

Advanced Physical Chemistry (fizkemhk17em)

Electronic Structure

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Density Functional Theory (DFT)

Wave function vs. density

The wave function is a $4N$ dimensional function which determines all properties of the system:

$$\Psi = \Psi(\tau_1, \tau_2, \dots, \tau_N) \quad \tau_i = (\mathbf{r}_i, \sigma_i)$$

$$E = \langle \Psi | \hat{H} | \Psi \rangle \quad \text{i.e.} \quad E = E[\Psi]$$

On the other hand, the density is a three dimensional function:

$$\rho(\mathbf{r}_1) = N \cdot \int \int \dots \int \Psi(\tau_1, \tau_2, \dots, \tau_N)^* \Psi(\tau_1, \tau_2, \dots, \tau_N) d\sigma_1 d\tau_2 \dots d\tau_N,$$

which gives the probability of finding a single electron at a given point.

The density can be calculated from the wave function:

$$\Psi \rightarrow \rho(\mathbf{r})$$

Intuitively, one would assume that it also gives all properties of the systems:

$$\rho \stackrel{?}{\rightarrow} E \quad \text{i.e.} \quad E \stackrel{?}{=} E[\rho]$$

Splitting up of the Hamiltonian

$$\hat{H} = \underbrace{-\sum_i \frac{1}{2} \Delta_i}_{\hat{T}} + \underbrace{\sum_{i < j} \frac{1}{r_{ij}}}_{V_{ee}} - \underbrace{\sum_i \sum_A \frac{Z_A}{r_{iA}}}_{V(\mathbf{r})}$$

- \hat{T} kinetic energy, not system specific;
- V_{ee} electron-electron repulsion, defined by N , not system specific;
- $V(\mathbf{r})$ depends only on the nuclei, called the „external potential”.

The first two terms is the same for all system, while the „external potential” defines which molecule we consider (where are the nuclei, what is their charge).

First theorem of Hohenberg-Kohn (HK1)

$$\begin{array}{ccc} V(\mathbf{r}), N & \rightarrow & \hat{H} \\ & & \downarrow \text{Schrodinger equation} \\ \rho(\mathbf{r}) & \leftarrow & E, \Psi \end{array}$$

The energy of the system, its wave function and therefore also the density is determined by the „external potential”, i.e. by the molecule.

HK1:

A $V(\mathbf{r})$ „external potential” (disregarding a trivial constant term) is defined completely by the electron density.

Therefore, considering also the relations in the above figure:

$$V(\mathbf{r}) \leftrightarrow \rho(\mathbf{r})$$

Energy as functional of the density

Molecule \rightarrow position of the nuclei $\rightarrow V(\mathbf{r}) \rightarrow \rho(\mathbf{r}) \rightarrow$ energy

Therefore the energy is a functional of the density:

$$E[\rho] = T[\rho] + E_{ee}[\rho] + E_{ne}[\rho]$$

- $T[\rho]$ is the kinetic energy, its form is unknown
- $E_{ee}[\rho] = J[\rho] + E_x[\rho]$: electron-electron interaction, summ of the Coulomb (J) and the exchange (E_x) contributions. The functional form is known for (J) but not for (E_x).
- $E_{ne}[\rho]$ interaction between electron and nuclei, form is known, can be calculated from V ($\int \rho V dr$)

$T[\rho]$ and $E_{ee}[\rho]$ are universal, $E_{ne}[\rho]$ system dependent.

Second theorem of Hohenberg-Kohn (HK2)

HK2:

The variational principle is also valid for the energy functional, i.e. the energy is minimal with the exact electron density

This means, the best density can be obtained by minimization, provided the form of the functional is known.

But the form of the functional is not known!

