

Density Functional Theory

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Ab initio Calculations

- Hamiltonian: (without external fields, non-relativistic)

$$\hat{H} = \sum_i \left(-\frac{\nabla_i^2}{2m} \right) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\ + \sum_i \left(-\frac{\nabla_i^2}{2M_i} \right) + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} \\ - \sum_{ij} \frac{Z_j}{|\mathbf{r}_i - \mathbf{R}_j|}$$

Electrons

Nuclei

Electron-Nuclei interaction

In principle, the system is fully determined by specifying the number, mass and charge of all its constituents.

We have to deal with 10^{23} mutually interacting particles !!!

Born Oppenheimer Approximation

- Nuclei are 3 orders of magnitude heavier than electrons
- Their motion will be much slower
- Electrons can adjust instantaneously to nuclear positions.
- When calculating the electronic motion, nuclear coordinates can be treated as parameters.
- Formally we set the nuclear mass to infinity: the kinetic energy of the nuclei drops out.
- We are still left with the full interacting electronic problem!

$$\hat{H} = \sum_i \left(-\frac{\nabla_i^2}{2m} \right) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i \left(\frac{\nabla_i^2}{2M_i} \right) + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} - \sum_{ij} \frac{Z_j}{|\mathbf{r}_i - \mathbf{R}_j|}$$

The Electronic Problem

$$\hat{H} = \underbrace{\sum_{i\sigma} \left(-\frac{\nabla_i^2}{2m} \right)}_T + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_W + \underbrace{v_0(\mathbf{r})}_V$$

lattice potential:
Coulomb potential of
the nuclei

T

W

V

Experiments show:

electrons (often) behave as
if they were independent particles

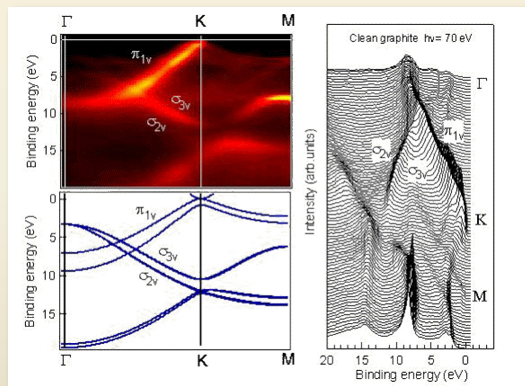


photo-emission

This suggests an effective single-particle
approach

Mean field approximation (Hartree)

- Replace e-e interaction by interaction with the average potential of the other electrons (Hartree approximation)

$$\frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \rightarrow \sum_i \int d^3 r' \frac{n(\mathbf{r})}{|\mathbf{r}_i - \mathbf{r}'|}$$

- Independent electrons in effective field
- Equations to be solved:

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + v_0(\mathbf{r}) + \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2$$

- Potential depends on the density: **Self-consistency !!**

Mean field approximation (Hartree)

- Total Energy:

$$\begin{aligned} E_H &= \sum_i^N \langle i | \hat{T} + \hat{V}_0 | i \rangle + \frac{1}{2} \sum_{i,j}^N \langle ij | \hat{U} | ij \rangle \\ &= \sum_i^N \epsilon_i - \frac{1}{2} \sum_{i,j}^N \langle ij | \hat{U} | ij \rangle \end{aligned}$$

double counting term

- Very crude approximation
 - Quantum many-body effects completely neglected
 - Self-Interaction error

Mean field approximation (Hartree-Fock)

- Improvement: Take Pauli principle into account

- Antisymmetrized wave function:

$$\Phi^{(A)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P [\varphi_{P(1)}(\mathbf{r}_1) \varphi_{P(2)}(\mathbf{r}_2) \dots \varphi_{P(N)}(\mathbf{r}_N)]$$

- Slater Determinant

$$\Phi^{(A)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \dots & \varphi_1(\mathbf{r}_N) \\ \vdots & & \vdots \\ \varphi_N(\mathbf{r}_1) & \dots & \varphi_N(\mathbf{r}_N) \end{vmatrix}$$

- Variational approach

$$\frac{\delta}{\delta \varphi_j^*(\mathbf{r})} \left[\langle \Phi | \hat{H} | \Phi \rangle - \sum_i^N \epsilon_i \int d^3 r |\varphi_i(\mathbf{r})|^2 \right] = 0$$

