Electronic Structure of Condensed Matter
Fudan University - April 2010

DFT-II - Kohn-Sham-DFT
What is E_{xc} – Approximations for E_{xc}

Instructor: Richard M. Martin
University of Illinois
Stanford University

rmartin@illinois.edu
and
Rmartin42@gmail.com

Functional $E_{xc}[n]$ in Kohn-Sham Eqs.

- **First: What is the basic relation of E_{xc} to exchange and correlation**
  - **Requires information on the many-body system of interacting electrons**
- **Next: Examples of approximate functionals $E_{xc}[n]$**
  - **Local Density Approximation - LDA**
    - Assume the functional is the same as a model problem – the homogeneous electron gas
    - E_{xc} has been calculated as a function of density using quantum Monte Carlo methods (Ceperley & Alder)
  - **Improvements: Gradient approximations - GGA**
    - Various theoretical improvements for electron density that is varies in space
  - **Orbital functionals – Van der Waals functionals**

Relation of $E_{xc}[n]$ to exchange and correlation I

- **Exchange and correlation denote the correlation among the electrons**
- **Around each electron there is a "hole" - depletion of other electrons described by the density reduction $n_{xc}(r)$**
- **For parallel spins , there is exclusion due to the Pauli exclusion principle**
  Also correlation tends to push other electrons away
- **For opposite spins correlation is a depletion of other electrons due to repulsion (a larger correlation effect than for parallel spins)**
- **Requires information on the many-body system of interacting electrons**

Relation of $E_{xc}[n]$ to exchange and correlation II

- **E_{xc} is the reduction in the energy due to exchange and correlation**
- **The energy is insensitive to the shape of the xc hole $n_{xc(}r)$**
- **E_{xc} depends only upon the spherical aaverage of the xc density**

$$E_{xc} = 4\pi \int dr\, r^2\, (1/r)\, n_{xc}(r)$$

- **Requires information on the many-body system of interacting electrons**
  But only the spherical average – a great simplification

Homogeneous Gas – Basic definitions

Interacting electron problem – with no external potential
(a constant V is just a shift in the energy)

A homogeneous system is completely specified by its density $n = N_e/\Omega$, which can be characterized by the parameter r_s, defined as the radius of a sphere containing one electron on average,

$$\frac{4\pi}{3}r_s^3 = \Omega/N_e = \frac{1}{n}; \quad \text{or} \quad r_s = \left(\frac{3}{4\pi n}\right)^{1/3}. \tag{5.1}$$

Table 5.1. Typical r_s values in elemental solids in units of the Bohr radius a_0. The valence is indicated by Z. The alkalis have bcc structure; Al, Cu, and Pb are fcc; the other group IV elements have diamond structure, and other elements have various structures. The values for metals are taken from [86] and [88]; precise values depend upon temperature

Z = 1	Z = 2	Z = 1	Z = 2	Z = 3	Z = 4
Li 3.23	Be 1.88			B	C 1.31
Na 3.93	Mg 2.65			Al 2.07	Si 2.00
K 4.86	Ca 3.27	Cu 2.67	Zn 2.31	Ga 2.19	Ge 2.08
Rb 5.20	Sr 3.56	Ag 3.02	Cd 2.59	In 2.41	Sn 2.39
Cs 5.63	Ba 3.69	Au 3.01	Hg 2.15	Tl	Pb 2.30

Local Density Approximation

Assume $E_{xc}[n]$ is a sum of contributions from each point in space *depending only upon the density at each point independent of other points.* Then

$$E_{xc}[n] = \int d^3r n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r})) \tag{26}$$

where $\epsilon_{xc}(n)$ is the x-c energy per electron

- Since $\epsilon_{xc}(n)$ is assumed to be universal, *must be the same as for homogeneous electrons of density n.*
- Exchange (e.g., Aschroft and Mermin, p. 411)

$$\epsilon_x(n) = -\frac{0.458}{r_s}\ Hartree, \tag{27}$$

where r_s is the average distance between electrons given by $\frac{4\pi}{3}r_s^3 = \frac{1}{n}$.

