Density Functional Theory and the Local Density Approximation

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Outline

- Born-Oppenheimer approximation
- Hohenberg-Kohn theorems
- Kohn-Sham implementation
- The E_{xc} functional
- The local density approximation (LDA)
- Limits of current implementations of DFT

The *First Principles* Approach

- 🟩 it is free of adjustable parameters
- 🟩 it treats the electrons explicitly
- 🟥 cost of the calculation limits system size and simulation time

electron → • r

nucleus
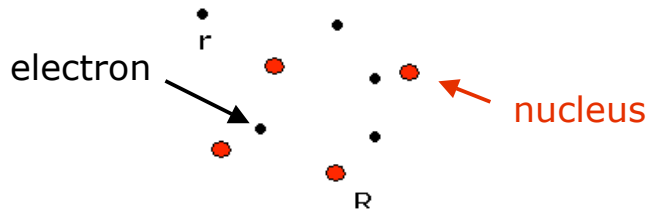
$$\hat{H}_{N,e}\Psi_{N,e}\left(\{\mathbf{R}_J\},\{\mathbf{r}_i\}\right)=E_{N,e}\Psi_{N,e}\left(\{\mathbf{R}_J\},\{\mathbf{r}_i\}\right)$$

where $\quad \hat{H}_{N,e}=\hat{T}_N+\hat{T}_e+\hat{V}_{N-N}+\hat{V}_{N-e}+\hat{V}_{e-e}$

Born-Oppenheimer Approximation

$$\hat{H}_{N,e}\Psi_{N,e}\left(\{\mathbf{R}_J\},\{\mathbf{r}_i\}\right)=E_{N,e}\Psi_{N,e}\left(\{\mathbf{R}_J\},\{\mathbf{r}_i\}\right)$$

Electron mass much smaller than nuclear mass:
➡ Timescale associated with nuclear motion much slower than that associated with electronic motion
➡ Electrons follow instantaneously the motion of the nuclei, remaining always in the same stationary state of the Hamiltonian

$$\Psi_{N,e}\left(\{\mathbf{R}_J\},\{\mathbf{r}_i\}\right)=\Theta_N\left(\{\mathbf{R}_J\}\right)\Phi\left(\{\mathbf{r}_i\}\right)$$

⬇

depends only *parametrically* on $\{\mathbf{R}_J\}$

Born-Oppenheimer approximation decouples the electronic problem from the ionic problem. The electronic problem is:

$$\hat{H}\,\Phi\left(\{\mathbf{r}_i\}\right)=E\,\Phi\left(\{\mathbf{r}_i\}\right)$$

The Electronic Problem

Time-independent, non-relativistic Schroedinger equation in the Born-Oppenheimer approximation [in atomic units: $e = m_e = \hbar = 1$]:

$$\hat{H}\,\Phi(\{\mathbf{r}_i\}) = E\,\Phi(\{\mathbf{r}_i\})$$

$$\hat{H} = \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{N-e}$$

where $\quad \hat{T}_e = -\dfrac{1}{2}\sum_i^N \nabla_i^2 \qquad \hat{V}_{e-e} = \sum_{i<j}^N \dfrac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$

$$\hat{V}_{N-e} = -\sum_\alpha^{N_{at}} \dfrac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} \quad \longleftarrow \quad \text{External potential}$$

The external potential and the number of electrons, N, completely determine the Hamiltonian

Density functional theory (DFT) offers a solution …

Density Functional Theory: the Theorems

Theorem 1.

The external potential is uniquely determined by the electronic charge density - $n(\mathbf{r})$ - so the total energy is a unique functional of the density - $E[n]$!

Theorem 2.

The density which minimises the energy is the ground state density and the minimum energy is the ground state energy:

$$\underset{n}{Min}\, E[n] = E_0$$

there is a *universal* functional $E[n]$ which could be minimised to obtain the *exact* ground state density and energy.

Hohenberg & Kohn, PRB **136**, 864 (1964)

What is the Functional?

$$E[n] = T_e[n] + V_{e-e}[n] + V_{ext}[n].$$

where $T_e[n]$ is the kinetic energy and V_{e-e} is the electron-electron interaction.