Mean field approximation (Hartree-Fock)

- Hartree-Fock equations:

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + v_0(\mathbf{r}) + \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right) \varphi_i(\mathbf{r}) - \int d^3 r' \frac{\rho(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \varphi_i(\mathbf{r}') = \epsilon_i \varphi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2 \quad \rho(\mathbf{r}, \mathbf{r}') = \sum_i^N \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}')$$

- Total Energy:

Coulomb and exchange energy

$$\begin{aligned} E_{HF} &= \sum_i^N \langle i | \hat{T} + \hat{V}_0 | i \rangle + \frac{1}{2} \sum_{i,j}^N \left[\langle ij | \hat{U} | ij \rangle - \langle ij | \hat{U} | ji \rangle \right] \\ &= \sum_i^N \epsilon_i - \frac{1}{2} \sum_{i,j}^N \left[\langle ij | \hat{U} | ij \rangle - \langle ij | \hat{U} | ji \rangle \right] \end{aligned}$$

double counting term

Mean field approximation (Hartree-Fock)

- First order perturbation theory
- No self-interaction error:
 - Self-Coulomb and self-exchange cancel
- Still misses many-body correlations: (important in solids)
 - Overestimate gaps
 - Homogeneous e-gas is non-metallic in Hartree-Fock
- Systematic starting point for many-body calculations

Beyond Hartree-Fock:

Many-body perturbation theory:

- Finite systems: Atoms and Molecules
 - consider higher order terms (finite systems): configuration interaction (CI), coupled clusters, etc.
 - very expensive!!
- Extended systems: Solids
 - finite order diverges
 - infinite order resummation possible (RPA) (See GW)

Alternative: **Density Functional Theory**

Density Functional Theory: Motivation

Can we use the many body wavefunction?

Consider Nitrogen atom:

- 7 electrons: 21 coordinates
- Coarse tabulation: 10 data points per coordinate
- 10^{21} data points
- 8 Byte per point: 8×10^{12} GByte
- 2×10^{12} DVD's (10^8 tons)

Absolutely impossible!

Hohenberg-Kohn Theorem

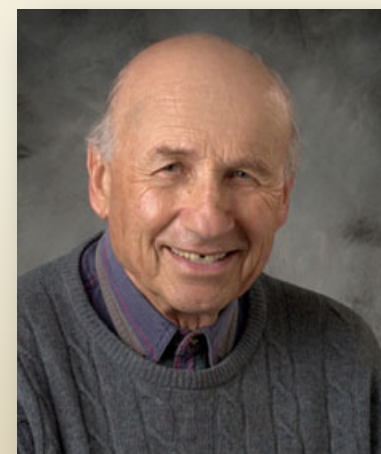
The ground state density alone completely determines the physical system

this is a remarkable result:

The density is a simple function in three dimensional space.

Chemistry Nobel Prize 1999:

W. Kohn
J. Pople



Hohenberg-Kohn Theorem

- One to one mapping between density and external potential:

$$v(\mathbf{r}) \longleftrightarrow n(\mathbf{r})$$

- Therefore the many-body wave function is a functional of the density:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Psi[n](\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

- Observables are functionals of the density $n(\mathbf{r})$

$$A[n] = \langle \Psi[n] | \hat{A} | \Psi[n] \rangle$$

Hohenberg-Kohn Theorem

- In particular: Ground state energy is a functional of $n(\mathbf{r})$

$$E_0[n] = \langle \Psi[n] | \hat{H} | \Psi[n] \rangle$$

- Ground state energy for given external potential:

$$\begin{aligned} E_{v_0}[n] &= \langle \Psi[n] | \hat{T} + \hat{W} + \hat{V}_0 | \Psi[n] \rangle \\ &= \underbrace{\langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle}_{=F[n]} + \int d^3r n(\mathbf{r}) v_0(\mathbf{r}) \end{aligned}$$

- Functional $F[n]$ is universal:
 - It does not depend on the external potential
 - It is the same for *all* electronic systems
 - The exact form is unknown. It has to be approximated!

