

# Density functional theory

# Explicit electronic structure

- When does one have to solve the electron structure explicitly?
  - Chemical reactions: Breaking and creation of chemical bonds
  - Changing coordination
  - Changing type of interaction
  - Difficult chemistry of elements
- However, the complexity of the problem grows immensely: Nuclei localised (only coordinates needed), explicit electron structure means solving the full Schrödinger equation

⇒ Compromises, approximations

# Many body electronic structure theory

- Born-Oppenheimer *Ansatz* leads to a many body Schrödinger equation

$$\mathcal{H}^e \Psi_{\{\mathbf{R}_I\}}(\{\mathbf{r}_i\}) = E_{\{\mathbf{R}_I\}}^e \Psi_{\{\mathbf{R}_I\}}(\{\mathbf{r}_i\})$$

with Hamiltonian

$$\begin{aligned} \mathcal{H}^e &= \hat{\mathcal{T}}_e + \hat{V}_{\text{ext}} + \hat{V}_{\text{ee}} \\ &= \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + V_{\text{ext}}(\mathbf{r}) + \frac{1}{4\pi\epsilon_0} \sum_{ij} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \end{aligned}$$

- Wave function

$$\Psi_{\{\mathbf{R}_I\}}(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

depends on all the coordinates of the electrons; it has to satisfy

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_1, \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)$$

and the ground state energy is obtained via minimisation

$$E_0 = \min_{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)} \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle$$

subject to the constraint on normalisation

# Many body wave function

## Explicit presentation

- Imagine storing the full many body wave function, not even speaking of solving it
  - For example 10 orbitals (20 electrons with spin degeneracy), 100 points per orbital
    - $100^{10}$  points, 4 bytes per value  $\Rightarrow \approx 300'000$  PB
- $\Rightarrow$  The data amount is impossible to handle, simplification and/or approximations required

# Quantum chemistry approaches

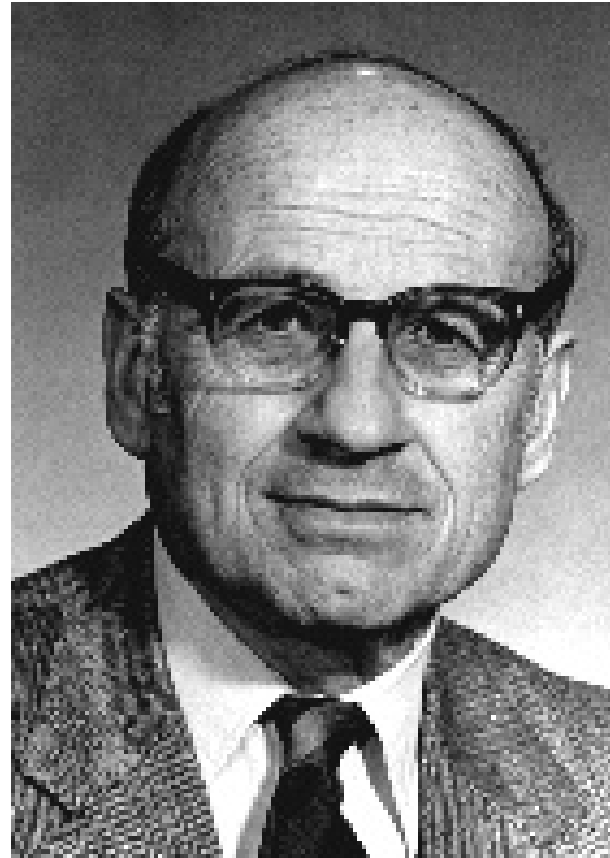
- Hartree-Fock: Approximate wave function with a single determinant; anti-symmetric property automatically fulfilled
- Correlation:
  - MP2, MP3, MP4
  - MC-SCF
  - FCI
  - Coupled-cluster
  - ...

## Alternative route: *via density*

- Density is a basic property of the system and the coordinate space does not grow with the number of particles
- It is enough to know only the (electron) density?

$$n_1(\mathbf{r}) = N \int \dots \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N$$

Solution: Walter Kohn







# Contributions of Walter Kohn

- The foundations could be found already in the literature (Thomas-Fermi, ...), but the essentials were still missing
  - Hohenberg-Kohn theorems (1964)
  - Kohn-Sham scheme (1965)
- Also other contributions in the field of physics: Kohn anomaly, ...

# Hohenberg-Kohn theorem I

The electron many body (ground state) wave function  $\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)$  of a system of  $N$  interacting electrons is a unique functional of the electronic density  $n(\mathbf{r})$

Thus the *density* can be used instead of the (external) potential to characterise all the properties of an electronic structure

(That the density defines the potential is trivial)

# Hohenberg-Kohn theorem I: Proof

By *reduction ad absurdum*:

- Suppose two different potentials,  $v_{\text{ext},1}$  and  $v_{\text{ext},2}$ , yielding the same density, but with different ground state wave functions  $\Psi_1$  and  $\Psi_2$
- Now try  $\Psi_2$  with the potential  $v_{\text{ext},1}$ ; by variational principle,

$$\langle \Psi_2 | \hat{T} + \hat{V}_{ee} + v_{\text{ext},1} | \Psi_2 \rangle > \langle \Psi_1 | \hat{T} + \hat{V}_{ee} + v_{\text{ext},1} | \Psi_1 \rangle$$

Since the density is the same,

$$\langle \Psi_2 | \hat{T} + \hat{V}_{ee} | \Psi_2 \rangle > \langle \Psi_1 | \hat{T} + \hat{V}_{ee} | \Psi_1 \rangle$$

Swap 1 and 2,

$$\langle \Psi_1 | \hat{T} + \hat{V}_{ee} | \Psi_1 \rangle > \langle \Psi_2 | \hat{T} + \hat{V}_{ee} | \Psi_2 \rangle$$