$V_{ext}[n]$ is trivial:

$$V_{ext}[n] = \int \hat{V}_{ext} \, n(\mathbf{r}) d\mathbf{r}$$

where

$$\hat{V}_{ext} = -\sum_{\alpha}^{N_{at}} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|}$$

T and V_{e-e} need to be approximated !

$E[n]$ – The Kohn Sham Approach

Write the density in terms of a set of N non-interacting orbitals:

$$n(\mathbf{r}) = \sum_{i}^{N} |\phi_i(\mathbf{r})|^2$$

The non interacting kinetic energy and the classical Coulomb interaction

$$T_s[n] = -\frac{1}{2}\sum_{i}^{N} \left\langle \phi_i \left| \nabla^2 \right| \phi_i \right\rangle \qquad V_H[n] = \frac{1}{2}\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

This allows us to recast the energy functional as:

$$E[n] = T_s[n] + V_{ext}[n] + V_H[n] + E_{xc}[n]$$

where we have introduced the exchange-correlation functional:

$$E_{xc}[n] = (T[n] - T_s[n]) + (V_{e-e}[n] - V_H[n])$$

The Kohn-Sham Equations

Vary the energy with respect to the orbitals and ….

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

where:

$$V_{xc}(\mathbf{r}) = \frac{\partial E_{xc}[n]}{\partial n(\mathbf{r})}$$

KS equations are solved via an iterative procedure until self-consistency is reached

No approximations, So…

If we knew $E_{xc}[n]$ we could solve for the **exact** ground state energy and density !

Kohn & Sham, PRA **140**, 1133 (1965)

The Non-interacting System

There exists an effective mean field potential which, when applied to a system of non-interacting fermions, will generate the exact ground state energy and charge density !!!

$$\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots)$$

$$V_{xc}(\mathbf{r})$$
$$\phi_i(\mathbf{r})$$

E[n], n(r)
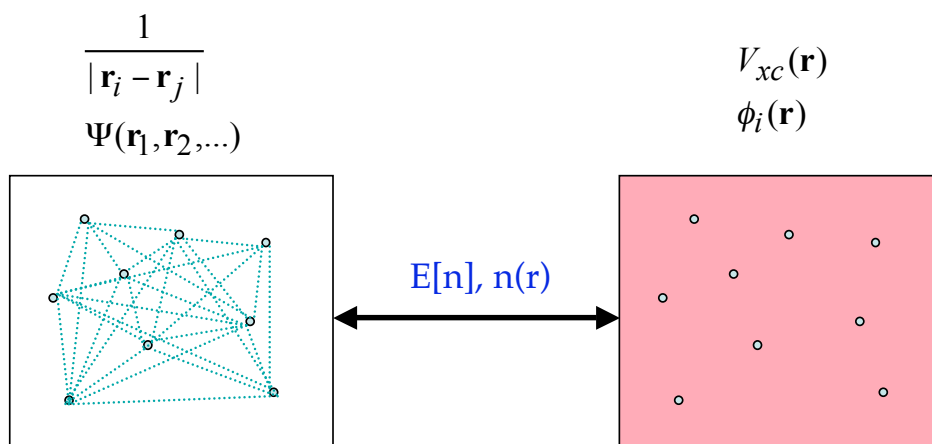
Density Functional Theory: The History

Thomas-Fermi-Dirac Model (1929):
First model where the energy is expressed in terms of the electron density

E. Fermi, Nobel laureate 1938

Kohn-Hohenberg-Sham (1964):
Exact univoque relationship between ground state energy and electron density

W. Kohn, Nobel laureate 1998

$E_{xc}[n]$ - Properties

$$E_{xc}[n] = (T[n] - T_s[n]) + (V_{e-e}[n] - V_H[n])$$

– Does not depend on V_{ext}(the specific system): it is a 'universal' functional.