Hohenberg-Kohn Theorem

- Variational principle:

$$\begin{aligned} E_{HK}[n_0] &= E_0 \\ E_{HK}[n] &> E_0 \quad \text{for } n \neq n_0 \end{aligned}$$

- Ground state density and energy can, in principle, be found by minimizing the energy functional:

$$E_0 = \min_n E_{HK}[n] \quad \text{with} \quad N = \int d^3r n(\mathbf{r})$$

Euler-Lagrange equation:

$$\begin{aligned} \frac{\delta}{\delta n(\mathbf{r})} \left(E_{HK}[n] - \mu \int d^3r' n(\mathbf{r}') \right) \Big|_{n \equiv n_0} &= 0 \\ \frac{\delta F[n]}{\delta n(\mathbf{r})} \Big|_{n \equiv n_0} + v_0(\mathbf{r}) - \mu &= 0 \end{aligned}$$

- But:** Free minimization is difficult!

Hohenberg-Kohn Theorem

Summary:

1. **One-to-one mapping:**

$$v(\mathbf{r}) \longleftrightarrow n(\mathbf{r})$$

$$A[n] = \langle \Psi[n] | \hat{A} | \Psi[n] \rangle$$

2. **Variational principle:**

$$E_0 = \min_n E_{HK}[n] \quad \text{with} \quad N = \int d^3r n(\mathbf{r})$$

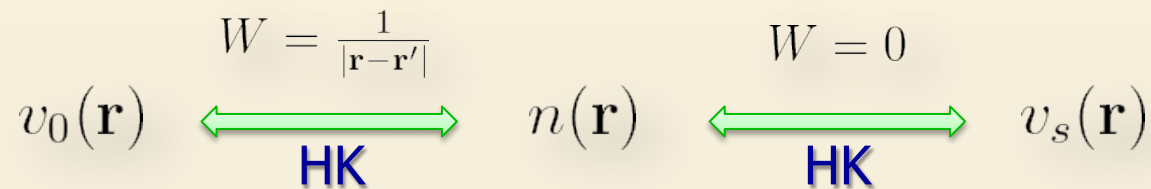
$$\left. \frac{\delta F[n]}{\delta n(\mathbf{r})} \right|_{n \equiv n_0} + v_0(\mathbf{r}) - \mu = 0$$

3. **Universal functional:** $F[n] = T[n] + W[n]$

Extensions to degenerate ground states.

Kohn-Sham Approach

- The Hohenberg-Kohn (HK) theorem:
independent of the interaction $W(\mathbf{r},\mathbf{r}')$
- Apply HK twice:



- Defines effective potential of a non-interacting system (Kohn-Sham system) which reproduces the exact ground state density of the full system.

Kohn-Sham Approach

Consider non-interacting system:

Two ways to calculate the density:

1. *Schrödinger equation:*

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + v(\mathbf{r}) \right) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad n(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2$$

2. *Euler-Lagrange equation:*

$$\left. \frac{\delta F_s[n]}{\delta n(\mathbf{r})} \right|_{n \equiv n_0} + v(\mathbf{r}) - \mu = 0$$

with $F_s[n] = T_s[n]; \quad W[n] = 0$

Kohn-Sham Approach

Rewrite universal functional $F[n]$:

$$\begin{aligned} F[n] &= \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle \\ &= T_W[n] + W[n] \\ &= T_s[n] + \frac{1}{2} \int d^3r \int d^3r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') + E_{xc}[n] \end{aligned}$$

Kinetic energy

Classical Coulomb energy

exchange energy

Exchange-correlation energy:

$$\begin{aligned} E_{xc}[n] &= T_W[n] - T_s[n] \\ &+ W[n] - \frac{1}{2} \int d^3r \int d^3r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \end{aligned}$$

contains all many body effects, but is unknown.

