

Density functional theory

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Foundations of density functional theory

No proofs ...

... although simple and enlightening.

Definitions and notations

Operators

- $H = T + V_{ne} + V_{ee}$: Hamiltonian
- $T = -(1/2) \sum_{i=1}^N \nabla_i^2$: Kinetic energy
- $V_{ne} = \sum_{i=1}^N v_{ne}(r_i)$: Interaction between electrons and nuclei
- $V_{ee} = \sum_{i<j}^N 1/|r_i - r_j|$: Interaction between electrons

Wave function and density

- Ψ : general wave function
- ϕ_i : orbitals
- Φ : Slater determinant
- $\rho_{\Psi}(r_1) = N \int \cancel{d^3 r_1} d^3 r_2 \dots |\Psi|^2$: density

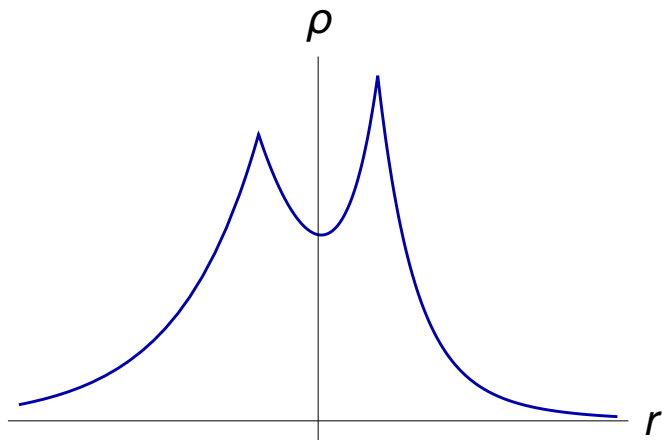
$$\rho_{\Phi} = \sum_{i=1}^N |\phi_i|^2$$

Remark

$$\int \rho(r) d^3 r = N$$

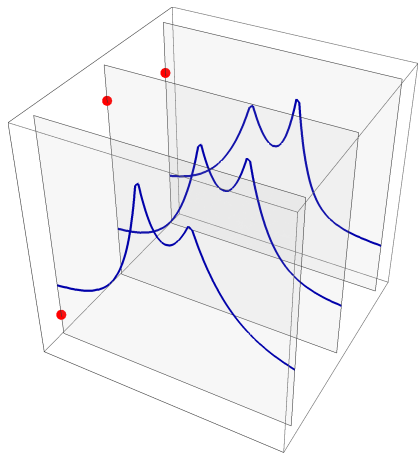
Particle Density, $\rho(r)$

average number of particles in the volume element around r
volume of that element



Density Functional

$$\rho(r) \mapsto F$$



Theory

Hohenberg-Kohn theorem: obtaining the ground state energy and density by a variation principle.

$$E_0 = \min_{\Psi} \langle \Psi | T + V_{ne} + V_{ee} | \Psi \rangle = \min_{\rho} \left(F[\rho(r)] + \int \rho(r) v_{ne}(r) d^3r \right)$$

Usually, E_0 from N and v_{ne} that give H

HK: E_0 from ρ and v_{ne} .

Trivial, as $\rho \rightarrow N$? No.

- Simple form of the only term where v_{ne} enters: all effort has to be put into F , independent of v_{ne} .
- Extra effort for obtaining F is considerable. Guideline for cheap approximations?

