

Density Functional Theory

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DFT

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Introduction

Basics in Quantum
Mechanics

DFT

Self Consistent Field
(SCF) Cycle

Numerical Effort

Post Processing

DENSITY FUNCTIONAL THEORY is a method to successfully describe the behavior of atomic and molecular systems and is used for instance for:

- structural prediction of chemical compounds
- simulation of chemical reactions
- folding of proteins
- ...

This method is used a lot nowadays and even on high end computers computations can take up to months. But these computations are absolutely necessary in modern chemistry, pharmacy and also physics.

Classically atoms and molecules can be simulated rather easy with potentials, which can be derived from statistical physics.

Advantages

- low computational effort
- so it is possible to simulate a large amount of particles
- easy to implement

Disadvantages

- mostly pairwise potentials
- do not represent the true interaction of particles
- small scale effects (bonding etc.) cannot be simulated

So we need to take quantum mechanical behavior into account.

Classical Mechanics

- every system is determined by \vec{x} and \vec{p}
- every state can be measured and predicted exactly
- state and measurement of a system are the same

But some effects cannot be explained with the Classic Model

- Black Body Radiation
- Self Interaction of Electrons
- The Photoelectric Effect
- ...

And this effects can only be described by Quantum Physics!

- in Quantum Mechanics Newton's Laws do not apply in the same way

Heisenberg's Uncertainty Principle

$$\Delta x \Delta p \geq \frac{\hbar}{2} \quad (1)$$

where Δx is the uncertainty in position and Δp is the uncertainty in momentum

$\hbar = \frac{h}{2\pi}$ is the reduced Planck constant

- position and momentum can only be measured to a certain energy difference
- an nearly exact measurement for x results in a very fuzzy result for p and vice versa
- the measurement itself changes the state of the object

Quantum objects can only be described as *Wave Functions* ψ

Properties

$$\psi \in \mathbb{C} \quad (2)$$

$$\int \psi \psi^* d\vec{x} = 1 \quad (3)$$

Eq.(3) has to be fulfilled, because $\psi\psi^*$ represents a probability density.

ψ can be:

- a finite or infinite vector $\vec{\psi}$
- a function with a finite or infinite number of variables $\psi(x_1, \dots, x_n, \dots)$
- can be defined in spacial dimensions ($\psi(\vec{x})$) and momentum space ($\psi(\vec{p})$)

- basis formulation

general Schrödinger Equation

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{x}, t) = \mathbf{H} \psi(\vec{x}, t) \quad (4)$$

but we just need the

stationary solution

$$E_i \psi_i(\vec{x}) = \mathbf{H} \psi_i(\vec{x}) \quad (5)$$

- E_i are Eigenvalues with the eigenvectors ψ_i
- \mathbf{H} is an Operator acting on ψ
- all ψ_i are perpendicular to each other
- ψ_0 with the lowest energy E_0 represents the ground state

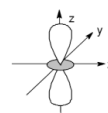
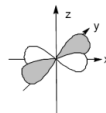
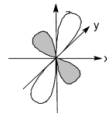
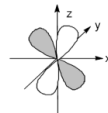
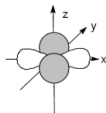
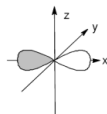
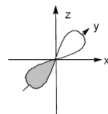
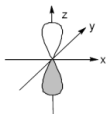
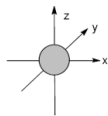
The Hamilton Operator returns the kinetic and potential energy of a system. Classically we would derive the Hamiltonian by the sum of kinetic and potential energy, but in quantum mechanics the kinetic energy is evaluated by the Laplacian (Differential Operator)

$$\mathbf{H} = -\frac{1}{2}\Delta + V(\vec{x}) \quad (6)$$

so that the Schrödinger equation looks like

$$\mathbf{H}\psi_i = -\frac{1}{2}\Delta\psi_i + V\psi_i \quad (7)$$

Solving the Schrödinger equation analytically is only possible for hydrogen like systems as H , He^+ , Li^{2+} ...



- In a molecule the wave function ψ depends on the position of the electrons (\vec{x}) and the atomic nuclei (\vec{R}) and the spin of the electrons ($\vec{\sigma}$)
- the problem has so $3N_e + 3N_n$ dimensions
- The nuclei are much heavier (at least ≈ 2000 times) than the electrons and so they are not as mobile as the electrons

Born-Oppenheimer-Approximation

The nuclei are treated as static in the molecule so that the electrons move in a system of of non-moving nuclei.