Kohn-Sham Approach

Insert this in Euler equation

$$\left. \frac{\delta F[n]}{\delta n(\mathbf{r})} \right|_{n \equiv n_0} + v_0(\mathbf{r}) - \mu = 0$$

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_0(\mathbf{r}) + \int d^3 r' w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} - \mu = 0$$

This corresponds to

$$\left. \frac{\delta F_s[n]}{\delta n(\mathbf{r})} \right|_{n \equiv n_0} + v_s[n](\mathbf{r}) - \mu = 0$$

with

$$v_s[n](\mathbf{r}) = v_0(\mathbf{r}) + \int d^3 r' w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

Solve this with method 1. (Schrödinger equation)

Kohn-Sham Approach

Kohn-Sham equations: (to be solved self-consistently)

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + v_s[n](\mathbf{r}) \right) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2$$

$$v_s[n](\mathbf{r}) = v_0(\mathbf{r}) + \int d^3r' w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

Total Energy: (electronic contribution)

$$E_0[n] = \sum_i^{occ} \varepsilon_i - \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] - \int d^3r n(\mathbf{r}) v_{xc}[n](\mathbf{r})$$

single particle energy

+ double counting terms

Kohn-Sham Approach

Remarks: “Kohn-Sham quasi-particles”

- KS system is a auxiliary system, defined to reproduce the ground state density
- “KS quasi particles” do not represent the physical quasi particles:
 - Infinite lifetime
 - In general wrong excitation energies
- DFT (as discussed) is a ground state theory !
- In many cases KS quasi-particles are good approximations to the physical quasi particles, but they should be used with care.

Extensions

Spin-DFT for magnetic systems

- in principle, the magnetization is a functional of n
- in practice, this functional is unknown (and would have to be complicated)
- Therefore:
 - include magnetization $\mathbf{m}(\mathbf{r})$ as additional density.
 - include conjugate field $\mathbf{B}(\mathbf{r})$ which couples to $\mathbf{m}(\mathbf{r})$

$$\hat{V} = \int d^3r (\hat{n}(\mathbf{r})v(\mathbf{r}) - \hat{\mathbf{m}}(\mathbf{r})\mathbf{B}(\mathbf{r}))$$

- xc functional: $E_{xc}[n, \mathbf{m}]$
- effective magnetic field $\mathbf{B}_{\text{eff}}(\mathbf{r}) = \mathbf{B}_{\text{ext}}(\mathbf{r}) + \frac{\delta E_{xc}[n, \mathbf{m}]}{\delta \mathbf{m}(\mathbf{r})}$
- effective field can maintain finite magnetization even without external field

Extensions

Spin-DFT for magnetic systems

- collinear magnetism: magnetization in z-direction

$$\begin{aligned}n(\mathbf{r}) &= n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r}) \\m_z(\mathbf{r}) &= -\mu_0 (n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r}))\end{aligned}$$

- Kohn-Sham equation:

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + v_s^{\sigma}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) - \sigma \mu_0 B_z(\mathbf{r}) \right) \varphi_i^{\sigma}(\mathbf{r}) = \epsilon_i^{\sigma} \varphi_i^{\sigma}(\mathbf{r})$$

- effective potential:

$$v_s^{\sigma}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) = v_0(\mathbf{r}) + \int d^3 r' w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') + v_{xc}^{\sigma}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}).$$

Extensions

Current-DFT

- include current density
- describes orbital magnetism

Multi-Component DFT

- goes beyond Born-Oppenheimer approximation
- includes nuclei as quantum mechanical particles

DFT for Superconductors

- based on multi-component DFT for electrons and nuclei
- includes superconducting order parameter as additional density
- ab initio description of superconducting properties

Density Functional Theory

- Is it the exact solution?
- Where has the difficulty many-body problem gone?
- exchange-correlation functional $E_{xc}[n]$
 - all many body effects are ‘hidden’ in here
 - the exact form is unknown
 - one needs good approximations

Exchange-correlation (xc) Functionals

Local Density Approximation (LDA):

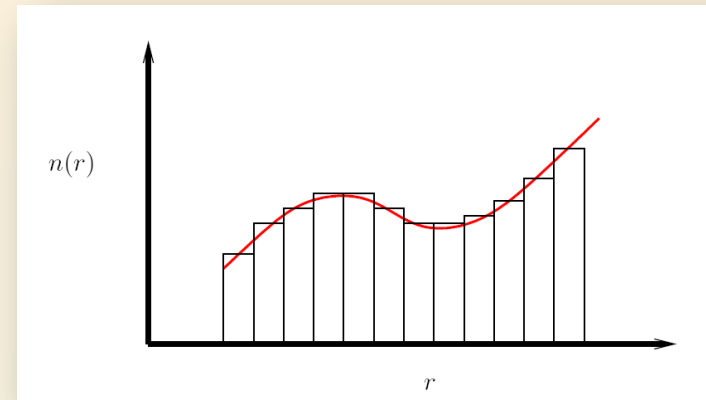
- Approximate the system locally as homogeneous e-gas