– The exact dependence on $n(\mathbf{r})$ is unknown

E_{xc} must be approximated in applications

Local Density Approximation (LDA)

The idea: build E_{xc} from the knowledge of the exchange-correlation energy per particle, ε_{xc}, of the homogeneous electron gas

Kohn & Sham, PRA **140**, 1133 (1965)

For the homogeneous electron gas the exact dependence of $\varepsilon_{xc}(n)$ can be computed by Quantum Monte Carlo.
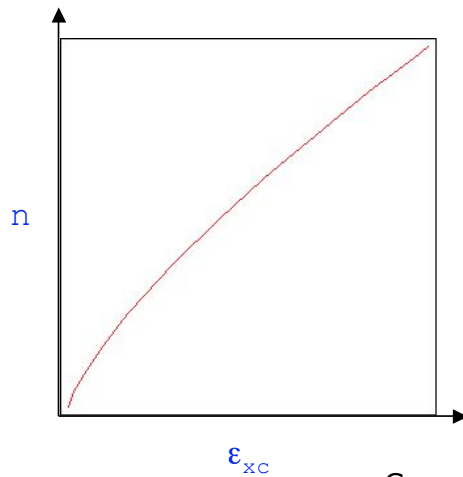
Ceperley & Alder, PRL **45**, 566 (1980)

LDA to E_{xc}: How it is built

$$E_{xc}^{LDA} = \int \varepsilon_{xc}\big(n(\mathbf{r})\big) n(\mathbf{r}) d\mathbf{r}$$
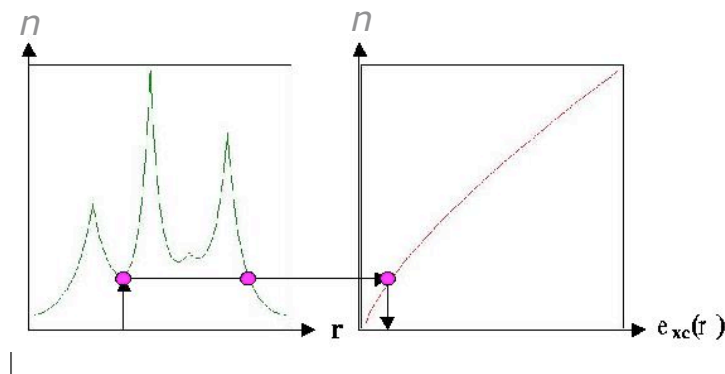
Picture courtesy of Andreas Savin

Kohn & Sham, PRA **140**, 1133 (1965)

LDA: Performance

Kohn & Sham, PRA **140**, 1133 (1965): "We do not expect an accurate description of chemical bonding"

In reality:

- Covalent bonds ⎫
- Metallic bonds ⎬ generally well described
- Ionic bonds ⎭ (tends to overbind slightly)

- Hydrogen bonds: LDA not adequate

- Van der Waals bonds: DFT not adequate – but this is not just a LDA problem…

Why does LDA work in most cases ?

The Exchange-Correlation Hole

The exchange correlation hole, $P_{xc}(\mathbf{r}_1,\mathbf{r}_2)$, is the probability of finding an electron at $\mathbf{r}_2$ given that there is an electron at $\mathbf{r}_1$.

It is the hole the electron at $\mathbf{r}_1$ digs for itself in the surrounding electronic density.

There are a number of properties which will be satisfied by the exact exchange correlation hole. For instance it should normalise to exactly one electron:

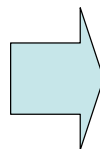$$\int P_{xc}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 = -1$$

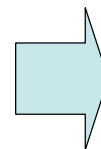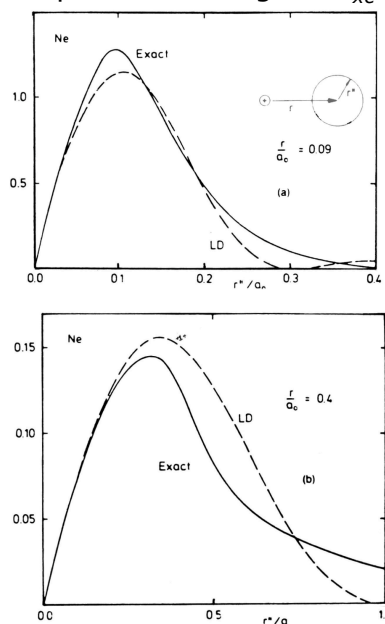LDA satisfies this rule.

