

Density functional theory – An introduction

**Presentation for the Praktikum in
Theoretical Chemistry**

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1. Introduction

Theory:

In science, a theory is a proposed description, explanation, or model of the manner of interaction of a set of natural phenomena, capable of predicting future occurrences or observations of the same kind, and capable of being tested through experiment or otherwise falsified through empirical observation.

www.en.wikipedia.org

1. Introduction

Functional:

The initial meaning is a function that takes functions as its argument

Function: $f := x \rightarrow f(x)$

Functional: $F := f(x) \rightarrow F[f]$

examples: integral as functional $F[f] = \int_{-\infty}^{\infty} f(x) dx$

expectation value of an operator \hat{O}

$$\langle \hat{O} \rangle = \langle \Psi | \hat{O} | \Psi \rangle = \int \dots \int \Psi^* \hat{O} \Psi d\vec{x}_1 d\vec{x}_2 \dots d\vec{x}_N$$

1. Introduction

Density: $n(\mathbf{r})$, also written as $\rho(\mathbf{r})$

here electron density or exactly electron probability density

Defined as probability to find an electron with spin σ in volume element $d\mathbf{r}$ at \mathbf{r} :

$$n_{\sigma}(\mathbf{r}) = N \sum_{\sigma_2 \dots \sigma_N} \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N |\Psi(\mathbf{r}\sigma, \mathbf{r}_2\sigma_2, \dots, \mathbf{r}_N\sigma_N)|^2$$

$$n(\mathbf{r} \rightarrow \infty) = 0$$

$$\sum_{\sigma} \int n_{\sigma}(\mathbf{r}) d\mathbf{r} = N$$

$$\langle \hat{V}_{\text{ext}} \rangle = \langle \Psi | \sum_{i=1}^N v(\mathbf{r}_i) | \Psi \rangle = \int n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}$$

The electron density is an observable and thus can be measured experimentally

Additional properties: electron density has cusps at the positions of the nuclei, the charge of the nuclei can be determined by Kato's cusp condition

1. Introduction

Why using electron density?

„Conventional approach“: Construction Hamiltonian, solving Schrödinger's equation

=> wavefunction $\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \dots, \mathbf{r}_N\sigma_N)$

=> energy, molecular properties, frequencies, ...

Problems:

- in most cases, the solution must be approximated
- complicated, as there are $3N$ spatial + N spin variables
- even more complicated if ee-interaction is taken care of
- large computational demand, impossible for large systems

But: Hamiltonian acts only on one or two particles and thus its form is independent of the size of the system

=> electron density, depends only on 3 spatial variables

Needed: proof, that $n(\mathbf{r})$ determines the Hamiltonian and thus the entire system

plausible argument (not proof): $n(\mathbf{r})$ contains all information to construct the Hamiltonian (number of electrons, position (and so number) and charge of nuclei)₆

2. Basics of DFT

The Hohenberg-Kohn Theorems

Given an external potential $v_{\text{ext}}(\mathbf{r})$.

1) The external potential $v_{\text{ext}}(\mathbf{r})$ is (to within a constant) a unique functional of the ground-state density $n_0(\mathbf{r})$. Since $v_{\text{ext}}(\mathbf{r})$ determines the Hamiltonian, the ground-state wave function is also a unique functional of $n_0(\mathbf{r})$: $\Psi_0 = \Psi[n_0]$

Thus, the expectation value of any observable \hat{O} is also a functional of $n_0(\mathbf{r})$.