- density is constant: $n(\mathbf{r})=n$
- xc energy per particle is a function of n

- Ansatz for $E_{xc}[n]$:

$$E_{xc}^{LDA}[n] = \int d^3r n(\mathbf{r}) e_{xc}^{hom}(n(\mathbf{r}))$$

- $e_{xc}(n)$ calculated from Quantum Monte Carlo (Ceperley, Alder) and then parameterized.



xc Functionals

Local Spin-Density Approximation (LSDA):

- Approximate the system locally as homogeneous magnetic e-gas
 - spin-densities are constant
 - xc energy per particle is a function of $(n_{\uparrow}, n_{\downarrow})$
 - Ansatz for $E_{xc}[n_{\uparrow}, n_{\downarrow}]$:

$$E_{xc}^{\text{LSD}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r (n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})) \epsilon_{xc}^{\text{hom}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}))$$

- $e_{xc}(n_{\uparrow}, n_{\downarrow})$ is parametrisation of Quantum Monte Carlo data

xc Functionals

Generalized Gradient Approximations (GGA)

- L(S)DA is first term in an expansion in gradients of the density
- Inclusion of higher terms worsens results
- Reason: exact relations, fulfilled by L(S)DA !
- GGA's are constructed to incorporate some of these relations

$$E_{xc}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int d^3r f(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow})$$

xc Functionals

Orbital functionals:

- Kinetic energy:
 - KS already treats kinetic energy as orbital functional:

$$T_s[n] = T_s[\{\varphi_i(\mathbf{r})\}] = -\frac{\hbar^2}{2m} \int d^3r \sum_i \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r})$$

- Exact exchange (Fock term):
 - unknown as density functional, but
 - exact representation in terms of orbitals.

$$E_x[\{\varphi_i(\mathbf{r})\}] = \sum_{ij} \int d^3r \int d^3r' \frac{\varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- implicit functional of the density: $E_x[n] = E_x[\{\varphi_i[n](\mathbf{r})\}]$

xc Functionals

Orbital functionals:

- optimized effective potential:
apply chain rule for functional derivative:

$$v_{xc}(\mathbf{r}) = \sum_i \iint \frac{\delta E_{xc}[\{\varphi_i(\mathbf{r})\}]}{\delta \varphi_i(\mathbf{r}')} \frac{\delta \varphi_i(\mathbf{r}')}{\delta v_{eff}(\mathbf{r}'')} \frac{\delta v_{eff}(\mathbf{r}'')}{\delta n(\mathbf{r})} + c.c$$

inverse response function $\frac{\delta v_{eff}(\mathbf{r}'')}{\delta n(\mathbf{r})} = \chi_0^{-1}(\mathbf{r}, \mathbf{r}')$

- OEP integral equation

$$\int \chi_0(\mathbf{r}, \mathbf{r}') v_{xc}^{OPM}(\mathbf{r}') = \sum_{i \neq k} \int \frac{\delta E_{xc}[\{\varphi_i(\mathbf{r})\}]}{\delta \varphi_i(\mathbf{r}')} \frac{\varphi_k(\mathbf{r}') \varphi_k^*(\mathbf{r})}{\epsilon_k - \epsilon_i} \varphi_i(\mathbf{r}) + c.c.$$

- So far: no good orbital functional for correlations
(adding LDA/GGA correlations removes some error cancellation)

Beyond Kohn-Sham

LDA /GGA underestimate correlations for localized states:

- Failure to open gaps in some transition metal oxides
- General underestimation of gaps
- d- and f- electrons are too delocalized
- One reason: Spurious self-interaction (see Hartree-approx.)

$$U[n_\alpha] + E_{xc}^{LSD}[\bar{n}_\alpha] \neq 0 \quad n_\alpha \text{ is single electron density}$$