What we know is that the relations can be rationalized through the Schrödinger equation, but we do not know whether an analytical form exists at all (most probably it does not exist!!)

$$\begin{array}{ccc}
 V(\mathbf{r}), N & \rightarrow & \hat{H} \\
 \updownarrow & & \downarrow \textit{Schrodinger egyenlet} \\
 \rho(\mathbf{r}) & \leftarrow & E, \Psi
 \end{array}$$

Kohn-Sham (KS) DFT

Construct the functional of the kinetic energy for a system with non-interacting particles, assuming the same density as of the investigated system:

$$T_S = \sum_i^{\text{occ}} \langle \varphi_i | -\frac{1}{2}\Delta | \varphi_i \rangle$$

and

$$\rho(\mathbf{r}) = \sum_i^{\text{occ}} \varphi_i^*(\mathbf{r})\varphi_i(\mathbf{r})$$

Note that we have introduced orbitals, from now on we not simply treat the density.

T_S is not the same as $T[\rho]$ it is just an approximation:

$$T[\rho] = T_S[\rho] + E_c[\rho]$$

with correction E_c being the „correlation contribution” which is *not known*!!

$$E_{xc}[\rho] = T[\rho] - T_S[\rho] + E_x[\rho]$$

is the so called *exchange-correlation* functional, which collects all the the unknown contributions. **We have no idea how it looks like!!!**

Kohn-Sham (KS) DFT

Thus, the so called *Kohn-Sham energy functional* has the form:

$$E_{KS}[\rho] = T_S[\rho] + J[\rho] + E_{ne}[\rho] + E_{xc}[\rho]$$

Applying the variational principle (look for the „best” density which gives the lowest energy), we arrive at one-particle equations which are similar to that of the Hartree-Fock method and called the Kohn-Sham equation:

$$\begin{aligned}\hat{h}_{KS} \varphi_i &= \varepsilon_i \varphi_i \\ \hat{h}_{KS} &= -\frac{1}{2}\Delta + \hat{V}_{ne} + \hat{J} + \hat{V}_{xc}\end{aligned}$$

Comparing to the Fock operator

$$\hat{f} = -\frac{1}{2}\Delta + \hat{V}_{ne} + \hat{J} - \hat{K}$$

the only difference is that the exchange (\hat{K}) is replaced by „exchange-correlation” potential (V_{xc}).

Kohn-Sham (KS) DFT

$$\begin{aligned}\hat{h}_{KS} \varphi_i &= \varepsilon_i \varphi_i \\ \hat{h}_{KS} &= -\frac{1}{2}\Delta + \hat{V}_{ne} + \hat{J} + \hat{V}_{xc}\end{aligned}$$

From the Kohn-Sham equation we get orbitals and orbital energies and we can calculate the density from the orbitals. Using the density, all the properties can be calculated.

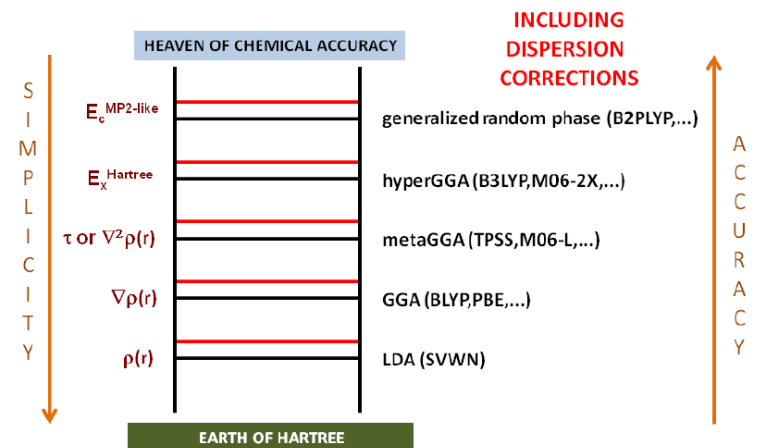
Problem: if we don't know E_{xc} , we do not know V_{xc} , either!!!!

The different DFT methods differ in the choice of the functional V_{xc} .