2) Especially, the ground-state energy is a functional of $n_0(\mathbf{r})$:

$$E_{v,0} = E_v[n_0] = \langle \Psi[n_0] | \hat{H} | \Psi[n_0] \rangle$$

3) For a given $v_{\text{ext}}(\mathbf{r})$, the correct density $n_0(\mathbf{r})$ minimizes the true ground-state energy E_0 (variational principle, proof also via wave-function variational principle):

$$E_v[n'] = T[n'] + V_{\text{ext}}[n'] + V_{\text{ee}}[n']$$

$$E_v[n_0] \leq E_v[n']$$

2. Basics of DFT

Proof:

Original proof via reductio ad absurdum

Alternate, more constructive proof: Constrained Search (Levy)

Recall: Hamiltonian for N-electron system in Born-Oppenheimer-Approximation:

$$\hat{H}_{\text{elec}} = \underbrace{-\frac{1}{2} \sum_{i=1}^N \nabla_i^2}_{\hat{T}_e} - \underbrace{\sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_i - R_A}}_{\hat{V}_{Ne}} + \underbrace{\sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}}_{\hat{V}_{ee}} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{ee}$$

Variational principle: $E_0 = \min_{\Psi \rightarrow N} \langle \Psi | \hat{H} | \Psi \rangle = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{ee} | \Psi \rangle$

Split into 2 steps: $E_0 = \min_{n \rightarrow N} \left(\min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{ee} | \Psi \rangle \right)$

$$\min_{\Psi \rightarrow n} \langle \Psi | \hat{H} | \Psi \rangle = \min_{\Psi \rightarrow n} \underbrace{\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle}_{F[n]} + \underbrace{\int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}}_{V_{\text{ext}}} = F[n] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \langle \Psi_n^{\text{min}} | \hat{T} + \hat{V}_{ee} | \Psi_n^{\text{min}} \rangle = T[n] + E_{ee}[n]$$

$$E_0 = \min_n E_v[n] = \min_n \left\{ F[n] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right\}$$

„universal functional“:
if known exactly, it
would solve SE

2. Basics of DFT

Prerequisites:

$$\text{Definition: } F[n] = \underbrace{T_S[n]}_{\text{non-interacting}} + \underbrace{E_H[n]}_{\text{Hartree/Coulomb energy}} + \underbrace{E_{xc}[n]}_{\text{Exchange-correlation functional}}$$

$E_{ee}[n]$

with Hartree-electrostatic self-repulsion $E_H[n] = \frac{1}{2} \int \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$

T_S can be treated exactly, but E_{xc} must be approximated

$$\text{So } E[n] = F[n] + \underbrace{\int v[\mathbf{r}]n[\mathbf{r}]d\mathbf{r}}_{V_{\text{ext}}} = T_S[n] + V_{\text{ext}} + E_H[n] + E_{xc}[n]$$

$$\text{and } E_{xc}[n] = \underbrace{E[n]}_{T[n] + V_{\text{ext}}[n] + E_{ee}[n]} - T_S[n] - V_{\text{ext}} - E_H[n] = \underbrace{(T[n] - T_S[n])}_{T_C} + \underbrace{(E_{ee}[n] - E_H[n])}_{E_{\text{ncl}}}$$

$$\text{Furthermore: } E_{xc} = E_x + E_c$$
$$T[n] = T_S[n] + T_C[n] \quad (T_C \text{ is part of } E_c)$$

2. Basics of DFT

Kohn-Sham (KS) non-interacting system:

N fermions which do not interact (no Coulomb repulsion) moving in a potential v_s and residing in single-particle-orbitals $\phi_i \Rightarrow V_{ee}=0$

For a non-interacting system, a Slater-determinant delivers the exact wave function (as in Hartree-Fock), so ϕ_i are constructed as Slater-determinants.