$\Rightarrow$  *Absurdum!*

## Hohenberg-Kohn theorem II

From all the densities, the one  $n$  that minimizes the energy functional with a given external potential is the ground state density, *i. e.* the density which corresponds to the solution of the Schrödinger equation;  $E[\tilde{n}] \geq E_0$

## Hohenberg-Kohn theorem II: Proof

- From the first theorem it follows that  $n(\mathbf{r})$  defines its own potential  $v_{\text{ext}}$  and thus  $\hat{H}$  and ultimately the wave function. Hence, any property is a functional of  $n$ . Now, apply another wavefunction  $\tilde{\Psi}$  to  $\hat{H}$ , the variational principle states,

- 

$$\langle \tilde{\Psi} | \hat{T} + \hat{V}_{ee} + v_{\text{ext}} | \tilde{\Psi} \rangle \geq E[n]$$

One can also use define a universal functional  $F[n] = \hat{T} + \hat{V}_{ee}$ , *i. e.* it is independent of  $v_{\text{ext}}(\mathbf{r})$ . So if you find it... Many problems solved! (And you'll get a paid visit to Stockholm!)

# Chemical potential

- All the variations with respect to density must be done at a constant number of electrons  $N$
- This can be done applying a Lagrangean multiplier  $\mu$

$$E'[n] = E[n] - \mu \left[ \int_{\mathbf{r}} n(\mathbf{r}) d\mathbf{r} - N \right]$$

- Variation yields

$$\begin{aligned} \delta E'[n] &= \delta E[n] - \mu \int_{\mathbf{r}} \delta n(\mathbf{r}) d\mathbf{r} \\ &= \delta \left\{ E[n] - \mu \int_{\mathbf{r}} n(\mathbf{r}) d\mathbf{r} \right\} \\ &= \int_{\mathbf{r}} \frac{\delta E[n]}{\delta n(\mathbf{r})} \delta n(\mathbf{r}) - \mu \int_{\mathbf{r}} \delta n(\mathbf{r}) d\mathbf{r} \\ &= \int_{\mathbf{r}} \left\{ \frac{\delta E[n]}{\delta n(\mathbf{r})} - \mu \right\} \delta n(\mathbf{r}) d\mathbf{r} = 0 \end{aligned}$$

$\Rightarrow$

$$\mu = \frac{\delta E[n]}{\delta n(\mathbf{r})} = v_{\text{ext}}(\mathbf{r}) + \frac{\delta T[n]}{\delta n(\mathbf{r})} + \frac{\delta V_{ee}[n]}{\delta n(\mathbf{r})}$$

# Kohn-Sham *Ansatz*

- Assume that one electron orbitals  $\{\phi_i\}$  which are multiplicative in their Slater determinant wave function (*i. e.* non-interacting),

$$\Psi_s = \frac{1}{N!} |\phi_1 \phi_2 \dots \phi_N|.$$

- Orbitals  $\phi_i$  are eigenstates of an effective (Kohn-Sham) potential  $v_s$  and orthonormal,

$$\begin{aligned} \hat{H}_s \phi_i &= \epsilon_i \phi_i & \hat{H}_s &= -\frac{1}{2} \nabla^2 + v_s(\mathbf{r}) \\ \langle \phi_i | \phi_j \rangle &= \delta_{ij} & n(\mathbf{r}) &= \sum_i^N |\phi_i(\mathbf{r})|^2 \end{aligned}$$

# Kohn-Sham scheme: Total energy

- This *Ansatz* leads to the total energy

$$E_{\text{KS}}[n] = \int_{\mathbf{r}} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} + T_s[n] + E_H[n] + E_{xc}[n]$$

or, according to Hohenberg & Kohn

$$E[n] = \int_{\mathbf{r}} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} + F_{\text{universal}}[n].$$

- The first term corresponds to interaction between electrons and external potential (ionic density + perturbations), and

$$T_s = -\frac{1}{2} \min_{\{\phi_i\} \mapsto n} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle; \text{ kinetic energy of non-interacting electrons}$$

$$E_H[n] = \frac{1}{2} \int_{\mathbf{r}} \int_{\mathbf{r}'} \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r}; \text{ the classical Coulomb interaction, or Hartree term}$$

$E_{xc}[n]$ ; all the remainder, *i. e.*

$$E_{xc}[n] = (T[n] - T_s[n]) + (E_{ee} - E_H[n])$$



# Kohn-Sham potential

- Variational principle: for infinitesimally small variation  $\delta n(\mathbf{r})$  (conserving  $N$ , i. e.  $\int_{\mathbf{r}} \delta n(\mathbf{r}) d\mathbf{r} = 0$ ),

$$\delta E_v = \delta T_s + \int_{\mathbf{r}} \left( v_{\text{ext}}(\mathbf{r}) + \frac{\delta E_H}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \right) \delta n(\mathbf{r}) d\mathbf{r} = 0$$

- At the minimum

$$v_H(\mathbf{r}) = \frac{\delta E_H}{\delta n(\mathbf{r}')} = \int_{\mathbf{r}'} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'; \text{ Hartree potential}$$
$$v_{xc} \equiv \frac{\delta E_{xc}}{\delta n(\mathbf{r})}; \text{ exchange-correlation potential}$$

- We need still the variation  $\delta T_s$  of the kinetic energy part

# Kohn-Sham potential

Kinetic part  $\delta T_s$ ?

