

FOUNDATIONS OF DENSITY-FUNCTIONAL THEORY

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Overview I

- **Hohenberg-Kohn theorem**
- **Hellmann-Feynman theorem**
 - Forces on atoms
 - Stresses on unit cell
- **Local-density approximation: density only**
 - Thomas-Fermi theory and beyond
- **Local-density approximation: Kohn-Sham theory**
 - Kohn-Sham equations
 - Variational conditions
 - Kohn-Sham eigenvalues

Overview II

- Exchange-correlation functionals
 - Local-density approximation (LDA)
 - Generalized gradient approximation (GGA), meta-GGA
 - Hybrid-functionals
- Limitations of DFT
 - Band-gap problem
 - Overbinding
 - Neglect of strong correlations
 - Neglect of van-der-Waals interactions
- Beyond LDA
 - LDA+U
 - GW, SIC, ...

Density-functional theory - HKS theorem

Hohenberg-Kohn-Sham theorem:

(1) The ground-state energy of a many-body system is a unique functional of the particle density, $E_0 = E[\vec{n}]$.

(2) The functional $E[\vec{n}]$ has its minimum relative to variations $\delta n(\vec{r})$ of the particle density at the equilibrium density $n_0(\vec{r})$,

$$E = E[n_0(\vec{r})] = \min \{E[\vec{n}]\} \tag{1}$$
$$\frac{\delta E[n(\vec{r})]}{\delta n(\vec{r})} \Big|_{n(\vec{r})=n_0(\vec{r})} = 0$$

Proof - HKS theorem

Reductio ad absurdum:

$$H = T + V_{ee} + V \quad (2)$$

is the Hamiltonian of a many-electron system in an external potential $V(\vec{r})$ and with an electron-electron interaction V_{ee} . In the ground-state this system has the energy E_0 , with $E_0 = \langle \psi_0 | H | \psi_0 \rangle$ and the particle density $n_0(\vec{r}) = |\langle \psi_0 | \vec{r} \rangle|^2$. Let us assume that a different external potential V' leads to a different ground-state ψ'_0 , but to the same particle density: $n'_0(\vec{r}) = |\langle \psi'_0 | \vec{r} \rangle|^2 = n_0(\vec{r})$. According to the variational principle it follows that

$$\begin{aligned} E'_0 < \langle \psi_0 | H' | \psi_0 \rangle &= \langle \psi_0 | (H + V' - V) | \psi_0 \rangle \\ &= E_0 + \langle \psi_0 | (V' - V) | \psi_0 \rangle \end{aligned} \quad (3)$$

Proof - HKS theorem

$$E'_0 < E_0 + \int n_0(\vec{r})[V'(\vec{r}) - V(\vec{r})]d^3r \quad (4)$$

Starting from

$$E_0 < \langle \psi'_0 | H | \psi'_0 \rangle \quad (5)$$

and using $n'_0(\vec{r}) = n_0(\vec{r})$ it follows

$$\begin{aligned} E_0 &< E'_0 + \int n'_0(\vec{r})[V(\vec{r}) - V'(\vec{r})]d^3r \\ &= E'_0 + \int n_0(\vec{r})[V(\vec{r}) - V'(\vec{r})]d^3r \end{aligned} \quad (6)$$

in direct contradiction to the results obtained above. Hence $n'_0(\vec{r})$ and $n_0(\vec{r})$ must be different and $V(\vec{r})$ is a unique functional of $n(\vec{r})$.

The variational property of the Hohenberg-Kohn-Sham functional is a direct consequence of the general variational principle of quantum mechanics.

HKS theorem - Variational principle

With

$$\begin{aligned} F[n(\vec{r})] &= \langle \Psi | T + V_{ee} | \Psi \rangle \\ E[n(\vec{r})] &= F[n(\vec{r})] + \int n(\vec{r})V(\vec{r})d^3r \end{aligned} \quad (7)$$

it follows

$$\begin{aligned} E[(n'(\vec{r}))] &= \langle \Psi' | T + V_{ee} | \Psi' \rangle + \langle \Psi' | V | \Psi' \rangle \\ &= F[n'(\vec{r})] + \int n'(\vec{r})V(\vec{r})d^3r \\ &> \langle \Psi_0 | T + V_{ee} | \Psi_0 \rangle + \langle \Psi_0 | V | \Psi_0 \rangle = E[n_0(\vec{r})] \\ &= F[n_0(\vec{r})] + \int n_0(\vec{r})V(\vec{r})d^3r \end{aligned} \quad (8)$$

and hence

$$\begin{aligned} E_0 = E[n_0(\vec{r})] &= \min \{E[n(\vec{r})]\} \\ \frac{\delta E[n(\vec{r})]}{\delta n(\vec{r})} \Big|_{n(\vec{r})=n_0(\vec{r})} &= 0 \end{aligned} \quad (9)$$

