

Materials design and selection for circular economy

Mod. 2 Design and selection of functional molecules and materials
for sustainable synthesis and circularity

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An electron is quantum mechanically described by a wavefunction.

Thus, we need first a **good wavefunction** for the system of interest.

The wavefunction $\Psi(\mathbf{r})$ can be obtained by quantum mechanics calculations.

Which QM method?

Are there recipes of *computational cooking*?



The description of electron distribution in detail requires quantum mechanics!

Solution of the time independent Schroedinger equation (TISE or simply SE):

Schroedinger equation for a system of N electrons:

$$\hat{H}\Psi(x_1, x_2, \dots x_N) = E\Psi(x_1, x_2, \dots x_N)$$

$\hat{H}$ Molecular Hamiltonian

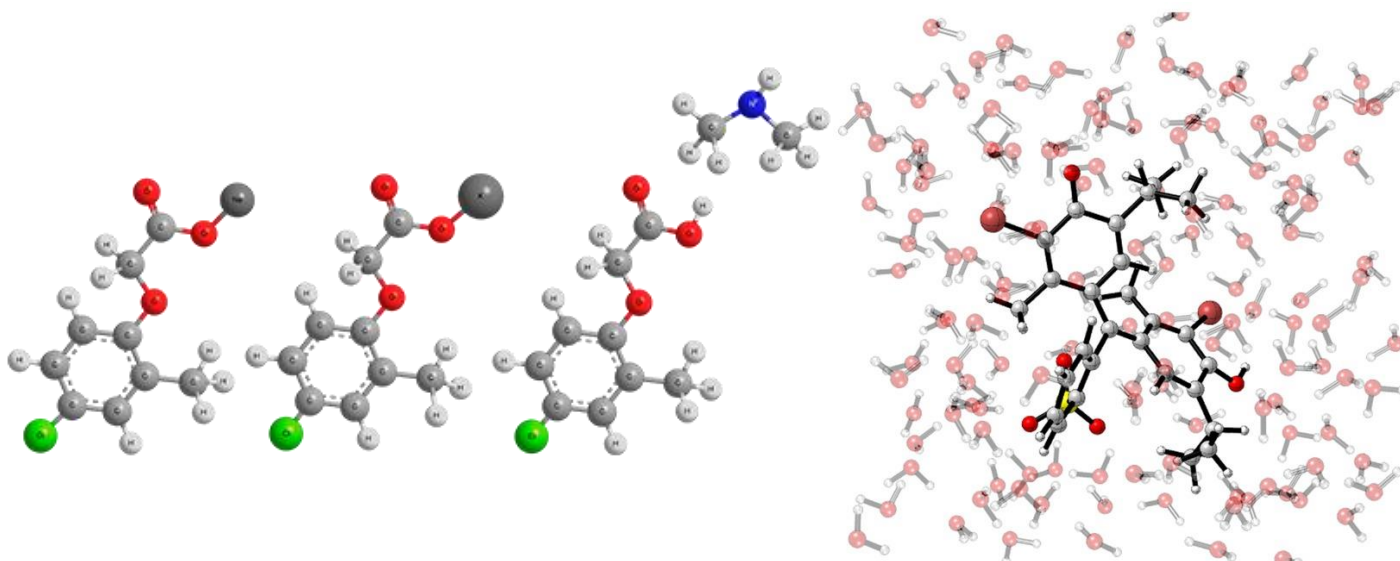
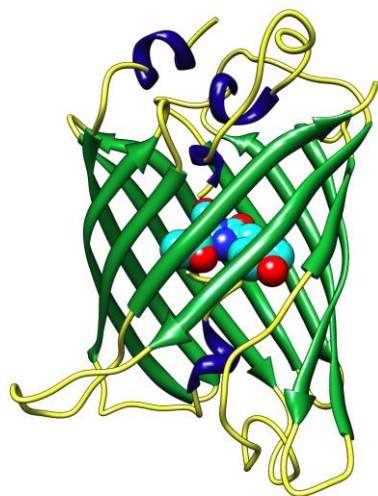
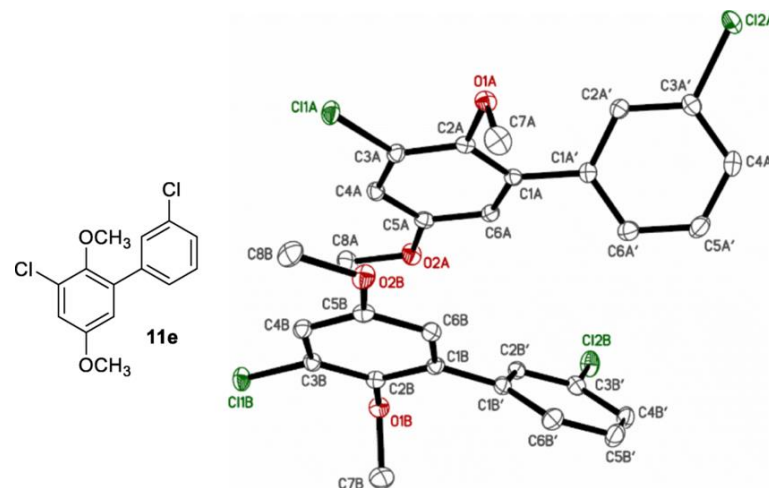
- Solutions are generated without reference to experimental data: *ab initio methods*
- Other approaches are *semi-empirical* models and *density functional theory (DFT)* models

Which molecular structure?