- HK theorem: associate to  $n_{\text{NI}}$  a potential  $v_s[n]$  and minimise energy functional  $E_s$ ,

$$E_s[n] = \sum_i \langle \phi_i | -\frac{1}{2} \nabla^2 + v_s[n] | \phi_i \rangle = T_s[n] + \int_{\mathbf{r}} v_s(\mathbf{r}, [n]) n(\mathbf{r}) d\mathbf{r}$$

and, due to the variational principle,

$$\delta E_s = \delta T_s + \int_{\mathbf{r}} v_s(\mathbf{r}) \delta n(\mathbf{r}) d\mathbf{r} = 0 .$$

- Hence

$$\delta T_s = - \int_{\mathbf{r}} v_s(\mathbf{r}) \delta n(\mathbf{r}) d\mathbf{r}$$

# Kohn-Sham potential

- Substitute  $\delta T_s$ ,

$$\delta E_v = - \int_{\mathbf{r}} v_s(\mathbf{r}) \delta n(\mathbf{r}) d\mathbf{r} + \int_{\mathbf{r}} \left( v_{\text{ext}}(\mathbf{r}) + \frac{\delta E_H}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \right) \delta n(\mathbf{r}) d\mathbf{r} = 0.$$

- The condition for  $n$  to be  $n_0$ , i. e. the density which minimizes  $E_v$ , is that the integrands equate,

$$v_s[n_0](\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int_{\mathbf{r}'} \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}[n_0](\mathbf{r})$$

A *self-consistent* evaluation for  $n_0$  is required

- Hohenberg-Kohn theorem: The densities have to be the same

$$n_0(\mathbf{r}) = n_{\text{NI}} [v_s(\mathbf{r}, [n_0])] (\mathbf{r}) = n_{\text{NI}} \left[ v_{\text{ext}}(\mathbf{r}) + \int_{\mathbf{r}'} \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}[n_0](\mathbf{r}) \right] (\mathbf{r}) .$$

# Ground state energy

Alternative expression

- $E_0 = E_v[n_0]$  is given by

$$E_0 = \int_{\mathbf{r}} v_{\text{ext}} n_0 d\mathbf{r} + T_s[n_0] + E_H[n_0] + E_{xc}[n_0]$$

- While also,

$$E_s[n_0] = T_s[n_0] + \int_{\mathbf{r}} v_s[n_0] n_0 d\mathbf{r} = \sum_i^N \epsilon_i$$

# Ground state energy

## Alternative expression

$$\begin{aligned} E_0 &= \int_{\mathbf{r}} v_{\text{ext}} n_0 d\mathbf{r} + T_s[n_0] + E_H[n_0] + E_{xc}[n_0] \\ &= \int_{\mathbf{r}} v_{\text{ext}} n_0 d\mathbf{r} + \sum_i^N \epsilon_i - \int_{\mathbf{r}} v_s[n_0] n_0 d\mathbf{r} + E_H[n_0] + E_{xc}[n_0] \\ &= \int_{\mathbf{r}} (v_{\text{ext}} - v_s) n_0 d\mathbf{r} + \sum_i^N \epsilon_i + E_H[n_0] + E_{xc}[n_0] \\ &= \int_{\mathbf{r}} \left[ v_{\text{ext}} - \left( v_{\text{ext}} + \int_{\mathbf{r}'} \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc} \right) \right] n_0 d\mathbf{r} + \sum_i^N \epsilon_i + E_H[n_0] + E_{xc}[n_0], \\ &= - \int_{\mathbf{r}} \int_{\mathbf{r}'} \frac{n_0(\mathbf{r}') n_0(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} - \int_{\mathbf{r}} v_{xc} n_0 d\mathbf{r} + \sum_i^N \epsilon_i + E_H[n_0] + E_{xc}[n_0] \\ &= -2E_H[n_0] - \int_{\mathbf{r}} v_{xc} n_0 d\mathbf{r} + \sum_i^N \epsilon_i + E_H[n_0] + E_{xc}[n_0] \end{aligned}$$

$$E_0 = - \int_{\mathbf{r}} v_{xc} n_0 d\mathbf{r} + \sum_i^N \epsilon_i - E_H[n_0] + E_{xc}[n_0]$$

# Kohn-Sham scheme

## Observations

- The Kohn-Sham equations must be solved *self-consistently*:

$$n(\mathbf{r}) \Rightarrow v_s[n] \Rightarrow \{\phi_i\} \Rightarrow n(\mathbf{r}) \Rightarrow \dots$$

- The Kohn-Sham potential is *local*
- The eigenvalues are *not* physical, except for the one of the highest occupied orbital, which is (should be) the ionisation potential
- The eigenvectors  $\phi_i$  are *not* any single-particle orbitals
- Please remember: DFT is a *ground state theory*
- The exact functional is not known (at the time being)

# Exchange-correlation functional

# Approximations to $v_{xc}$

## Local Density Approximation

- Approximate the exchange-correlation functional with its counter-part for homogeneous electron gas

$$E_{xc}^{LDA} = \int_{\mathbf{r}} \epsilon_{xc}(n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}$$

$\epsilon_{xc}$  is the exchange and correlation energy per electron of the homogeneous electron gas with density  $n$

- Idea: Evaluate the exchange-correlation function(al) at each point of space  $\mathbf{r}$  using the *local* density at that point as if the density around was homogeneous, irrespective of the true surroundings
- The *function* can be separated into the exchange and correlation parts, and they are both well defined separately:

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



# Approximations to $v_{xc}$

## Performance of the Local Density Approximation

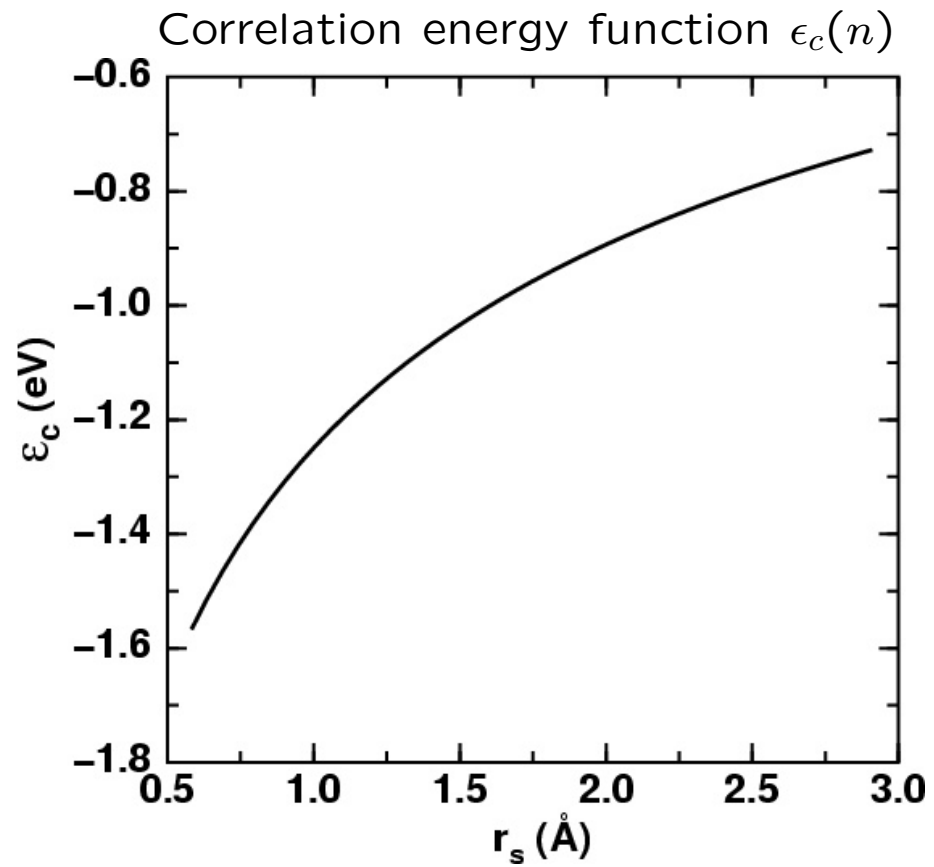
- The LDA exchange energy is due to Slater and Dirac,

$$\epsilon_x(n) = C_x n^{1/3}, \quad \text{where } C_x = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3}$$

- The exact analytical form of the correlation energy  $\epsilon_c(n)$  of the homogeneous electron gas is not known! The correlation energy is therefore fitted to quantum Monte-Carlo results (Ceperley & Alder) and analytical high- and low-density limits
  - There are several parametrisations: Vosko, Wilk & Nusair (1980); Perdew & Zunger (1981); Perdew & Wang (1992))
  - Default LDA in CPMD reproduces the Perdew-Wang functional [S Goedecker, M Teter & J Hutter, *PRB* **54**, 1703 (1996)]

# Approximations to $v_{xc}$

Local Density Approximation



# Approximations to $v_{xc}$

## Performance of the Local Density Approximation

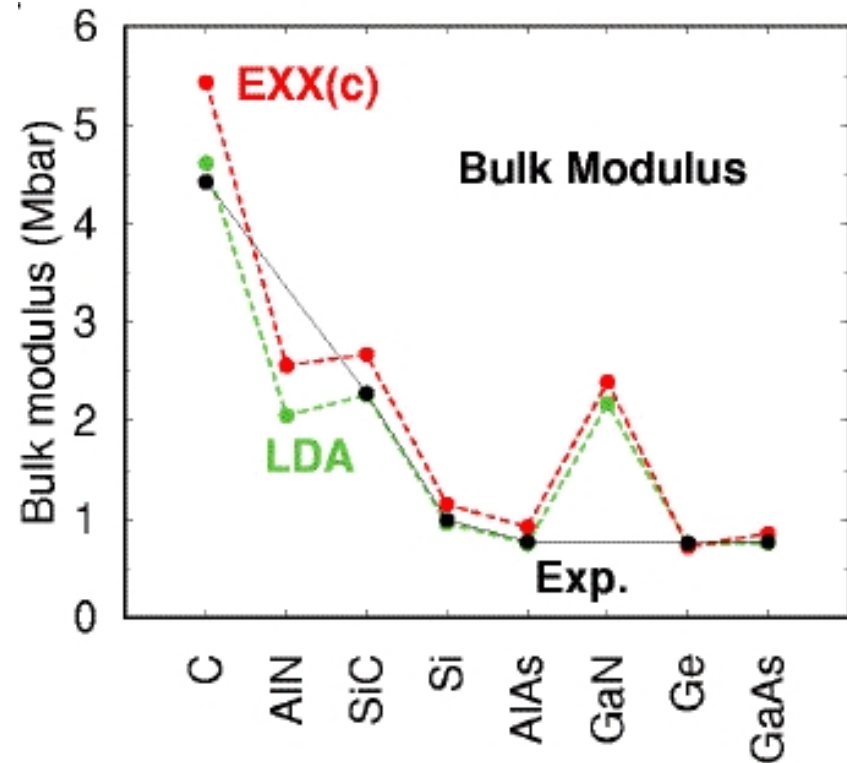
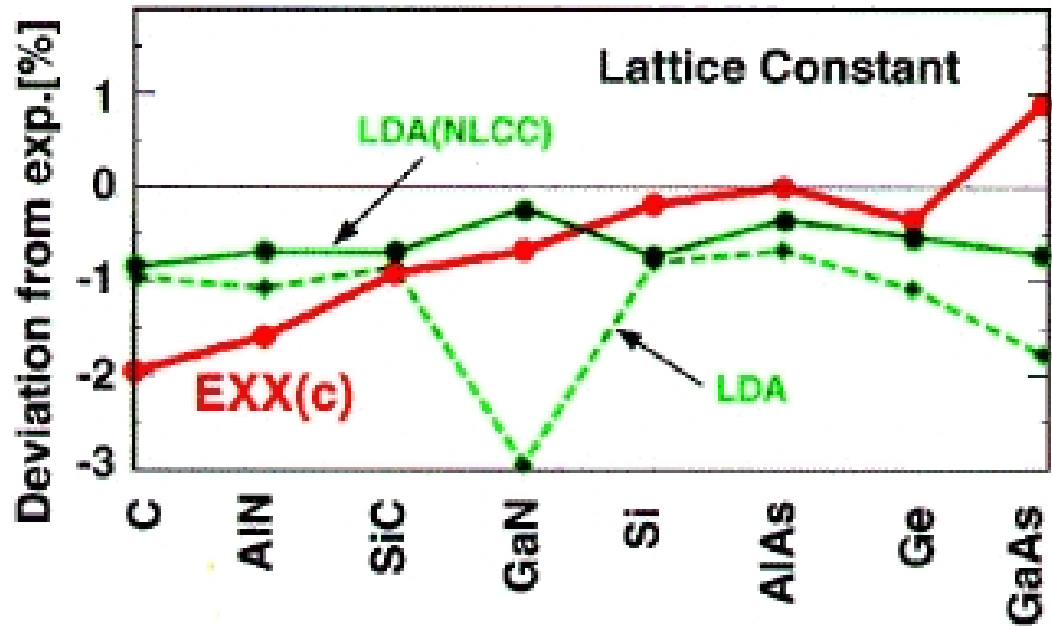
- The asymptotic decay of the exact functional is  $\propto \frac{1}{r}$  outside  $n$  (Almbladh and von Barth, 1985), whereas for LDA exponential (Tong and Sham, 1966; Lang and Kohn, 1970; Lang and Kohn, 1971) due to the exponential decay of the density
- Tail is crucial for IP's, work functions of surfaces and stability of negative atoms
- Overestimation of intramolecular forces  $\rightarrow$  too large binding energies, cohesion, van der Waals complexes
- Vibrational frequencies, phonons in solids, molecular geometries are ok; too small lattice constants and bulk compressibility or modulus too large
- $sd$  energy differences, spin-states bad  $\leftrightarrow$  magnetic properties
- Reaction barriers underestimated or even negative ( $\text{H}_2 + \text{H}$  reaction)