- Possible cures:
Hybrid Functionals, LSDA+U, LSDA+DMFT, SIC-LSD

LDA/GGA are not designed for spectroscopy

- TDDFT (still within Kohn-Sham)
- Many-body methods: GW, LDA+DMFT

Hybrid Functionals

- Observation: Fock term cancels self-interaction
- Add some exact exchange to the LDA

$$E_{xc}^{\text{hyb}} = E_{xc}^{\text{DFA}} + a_0(E_x - E_x^{\text{DFA}})$$

- Determine optimal amount by fitting to experimental results for a set of reference systems
- High accuracy for molecules
- Improved excitation energies
- Can be expensive (Fock term)
- Introduction of parameters

LDA+U

- Motivation: Hubbard model (standard model for correlated systems)

$$H_{\text{Hubbard}} = \sum_{k\sigma} \epsilon_{k\sigma} \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

- Add Hubbard term to LSD Hamiltonian
- Treat this term in mean field approximation

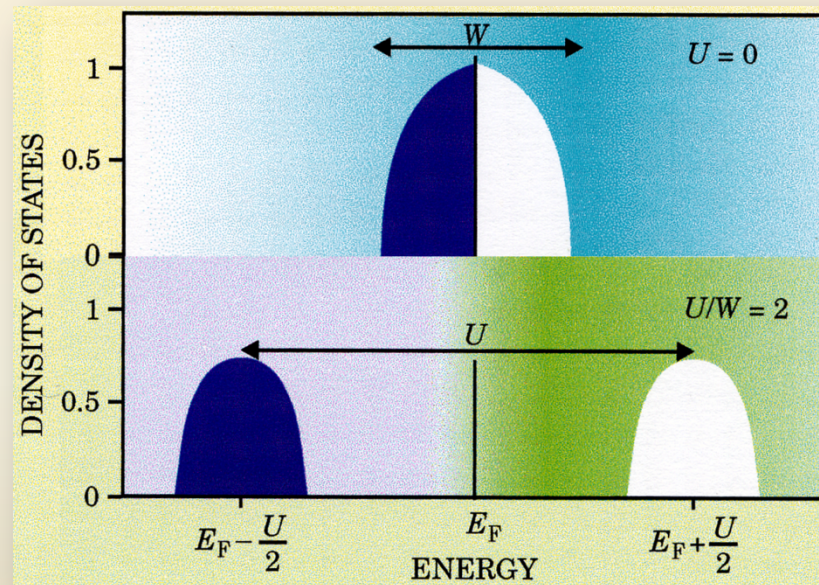
$$E^{\text{LDA+U}}[n] = E^{\text{LSD}}[n] + \sum_i E^{\text{corr}}(\underline{N}_i)$$
$$E^{\text{corr}}(\underline{N}) = \frac{1}{2} U \sum_{k \neq l} N_k N_l + E_{\text{dc}}$$

where $\underline{N} = \{N_k\}$ are the occupation of chosen correlated orbitals $|f_k\rangle$

$$N_k = \sum_{\alpha}^{\text{occ.}} |\langle \psi_{\alpha} | f_k \rangle|^2$$

LDA+U

- Main applications: transition metal oxides
- Hubbard U splits bands into upper and lower Hubbard band



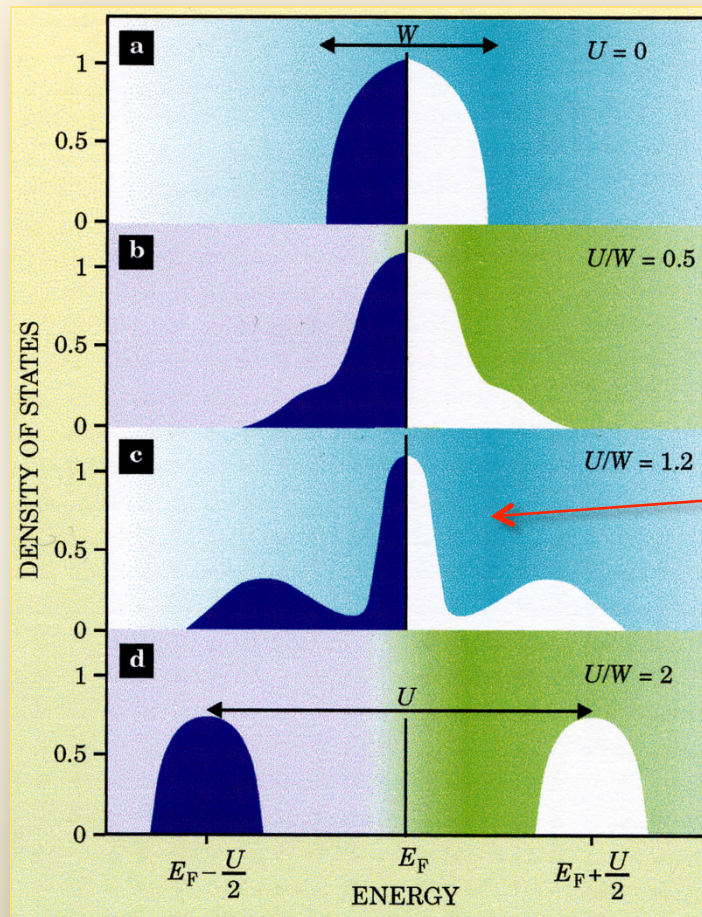
G. Kotliar and D. Vollhardt,
Physics Today 57, No. 3 (March), 53 (2004)

