

ASESMA – 2010

Exchange correlation functionals

The ones use in our project

What do we want to understand?

What do we want to calculate?

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Overview – Key points for using functionals I

- **Why are there so many functionals?**

- **Because that is a hard problem!**

- Every functional is an approximation

- No practical functional can work for everything!

- **Because there are so many types of materials where it is important to have accurate results for the energy, forces, etc.**

- Molecules (small - large)

- (Most of the functionals are made for these problems)

- **Walter Kohn got the Nobel Prize in Chemistry**

- Solids (more localized – delocalized states)

- **What do we want to study**

- For this project we want to study solids that contain Si and O

- We want accurate energies for different phases

- The appropriate choices are ones that work in such systems

- **Check the literature for which ones have been tested!**

Overview – Key points for using functionals II

- Which methods will we use?

- Pseudopotentials, Plane waves

- The pseudopotential must be accurate --- must be tested

- We will use ones that have been tested

- The pseudopotential must be consistent with the functional!

- We will use ones generated for the chosen functionals

- at least one especially for us (you

- Thanks Renata, Paolo, Stefano!

- As ALWAYS --- we must be sure that all aspects are done correctly and to the needed accuracy

- Energy cutoff, k-points, . . .

Local Density Approximation - LDA

- Described in the lectures by Daniel Joubert
- Two main functional forms
 - Both are fitted to the same data calculated with Quantum Monte Carlo methods – Ceperley – Alder (1980)
 - The QMC results are essentially exact
 - The difference is the functional form fitted to the data
 - Perdew - Zunger (PZ) Phys Rev 23, 5048 (1981)
 - Vosko – Wilkes - Nusair (VWN) Can. J. Phys. 58, 1200 (1988)
 - (See original papers, my book – Ch. 8 and App. B)
 - The results should be VERY similar
- This is the ONLY functional that is unique
(except for the very small differences in the forms)
- ALL others have additional features that are special to the particular form

Local Density Approximation - LDA

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

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

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., Ashcroft and Mermin, p. 411)

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

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

- Correlation found by:
Ceperley and Alder, 1980

Generalized Gradient Approximation(s)

There are many GGA's because the approximations are not universal. The effect of all of them is too:

- Increase the magnitude of the exchange energy, i.e., lower the total energy
- Decrease the magnitude of the correlation energy, i.e., raise the total energy. But this is a smaller effect than the exchange.

ϵ_x The effects can be expressed as a factor F_{xe} multiplying the usual local exchange energy

$$E_{xe}^{GGA}[n^\uparrow, n^\downarrow] = \int d^3r n(\mathbf{r}) \epsilon_{xe}(n^\uparrow, n^\downarrow, \nabla n^\uparrow, \nabla n^\downarrow)$$

$F_{xc} = F_x + F_c$ $\equiv \int d^3r n(\mathbf{r}) \epsilon_x^{hom}(n) F_{xe}(n^\uparrow, n^\downarrow, \nabla n^\uparrow, \nabla n^\downarrow),$ (34)

where F_{xe} is dimensionless, $\epsilon_x^{hom}(n)$ is the exchange energy of the unpolarized gas, and we can define a reduced dimensionless gradient proportional to the fractional variation in density normalized to the average distance between electrons $r_s \propto 1/k_F$.

$$s = \frac{|\nabla n|}{(2k_F)n} = \frac{|\nabla n|}{2(3\pi^2)^{1/3}(n)^{4/3}}. \quad (35)$$

Generalized Gradient Approximation(s)

- **Why is it “generalized”**

- **A direct expansion does NOT WORK**
- **For large gradients it causes large errors**
- **“Generalized” means the functional is defined in some way that reduces the effects for large gradients**