Accuracy often similar as in Hartree-Fock but cheaper and more physical insight (density).

# Approximations to $v_{xc}$

Local Density Approximation

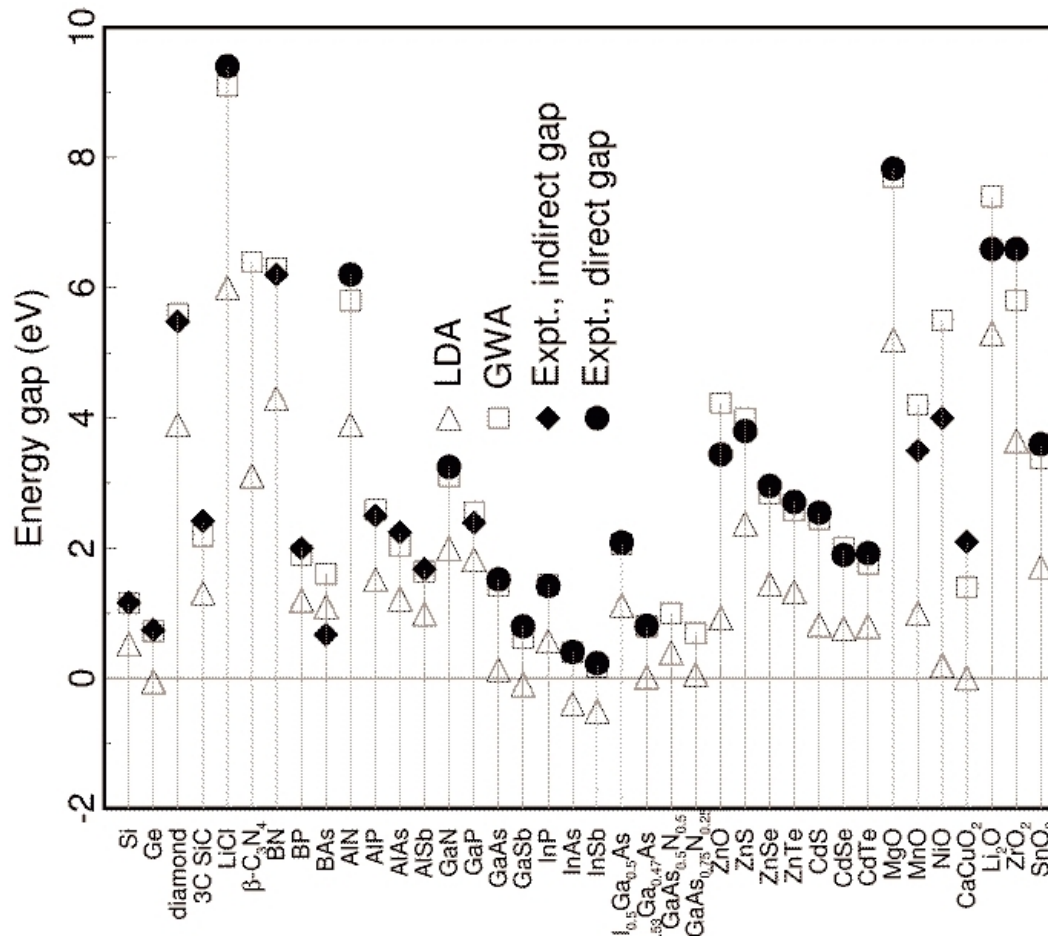
Structural properties



# Approximations to $v_{xc}$

Local Density Approximation

## Band gaps



Please remember: Ground state theory...!