Hellmann-Feynman theorem: Forces and stresses

The external potential V is created by the ions located at the positions \vec{R}_I , $V(\vec{r}) = \sum_I v(\vec{r} - \vec{R}_I)$. The ground-state energy and wavefunction depend on the ionic coordinates, $\vec{R} = \{\vec{R}_I\}$ as parameters. The force \vec{F}_I acting on an atom located at \vec{R}_I is given by

$$\begin{aligned} -\vec{F}_I &= \nabla_I E_0(\vec{R}) = \frac{\partial}{\partial \vec{R}_I} \langle \Psi_0(\vec{R}) | H(\vec{R}) | \Psi_0(\vec{R}) \rangle \\ &= \langle \nabla_I \Psi_0 | H | \Psi_0 \rangle + \langle \Psi_0 | \nabla_I H | \Psi_0 \rangle + \langle \Psi_0 | H | \nabla_I \Psi_0 \rangle \quad (10) \\ &= \langle \Psi_0(\vec{R}) | \nabla_I H(\vec{R}) | \Psi_0(\vec{R}) \rangle \end{aligned}$$

First and third terms in the derivative vanish due to variational property of the ground-state \rightarrow **Forces acting on the ions are given by the expectation value of the gradient of the electronic Hamiltonian in the ground-state.** The ground-state must be determined very accurately: errors in the total energy are 2nd order, errors in the forces are 1st order !

Hellmann-Feynman theorem: Forces and stresses

The **stress tensor** σ_{ij} describes the variation of the total energy under an infinitesimal distortion of the basis vectors $\vec{a}_{(k)}$ under a strain t_{ij} :

$$\begin{aligned}\sigma_{ij} &= -\frac{\partial E(\vec{a}'_{(k)})}{\partial t_{ij}} \\ a'_{(k),i} &= \sum_j (\delta_{ij} + t_{ij}) a_{(k),j} \\ \sigma_{ij} &= -\langle \Psi_0 | \frac{\partial}{\partial t_{ij}} H(\vec{a}'_{(k)}) | \Psi_0 \rangle\end{aligned}\tag{11}$$

DFT functional

Total-energy functional

$$E[n] = T[n] + E^H[n] + E^{xc}[n] + \int V(\vec{r})n(\vec{r})d^3r \quad (12)$$

$T[n]$... kinetic energy,

$E^H[n]$... Hartree energy (electron-electron repulsion),

$E^{xc}[n]$... exchange and correlation energies,

$V(\vec{r})$... external potential

- the exact form of $T[n]$ and E_{xc} is unknown !

Local density approximation - "density only":

- Approximate the functionals $T[n]$ and $E_{xc}[n]$ by the corresponding energies of a homogeneous electron gas of the same local density

→ Thomas-Fermi theory

Thomas-Fermi theory

Kinetic energy:

$$\begin{aligned} T[n] &= \int t[n(\vec{r})] d^3 r \\ t[n] &= \frac{3\hbar^2}{10m} (3\pi^2)^{2/3} [n(\vec{r})]^{5/3} \end{aligned} \quad (13)$$

where $t[n]$ is the kinetic energy of a noninteracting homogeneous electron gas with the density n .

Electron-electron interaction: Coulomb repulsion only

$$E^H[n] = \frac{e^2}{2} \int \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r d^3 r' \quad (14)$$

Add exchange-correlation term in modern versions. Variation of $E[n]$ with leads to the Thomas-Fermi equation

$$\frac{5}{3} C [n(\vec{r})]^{2/3} + e^2 \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' + V(\vec{r}) = 0 \quad (15)$$

Kohn-Sham theory

$$E[n(\vec{r})] = \int n(\vec{r})V(\vec{r})d^3r + \frac{e^2}{2} \int \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3rd^3r' + T[n(\vec{r})] + E^{xc}[n(\vec{r})] \quad (16)$$