- Correlation found by:
  - RPA approximation - good at high density
  - Interpolation between low and high density - Wigner (1934),
  - Essentially exact Monte Carlo Calculations done by Ceperley and Alder, 1980

Hole due to Exchange and Correlation

Results from quantum Monte Carlo Calculations

Opposite spin

Parallel spin

Key point – the xc hole is rather localized – extentds to ~ 2 r_s ~ distance to neighboring electrons

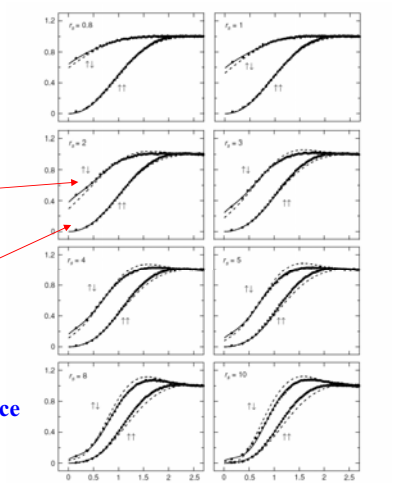
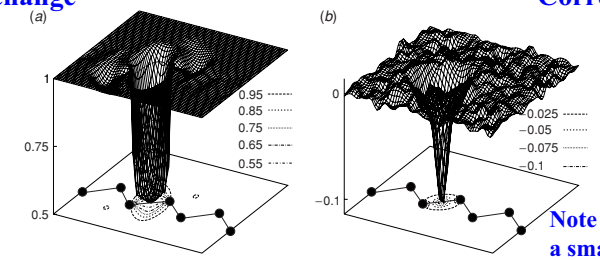


Figure 5.5. Spin-resolved normalized pair-correlation function $g_{\sigma\sigma'}(r)$ for the unpolarized homogeneous electron gas as a function of scaled separation r/r_s, for r_s varying from $r_s = 0.8$ to $r_s = 10$. Dots, QMC data of [302]; dashed line Perdew–Wang model; solid line coupling constant integrated form of [303]. From [303].

Exchange-correlation (x-c) hole in silicon

- Calculated by Monte Carlo methods

Exchange **Correlation**



Note this is on a smaller scale

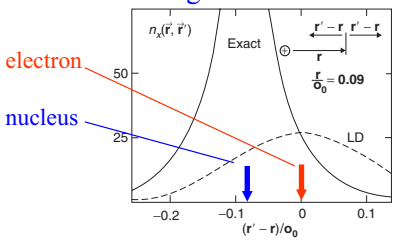
Hole is reasonably well localized near the electron
Supports a local approximation

Fig. 7.3 - Hood, et. al. [349]

Exchange and Correlation in an atom

- Exchange and correlation → around each electron, other electrons tend to be excluded – "x-c hole"
- E_{xc} is the interaction of the electron with the "hole" – which involves only a spherical average

Exchange hole in Ne atom



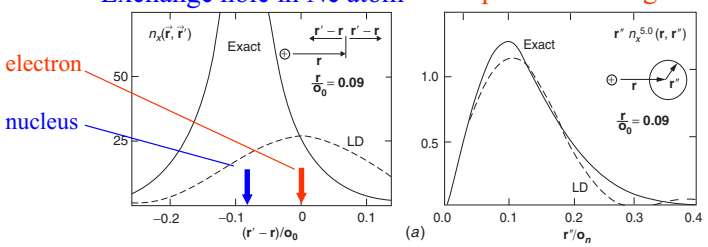
Is the local density approximation a good approximation?

