$ so $E <$

$E' + \int d^3 r (V(r) - V'(r))\rho'(r)$. We can use the same logic starting from H' , ψ' and E' . This leads to equation $E < E' + \int d^3 r (V(r) - V'(r))\rho(r)$. if $\rho = \rho'$ then we will have an absurd result $E + E' < E + E'$, so the wave function will determine the density uniquely.

- 3) The later statement can be inverted: $\rho \rightarrow \psi$, so the energy depend only on the density $E(\rho)$

Note: DFT is valid only for the **ground state**. It cannot be used for excited states.

It has turned out that the $E(\rho)$ is directly not very useful. Formally we can write the total energy as

$$E[\rho] = T[\rho] + W[\rho] - \int d^3 r V(r, R_I)\rho(r)$$

where T is the kinetic energy of the systems and W is the electron-electron interaction.

$$T[\rho] = - \sum_i \langle \psi | \nabla_i^2 | \psi \rangle; \quad W[\rho] = \int \frac{\rho(r)\rho(r')}{|r - r'|} d^3 r d^3 r' + E_{xc}(\rho)$$

In this form the $T[\rho]$ and $E_{xc}(\rho)$ are unknown. For $E_{xc}(\rho)$ there are reasonable approximations but $T[\rho]$ is not well known.

This so called density-only-DFT (or orbital free DFT, OF-DFT) can be used in some approximations but it is not very accurate. There are now some research projects trying to improve the OF-DFT. It is unlikely that the OF-DFT will be very accurate but it should be very fast and it should be very useful for screening calculations.

The Kohn-Sham method

Kohn and Sham proposed (1964) a very useful DFT scheme. We can assume that there is a **non-interacting** system that will **produce the correct density** (and the correct density will produce the correct energy). For a non-interaction system the Slater determinant IS the correct wave function, $\Psi_{KS} = \det[\varphi_{1,KS}, \varphi_{2,KS}, \dots \varphi_{N,KS}]$ and the density is

$$\rho(r) = \sum_{n=1}^N \varphi_{n,KS}^*(r)\varphi_{n,KS}(r)$$

This lead to Kohn-Sham equations to the orbital

$$\left[-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + V_{KS}[\rho; R](r) \right] \varphi_n^{KS}(r_i; R_I) = E_n \varphi_n^{KS}(r_i; R_I)$$

(KS1)

Here the $V_{KS}(r)$ is an unknown potential, r is electron positions and R are atomic positions. It is usually written as:

$$\left[-\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + 2 \int d^3 r_j \frac{\rho(r_j)}{|r_i - r_j|} - \sum_{ij} \frac{Z_i e^2}{4\pi\epsilon_0 |r_i - R_j|} + V_{xc}[\rho](r) \right] \varphi_n^{KS}(r_i; R_I) = E \varphi_n^{KS}(r_i; R_I), \quad (KS)$$

We have taken the large and known terms separately but the $V_{xc}(r)$ is still unknown. Fortunately it is not very large and with good approximations good results can be obtained. Note that Exc is not the same as in traditional quantum chemistry ($E_{xc} = \int V_{xc}(r) \rho(r) d^3 r$)

$$E_{xc}^{DFT}[\rho] = T[\rho] - T_{KS}[\rho] + E_{xc}^{QC}[\psi]$$

Since we do not know the exact kinetic energy either. Secondly the quantum chemical XC function is very, very complex and it is not easy to approximate it with density functional. For example we know exactly the exchange function (it is the HF theory).

One can write a formal equation for E_{xc}

$$E_{xc} = \frac{1}{2} \int \frac{\rho(r) \varrho_{xc}(r, r')}{|r - r'|} d^3 r d^3 r'$$

Where $\varrho_{xc}(r, r')$ is so called xc-hole. It can be shown that an integral of the xc-hole is

$$\int \varrho_{xc}(r, r') d^3 r' = -1$$

The asymptotic limit of the x-potential is known but c-potential is not known

$$V_x(r) \xrightarrow{r \rightarrow \infty} \frac{1}{r}$$

Approximations for V_{xc}

We need to have the xc energy and potential, E_{xc} , $E_{xc} = \int V_{xc}(r) \rho(r)$ and $V_{xc}(r) = \delta E_{xc} / \delta \rho(r)$

Local density approximation (LDA): The total energy of a homogenous electron gas can be computed very accurately. So we know the homogenous electron gas $E_{xc,homog}(\rho)$. Now we make a big approximation and use that function locally at every point in space.