- Crystallographic structure
- Fully *optimized* molecular structure
- Protein cluster
- Solvated molecular structure

The choice may profoundly affect your results!

How would you describe a molecule to the computer?



Which QM methodology?

Density Functional Theory (DFT) are the most popular QM methods because they represent....

an optimal compromise between effort and accuracy

Certainly, an important reason is that **it represents a first-principles method whose practical implementation combines a high efficiency** (a favorable order- N^3 or better scaling of the computational cost, where N is a size parameter, e.g., the number of electrons) **with a relatively high accuracy** (often agreeing with experiment within a few kcal/mol)



Hohenberg-Kohn theorems (1964)



The ground state energy E is uniquely determined by the corresponding electron density $\rho(\mathbf{r})$, that is, $E = E[\rho(\mathbf{r})]$.



For a well-behaved trial density $\rho_{\text{trial}}(\mathbf{r})$, the energy functional yields an energy that is higher than or equal to that belonging to the exact ground state density $\rho(\mathbf{r})$, that is, $E[\rho_{\text{trial}}(\mathbf{r})] \geq E[\rho(\mathbf{r})]$.

The exact ground state electronic energy and density can be calculated without recourse to the Schrödinger equation, at least in principle. That is, the first Hohenberg-Kohn theorem merely proves the existence of such a functional relationship between E and $\rho(\mathbf{r})$, but it does not give any prescription how to systematically construct or find $E[\rho(\mathbf{r})]$

The introduction in **1965** by **Kohn and Sham** of a practical computational scheme may, therefore, be considered to be the next major milestone in the development of formal DFT.

$$\left[-\frac{1}{2} \nabla^2 + v_S(\mathbf{r}) \right] \varphi_i = \varepsilon_i \varphi_i$$

The essential ingredient in this approach is the postulation of a reference system of N non-interacting electrons, moving in an effective external potential $v_S(\mathbf{r})$ the so-called **Kohn-Sham potential**, instead of the electrostatic potential $v(\mathbf{r})$ of the nuclei:



Interacting...



Non-interacting

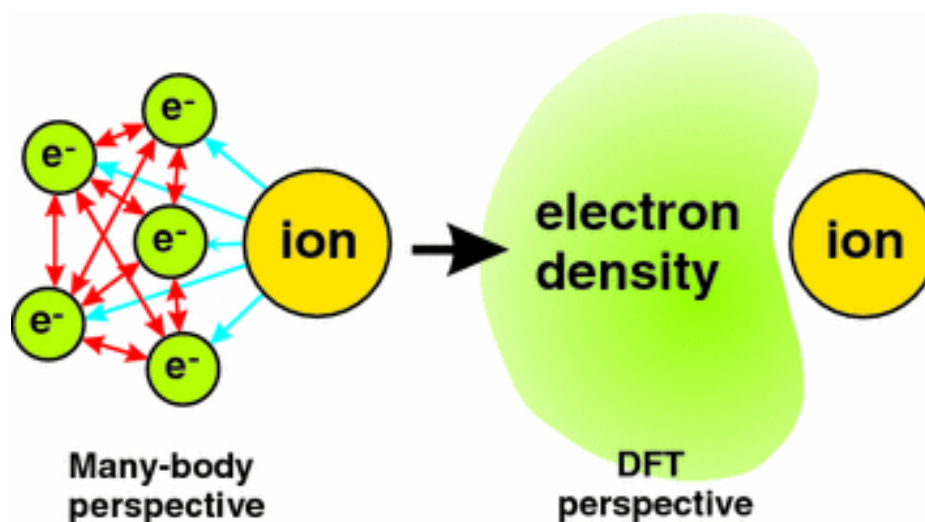
$$\left[-\frac{1}{2} \nabla^2 + v_S(\mathbf{r}) \right] \varphi_i = \varepsilon_i \varphi_i$$

- The first term in brackets is the usual kinetic energy operator.
- The non-interacting reference system has the property that its one-determinantal wavefunction of the lowest N orbitals yields the exact density of the interacting system with external potential $v(\mathbf{r})$ as a sum over densities of the occupied orbitals, that is, $\rho(\mathbf{r}) = \sum |\varphi_i|^2$, and the corresponding exact energy $E[\rho(\mathbf{r})]$. The Kohn-Sham potential should account for all effects stemming from the electron-nuclear and electron-electron interactions

Not only does the Kohn-Sham potential contain the attractive potential $v(\mathbf{r})$ of the nuclei and the classical Coulomb repulsion $v_{\text{Coul}}(\mathbf{r})$ within the electron density $\rho(\mathbf{r})$, but it also accounts for all exchange and correlation effects, which have so to say been “folded into” a local potential $v_{\text{xc}}(\mathbf{r})$

$$v_{\text{S}}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{Coul}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$$

This leaves us with an effective one-electron formulation of the quantum many-body problem, which is used in essence by all current implementations of DFT.