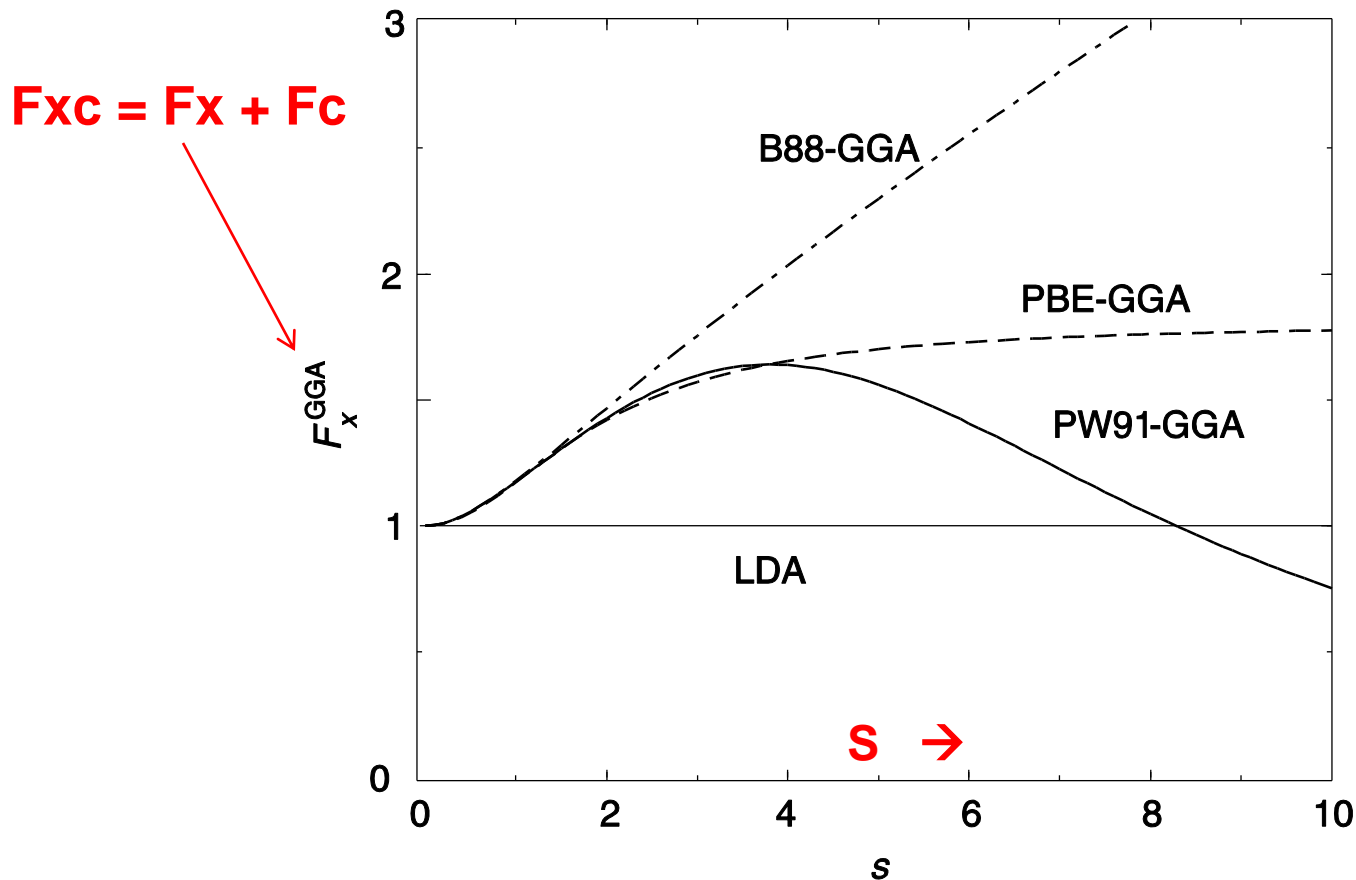
- **Why is it so hard?**

- **One reason is that there is a lot of cancellation between exchange and correlation**
- **You might think that exchange is only Hartree-Fock and I can do that very well**
- **The results get WORSE unless you combine with correlation in a physical, accurate way**
- **In fact partial inclusion of Hartree-Fock is exactly what is called “Hybrid Functionals”**

J. P. Perdew and K. Burke, ‘Comparison shopping for a gradient corrected density functional’, *Int. J. Quant. Chem.* 57:309–319, 1996.