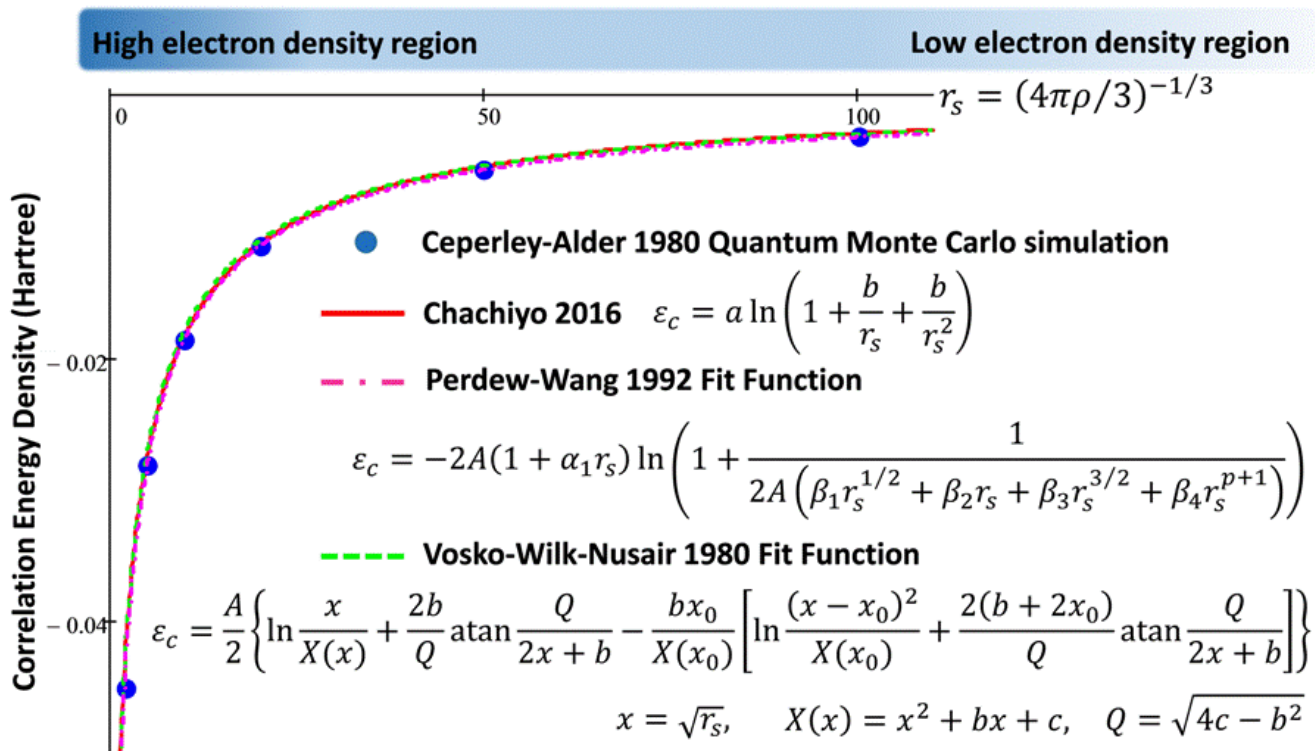
$$E_{xc}^{LDA} = \int E_{xc,homog}(\rho(r)) * \rho(r) d^3r \quad (LDA)$$

The xc is not a local function but the LDA still contain correlation. In fact LDA is a surprisingly good approximation. It will give good bonding geometries and dipole moments. Even the energies are reasonable.