This step reduces the original dimensionality to $3N_e$

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Finding Electronic Structure

- energy states
- occupation numbers
- electron distribution

Geometry Optimization

- conformation changes
- oscillation spectra
- simulation of Van-der-Waals forces

Molecular Dynamics

- direct simulation of reactions
- fully dynamic observation of the molecule

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Hartree-Fock

- direct usage of ψ to calculate potentials and energies
- advantage: allows further refinement of done calculation (not possible in DFT)
- disadvantage: doesn't include the electron correlation and computational expensive

Configuration Interaction

- precise method
- but computational extremely intensive → just used for small systems

So DFT is our method of choice for larger molecular systems, because all necessary properties of the system are based on a single scalar function → computational advantage.

First theorem

All properties of a system with the Born-Oppenheimer approximation are determined by the electron density ρ

$$\rho(\vec{x}) = \sum_i \psi_i \psi_i^* \quad (8)$$

where ψ_i are the solutions of the Schrödinger equation

Second Theorem

$$E(\rho) \geq E(\rho_0) \quad (9)$$

The Energy functional E is for any valid state always larger than the one for the ground state

So the Kohn-Sham approach is just based on the 3 dimensional electron density $\rho(\vec{x})$ and we avoid to compute with high-dimensional wave functions.

They are derived from the Schrödinger equation:

$$\begin{aligned} \mathbf{H}_\sigma \psi_\sigma &= (\mathbf{H}_{kin} + \mathbf{V}_{ne} + \mathbf{V}_{coul} + \mathbf{V}_{xc}) \psi_\sigma \\ &= \left(-\frac{1}{2} \Delta + \sum_n \frac{Z_n}{|\vec{x} - \vec{R}_n|} + \int \frac{\rho(\vec{x}')}{|\vec{x} - \vec{x}'|} d\vec{x}' + \mathbf{V}_{xc}(\rho) \right) \psi_\sigma \\ &= \epsilon_\sigma \psi_\sigma \end{aligned}$$

- one equation for each spin component of σ
- ψ_σ are the Kohn-Sham orbital functions
- they are one electron wave functions
- \mathbf{V}_{xc} is the Exchange correlation potential
- all properties do just depend on the density ρ

The energy computation is necessary for the post processing and for the iteration of the exchange correlation potential.

Energy

$$E = E_{kin} + E_{nn} + E_{ne} + E_{coul} + E_{xc} \quad (10)$$

$$= H_{kin}\psi_{\sigma} + \sum_{i>j} \frac{Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \int \rho V_{ne} d\vec{x} \quad (11)$$

$$+ \frac{1}{2} \int \rho V_{coul} d\vec{x} + \int \rho \epsilon_{xc} d\vec{x}$$

Again we have an exchange correlation part ϵ_{xc} in there.

E_{xc}

- should catch the error we make by representing the system as a sum of one electron wave functions
- is the only not exactly known propertie of DFT

If we would know E_{xc} exactly we would be able to describe a microscopical system exactly as well!

Calculation of E_{xc}

- can be guessed
- can be approximated iteratively
- its calculation is one main part of DFT

Exchange correlation potential:

$$V_{xc} = \frac{\delta E_{xc}}{\delta \rho}$$

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Basis Functions

Exchange Correlation Energy
Eigenproblem

Numerical Effort

Post Processing

Right now we have the basic ingredients to calculate the energy and electron structure of a system. We will now discuss the numerical algorithm and the problems there.

Main problem:

$$V = V(\rho) = V(\rho(\psi)) \Leftrightarrow \psi = \psi(V)$$

Solution:

Iterative scheme which leads to self-consistency of ρ .

- 1 choose set of basis functions \mathbf{w}
- 2 set initial ρ
- 3 calculate $V_{class} = V_{coul} + V_{ne}$
- 4 determine V_{xc}
- 5 build Hamilton matrix \mathbf{H}
- 6 solve Kohn-Sham equation $\mathbf{H}\psi = (\mathbf{H}_{kin} + V_{class} + V_{xc})\psi$
- 7 determine occupation numbers n_i of the orbitals ψ_i
- 8 calculate $\rho = \sum n_i \psi_i^* \psi$
- 9 if the convergence criteria are not met: GOTO 3
else: calculate energy E and do postprocessing

Slater Functions

$$f(\vec{x} - \vec{x}')e^{-\alpha|\vec{x}-\vec{x}'|} \quad (12)$$

f can be any function like spherical harmonics or cartesian polynomials.