Generalized Gradient Approximation(s)

EXCHANGE is INCREASED in MAGNITUDE— more NEGATIVE
Examples



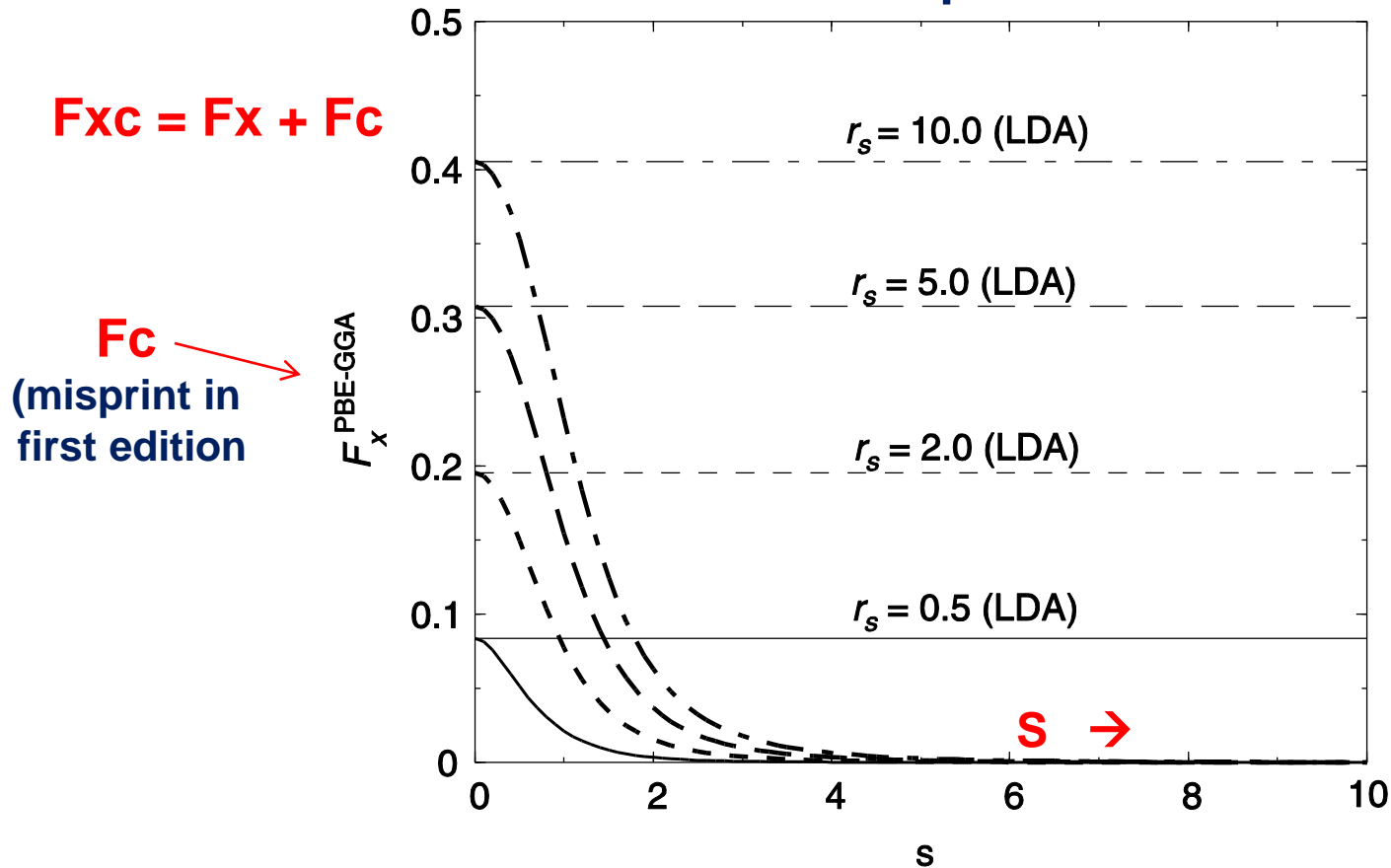
Most relevant range for typical materials $s \sim 0$ to 3

Larger for larger gradients

Larger for atoms, molecules, localized states in solids for example 3d)

Generalized Gradient Approximation(s)

CORRELATION is DECREASED in MAGNITUDE– less NEGATIVE
Examples



Most relevant range for typical materials S ~ 0 to 3

SMALLER for larger gradients

SMALLER for atoms, molecules, localized states in solids for example 3d)

Generalized Gradient Approximation(s)

- **EXCHANGE is LARGER** in magnitude than **CORRELATION**
 - A big surprise to me!
 - But not really a surprise **AFTER** you think hard about it
 - It is due to the fact that we have a **self-interaction** (an electron interacts with itself!) this is a large positive energy that is **WRONG**
 - Exchange is the negative energy that removes this error!
 - Approximate exchange functionals do not correct it completely - improved by “Self Interaction Correction”
- **CORRELATION SMALLER** for large gradients
 - Not really a surprise **AFTER** you think hard about it (You can ask me sometime)