$$\text{Using } \phi_i: T_s[n] = -\frac{1}{2} \sum_i^N \int d\mathbf{r} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) = -\frac{1}{2} \langle \phi | \nabla^2 | \phi \rangle$$

$$E_x[\phi_i[n]] = -\frac{1}{2} \sum_{jk} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\phi_j^*(\mathbf{r}_1) \phi_k^*(\mathbf{r}_2) \phi_j(\mathbf{r}_1) \phi_k(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}'|}$$

$$\text{Now: } E[n] = T_s[\phi_i[n]] + V_{\text{ext}} + E_H[n] + E_{xc}[n]$$

$E[n]$ can no longer be minimized directly, as it's now a functional of ϕ_i

2. Basics of DFT

Indirect approach to solve $E[n]$:

$$0 = \frac{\delta E}{\delta n} = \frac{\delta T_S}{\delta n} + \frac{\delta V_{\text{ext}}}{\delta n} + \frac{\delta E_H}{\delta n} + \frac{\delta E_{\text{xc}}}{\delta n} = \frac{\delta T_S}{\delta n} + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$$

For KS-system in $v_S(\mathbf{r})$: $0 = \frac{\delta E}{\delta n_S} = \frac{\delta T_S}{\delta n_S} + v_S(\mathbf{r})$

$$n_S(\mathbf{r}) = n(\mathbf{r}) \quad \text{if} \quad v_S(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$$

Orbitals ϕ_i can be determined by self-consistent solution of Kohn-Sham-equation:

$$\left(-\frac{1}{2} \nabla^2 + v_S(\mathbf{r}) \right) \phi_j(\mathbf{r}) = \epsilon_j \phi_j(\mathbf{r}) \quad \text{„direct“ solution impossible as } v_S \text{ depends on } n$$

$$\text{and} \quad n(\mathbf{r}) \equiv n_S(\mathbf{r}) = \sum_{j=1}^N |\phi_j(\mathbf{r})|^2$$

For a converged solution n_0 :

$$E_0 = \sum_i^N \epsilon_i - \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{n_0(\mathbf{r}_1) n_0(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} - \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n_0(\mathbf{r}) + E_{\text{xc}}[n_0]$$

2. Basics of DFT

Results:

$$v_S(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$

$$\left(-\frac{1}{2} \nabla^2 + v_S(\mathbf{r}) \right) \phi_j(\mathbf{r}) = \epsilon_j \phi_j(\mathbf{r})$$

Iteration until self-consistency is reached
delivers ϕ_j , $n(\mathbf{r})$ and ϵ

$$n(\mathbf{r}) \equiv n_S(\mathbf{r}) = \sum_{j=1}^N |\phi_j(\mathbf{r})|^2$$

IF E_{xc} and v_{xc} were known, the Kohn-Sham system would deliver the exact ground state energy, so the correct eigenvalue of the Hamiltonian and thus, it would exactly solve Schrödinger's equation!

Unfortunately, v_{xc} is unknown, and so is E_{xc} , as $v_{xc} = \frac{\delta E_{xc}}{\delta n}$

Finding good and always better approximations
for E_{xc} and v_{xc} is the goal of modern DFT.

3. Practical approaches

Practical approaches: LDA

Assumption: uniform or slowly varying electron gas

$$E_{xc}^{\text{LDA}}[n] = \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) d\mathbf{r}$$

$$\epsilon_{xc}(n(\mathbf{r})) = \epsilon_x(n(\mathbf{r})) + \epsilon_c(n(\mathbf{r}))$$

ϵ_{xc} : exchange – correlation energy per particle in a uniform electron gas

exchange part:

$$\epsilon_x^{\text{LDA}}[n] = -C_x n^{1/3} \quad \text{with} \quad C_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3}$$

$$E_x^{\text{LDA}}[n] = -C_x \int n^{4/3}(\mathbf{r}) d\mathbf{r}$$

often called
Slater exchange functional S

correlation part fitted to QMC calculation of Ceperley&Alder, quite complex
e.g. Vosko-Wilk-Nusair with 12 fitting constants

3. Practical approaches

Practical approaches: “Jacob's Ladder”

Heaven (chemical accuracy)



Earth („Hartree world“)