(1) Parametrize the particle density in terms of a set of **one-electron orbitals representing a non-interacting reference system**

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2 \quad (17)$$

(2) Calculate **non-interacting kinetic energy** in terms of the $\phi_i(\vec{r})$'s, i.e.

$$T[n] \sim T_0[n],$$

$$T_0[n] = \sum_i \int \phi_i^*(\vec{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \phi_i(\vec{r}) d^3r \quad (18)$$

Kohn-Sham theory II

(3) Local-density approximation for **exchange-correlation energy**

$$E^{xc}[n(\vec{r})] = \int n(\vec{r}) \epsilon_{xc}[n(\vec{r})] d^3 r, \quad (19)$$

where $\epsilon_{xc}[n(\vec{r})]$ is the exchange-correlation energy of a homogeneous electron gas with the local density $n(\vec{r})$. For the exchange-part, a Hartree-Fock calculation for a homogeneous electron gas with the density n leads to

$$\epsilon_x[n(\vec{r})] = -\frac{3e^2}{4\pi} (3\pi^2 n(\vec{r}))^{1/3} \quad (20)$$

(4) Determine the **optimal one-electron orbitals using the variational condition under the orthonormality constraint** $\langle \phi_i | \phi_j \rangle = \delta_{ij}$

$$\delta \left\{ E[n(\vec{r})] - \sum_{i,j} \epsilon_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}) \right\} = 0 \quad (21)$$

Kohn-Sham theory III

→ Kohn-Sham equations (after diagonalizing ϵ_{ij}):

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) + e^2 \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' + \mu_{xc}[n(\vec{r})] \right\} \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \quad (22)$$

with the **exchange-correlation potential** $\mu_{xc}[n(\vec{r})] = \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})}$

Total energy:

$$E = \underbrace{\sum_i \epsilon_i}_{(1)} - \underbrace{\frac{1}{2} \int \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r d^3 r' + \int n(\vec{r}) \{ \epsilon_{xc}[n(\vec{r})] - \mu_{xc}[n(\vec{r})] \} d^3 r}_{(2)} \quad (23)$$

(1)... sum of "one-electron energies"

(2)... "double-counting corrections"

Kohn-Sham theory IV

Variational conditions

- Total energy $E[n]$

$$\frac{\delta E[n(\vec{r})]}{\delta n(\vec{r})} \Big|_{n(\vec{r})=n_0(\vec{r})} = 0 \quad (24)$$

- Kohn-Sham eigenvalues ϵ_i

$$\delta\{\langle \phi_i | H^{KS} | \phi_i \rangle\} = 0 \quad \text{with} \quad \langle \phi_i | \phi_j \rangle = 0 \quad \forall \epsilon_i < \epsilon_j \quad (25)$$

- Norm of residual vector $|R_i\rangle$

$$|R(\phi_i)\rangle = (H^{KS} - \epsilon_i^{app}) | \phi_i \rangle, \quad \epsilon_i^{app} = \langle \phi_i | H^{KS} | \phi_i \rangle \quad (26)$$
$$\delta\{\langle R(\phi_i) | R(\phi_i) \rangle\} = 0$$

No orthogonality constraint !

Kohn-Sham theory V

Interpretation of the "one-electron energies" ϵ_i

- Hartree-Fock theory - Koopman's theorem

$$\epsilon_i^{HF} = E^{HF}(n_i = 1) - E^{HF}(n_i = 0) \quad (27)$$

ϵ_i^{HF} = Ionisation energy if relaxation of the one-electron orbitals is neglected.

- Kohn-Sham theory:

Total energy is a nonlinear functional of the density \longrightarrow Koopmans theorem not valid.

$$\frac{\delta E[n(\vec{r})]}{\delta n_i(\vec{r})} = \epsilon_i, \quad n_i(\vec{r}) = \phi_i^*(\vec{r})\phi(\vec{r}) \quad (28)$$

Exchange-correlation functionals I

Definition of the exchange-correlation functional:

$E^{xc}[n]$ accounts for the difference between the exact ground-state energy and the energy calculated in a Hartree approximation and using the non-interacting kinetic energy $T_0[n]$,

$$E^{xc}[n] \equiv T[n] - T_0[n] + U^{xc}[n] \quad (29)$$

$T[n]$, $T_0[n]$... exact and non-interacting kinetic energy functional

$U^{xc}[n]$... interaction of the electrons with their own exchange-correlation hole n_{xc} defined as (ρ_2 is the two-particle density matrix)

$$\rho_2(\vec{r}, s; \vec{r}', s') \equiv n_s(\vec{r})(n_{s'}(\vec{r}') + n_{xc}(\vec{r}, s; \vec{r}', s')) \quad (30)$$