Note that Exc[n] includes both Exchange and Correlation

- Exchange and correlation → around each electron, other electrons tend to be excluded – "x-c hole"
- E_{xc} is the interaction of the electron with the "hole" – which involves only a spherical average

Exchange hole in Ne atom

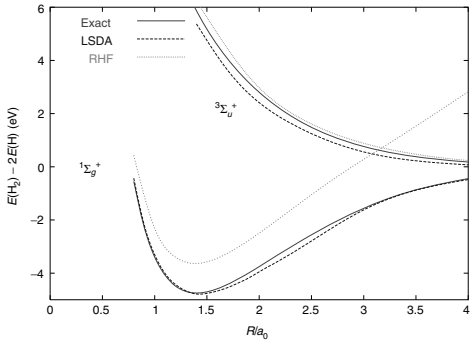
Spherical average



Supports the local density approximation! (Gunnarsson, et. al.)

Example of H_2 Molecule

- It seems ridiculous to approximate the correlation of the two electrons by the LDA derived from the homogeneous gas!
- How good are the results?



Very Good!

Supports a local approximation – exact is the homogeneous limit and amazingly good for the H_2 molecule!

Reasons L(S)DA is so successful

- **It is remarkable that the local approximation – based on the homogeneous gas is so good for inhomogeneous systems**
- **Why is it so good? Rationalizations:**
  - Only the spherical average matters for the energy
    It can be terrible for the actual non-spherical correlation !
  - It works for Ne and H2 (no one knows why!
  - It is based upon an actaul system, so it obeys sum rules, unlike many attempts at improvements

But it is really NOT so good when examined closely!

- It does not give "chemical accuracy"
  Next slide – improvements!

Generalized Gradient Approximations

- **Why are there many GGAs whereas there is only one LDA**
  (we ignore the small differences in the way the LDA is parametrized)
- **Why is it "generalized"?**
  - The direct expansion is a disaster -- if it is correct for small gradients it increases much too much for large gradients
- **The various GGAs differ mainly in how the expansion is cut off for large gradients**
- **Next slides**
  - Definition of terms
  - Behavior of GGAs as a function of the magnitude of the gradient

Generalized Gradient Approximations

- **Useful way to define a GGA**

$$E_{xc}^{GGA}[n^{\uparrow}, n^{\downarrow}] = \int d^3r n(\mathbf{r}) \epsilon_{xc}(n^{\uparrow}, n^{\downarrow}, \nabla n^{\uparrow}, \nabla n^{\downarrow})$$
$$\equiv \int d^3r n(\mathbf{r}) \epsilon_x^{hom}(n) F_{xc}(n^{\uparrow}, n^{\downarrow}, \nabla n^{\uparrow}, \nabla n^{\downarrow}),$$

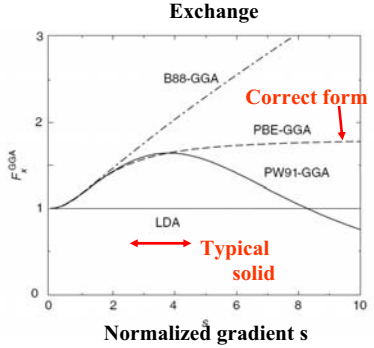
$F_x = F_c = 1$ for LDA, $F_x > 1$, $F_c < 1$
Why?

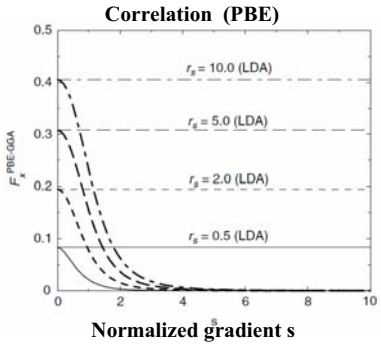
- **Normalized gradient**

$$s = \frac{|\nabla n|}{(2k_F)n} = \frac{|\nabla n|}{2(3\pi^2)^{1/3}(n)^{(4/3)}}.$$