- | | | |
|-----|-----------|---|
| (5) | | + explicit dependence on unoccupied orbitals (exact partial correlation) |
| (4) | hyper-GGA | + explicit dependence on occupied orbitals (exact exchange energy density)
example: hybrid functionals |
| (3) | meta-GGA | + explicit dependence on kinetic energy density |
| (2) | GGA | + explicit dependence on gradients of the density |
| (1) | LDA | local density only |

b) Jacob's ladder

3. Practical approaches

Practical approaches: GGA

Ansatz: adding gradient expansion

$$E_{XC}^{GGA}[n] = \int f^{GGA}(n(\mathbf{r}), \nabla n(\mathbf{r})) d\mathbf{r}$$

Depending on the method of construction of f , very different GGAs are obtained.

Two main classes of realisation of f :

Always: Find a suitable functional form

Either: Parameters are then fitted to sets of experimental data (e.g. G2) [Chemistry]

Or: Exact physical constraints are taken into account, no fitting [Physics]

$$E_{XC}^{GGA}[n] = E_X^{GGA} + E_C^{GGA}$$

$$E_X^{GGA}[n] = E_X^{LDA} - \sum_{\sigma} \int F(s_{\sigma}) n_{\sigma}^{4/3}(\mathbf{r}) d\mathbf{r}$$

with reduced density gradient $s_{\sigma}(\mathbf{r}) = \frac{|\nabla n_{\sigma}(\mathbf{r})|}{n_{\sigma}^{4/3}(\mathbf{r})}$

(local inhomogeneity parameter)

c) GGA

3. Practical approaches

GGA – example: Constraints for the construction of the PBE-functional
(see „GGA made simple“, Perdew, 1996)

Correlation term: $E_C^{GGA}[n\uparrow, n\downarrow] = \int n[\epsilon_C^{LDA}(r_s, \zeta) + H(r_s, \zeta, t)]$

With: local Seitz radius r_s ($n = \frac{3}{4\pi r_s^3} = \frac{k_F^3}{3\pi^2}$), relative spin polarisation $\zeta = \frac{n\uparrow - n\downarrow}{n\uparrow + n\downarrow}$

Dimensionless density gradient $t = \frac{|\nabla n|}{22\phi k_s n}$ with $k_s = \sqrt{\left(\frac{4k_F}{\pi}\right)}$

and $\phi(\zeta) = \frac{1}{2}[(1+\zeta)^{2/3} + (1-\zeta)^{2/3}]$

- Slowly varying limit ($t \rightarrow 0$): $H \rightarrow \beta_{MB} \phi^3 t^2$ with $\beta_{MB} = 0.066725$
- Rapidly varying limit ($t \rightarrow \infty$, no correlation): $H \rightarrow -\epsilon_C^{LDA}(r_s, \zeta)$
- Uniform scaling to the high-density limit [$n(\mathbf{r}) \rightarrow \lambda^3 n(\lambda \mathbf{r})$ and $\lambda \rightarrow \infty$]:

E_C must scale to a constant

„Simple Ansatz“: $H = c_0 \phi^3 \ln \left[1 + \frac{\beta_{MB}}{c_0} t^2 \left[\frac{1 + At^2}{1 + At^2 + A^2 t^4} \right] \right]$ $A = \frac{\beta_{MB}}{c_0 \exp(-\epsilon_C^{LDA}(r_s, \zeta) / c_0 \phi^3) - 1}$ 16

3. Practical approaches

GGA – example: Constraints for the construction of the PBE-functional
(see „GGA made simple“, Perdew, 1996)

Exchange term:
$$E_X^{\text{GGA}}[n] = \int n \epsilon_X^{\text{LDA}} F_X(s) \, d\mathbf{r}$$

$$\epsilon_X^{\text{LDA}} = -\frac{3}{4} \sqrt{\frac{3n}{\pi}}$$

- Exact energy obeys spin scaling relationship:

$$E_X[n\uparrow, n\downarrow] = \frac{1}{2} (E_X[2n\uparrow] + E_X[2n\downarrow])$$