DFT functionals

There are several levels of the approximation (Jacob's ladder of DFT):

1. Assuming homogeneous electron gas – V_{xc} can be calculated from the density;
2. Gradient-corrected (GGA - General Gradient Approximation) functionals:
 - functional V_{xc} depends not only on the density but also on its gradients
 - expansion according to these quantities
 - empirical parameters ← fitted on chemical systems
3. Hybrid methods
 - exchange part of the potential from Hartree-Fock („exact exchange”)
 - new parameters ← fitted on chemical properties
4. Correction for long distance interactions
 - empirical
 - from wave function methods



DFT functionals

Approximation	exchange V_x	correlation V_c
1) homogeneous electron gas	LDA	VWN
2) Gradient-corrected (GGA)	PW86 B88 PBE	LYP PW91 PBE
3) Hybrid methods	B3 PBE0	B3
4) Correction for long distance interactions		DFT-D Double-hybrid DFT M06 M06-2X M06-L M06-HF

The name of the functional is the combination of the names of the exchange and correlation part (e.g. B3-LYP). Abbreviations on the following page

DFT functionals

Abbreviations:

LDA – Local Density Approximation (used mostly in solid state physics)

VWN – Vosko, Wilk, Nusair correlation functional

PW86 – Perdew and Wang functional from 1986

LYP – Lee, Young and Parr correlation functional

B88 – Becke's exchange functional from 1988

PW90 – Perdew and Wang functional from 1991

PBE – Perdew, Burke and Erzenhof functional

B3 - Becke's hybrid functional

PBE – Perdew, Burke and Erzenhof hybrid exchange functional

DFT-D – dispersion-corrected functional (Grimme)

M06-yy – Truhlar's (Minnesota) series of functionals

Performance of the DFT methods (kcal/mol)*

Method	Mean abs. dev.	Maximum error
G2**	1.6	8.2
SVWN (LDA-VWN)	90.9	228.7
BLYP	7.1	28.4
BPW91	7.9	32.2
B3LYP	3.1	20.1
B3PW91	3.5	21.8

* Using atomization and ionization energy as well as electron affinity of 126 molecules.

** combination of wave function methods (best one can do, very expensive).

Basis sets used in computational chemistry

The LCAO-MO approximation

Above we have discussed the approximation: molecular orbitals are expanded on atomic bases:

$$\varphi_i = \sum_a c_{ai} \chi_a$$

This is the so called LCAO-MO (Linear Combination of Atomic Orbitals for Molecular Orbitals) approximation, which is almost always used in computational chemistry, both in Hartree-Fock and DFT calculations.

The quality of the basis largely determines the quality of the results.

Form of the basis functions

According to the chemical intuition, MO's can be obtained from AO's. Best choice would be to use atomic orbitals obtained for the atoms within the IPA calculation.

STO: Slater-type orbitals

$$\chi_{n,l,m}(r, \theta, \varphi) \sim r^{n-1} e^{-\zeta r} Y_l^m(\theta, \varphi)$$

ζ is the parameter of the function. A few Slater functions give already a quite good qualitative description.

Problem: calculation of the electron-electron interaction is complicated with these functions.

Form of the basis functions

GTO: Gauss-type orbitals

$$g_b = \chi_{ijk} = x^i y^j z^k e^{-\zeta r^2}$$

This form is based on Cartesian coordinates, and instead of quantum number l , the exponent of x , y , z coordinates are used to form the necessary functions:

- s function $i = j = k = 0$;
- p function, e.g. $i = 1, j = k = 0$;
- d function, e.g. $i = 1, j = 1, k = 0$.

Here also ζ is the only parameter.

Advantage: product of two Gaussian functions placed in different points of space is also a Gaussian function, therefore the electron-electron interaction can be calculated easily!

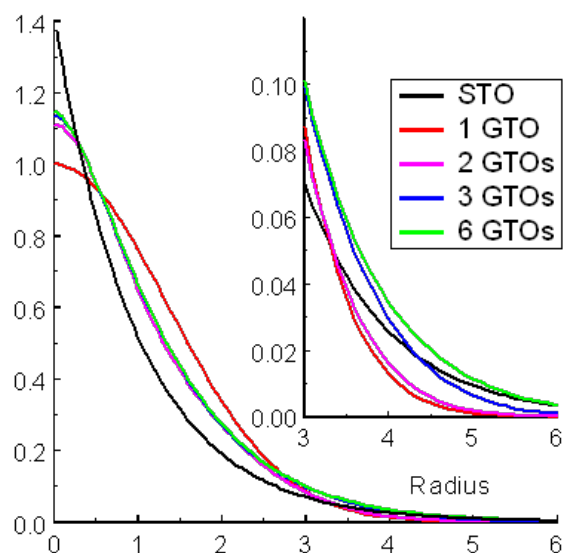
Disadvantage: falloff is too fast, and there is no *cusp* \rightarrow for the same quality more Gaussian functions are needed than Slater functions.