Accurate functionals

$$F[\rho] = \min_{\Psi \rightarrow \rho(r)} \langle \Psi | T + V_{ee} | \Psi \rangle$$

Examples

N	V_{ee}	F	$\int \rho v$	E	comment
1	0	0.5	-1	-0.5	H atom, $\rho = \frac{N}{\pi} e^{-2r}$
2	0	1	-2	-1	Non-interacting H^- , $\rho = \frac{N}{\pi} e^{-2r}$
2	$1/r_{12}$	0.84	-1.37	-0.53	Interacting H^- , v known, ρ calc. ^a
2	$1/r_{12}$	1.59	-3.26	-1.67	$\rho = \frac{N}{\pi} e^{-2r}$, ρ known, v calc. ^b

^aFreund+Huxtable+Morgan,1984; Umrigar+Gonze, 1994

^bColonna+AS, 1999

Response functions, χ

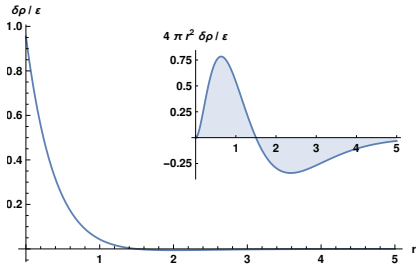
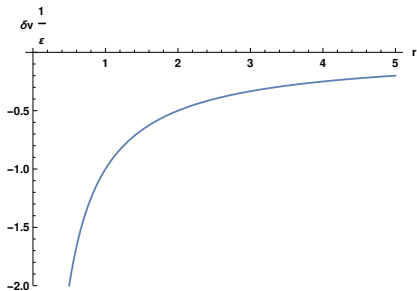
Relationship between small changes in the potential and in the density:

$$\delta\rho(r) = \int \chi(r, r') \delta v(r') d^3 r'$$

Result of first-order perturbation theory

Density in r is affected by a change of potential in r'

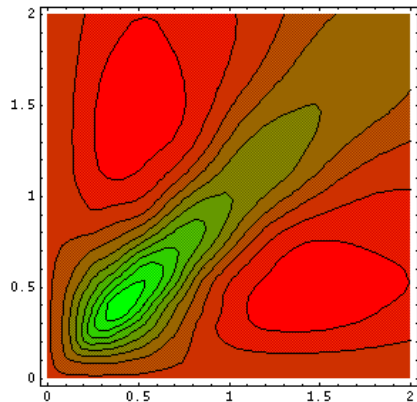
Hydrogen atom $Z = 1 \rightarrow Z = 1 + \epsilon$



Understanding the response functions, χ

Even $\delta v(r) = \delta(r - r_0)$ produces changes in $r \neq r_0$: $\delta\rho(r) = \chi(r, r_0)$

$\chi(r, r_0)r^2r_0^2$ for He



Colonna+Allavena+AS, 2001

Methods used in the framework of density functional theory

The Kohn-Sham method

$$E_0 = \min_{\Psi} \langle \Psi | T + V_{ne} | \Psi \rangle + E_{hxc}[\rho_{\Psi}(r)]$$

E_{hxc} corrects for the part missing in $\langle \Psi | T + V_{ne} | \Psi \rangle$

Features

- A choice
- Still exact, in principle
- Variation of Ψ gives a Schrödinger equation for non-interacting particles:

$$(T + V_{KS})\Psi_{KS} = E_{KS}\Psi_{KS}$$

Functionals for the kinetic, exchange, correlation energies

$$E_h[\rho] = \frac{1}{2} \int \int d^3 r_1 d^3 r_2 \rho(r_1)\rho(r_2)/r_{12}$$

$$E_{xc}[\rho] = E_{hxc}[\rho] - E_h[\rho]$$

$$E_x[\rho] = \langle \Psi_{KS} | V_{ee} | \Psi_{KS} \rangle - E_h[\rho]$$

$$E_c[\rho] = E_{xc}[\rho] - E_x[\rho]$$

... and hybrids

Motivations

- E_h : electrostatics ($\langle V_{ne} \rangle, \langle V_{nn} \rangle$ always treated exactly)
- E_{xc} : treating on same footing exchange and correlation; exchange is statistically "correlation");
also compensation in approximations
- E_c : smaller contribution to approximate
- hybrids (some E_x): partitioning is arbitrary, anyhow.