# Approximations to $v_{xc}$

## Performance of the Local Density Approximation

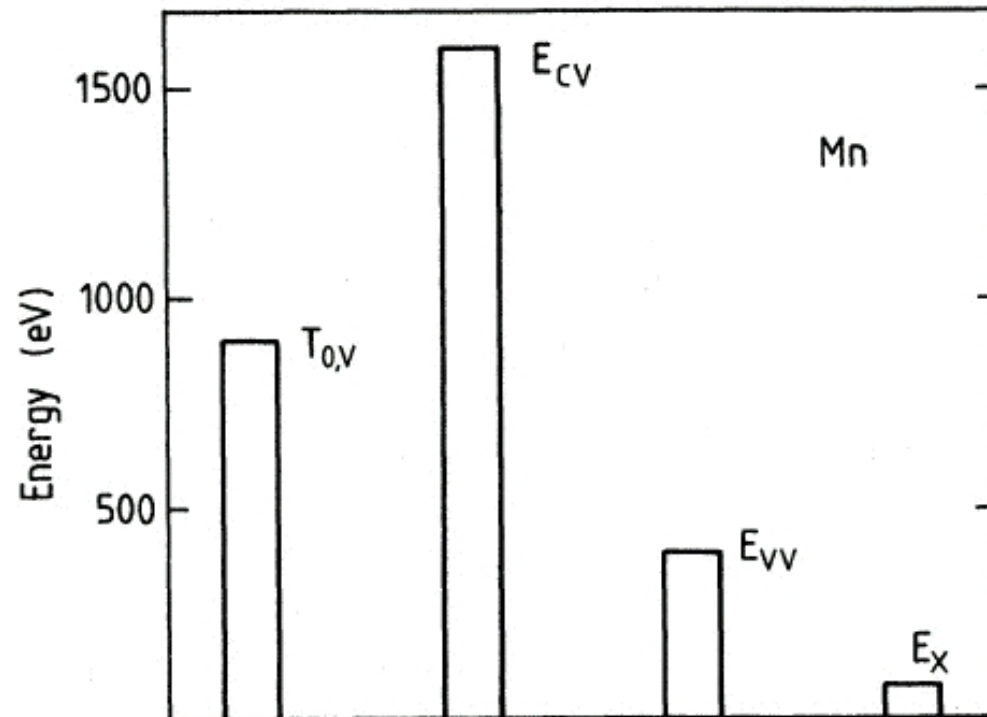
Why does it albeit work so well?

- The XC contribution is the smallest (that's why it was packed aside in the first place)
- LDA, despite its simplicity, still fulfills many important requirements set for the exact functional; scaling relations, sum rules, . . .
- There is a major error cancellation between the exchange and correlation (Warning: Same occurs with many other functionals also; thereby best keeping the same “level of sophistication” in both parts)

# Approximations to $v_{xc}$

Proportions of energies

Energy components in Mn atom;  $E_C \approx E_x$



# Approximations to $v_{xc}$

## Performance of the Local Density Approximation

Why does it albeit work so well?

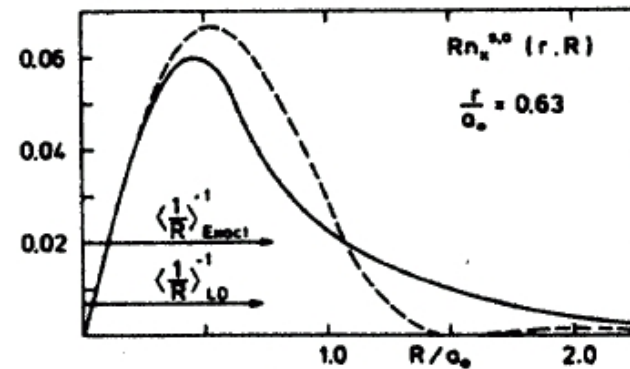
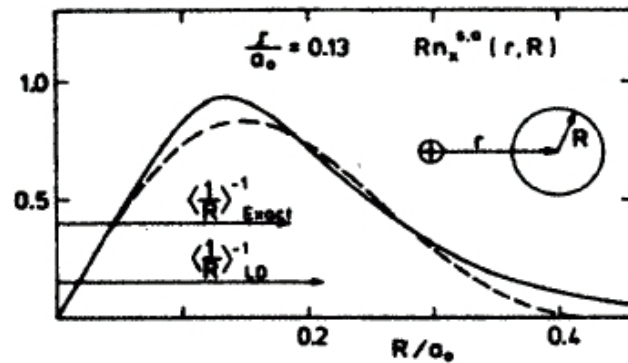
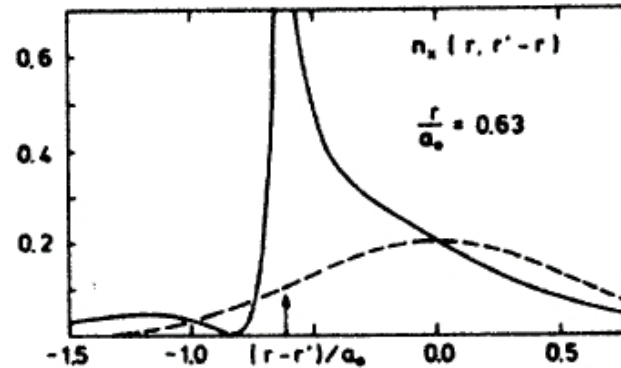
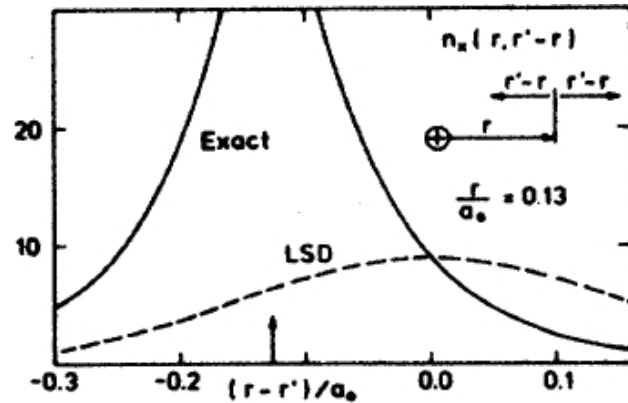
- The XC contribution is the smallest (that's why it was packed aside in the first place)
- LDA, despite its simplicity, still fulfills many important requirements set for the exact functional; scaling relations, sum rules, . . .
- There is a major error cancellation between the exchange and correlation (Warning: Same occurs with many other functionals also; thereby best keeping the same “level of sophistication” in both parts)