The exchange is easy

$$E_x^{LDA} = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \rho(r)^{4/3} d^3r, \quad k_F = (3\pi^2\rho)^{1/3}$$

the correlation is more complex and it is traditionally fitted to Quantum Monte Carlo calculations. There is also very simple Chachiyo correlation functional ($a=\ln(2)-1/2\pi^2$, $b=20.456325..$) which works well.



Picture form: https://en.wikipedia.org/wiki/Local-density_approximation

The next level is to include the gradient of the density to the model. We also know that the xc potential

GGA for V_{xc}

The LDA can be model can be improved including the gradient of the density

$$E_{xc}^{GGA} = E_{xc}^{LDA} + \int E_{xc}(\rho(r), \nabla\rho) * \rho(r) d^3r \quad (\text{GGA})$$

This looks simple but is has been hard to find good approximation. One of the simplest one that works is due to Axel Becke (1986),

$$E_x^{GGA} = \int E_{x,homog}(\rho) * f_x(\xi) d^3r, \quad \xi = \frac{(\nabla\rho)^2}{(2k_F\rho)^2}, \quad k_F = (3\pi^2\rho)^{1/3}, \quad f_x^{B86}(\xi) = 1 + \frac{a\xi}{1+b\xi}$$

Where a and b are parameters, a=0.2351 and b=0.24308. 1988 Becke proposed an improvement to this equation

$$f_x^{B88}(\xi) = 1 + \frac{a\xi}{1 + b\sqrt{\xi} \operatorname{arsh}(2(6\pi^2)^{1/3}\sqrt{\xi})}$$

Now a=0.2743 and b=9a/4π. This is very much used approximation for x-energy. The correlation have also several models. One very used model is PBE (Perdew-Burke-Ernzerhof)

$$E_c^{GGA} = \int \rho(r) * f_c(t) d^3r, \quad t = \frac{|\nabla\rho|}{2k_F\rho},$$

$$f_c^{PBE}(t) = \frac{\beta^2}{2\alpha} \ln \left[1 + \frac{2\alpha}{\beta} \frac{t^2 + At^4}{1 + At^2 + A^2t^4} \right], \quad A = \frac{2\alpha}{\beta} \left[\exp \left(-\frac{2\alpha \epsilon_c^{homog}(\rho)}{\beta^2 \rho} \right) - 1 \right]^{-1}$$

α and β are constants.

There are far too many DFT approximations. Some of them have empirical parameters like the B86, B86, and HCTH. The HCTC model contain several parameters that have been fitted to accurate quantum chemical results (like CCSD(T)).

See:

<http://www.tddft.org/programs/octopus/wiki/index.php/Libxc>

Hybrid functionals

The Hartree-Fock model will describe the exchange exactly, so it would be tempting to use the HF for it and a DFT/GGA model for correlation:

$$E_{xc}^{hyb} = E_x^{HF} + E_c^{GGA}$$

This model is not very good because there is some error cancelation in the E_x and E_c terms and it is hard to model only E_c . Much better results can be obtained if the HF and DFT:n E_x are mixed.

$$E_{xc}^{hyb} = aE_x^{HF} + (1-a)E_x^{GGA} + bE_c^{GGA}$$

Sometimes the LDA and GGA have different weights. The most important hybrid is B3LYP

$$E_{xc}^{hyb} = aE_x^{HF} + (1-a)E_x^{LDA} + bE_x^{B88} + (1-c)E_c^{LDA} + cE_c^{LYP}$$

The constants are $a=0.20$, $b=0.72$, $c=0.81$. (Note LYP-GGA includes LDA, so in normal BLYP calculation $a=0.0$, $b=1.0$ and $c=1.0$).

Most of the hybrid functional are variant of the equation above. The PBE0 (should be PBE1PBE)

$$E_{xc}^{hyb} = aE_x^{HF} + (1-a)(E_x^{LDA} + E_x^{PBE}) + E_c^{LDA} + E_c^{PBE}$$

where $a=0.25$. This is simple. There are also some reasonable arguments that a should be $= 0.25$. This is the reason for name PBE0.