Exact properties of functionals

Useful when constructing approximations (M. Levy, et al.) Scaling

$$\Psi_\lambda(r_1, r_2, \dots) = \lambda^{3N/2} \Psi(\lambda r_1, \lambda r_2, \dots)$$

Ψ_λ is normalized to 1

Basic idea: \min_Ψ contains $\min_\lambda \Psi_\lambda(r)$

Examples

- $\rho_\lambda(r) = \rho(r, \Psi_\lambda) = \lambda^3 \rho(\lambda r)$
- $E_h[\rho_\lambda] = \lambda E_h[\rho]$
- $E_x[\rho_\lambda] = \lambda E_x[\rho]$

Tools for constructing approximations, and extending DFT

Adiabatic connection

With $H(\mu) = T + V(\mu) + W(\mu)$ there is a Hohenberg-Kohn theorem, and functional $F_\mu[\rho]$.

Choose $\mu = 0$ for the Kohn-Sham system, $\mu = \infty$ for the physical system.

$$E_{hxc} = \int_0^\infty d\mu \langle \Psi(\mu) | W'(\mu) | \Psi(\mu) \rangle$$

$\Psi(\mu)$ is the eigenfunction of $H(\mu)$

Langreth+Perdew 1975, Yang 1998, ...

Hybrids

- Reason to start the adiabatic connection with the Kohn-Sham system: non-interacting system is computationally efficient
- Reason to start the adiabatic connection somewhere else: getting closer to the physical system

$$E_{hxc}(\mu_0) = \int_{\mu_0 > 0}^{\infty} d\mu \langle \Psi(\mu) | W'(\mu) | \Psi(\mu) \rangle$$

Approximations for density functionals

Local Density Approximation

Assumption of universality for the ansatz

$$E_{\dots} \approx \int d^3r e_{\dots}(\rho(r)) = \int d^3r \rho \varepsilon_{\dots}(\rho(r))$$

Change of notation: $e_{\dots}(\rho) = \rho \varepsilon_{\dots}(\rho)$

Uniform electron gas: a reasonable choice for finding ε

$\rho(r)$ independent of r

$$E_{\dots} \approx \int d^3r \rho \varepsilon_{\dots}(\rho) = \varepsilon_{\dots}(\rho) \int d^3r \rho = N \varepsilon_{\dots}(\rho)$$

$$\varepsilon_{\dots}(\rho(r)) = (E_{\dots}(\rho(r))/N)_{UEG}$$

Semi-local approximations

Some ansatz of the form:

$$E_{\dots} \approx \int d^3r e_{\dots}(\rho(r), |\nabla\rho|, \dots)$$

i.e., including derivatives, too.

Hybrids

Correct the energy of the model

$$H(\mu_0) = T + V(\mu_0) + W(\mu_0), \quad \mu_0 > 0$$

with some approximations both for

- the correction $E_{hxc}(\mu_0)$, and
- for the solution of $H(\mu_0)\Psi(\mu_0) = E(\mu_0)\Psi(\mu_0)$
 - Combination with Hartree-Fock:
 $\Psi(\mu_0)$ restricted to a single Slater determinant
 - Combination with multi-reference methods (CI, CC, PT, ...):
 $\Psi(\mu_0)$ as a linear combination of Slater determinants

Spin densities

Most functional approximations depend on ρ_{\uparrow} and ρ_{\downarrow} (spin-up and spin-down densities).

For a single Slater determinant

$$\rho_{\uparrow}(r) = \sum_{i, \text{spin up}} |\phi_i(r)|^2$$

$$\rho_{\downarrow}(r) = \sum_{i, \text{spin down}} |\phi_i(r)|^2$$

$$\rho_{\uparrow} + \rho_{\downarrow} = \rho$$

$$\rho_{\uparrow} - \rho_{\downarrow} = \sigma$$

σ : spin density

Methods for excited states

- Time-dependent DFT
- Δ SCF
- Orbital energy differences
- ...

Main limitations of approximations

Systematic improvement

What is systematic improvement?