P_{xc} is very poorly estimated the LDA
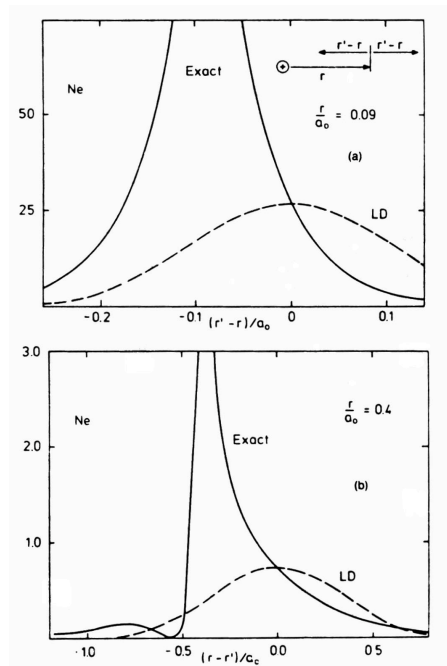
Jones & Gunnarsson, Rev. Mod. Phys. **61**, *689* (1979)

How can V_{e-e} be reasonable if P_{xc} is wrong ?

V_{e-e} depends only on the spherical average of P_{xc}
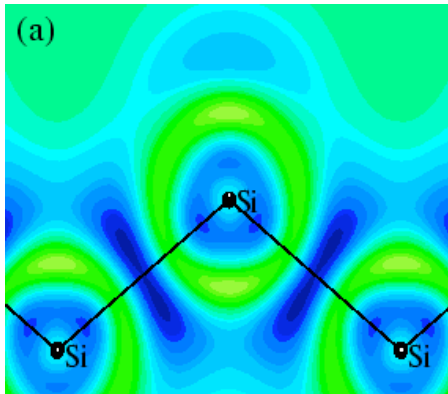
Spherical average of P_{xc}

LDA works in part because it generates a reasonable estimate of the spherical average
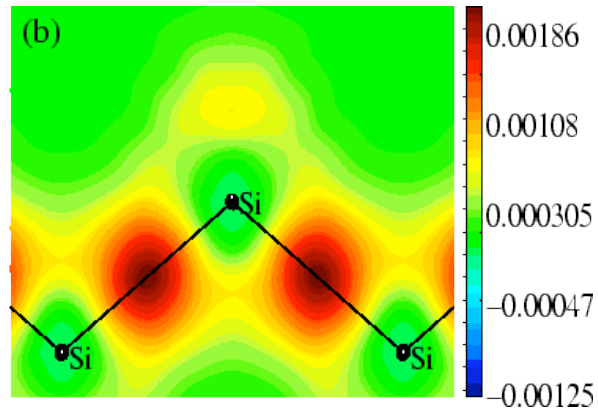
Jones *et. al.* 1979

The LDA energy densities

The difference between the exact (V-QMC) and LDA energy density in bulk silicon (au)

Exchange   **Correlation**

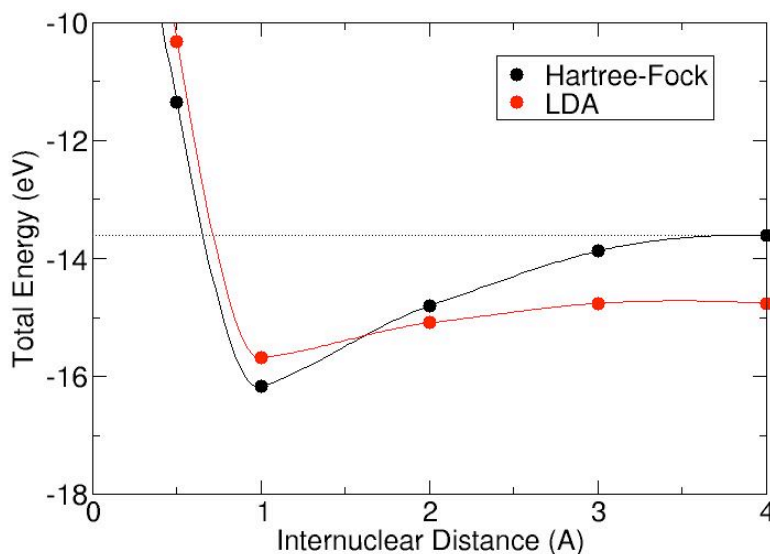Hood et al PRB **57** 8972 (1998)

So Why does the LDA work ?