Exchange-correlation functionals II

Properties of the exchange-correlation hole

- Locality

$$\lim_{|\vec{r}-\vec{r}'|} n_{xc}(\vec{r}, s; \vec{r}', s') = 0 \quad (31)$$

- Pauli principle for electrons with parallel spin

$$n_{xc}(\vec{r}, s; \vec{r}', s) = -n_s(\vec{r}) \quad (32)$$

- Antisymmetric non-interacting wavefunction

$$\int n_x(\vec{r}, s; \vec{r}', s') d^3 r' = -\delta_{s,s'} \quad (33)$$

- Normalization of two-particle density matrix

$$\int n_c(\vec{r}, s; \vec{r}', s') d^3 r' = 0 \quad (34)$$

Exchange-correlation functionals III

Properties of the exchange-correlation functional

- Adiabatic connection formula

$$E^{xc}[n] = \frac{1}{2} \int d^3 r n(\vec{r}) \int d^3 r' \int_0^1 d\lambda \frac{n_{xc,\lambda}(\vec{r}; \vec{r}')}{|\vec{r} - \vec{r}'|} \quad (35)$$

- Lieb-Oxford bound

$$E^{xc}[n] \geq -D \int n^{4/3}(\vec{r}) d^3 r, \quad 1.44 \leq D \leq 1.68 \quad (36)$$

plus scaling relations,.....

Local (spin-)density approximation - L(S)DA

$$E^{xc}[n(\vec{r})] = \int n(\vec{r}) \epsilon_{xc}[n(\vec{r})] d^3 r, \quad (37)$$

Exchange-functional (for spin-polarized systems,

$$n(\vec{r}, \uparrow) \neq n(\vec{r}, \downarrow), \quad n = n_{\uparrow} + n_{\downarrow})$$

$$\begin{aligned} \epsilon_x[n(\vec{r}, \uparrow), n(\vec{r}, \downarrow)] &= -\frac{3e^2}{4\pi} (3\pi^2)^{1/3} \left\{ \frac{n(\vec{r}, \uparrow)^{4/3} + n(\vec{r}, \downarrow)^{4/3}}{n(\vec{r})} \right\} \\ &= \epsilon_x^p + (\epsilon_x^f - \epsilon_x^p) \frac{(n_{\uparrow}/n)^{4/3} + (n_{\downarrow}/n)^{4/3} - (1/2)^{1/3}}{1 - (1/2)^{1/3}} \end{aligned} \quad (38)$$

with $\epsilon_x^p = \epsilon_x(n_{\uparrow} = n_{\downarrow} = n/2)$ for the paramagnetic (non-spinpolarized) and $\epsilon_x^f = \epsilon_x(n_{\uparrow} = n, n_{\downarrow} = 0)$ for the ferromagnetic (completely spin-polarized) limits of the functional.

Correlation functional $\epsilon_c[n(\vec{r}, \uparrow), n(\vec{r}, \downarrow)]$ fitted to the ground-state energy of a homogeneous electron gas calculated using quantum Monte Carlo simulations and similar spin-interpolations.

Semilocal functionals

Generalized gradient approximation - GGA

$$E^{xc}[n(\vec{r}, \uparrow), n(\vec{r}, \downarrow)] = \int f[n(\vec{r}, \uparrow), n(\vec{r}, \downarrow), \nabla n(\vec{r}, \uparrow), \nabla n(\vec{r}, \downarrow)] d^3 r, \quad (39)$$

There are two different strategies for determining the function f :

- (1) Adjust f such that it satisfies all (or most) known properties of the exchange-correlation hole and energy.
- (2) Fit f to a large data-set of exactly known binding energies of atoms and molecules.

Strategy (1) is to be preferred, but many different variants: Perdew-Wang (PW), Becke-Perdew (BP), Lee-Yang-Parr (LYP), Perdew-Burke-Ernzerhof (PBE).