Form of the basis functions

CGTO: Contracted Gauss-type orbitals

$$\chi_a = \sum_b d_{ab} g_b$$

i.e. the basis functions are fixed combination of so called primitive Gaussian functions (described on the previous slide). Coefficients d_{ab} are additional parameters of the basis set, they are obtained from a previous calculation. One possibility: expansion of Slater function on the Gaussian ones ($STO - nG$).



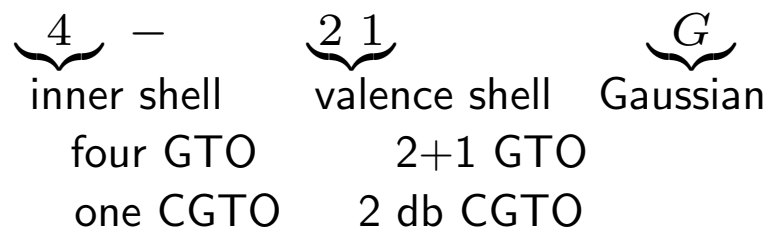
Gaussian basis functions used in practice

- **Minimal basis:** one function for all occupied sub-shell. For example:
 - H one s -type function
 - C two s , one set of p (all together five functions)
 - **Double zeta (DZ) basis:** two functions for all occupied sub-shell. For example:
 - H two s -type functions
 - C four s , two sets of p (all together ten functions)
 - O four s , two sets of p (all together ten functions)
 - **Triple zeta (TZ) basis:** three functions for all occupied sub-shell.
 - **Polarization functions:** include also functions with larger l than that of the occupied shells. For example, in case of DZP:
 - H two s -type functions and **one set of p**
 - C four s , two sets of p **one set of d**
 - O four s , two sets of p **one set of d**
- For the description of electron correlation, polarization functions are necessary!
- **Diffuse functions:** include additional functions with smaller *zeta* exponents. These decay slower and required to describe extended wave function (e.g. anions).

Gaussian basis functions used in practice

- Split-valence basis

Chemistry takes place in the valence shell, therefore it is not necessary to use too many functions for the inner shells. Leave out the functions describing the core from the optimization procedure, use them with a fixed coefficient. For example, use contraction like:



For example, the 3-21G basis:

	subshell	GTO		CGTO
<i>H</i>	1 <i>s</i>	3 Gaussians	→	two functions
	1 <i>s</i>	3 Gaussians	→	one function
<i>C</i>	2 <i>s</i>	3 Gaussians	→	two functions
	2 <i>p</i>	3x3 Gaussians	→	2x3 functions

Gaussian basis functions used in practice

- Split-valence basis (cont.)

Polarization functions

6 – 31 G^* ← polarization function on second row atoms

6 – 31 G^{**} ← polarization function als on H atom

Diffuse functions (small exponents, slow falloff)

6 – 31 $G+$ ← diffuse function on second row atoms

6 – 31 $G++$ ← diffuse function also on H atom

These are important for long range interactions, diffuse electron distributions (e.g. anions).

Gaussian basis functions used in practice

- „Correlation Consistent” basis: cc-pVXZ

cc: correlation consistent – for higher level (correlation) calculations

p: polarized – includes polarization function

V: valence – „split valence” type

XZ: DZ (double zeta), TZ (triple zeta), QZ, quadruple zeta, etc.

For example, cc-pVTZ is „triple zeta” type basis (polarization functions in red):

H three *s* type functions, two stes of *p*, one set of *d*

C one + three *s* type functions, three sets of *p*, two stes of *d*, one set of *f*

O one + three *s* type functions, three sets of *p*, two stes of *d*, one set of *f*

Further variants:

aug-cc-pVXZ: includes also diffuse functions

cc-pCVXZ: includes also „core” functions