LDA+DMFT

- Dynamical Mean-Field Theory (DMFT):
 - Hubbard model in infinite dimensions:
 - Self-energy becomes local
 - Exact mapping to Anderson Impurity Model (which can be solved by e.g. QMC)
 - Impurity in an effective medium (determined selfconsistently)
 - In ‘real systems’ (3 dimensional):
 - High coordination number: approximately local self-energy
 - Correlated orbitals are well localized
- LDA+DMFT:
 - Use LDA to obtain tight binding Hamiltonian
 - Use DMFT to solve that Hamiltonian

LDA+DMFT

- Hubbard bands plus 'Kondo peak'



Typical picture for
Heavy Fermion systems

G. Kotliar and D. Vollhardt,
Physics Today 57, No. 3 (March), 53 (2004)

Self-Interaction Corrected (SIC) LSD

- Explicitly subtract self-interaction for each occupied orbital

$$E_{\text{xc}}^{\text{SIC-LSD}}[\{\bar{n}_\alpha\}] = E_{\text{xc}}^{\text{LSD}}[\bar{n}] - \sum_{\alpha}^{\text{occ}} (U[n_\alpha] + E_{\text{xc}}[\bar{n}_\alpha])$$

- Minimise with respect to φ_α under constraint $\langle \varphi_\alpha | \varphi_{\alpha'} \rangle = \delta_{\alpha\alpha'}$

$$\left(-\frac{\nabla^2}{2} + v_{\text{eff}}[\{\bar{n}_\alpha\}](\mathbf{r}) \right) \varphi_\alpha(\mathbf{r}) = \sum_{\alpha'}^{\text{occ}} \lambda_{\alpha\alpha'} \varphi_{\alpha'}(\mathbf{r})$$

- with effective potential

$$v_{\text{eff}}[\{\bar{n}_\alpha\}](\mathbf{r}) = v_{\text{eff}}^{\text{LSD}}[\bar{n}](\mathbf{r}) - v_{\text{H}}[n_\alpha](\mathbf{r}) - v_{\text{xc}}^{\text{LSD}}[\bar{n}_\alpha](\mathbf{r})$$

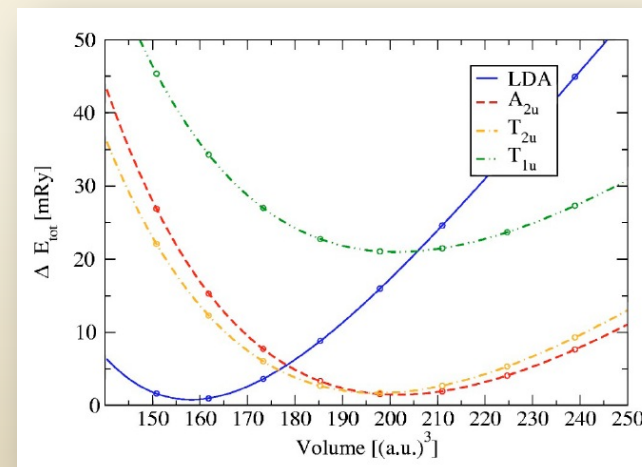
- SIC density: $n_\alpha(\mathbf{r}) = |\varphi_\alpha(\mathbf{r})|^2$