# Approximations to $v_{xc}$

Exchange-correlation hole

The “hole” the exchange and correlation dig around the reference electron



The hole (top) is badly described, however the spherical average (bottom), which is the property needed, agrees reasonably; notice, that in LDA the hole is centred at the reference electron!

# Approximations to $v_{xc}$

## Performance of the Local Density Approximation

Why does it *not* work so well?

- Missing integer discontinuity in the potential; thus bad excitation energies; (the first place)
- Self-interaction not excluded: The electron interacts directly with itself
- Thus for example  $d$  and  $f$  functions underbound (e. g. density of states in fcc Cu)
- Wrong tail: no Rydberg states, image states at metal surfaces

# Approximations to $v_{xc}$

## Generalised Gradient Approximation

Idea: Extend LDA to inhomogeneous systems by inclusion of density gradients.

- Straight-forward approach: Taylor expansion around the density.  
→ Gradient Expansion Approximation (GEA) by Hohenberg and Kohn (1964)
- However, performance usually worse than LDA
- Improve through increased freedom in functional form and approximation:  
Generalised Gradient Approximation, GGA  
→ many different functionals, e. g. BLYP, P86, PW91, PBE

# Approximations to $v_{xc}$

## GGA - PBE

Perdew, Burke & Ernzerhof, *Physical Review Letters* (1996):

- Like Perdew-Wang'91: “Analytical” function, only “natural constants”
- Det vill säga, *no fitting*

$$E_{xc}^{\text{PBE}} = E_x^{\text{PBE}} + E_c^{\text{PBE}}$$

$$E_x^{\text{PBE}}(n, |\nabla n|) = \int_{\mathbf{r}} n \varepsilon_x^{\text{LDA}}(n) F_x^{\text{PBE}}(s) d\mathbf{r},$$

$$F_x^{\text{PBE}}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu s^2}{\kappa}},$$

$$\mu = \beta \left( \frac{\pi^2}{3} \right)$$

$$\begin{aligned}
E_C^{\text{PBE}}(n, |\nabla n|) &= \int_{\mathbf{r}} d\mathbf{r} n \left[ \varepsilon_{\text{xc}}^{\text{LDA}}(n) + H_C^{\text{PBE}}(r_s, \eta, t) \right], \\
H_C^{\text{PBE}}(r_s, \eta, t) &= \gamma \phi^3 \ln \left[ 1 + \frac{\beta}{\gamma} t^2 \left( \frac{1 + At^2}{1 + At^2 + A^2 t^4} \right) \right], \\
A(r_s, \eta) &= \frac{\beta}{\gamma} \frac{1}{e^{-\varepsilon_c^{\text{LDA}}/\gamma \phi^3} - 1}, \\
\phi(\eta) &= \frac{1}{2} \left[ (1 + \eta)^{2/3} + (1 - \eta)^{2/3} \right], \\
\gamma &= \frac{1 - \ln 2}{\pi^2}; \quad r_s = \left[ \frac{3}{4\pi n} \right]^{1/3} \text{ local Wigner-Seitz radius}
\end{aligned}$$

Here  $s(\mathbf{r}) = \frac{|\nabla n|}{2k_F n}$  and  $t(\mathbf{r}) = \frac{|\nabla n|}{2\phi k_s n}$ ,  $k_s = \sqrt{4k_F/\pi}$ , are dimensionless density gradients and  $\beta$  comes from the generalised gradient expansion for the correlation (Perdew *et al*, 1992) and  $\approx 0.066725$  (Wang & Perdew, 1991).  $\kappa$  is formally set by the Lieb-Oxford bound (1981) for the exchange energy

$$E_x[n] \geq E_{\text{xc}}[n] \geq -1.679 \int_{\mathbf{r}} n^{4/3} d\mathbf{r} .$$

Note: revPBE plays exactly with this parameter

# Approximations to $v_{xc}$

## Performance of GGA's

- core electrons are more strongly bound  $\rightarrow$  nucleus better screened  $\rightarrow$  valence electrons are less bound  $\rightarrow$  longer bond lengths, larger lattice constant ( $\rightarrow$  too low bulk moduli)
- vibrational frequencies similar to LDA
- reaction barriers larger than LDA
- intramolecular interactions weaker  $\rightarrow$  too low work functions and energies of surfaces, accurate to underestimated interaction energies for van der Waals complexes

# Further approximations to $v_{xc}$

## Climbing the ladder

- John Perdew's vision on the development of XC functionals

NIRVANA (chemical accuracy)		
explicit dependence on...		
unoccupied orbitals	rung 5	fully nonlocal
occupied orbitals	rung 4	<i>e. g.</i> hybrid functionals
kinetic energy density	rung 3	meta-GGAs
gradients of the density	rung 2	GGAs
local density only	rung 1	LDA
EARTH (Hartree theory)		