Meta-GGA functionals

The meta-GGA functionals are next level functional form GGA. They utilize information of second derivative of the density, $\nabla^2 \rho$, and/or kinetic energy density.

$$t_s(r) = \sum_k |\nabla \phi_k(r)|^2$$

The MGGA functional, like PKZB, TPSS, are rather complicated but they are usually a bit better than best GGA's.

Dispersion

Dispersion (or van der Waal interaction) describes weak non-dipolar interactions between molecules. It is the leading interaction between rare-gas atoms, it is important in aromatic molecules and it has some contribution in all molecules. The dispersion is based on virtual molecular excitations and it is very difficult to include to DFT. The dispersion is also absent in HF theory. In practice all DFT and hybrid models will lack dispersion. NOTE: many DFT models will result molecular binding e.g. for He dimer, but from wrong reason.

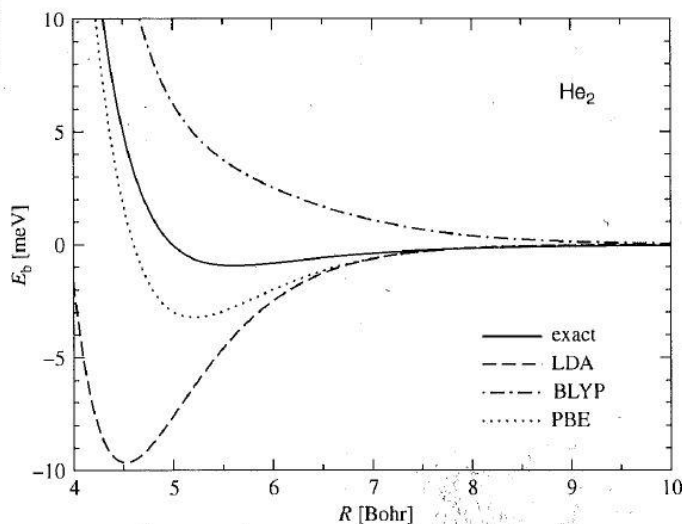


Fig. 6.2 Energy surface E_b of He_2 : Selfconsistent LDA [134], BLYP [219, 221] and PBE [207] data versus exact result [332].

The simplest way to add dispersion is the use empirical potentials. The most popular one is developed by Stefan Grimme and his research group.

$$E_{vdw}^{DFT} = E_{xc}^{GGA} + E_{grimme}^{vdw}(|R_I - R_J|)$$

This model need parameters for all atoms and the parameters depend on the GGA. Computationally the method is light. No information of the density or wave functions are needed. Also the approach of Tkatchenko and Scheffler is popular. There are DFT models that includes the dispersion but they are not much used.

More details:

<http://www.compchemhighlights.org/2014/04/approaches-to-dispersion-in-dft.html>

On the other hand, most of the quantum chemistry methods, like MP2, CCSD, etc. include dispersion interactions. Thus if they can be used they are convenient for testing the dispersion effects.

PROBLEMS WITH DFT

The main problem with DFT is rather obvious. There is not systematic way to improve the XC-potential. This is very clearly seen from the huge number of XC-models and their slow progress. We also know that the "exact" XC-potential is extremely complex. It is very unlikely that a universal and very good XC-potential will be ever found. But slowly better XC-models will be developed. One can crudely order the DFT model with increasing accuracy:

LDA (bad) < GGA < meta-GGA ~ hybrid functionals
GGA < GGA + dispersion

SI PROBLEM

One deep DFT problem is the self-interaction interaction. The main problem is that in DFT every electron will feel itself. The SI can formally be corrected by subtracting the orbital dependent SI

$$E_{xc}^{SIC-GGA} = E_{xc}^{GGA}[\rho_{\uparrow}, \rho_{\downarrow}] - \sum_{n,\sigma} \left\{ E_H(|\varphi_{k,\sigma}|^2) + E_{xc}^{GGA}(|\varphi_{k,\sigma}|^2, 0) \right\}$$

This correction is complicated since it depend on orbitals, not on density. It is not anymore a DFT model. This also causes several computational problems. It is very difficult to converge the SIC-DFT equations.

There are also new SI models but they are rather complex. On the other hand the HF model is free of SI error and thus the hybrid methods are working better than the pure GGA models.