Nicola Marzari
Next part of this lecture

Generalized Gradient Approximation(s)

- **LYP - functional for correlation**

- Lee, Yang, Parr, Phys Rev B 37, 785 (1998)

- Development of the Colle-Salvetti correlation-energy formula (**Derived from the He atom**) into a functional of the electron density

(Originally derived using a kinetic energy density – see later slide when this was used in newer “Meta-GGAs”)

- **BLYP**

- Added an expression for exchange by Becke constructed to apply to atoms and molecules

- **Fit to get the tails of the wavefunction right for atoms**

- Becke, Phys Rev A 38, 3098 (1988)

- **ALL information is from atoms!**

Generalized Gradient Approximation(s)

- **PBE**

J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 1996.

- A functional you can understand!
 - Reduces to the LDA for gradients $s = 0$
- Find a form for correlation first (!)
- Then find form for exchange that fits known limits
- Formulas in paper or book, App. B
- **A LL information is from the electron gas**

Generalized Gradient Approximation(s)

•WC

Wu and Cohen, Phys Rev B 73, 235116 (2006)

•Basic idea:

The exchange depends upon the density over some region around a given point

•Implementation: Higher powers of the reduced gradient s

$$F_X = 1 + \kappa - \kappa/(1 + x/\kappa), \quad (4)$$

$$x = \frac{10}{81}s^2 + \left(\mu - \frac{10}{81} \right) s^2 \exp(-s^2) + \ln(1 + cs^4), \quad (6)$$

Moving On – Beyond GGAs

- **Perdew's Ladder**
(Perdew)
- **RPA – many body methods**
- **Hybrid Functionals**
(include a fraction of Hartee-Fock exchange)
- **MetaGGAs**
(include kinetic energy density)
- **GGAs**
(include gradients)
- **LDA**

Meta -GGA(s)

•TPSS

Tao, Perdew, Staroverov, and Scuseria, PRL 91, 146401 (2003)

Functional of local density, gradient, Laplacian, and **Kinetic energy density**

From the original paper:

The first three rungs of “Jacob’s ladder” Find of approximations can be summarized by the formula

$$E_{xc}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n \epsilon_{xc}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \tau_{\uparrow}, \tau_{\downarrow}), \quad (1)$$

where $n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})$ is the total density, and

$$\tau_{\sigma}(\mathbf{r}) = \sum_i^{\text{occup}} \frac{1}{2} |\nabla \psi_{i\sigma}(\mathbf{r})|^2 \quad (2)$$

Kinetic energy density

Hybrid Functionals

- Mix Hartree-Fock with DFT

First example – Becke - 50% HF – 50% DFT - not used here

- Three parameter model of Becke -

J. Chem. Phys. 98, 5648 ~1993

$$E_{xc}^{hyb} = E_{xc}^{LSD} + a_0(E_x - E_x^{LSD}) + a_x(E_x^{GGA} - E_x^{LSD}) + a_c(E_c^{GGA} - E_c^{LSD}), \quad (4)$$

$$a_0 = 0.20, a_1 = 0.72, a_3 = 0.81$$

B3LYP

Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. J. Phys. Chem. 1994, 98, 11623.

$$E_{xc}^{B3LYP} = (1 - a_0)E_x^{LSDA} + a_0E_x^{HF} + a_x\Delta E_x^{B88} + a_cE_c^{LYP} + (1 - a_c)E_c^{VWN} \quad (2)$$

$$\text{Same } a_0 = 0.20, a_1 = 0.72, a_3 = 0.81$$

Hybrid Functionals

- **PBE0 -**

J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. 105, 9982 1996

$$E_{xc}^{hyb}(n=4) = E_{xc}^{DFA} + \frac{1}{4} (E_x - E_x^{DFA}).$$

- **Derived from theory – no parameters**
(note 0.25 close to 0.20 found by fitting in B3LYP)

A LL information is from the electron gas

Conclusions

- **You will test and compare**
- **Functionals derived from the electron gas vs ones derived from atoms and molecules**
- **Functionals with local (density plus gradients)**
- **Vs non-local exchange in Hartree Fock**
- **Functionals involving the kinetic energy density**