- Next level result better?
Not for most computed quantities in quantum chemistry.
- Defining a path toward the exact result?
In wave function methods, not in DFAs.
- Smaller rigorous error bars at the higher level?
No useful rigorous error bars in quantum chemistry.
- Smaller experience defined error bars at higher level?
In DFAs.

Treatment of degeneracy and size-consistency

Unsolved problem in DFAs. Also problem with spin-densities.

Methods related to DFT

Local potentials

Kohn-Sham produces local potentials that decay $\propto 1/r$: better than Hartree-Fock, e.g., for excited states.

Using Kohn-Sham like potentials

- optimized effective potentials
- “exact exchange”
- ...

Active field.

Random phase approximation

RPA much used in nuclear physics.

Proposes approximation for pair density.

As related to change of density with change in external potential (χ), considered connected to DFT.

Judging approximations

Concepts from statistics

Large data sets used for judging if a given approximation is better than another.

Caution !

Benchmarks and their limits

Two properties, A and B , and two questions

- 1 Is property B (e.g., bulk modulus) well reproduced, and is property A (e.g., lattice constant well) reproduced?
- 2 Is the bulk modulus good, when the lattice constant is good? (e.g., lattice constant can be checked, and trusted, but no information about the bulk modulus)

Check benchmark paper

In the table for A method X works best.

In the table for B , method X is also the best.

Should one use method X for the questions above?

Most benchmark papers do not allow us to answer such questions

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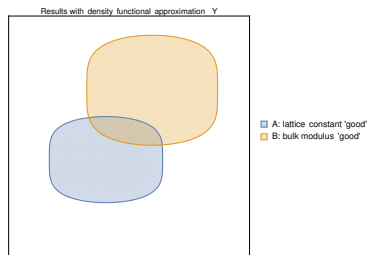
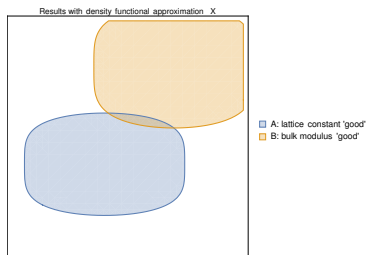
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- 1 $P(A \cap B)$
- 2 $P(B|A)$

while benchmark about $P(A)$ and $P(B)$.

Two properties: Maths



- $P(A) = n(A)/n(\text{total})$: probability to obtain a good lattice constant
- $P(A \cap B) = n(A \cap B)/n(\text{total})$: probability to obtain a good lattice constant and a good bulk modulus
- $P(A|B) = n(A \cap B)/n(A) = P(A \cap B)/P(A)$: probability to obtain a good bulk modulus if the lattice constant was good

$P(A \cap B)$ and $P(A|B)$ both refer to $n(A \cap B)$, but have different "normalization"

Two properties: DF example

Errors: Lattice constant $< 1\text{pm}$, bulk modulus $< 4\text{GPa}$

DF	$P(A)$	$P(B)$	$P(A \cap B)$	$P(B A)$
LDA	0.11	0.43	0.07	0.64
PBEsol	0.25	0.50	0.07	0.28

Errors: Lattice constant $< 2\text{pm}$, bulk modulus $< 4\text{GPa}$

DF	$P(A)$	$P(B)$	$P(A \cap B)$	$P(B A)$
LDA	0.39	0.43	0.29	0.74
PBEsol	0.39	0.50	0.14	0.36

Errors: Lattice constant $< 3\text{pm}$, bulk modulus $< 4\text{GPa}$

DF	$P(A)$	$P(B)$	$P(A \cap B)$	$P(B A)$
LDA	0.54	0.43	0.29	0.54
PBEsol	0.61	0.50	0.32	0.52

Remark: Sample size (28) is too small to draw conclusions about functionals

Conclusion

Speaker: I use DFT, because it is an easy to use black box, and does not require much thinking.

K. Ruedenberg: Why is it a bad thing to think?

35th Midwest Theoretical Chemistry Conference, Ames (2003)