- Linear response (small density variations around uniform density):

LSD is a good approximation => try to keep the LSD linear response

$$s \rightarrow 0: F_X(s) = 1 + \mu s^2 \quad \text{where} \quad \mu = \beta \frac{\pi^2}{3} \simeq 0.21951$$

- Lieb-Oxford bound:

$$E_X[n\uparrow, n\downarrow] \geq E_{\text{xc}}[n\uparrow, n\downarrow] \geq -1.679 \int n^{4/3} \, d\mathbf{r}$$

Choice of F to satisfy these constraints:
$$F_X(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2 / \kappa}$$

3. Practical approaches

Practical approaches: meta-GGA

$$E_{XC}^{MGGA} = \int n e_{XC}^{MGGA}(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r})) d\mathbf{r}$$

With Kohn-Sham orbital kinetic energy density

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla \phi_i(\mathbf{r})|^2$$

Exchange-correlation potential becomes orbital dependent
Hybrid functionals are meta-GGAs

Also for mGGAs: either fitting to experimental data
or derivating by physical constraints

3. Practical approaches

Practical approaches: Hybrid functionals

$$E_{xc}[n] = \frac{1}{2} \int \int \frac{n(\mathbf{r}) \bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' = \int_0^1 E_{ncl}^\lambda d\lambda$$

with coupling-constant average hole density

$$\bar{n}_{xc}(\mathbf{r}, \mathbf{r}') = \int_0^1 n_{xc}^\lambda(\mathbf{r}, \mathbf{r}') d\lambda \quad \text{where } \lambda \text{ is the coupling parameter}$$

At $\lambda=0$: No interaction (pure Kohn-Sham system)

at $\lambda=1$: full interaction („real“ system)

Any non-interacting system can be described exactly using Hartree-Fock

$$\text{If } E_{ncl}^\lambda \text{ is linear in } \lambda \text{ and HH: } E_{xc}^{HH} = \underbrace{\frac{1}{2} E_{xc}^{\lambda=0}}_{E_{xc}^{exact}} + \frac{1}{2} E_{xc}^{\lambda=1}$$

$$\text{If not: } E_{xc}^{hyb} = a E_x^{exact} + (1-a) E_x^{GGA} + E_c^{GGA}$$

with (here) 1 or more parameters to be determined (experimentally or theoretically)

3. Practical approaches

Performance of DFT

Comparison of different DFT methods by mean absolute deviations (kcal/mol)

Method	G2	LSDA	GGA	BPW91	B3PW91
Type				GGA	Hybrid
Atomization energies	1,2	35,7	3,9	5,7	2,4
Ionization energies	1,4	6,3	11,2	4,1	3,8
Proton Affinities	1,0	5,6	2,4	1,5	1,2

Different DFT methods (kcal/mol)

Method	Type	Mean abs. dev.	Maximum abs. dev.
G2		1,6	8,2
G2(MP2)		2	10,1
G2(MP2, SVP)		1,9	12,5
SVWN	LDA	90	228,7
BLYP	GGA	7,1	28,4
BPW91	GGA	7,9	32,2
B3LYP	Hybrid	3,1	20,1
B3PW91	Hybrid	3,5	21,8

Atomization energies (kcal/mol)

Molecule	LDA	GGA (PBE)	Exact
H ₂	113	106,08	108,38
CH ₄	461,21	419,7	419,7
NH ₃	336,68	302,09	297,48
H ₂ O	267,5	232,91	232,91
CO	299,78	269,81	258,28
O ₂	175,26	142,97	119,91

4. Outlook

What is possible to use DFT?

- Find better functionals, improve the existing ones
- Taking next step(s) on Jacob's ladder: find new functionals
- apply time-dependent DFT (TDDFT)
- apply relativistic DFT
- combine DFT with wave-function based methods (e.g. MP2, CI or CC)