Generalized Gradient Approximations

- **Examples of Functionals**
  (I like PBE because it has a simple derivation – no free parameters)
  See text





What is improved by GGAs

- **Strongly bound solids (Si, C, ….) not a large effect**
  - **Often slightly worse than LDA**
- **The large is for localized systems – atoms, molecules**
  - **The normalized gradient is large in the outer regions where the density is small**
  - **Often a very large effect – much closer to experiment**
- **This is why DFT is used so much in chemistry!**
  - **For large molecules**
  - **This is why Kohn got the Nobel prize in chemistry!**
  - **Much work to have "chemical accuracy"**

The main challenges for GGAs

- The main challenge is make a GGA that is accurate for both:
  - Extended states in solids - small but important gradients
  - Localized`states in molecules, atoms
- Examples:
  - Surfaces have both types of regions
  - Adsorption, catalysts, ……
- Examples of construction

See Ch. 8, App. B

  - PBE – defines correlation first! Finds exchange term that cancels an error in correlation
  - Empirical – many functions defined in chemistry literature that are fit the sets of molecules

Other functionals: Van der Waals (VdW)

- Van der Waals – very recent

Not in book

  - General idea: include the non-local correlated quantum fluctutations of the dipoles`that give $1/r^6$ interaction. This depends upon the polarizabilities χ

- Why was it difficult to find a good VdW functional
  - Difficult to find good expressions for $\chi[n]$ as a functional of the density
  - Difficult to find a form that goes continuously from the VdW limit to strongly bonded cases where GGA works

Reference: Langreth, et al

Other functionals: Hybrid, Orbital dependent

- Hybrid – mixed Hartree-Fock and DFT
  - Main improvement is in the excitation energies
  - Important for many problems – especially when typical GGAs give the wrong ground state

See Ch. 8

- Orbital dependent
  - General idea: Kohn-Sham introduced orbitals for the kinetic energy – the next step is orbitals in $E_{xc} \Longrightarrow E_{xc}[\psi_i]$
  - Can be large improvement if there are both localized and delocalized localized functions
  - Example – localized 3d states of transition metals
    - "LDA+U" adds extra repulsive interaction for 3d states

Magnetic Systems
Local Spin Density Approximation

In principle, in Hohenberg-Kohn the density is enough

But in Kohn-Sham one must put in a spin dependent E_{xc}

Why?

- The exchange energy is easily generalized since exchange is always a sum of terms for $\uparrow$ and $\downarrow$ spins.
- Correlation involves both spins, so it must be parametrized in terms of both $n_\uparrow$ and $n_\downarrow$.
- Thus we are led to the *LSD* form $E_{xc}[n_\uparrow, n_\downarrow]$. All widely used forms are based upon fitting the energies found by Quantum Monte Carlo calculations for interacting electrons done by Ceperley and Alder.
- Parametrized forms given by Perdew and Zunger, 1981, and Vosko, Wilk, and Nusair, 1980.

Experimental bands in Na – approximate gas

In principle, in Hohenberg-Kohn the density is enough

Back to the basic question:

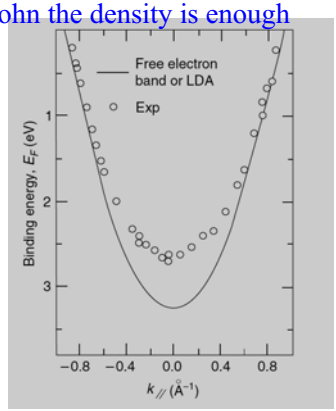
Are eigenvalues from KS calculations of any use?

Why do people often interpret them as approximate bands?

Test on the homogeneous gas

The KS bands MUST always be just the simple kinetic energy ~ k^2

Lets compare with real bands - Na



Not so bad!

Supports the idea that in systems not too different from the homogeneous gas the bands will be reasonable

C, Si, alkali metals, the s-p bands in transition metals (NOT the d bands), . .