Semilocal functionals

Meta-GGA

Include in addition a dependence on the kinetic energy density $\tau(\vec{r})$ of the electrons,

$$\tau(\vec{r}) = \sum_{i=1}^{n_{occ}} |\nabla\phi_i(\vec{r})|^2 \quad (40)$$

In the meta-GGA's, the exchange-correlation potential becomes orbital-dependent !

Hybrid functionals

General strategy: **Mixing exact-exchange (i.e. Hartree-Fock) and local-density energies**, as suggested by the adiabatic connection formula

$$E^{xc}[n] = \int_0^1 U_\lambda^{xc}[n] d\lambda \sim \frac{1}{2}U_0^{xc}[n] + \frac{1}{2}U_1^{xc}[n] \quad (41)$$

$U_0^{xc}[n]$... nonlocal exchange energy of Kohn-Sham orbitals

$U_1^{xc}[n]$... potential energy for exchange and correlation

Example: B3LYP functional

$$E^{xc}[n] = (1 - a)E_{LSDA}^x + aE_{exact}^x + bE_{B88}^x + cE_{LYP}^c + (1 - c)E_{VWN}^c \quad (42)$$

where E_{B88}^x stand for the exchange part of the Becke88 GGA functional, E_{LYP}^c for the correlation part of the Lee-Young-Parr local and GGA functional, and E_{VWN}^c for the local Vosko-Wilk-Nusair correlation functional. a , b , and c are adjustable parameters.

Limitations of DFT I

- **Band-gap problem:**

- HKS theorem not valid for excited states → band-gaps in semiconductors and insulators are always underestimated

- **Possible solutions:** - Hybrid-functionals lead to better gaps

- LDA+U, GW, SIC increase correlation gaps

- **Overbinding:**

- LSDA: too small lattice constants, too large cohesive energies, too high bulk moduli

- **Possible solutions:** - GGA: overbinding largely corrected (tendency too overshoot for the heaviest elements)

- The use of the GGA is mandatory for calculating adsorption energies, but the choice of the "correct" GGA is important.

Limitations of DFT II

- **Neglect of strong correlations**

- Exchange-splitting underestimated for narrow d - and f -bands
- Many transition-metal compounds are Mott-Hubbard or charge-transfer insulators, but DFT predicts metallic state
- **Possible solutions:** - Use LDA+U, GW, SIC, ...

- **Neglect of van-der Waals interactions**

- vdW forces arise from mutual dynamical polarization of the interacting atoms \longrightarrow not included in any DFT functional
- **Possible solution:** - Approximate expression of dipole-dipole vdW forces on the basis of local polarizabilities derived from DFT ??

Beyond DFT

DFT+U

Describe on-site Coulomb-repulsion by **Hubbard-Hamiltonian**

$$H = \frac{U}{2} \sum_{m,m',s} n_{m,s} n_{m',-s} + \frac{(U-J)}{2} \sum_{m \neq m',s} n_{m,s} n_{m',s} \quad (43)$$

where $n_{m,s}$ is the number operator for electrons with the magnetic quantum number m and spin s , $U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n)$ and J a screened exchange energy.

The DFT+U Hamiltonian includes contributions already accounted for in the DFT functional \rightarrow subtract double-counting, adopt rotationally invariant formulation \rightarrow

$$E_{DFT+U} = E_{DFT} + \frac{U-J}{2} \sum_s \text{Tr}[\rho^s - \rho^s \rho^s] \quad (44)$$

on-site density matrix ρ_{ij}^s of the d electrons

Beyond DFT II

Calculate quasiparticle-excitation energies by low-order many-body perturbation theory.

GW: Self-energy approximation approximated by

$$\Sigma(\vec{r}, \vec{r}'; \omega) = \frac{i}{2\pi} \int G(\vec{r}, \vec{r}'; \omega') W(\vec{r}, \vec{r}'; \omega') d\omega \quad (45)$$

where G is the full interacting Green's function and W the dynamically screened Coulomb interaction, described by the inverse dielectric matrix ϵ^{-1} and the bare Coulomb potential v ,

$$W(\vec{r}, \vec{r}'; \omega) = \int \epsilon^{-1}(\vec{r}, \vec{r}''; \omega) v(\vec{r}'' - \vec{r}) d^3 r'' \quad (46)$$

In practice, approximate forms of G and ϵ^{-1} have to be used.

SIC: Self-interaction corrections.

GW, SIC are not implemented in VASP. Results largely equivalent to LDA+U.