- commonly used and quite exact
- set of orthogonal functions
- they are LCAO (Linear Combination of Atomic Orbitals)
→ superposition of atomic orbitals represent the orbitals of the whole molecule (exponential part)
- asymptotic behavior is close to the exact orbital functions

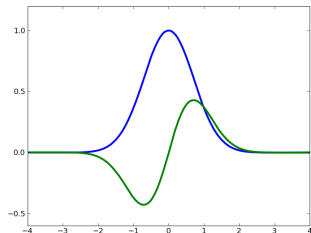
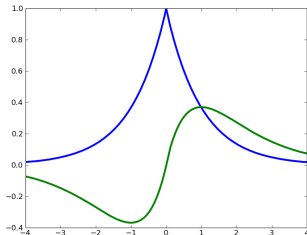
Disadvantages

They are numerically not easy to handle, because they require a numerical integration

Gaussian function

$$f(\vec{x} - \vec{x}')e^{-\alpha|\vec{x} - \vec{x}'|^2} \quad (13)$$

- easy to integrate analytically
- superposition of more than one Gauss function is necessary to represent one orbital
- their asymptotic behavior is not as good as that of the Slater functions



There is no strict way to determine them, but there are different approaches:

LDA (Local Density Approximation)

$$E_{xc} = \int \rho \epsilon_{xc}(\rho(\vec{x})) dV \quad (14)$$

- simple approximation
- its just using the density at a certain position \vec{r}
- still useful for determination of equilibrium structures, harmonic frequencies or charge moments

LSA (Local spin-density Approximation)

$$E_{xc} = \int \rho \epsilon_{xc}(\rho_{\uparrow}(\vec{x})\rho_{\downarrow}(\vec{x})) dV \quad (15)$$

- rather useful for molecules with odd number of electrons
- allow symmetry breaking of the spins

GGA (Generalized Gradient Approximation)

$$E_{xc} = \int \rho \epsilon_{xc}(\rho_{\uparrow}(\vec{x}), \rho_{\downarrow}(\vec{x}), \nabla \rho_{\uparrow}(\vec{x}), \nabla \rho_{\downarrow}(\vec{x})) dV \quad (16)$$

- are right now most commonly used
- but they are much harder to implement (ϵ_{xc} is a rather complicated function)
- more precise in general, especially for bonding energies

The choice of is differs with the system we like to simulate. There is a vast amount of functionals, each useful for another molecular system. With ϵ_{xc} we can compute V_{xc} and so H

Now we can calculate the Hamilton matrix \mathbf{H}

$$\mathbf{H}_{ij} = \int w_i \mathbf{H} w_j dV \quad (17)$$

and solve the Eigenproblem

$$\mathbf{H}\psi = \epsilon\psi \quad (18)$$

We get:

The Orbitals as linear combination of the basis functions and electron density

$$\psi_i = \sum_n w_n \psi_{in} \quad \rho = \sum_i \psi_i^* \psi_i \quad (19)$$

Diagonalisation

- $\mathcal{O}(N^3)$ operations necessary (N number of basis functions)
- one can use symmetries to reduce the problemsize

SCF

- numerically very intensive
- contains the diagonalisation in every iteration
- calculation of exchange correlation energies and potentials is also expensive

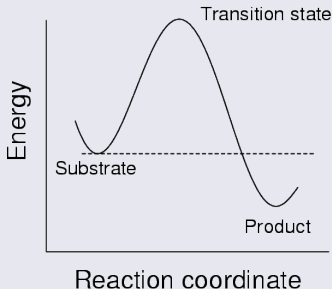
Post Processing

There also exist a number of post processing methods, which itself are already very computational intensive, even if classical models are used.

The parallelization and portation of this problems to super computers is absolutely necessary!

Chemical Reaction

In a chemical reaction, the system gets from the outside a activation energy. This energy pushes the system to a transition state, from which it goes to another state on the other side of the transition state.



These transition states are crucial for chemistry, because they mark exactly the activation energy needed for a molecule reaction.

One can approximate the energy landscape around a configuration \vec{R} quadratically.

With that we can:

- calculate the eigenmodes of a system
- determine oscillation spectra
- compare them to experiments
- good quality check

Thank You