Self-Interaction Corrected (SIC) LSD

- Orbital dependent potential differentiates between localised and delocalised electrons
- Gain in band formation vs. gain in localization energy
- Study of various localisation/delocalisation configurations
- Definition of the valence: $N_{\text{valence}} = Z - N_{\text{core}} - N_{\text{SIC}}$

Global energy minimum determines ground state configuration

- Example: Ce α - γ transition



Time-dependent DFT

One-to-one mapping $v(\mathbf{r}, t) \longleftrightarrow n(\mathbf{r}, t)$

- time evolution of interacting systems:
e.g. atoms and molecules in strong laser pulses
- time-dependent linear response:

$$n_1(\mathbf{r}, t) = \int d^3r' \int dt' \chi(\mathbf{r}, \mathbf{r}'; t - t') v_1(\mathbf{r}', t')$$

linear response function

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\eta \rightarrow 0^+} \sum_m \left(\frac{\langle 0 | \hat{\rho}(\mathbf{r}) | m \rangle \langle m | \hat{\rho}(\mathbf{r}') | 0 \rangle}{\omega - (E_m - E_0) + i\eta} - \frac{\langle 0 | \hat{\rho}(\mathbf{r}') | m \rangle \langle m | \hat{\rho}(\mathbf{r}) | 0 \rangle}{\omega + (E_m - E_0) + i\eta} \right)$$

response function has poles at the exact excitation energies

“two-particle” excitation energies can be calculated !

The GW approximation

- The Green's function: $G_\sigma(\mathbf{r}, t; \mathbf{r}'t') = -\langle \hat{T} \hat{\Psi}_\sigma^\dagger(\mathbf{r}, t) \hat{\Psi}_\sigma(\mathbf{r}', t') \rangle$

- describes propagation of an electron

- Bloch representation: $G(\mathbf{r}, \mathbf{r}', E) = \lim_{\eta \rightarrow 0} \sum_n \frac{\Psi_n^*(\mathbf{r}) \Psi_n(\mathbf{r}')}{E - E_n + i\eta}$

- useful properties:

- Density $n(\mathbf{r}) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} dE G(\mathbf{r}, \mathbf{r}, E)$

- DOS $n(E) = -\frac{1}{\pi} \text{Im} \int_{\text{cell}} d^3r G(\mathbf{r}, \mathbf{r}, E)$

- Bloch Spectral function

$$A(\mathbf{k}, E) = -\frac{1}{\pi} \text{Im} \int_{\text{cell}} d^3r \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} G(\mathbf{r}, \mathbf{r} + \mathbf{R}; E)$$

Green's function has poles at the exact single-particle excitation energies

The GW approximation

- Equation of motion: $(E - \hat{H}) G(\mathbf{r}, \mathbf{r}', E) = \delta(\mathbf{r} - \mathbf{r}')$
- Hedin's equations:

$$G(1, 2) = G_0(1, 2) + \int d(3, 4) G_0(1, 3) \Sigma(3, 4) G(4, 2)$$

Green's function

$$\Sigma(1, 2) = i \int d(3, 4) G(1, 3^+) W(1, 4) \Lambda(3, 2, 4)$$

Self-energy

$$W(1, 2) = u(1, 2) + \int d(3, 4) u(1, 3) P(3, 4) W(4, 2)$$

Screened interaction

$$P(1, 2) = -i \int d(3, 4) G(1, 3) \Lambda(3, 4, 2) G(4, 1^+)$$

Polarization function

$$\Lambda(1, 2, 3) = \delta(1 - 2) \delta(2 - 3) +$$

$$\int d(4, 5, 6, 7) \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Lambda(6, 7, 3)$$

Vertex function

exact description of the Green's function
(requires full self-consistency)

The GW approximation

- In practice:
 - Start from KS-Green's function:

$$G = G_s + G_s(\Sigma - v_{xc})G$$

- Only one-shot calculation:

$$\Sigma = G_s W_0$$

Self-energy

$$W_0 = u + u P_0 W_0$$

Screened interaction

$$P_0 = G_s G_s$$

Kohn-Sham
response function

- Imaginary part of Σ describes lifetime of excitations
- Real part of Σ describes shifts in the energy