# Solving the Kohn-Sham equations



# Resolution of the Kohn-Sham equations

## Diagonalisation

1 Take  $n^{old}$  as input for self-consistency equation,

$$v_s(\mathbf{r})^{old} = v_{\text{ext}}(\mathbf{r}) + \int_{\mathbf{r}'} d\mathbf{r}' \frac{n(\mathbf{r}')^{old}}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r}, [n^{old}])$$

2 Solve (by diagonalisation) Schrödinger equation for NI electrons  $\rightarrow \{\phi^{new}\}$

$$\left( -\frac{1}{2}\nabla^2 + v_s^{old} \right) \phi_i^{new} = \epsilon_i^{new} \phi_i^{new}$$

3  $n^{old} = \sum |\phi_i^{new}|^2$  and goto 1 unless converged

# Resolution of the Kohn-Sham equations

Constraint minimisation technique

Minimise

$$E[n] = \int_{\mathbf{r}} n v_{\text{ext}} d\mathbf{r} + T_s + E_H + E_{xc}$$

with respect to  $\{\phi_i\}$ ,  $E_0 = \min_{\{\phi_i\}} E[n]$ , and under the constraint that  $\langle \phi_i | \phi_j \rangle = \delta_{ij}$

Use Lagrange multipliers  $\Lambda_{ij}$  and minimise

$$E' = E[\{\phi_i\}] - \sum_{ij} \Lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij})$$

At the minimum,

$$\frac{\delta E}{\delta \phi_i^*} = \sum_j \Lambda_{ij} \phi_j$$

# Resolution of the Kohn-Sham equations

## Constraint minimisation technique

$$\begin{aligned}\frac{\delta E}{\delta \phi_i^*} &= -\frac{1}{2}\nabla^2\phi_i(\mathbf{r}) + \int_{\mathbf{r}'} d\mathbf{r}' \left( v_{\text{ext}}(\mathbf{r}') + \frac{\delta E_H}{\delta n} + \frac{\delta E_{xc}}{\delta n} \right) \frac{\delta n(\mathbf{r}')}{\delta \phi_i^*(\mathbf{r})}, \\ \frac{\delta n(\mathbf{r}')}{\delta \phi_i^*(\mathbf{r})} &= \delta(\mathbf{r} - \mathbf{r}')\phi_i(\mathbf{r}), \\ \rightarrow \frac{\delta E}{\delta \phi_i^*} &= \left[ -\frac{1}{2}\nabla^2 + v_s \right] \phi_i, \\ &= \hat{H}_s\phi_i\end{aligned}$$

Minimise  $E$  iteratively with gradient – but  $\hat{H}_s$  is not explicitly needed, at the minimum *any* set  $\{\phi_i\}$  satisfying

$$\delta E' = 0 \implies \hat{H}_s\phi_i = \Lambda_{ij}\phi_j,$$

is sufficient and hence called "minimal orbitals".

# Resolution of the Kohn-Sham equations

## Minimal vs canonical KS-orbitals

- Canonical  $\{\phi_i^c\}$  are those minimal orbitals which diagonalise Lagrange multiplier matrix,  $\Lambda_{ij}^c = \epsilon_i \delta_{ij}$ :

$$\hat{H}_s \phi_i = \epsilon_i \delta_{ij}.$$

They can be obtained by unitary transformation of any minimal (occupied) orbital set.

- For any minimal orbital set and any unitary transformation,  $\phi'_i = \sum_j U_{ij} \phi_j$ ,  $n$  (and consequently  $E_0$ ) is kept invariant ( $UU^\dagger = 1$ ).
- All minimal  $\{\phi'_i\}$  must satisfy that  $\hat{H}_s \phi'_i = \Lambda'_{ij} \phi'_j$ , with  $\Lambda' = U \Lambda U^\dagger$ .
- $\{\phi_i^c\}$  are good for interpretation but not needed for  $E_0$  and  $\mathbf{F}_I$ .

# Ionic forces

Hellmann-Feynman forces in DFT

$$\begin{aligned}\mathbf{F}_I &= -\frac{\partial E_0(\mathbf{R})}{\partial \mathbf{R}_I} = -\sum_i \int_{\mathbf{r}} d\mathbf{r} \frac{\delta F_{universal}}{\delta \phi_i^*} \frac{\partial \phi_i^*}{\partial \mathbf{R}_I} - \int_{\mathbf{r}} d\mathbf{r} n \frac{\partial v}{\partial \mathbf{R}_I}, \\ &= Z_I \int_{\mathbf{r}} d\mathbf{r} \frac{n(\mathbf{r}) (\mathbf{r} - \mathbf{R}_I)}{|\mathbf{r} - \mathbf{R}_I|^3}\end{aligned}$$

The first term vanishes because of stationary conditions.

# Density functional theory: Summary

- All (ground state) properties can be derived from the ground state density
- The Kohn-Sham scheme yields a set of self-consistent equations; however the effective, or Kohn-Sham potential is local and thus the scaling with system size not that bad
- Local density approximation yields in general good structural properties, less so for energetics
- Generalised gradient approximations usually yield more accurate results than the local density approximation at a similar cost
- There is no systematic way to improve the results (so far, that is)
- Yet the method of choice for systems with  $\simeq 10^2..10^4$  atoms

## Reminder: Kohn-Sham Equations

$$\left\{ -\frac{1}{2}\nabla^2 + v_s[n](\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

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

$$v_s[n](\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int_{\mathbf{r}'} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}[n](\mathbf{r})$$