- Exact properties of the xc-hole maintained

- The electron-electron interaction depends only on the spherical average of the xc-hole – this is reasonably well reproduced

- The errors in the exchange and correlation energy densities tend to cancel

Some things that do not work in this approach

- Van der Waals interactions: due to mutual dynamical charge polarisation of the atoms ⟶ not properly included in any existing approximations to E_{xc}

- Excited states: DFT is a ground state theory (ways forward: time-dependent DFT, GW, …)

- Non Born-Oppenheimer processes (i.e, non-radiative transitions between electronic states)

- Self-interaction problem: each electron lives in the field created by all electrons including itself (ways forward: SIC, hybrid DFT)
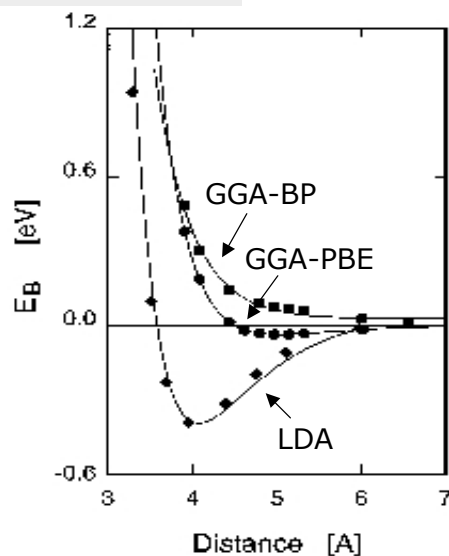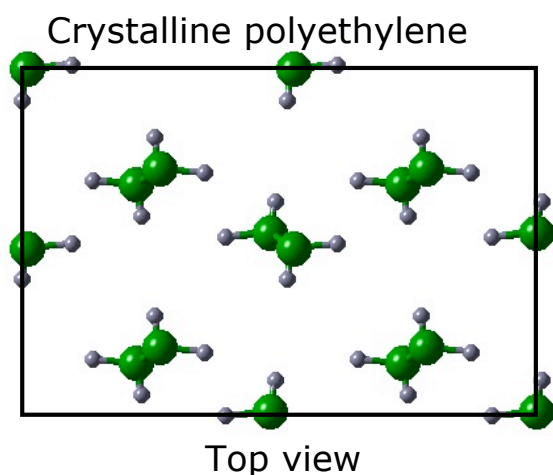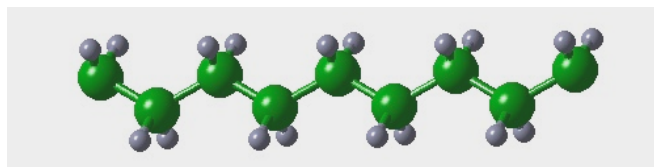

Self Interaction in H_2^+

- Self interaction leads to wrong dissociation limit:

- Self interaction problem particularly severe in the presence of *d* and *f* electrons

Courtesy of Ling Ge

Van der Waals Forces

Crystalline polyethylene


GGA-BP

GGA-PBE

LDA

Top view

B. Montanari *et al.* J. Chem. Phys. **108**, 6947 (1998)

Summary

- Born-Oppenheimer approximation
- Hohenberg-Kohn theorems
- Kohn-Sham implementation
- The E_{xc} functional
- The local density approximation (LDA): how it is built, why it works in many cases
- Limits of current implementations of DFT (self interaction, van der Waals forces, …)

Next

The magical world of electrons in crystals
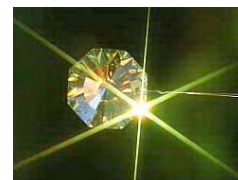
Useful References

- Hohenberg & Kohn, PRB **136**, 864 (1964)
- Kohn & Sham, PRA **140**, 1133 (1965)

- R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989)
- M. C. Payne et al., Rev. Mod. Phys **64**, 1045 (1992)

- R. M. Martin, *"Electronic Structure: basic theory and practical methods",* Cambridge University Press (2004)
- J. Kohanoff, *"Electronic Structure Calculations for Solids and Molecules: Theory and Computational Methods",* Cambridge University Press (2006)