A good reading....

Wiley Online Library

Angewandte
International Edition **Chemie**

GDCh

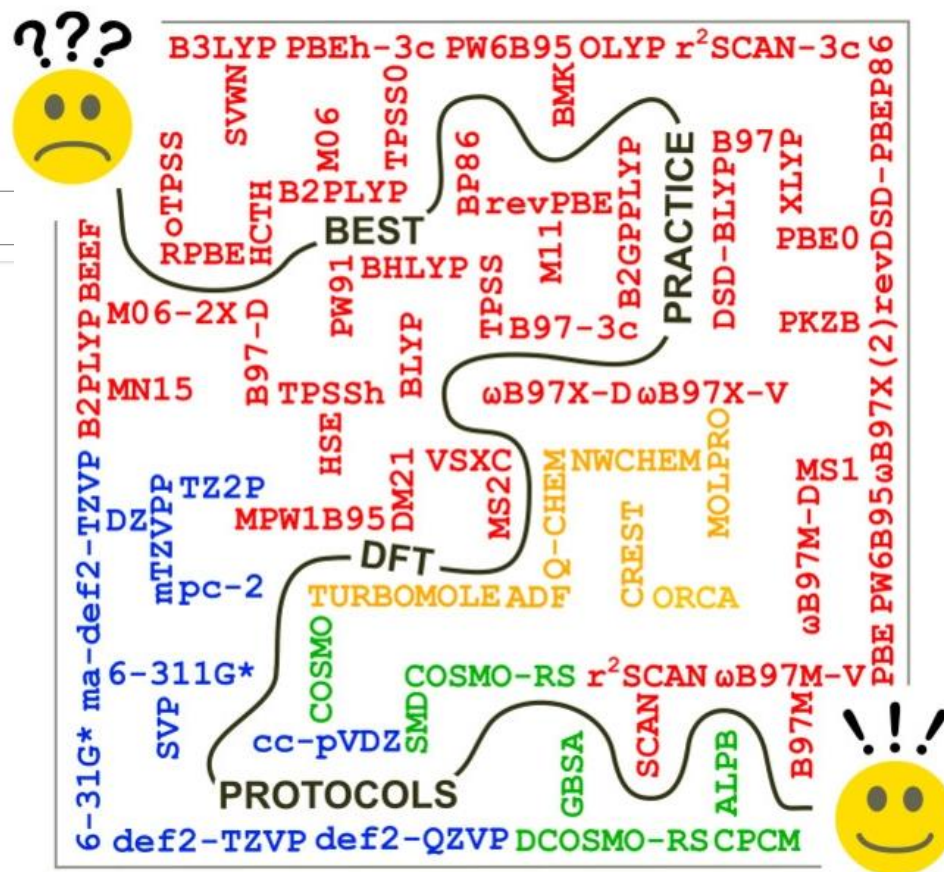
A Journal of the
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Best-Practice DFT Protocols for Basic Molecular Computational Chemistry**

Dr. Markus Bursch Dr. Jan-Michael Mewes Dr. Andreas Hansen Prof. Dr. Stefan Grimme

First published: 14 September 2022 | <https://doi.org/10.1002/anie.202205735>



Main families of density functionals

LDA Local Density Approximation: the density locally can be treated as a uniform electron gas, i.e. it is a slowly varying function.

GGA Generalized Gradient Approximation: The first derivative of the density is included as variable and in Addition. It is required that the fermi and Coulomb holes integrate to the required values of -1 and 0.

Meta-GGA: higher order gradient methods in which the exchange and correlation functionals depend on the Laplacian of the density /higher order derivatives.

Hybrid (or hyper GGA): the exchange energy is computed as HF exchange, but since HF and KS orbitals are different only a fraction of HF exchange is included. This improves also the self interaction error.

Performance of DFT methods

Accuracy, typical usage.

If covalent bonds, metallic bonds, ionic bonds :

2-3% for the geometry (bond lengths, cell parameters)

0.2 eV for the bonding energies (GGA)

problem with the band gap

For weak bonding situations (Hydrogen bonding, van derWaals), worse

Treatment of a few hundred atoms is OK on powerful parallel computers

Up to 50-100 atoms is OK on a PC.

What is DFT bad at?

Excited state properties:

- Band gaps [can do GW instead]
- Optical properties (electron-hole interactions) [can do BSE]

Other missing bits and trouble areas:

- Overbinding in LDA, underbinding in GGA
- Strongly correlated systems (narrow d- and f- bands)
- Lack of van der Waals interactions [can be added through the use of various schemes in addition to DFT]
- Presence of self-interaction error (electron interacts with its own charge density) [reduced by using hybrid functionals with some fraction of exact-exchange, but expensive]

Progress in improving ground state properties may lie in better exchange-correlation functionals, an active area of research