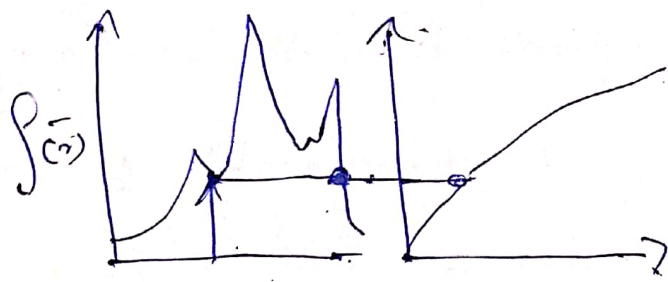
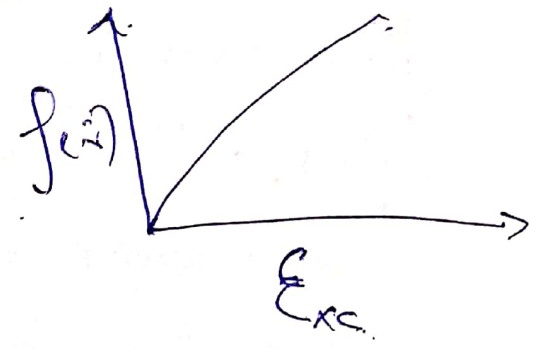


For the homogeneous electron gas
 2a) The exact dependence of $\epsilon_{xc}^{loc}(f(\vec{r}))$
 can be computed by Quantum Monte
 Carlo.



Kohn-Sham PRA, 110, 1133 (1965)



Ceperley and Alder PRL, 45, 566 (1980)

According to this approximation, the many electron system is divided into infinitesimally small regions located at positions \vec{r} , each of which contain a homogeneous interacting electron gas with a constant local density f .

Particularly, the LDA is exact approximation in the case of constant.

charge density, but surprisingly,

it also works well for other realistic cases.

Local Spin Density Approximation

Magnetic materials; where the spin-polarization of the material has been needed, are modelled using the Local spin density approximation. In such cases, Local electron density is divided into spin up and spin down electron densities ($\rho_{\uparrow}(\vec{r}), \rho_{\downarrow}(\vec{r})$).

The total electron density in this material is the sum of the two densities and the magnetization or the spin polarization. $\vec{m}(\vec{r})$ is also taken into account to characterize the system as:

$$\rho(\vec{r}) = \rho_{\uparrow}(\vec{r}) + \rho_{\downarrow}(\vec{r})$$

$$\vec{m}(\vec{r}) = \frac{\rho_{\downarrow}(\vec{r}) - \rho_{\uparrow}(\vec{r})}{\rho_{\uparrow}(\vec{r}) + \rho_{\downarrow}(\vec{r})}$$

39 ✓
So, exchange-correlation function
in the spin-polarized case takes
the form

$$E_{xc}^{LDA}[\rho(\vec{r}), \rho(\vec{r})] = \int \rho(\vec{r}) \epsilon_{xc}^{LDA}(\rho(\vec{r}), \rho(\vec{r})) d\vec{r}$$

The relation between exchange-correlation
functional and the spin dependent
exchange potential for a LDA is

$$V_{xc}(\rho(\vec{r}), \rho(\vec{r})) = \frac{\delta}{\delta \rho(\vec{r})} E_{xc}^{LDA}[\rho(\vec{r}), \rho(\vec{r})]$$

Draw Backs:

- Drastically fails — rapid variation in the electron density: in molecules at surfaces or for strongly correlated electron systems.
- Also leads — well known problem of the underestimation of the band gap in semiconductors and insulators.

200
200
200
i) Major drawback - study of defects. ^④
at semiconductor-oxide interfaces
where the electron density varies
rapidly.

To overcome this problem, many
approximations have been made. The most
widely used is generalized gradient
approximation (GGA).

Generalized Gradient Approximation:

"The electronic density is not
slowly varying".

In this approximation the exchange-
correlation functional is a function of both
the electron density and the gradient of
the electron density $|\nabla \rho(\vec{r})|$. Thus, in
many cases the GGA improves the total
energy, structural optimization, binding
energy of molecules, and also the

ground state properties of the transition metals elements as compared to LDA.

4a

The exchange-correlation functional in GGA can be written as

$$E_{xc}^{GGA} = \int f(\vec{r}) \cdot E_{xc}(\rho(\vec{r}), \nabla \rho(\vec{r})) d^3\vec{r}$$

In case of spin polarization it takes the form,

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

with magnetization term $g(\vec{r})$.

$$E_{xc}^{GGA}[\rho(\vec{r}), g(\vec{r})] = \int f(\vec{r}) E_{xc}(\rho(\vec{r}), \nabla_{\uparrow} \rho_{\uparrow}(\vec{r}), \nabla_{\downarrow} \rho_{\downarrow}(\vec{r}), g(\vec{r})) d^3\vec{r}$$

where $\rho(\vec{r}) = \rho_{\uparrow}(\vec{r}) + \rho_{\downarrow}(\vec{r})$.

It is worth noting that some systems are not correctly described with LDA and even with GGA, the case of CaO , where the band gap is much underestimated with respect to experiment.

3
LDA
4
Furthermore, for the Mott-Hubbard insulators, a band model gives a metallic picture with the LDA and the GGA.

Self-Interaction Correction (SIC)

The self-interaction error in DFT appears from the fact that the residual self-interaction in the Coulomb part and that in the exchange part do not cancel each other exactly. This error is responsible for the unphysical orbital energies of DFT and the failure to reproduce the potential energy curves of several physical processes.

A new algorithm is presented which is based on the Perdew-Zunger energy correction and which includes the self-interaction correction

→ A semi-empirical SIC method is designed to correct the orbital energies

The idea is that, explicitly subtract self-interaction terms for all occupied orbitals. (PRB 23, 5048 (1981)).

$$E_{xc}^{SIC} = E_{xc}^{LDA}[\rho(\vec{r})] - \sum_{i\sigma} \left(E_{xc}^{LDA}[\rho_{i\sigma}(\vec{r})] + \frac{e^2}{2} \int d^3r d^3r' \frac{\rho_{i\sigma}(\vec{r})\rho_{i\sigma}(\vec{r}')}{|\vec{r}-\vec{r}'|} \right)$$

where

$$\rho_{i\sigma}(\vec{r}) = |\Phi_{i\sigma}(\vec{r})|^2$$

where $\Phi_{i\sigma}(\vec{r})$ is orbital dependent potential.

Fully SIC requires "localization" of orbitals by minimizing the SIC total energy