DFT: Exchange-Correlation

Local functionals, exact exchange and other post-DFT methods

Outline

- Introduction
- What is exchange and correlation?
- Quick tour of XC functionals
 - (Semi-)local: LDA, PBE, PW91, WC, etc
 - Ab intitio non-local: HF, sX
 - Empirical non-local (hybrids): B3LYP, HSE
 - DFT+U
- When should they be used
- Closing statements

DFT and exchange-correlation

- Basically comes from our attempt to map 1 Nbody QM problem onto N 1-body QM problems
- Attempt to extract single-electron properties
 from interacting N-electron system
- These are quasi-particles, or Kohn-Sham eigenstates

Standard Definition

 $\int \frac{1}{2} \nabla^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} - \sum_{i,I} \frac{Z_I}{|r_i - R_I|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|} \Psi(r_1, r_2, ...) = E \Psi(r_1, r_2, ...)$ $n^{exact}(r) = \int ... \int \Psi^*(r_1, r_2, r_3, ...) \Psi(r_1, r_2, r_3, ...) dr_2 dr_3 ...$

Kohn-Sham Equations

$$\begin{pmatrix} -\frac{1}{2}\nabla_{i}^{2} + \frac{1}{2}\int\frac{n(r')}{|r-r'|}dr' - \sum_{I}\int\frac{Z_{I}n(r')}{|r'-R_{I}|}dr' + \frac{1}{2}\sum_{I\neq J}\frac{Z_{I}Z_{J}}{|R_{I}-R_{J}|} + \mu_{xc}[n(r)]\psi_{i}(r) = \varepsilon_{i}\psi_{i}(r) \\ n^{DFT}(r) = \sum_{i}\psi_{i}^{*}(r)\psi_{i}(r) \end{pmatrix}$$

$$n^{exact}(r) = n^{DFT}(r)$$

Exchange-Correlation Functionals

Alternative Exact Definition

Exact XC interaction is unknown

Within DFT we can write the <u>exact</u> XC interaction as

$$E_{xc}[n] = \frac{1}{2} \iint n(r) \frac{n_{xc}(r,r')}{|r-r'|} dr dr'$$

This would be excellent if only we knew what n_{xc} was!

This relation defines the XC energy.

It is simply the Coulomb interaction between an electron an *r* and the value of its XC hole $n_{xc}(r,r')$ at *r*'.

Exchange-Correlation Functionals

The XC hole

 From the Pauli exclusion principle we have for a given r

$$\int n_{xc}(r,r')dr' = -1$$

Which is known as the **sum rule**.



Non-local Nature of XC Hole



Exchange-Correlation Functionals

XC Interaction at Surfaces



As an electron approaches a surface (distance *x* away) then:
Coulomb interaction

•Coulomb interaction appears to have 1/x singularity.

•Fixed by properties of XC hole.

Generalities

All functionals are approximations

Reports of 'Failures of DFT' is actually a report of a failure of the XC functional

No functional (so far) is accurate(?) for all properties of interest

No matter what functional is 'invented' someone will always find a case where it fails

Any functional can be applied to any electronic structure problem

In this sense it is *ab initio* but we use experience and intuition to decide which one to use

Exchange-Correlation Functionals

Jacob's Ladder 1

The simplest XC functional is the local density approximation (LDA)

$$E_{xc}^{LDA}[n(r)] = \int n(r)\varepsilon_{xc}^{\text{hom}}[n(r)]dr$$

This is the simplest density functional. It was used for a generation in materials science, but is not accurate enough for many chemical purposes

Typical errors

Over-binds (binding energy too large)
 OUnderestimates lattice parameters
 OPhase stability incorrect order
 Energetics of magnetic materials in error

Jacob's Ladder 2

The **generalised gradient approximation** (GGA) contains the next term in a derivative expansion of the charge density:

$$E_{xc}^{GGA}[n(r)] = \int n(r) \varepsilon_{xc}^{GGA}[n(r), \nabla n(r)] dr$$

Typically (but not always) this is more accurate than the LDA

GGA greatly reduce the bond dissociation energy error, and generally improve transition-state barriers

But, unlike LDA, there is no single universal form

Exchange-Correlation Functionals

Why the GGA?

- LDA depends only on one variable (the density).
- GGA's require knowledge of 2 variables (the density and its gradient).
- In principle one can continue with this expansion.
- If quickly convergent, it would characterise a class of many-body systems with increasing accuracy by functions of 1,2,6,...variables.
- How fruitful is this? Depends on parameterisation used, but it will always be *semi-local*.

Jacob's Ladder 3

Next come the meta-GGA's

Instead of using $\nabla^2 n$ typically the kinetic energy is used (same idea, in principle)

 $E_{xc}[n(r), \nabla n(r), \nabla^2 n(r)]$ or $E_{xc}[n(r), \nabla n(r), \nabla^2 \psi(r)]$

Example: TPSS (J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **91**, 146401 (2003))

Hartree-Fock

Exchange is essentially the Pauli exclusion principle

Quantum mechanically, electrons are Fermions hence many particle wavefunction is anti-symmetric

$$\Psi(r_1,r_2) = -\Psi(r_2,r_1)$$

which after some generalisation we find the energy is

$$E_{X}^{non-local} = -\frac{1}{2} \sum_{ij,kq} \iint \frac{\psi_{ik}^{*}(r)\psi_{ik}(r')\psi_{jq}^{*}(r')\psi_{jq}(r)}{|r-r'|} dr dr'$$

Note: HF can get properties wrong in the opposite direction from DFT

Exchange-Correlation	Stewart Clark - University of	14
Functionals	Durham	

Moving off the ladder: Hybrid Functionals

If a method over-estimates your value of interest and another under-estimates it, then the answer you want can be obtained by taking a bit of both! (You may notice this is not *ab initio*)

This is where things start to go a bit crazy (welcome to the world of making up the answer you want to see – apparently some people call this science)

$$E_{xc} = \alpha E_x^{exact} + (1 - \alpha) E_x^{local} + E_c^{local}$$

[I'm being slightly over-critical here – there is some good science being done with these functionals]

Exchange-Correlation Functionals

Some properties of E_{xc}

The XC interaction for a HEG is known exactly (LDA). For solids, this in a very important limit.

The sum rule is required, but not usually implemented in empirical GGAs

Density scaling:

$$\left[n_l(x, y, z) = l^3 n(lx, ly, lz)\right]$$

Then, for example

$$\lim_{l \to \infty} E_{xc}[n_{l}] > -\infty$$

$$E_{xc}[n_{l}] > lE_{xc}[n]; l > 1$$

$$E_{xc}^{GGA}(n, \nabla n) \rightarrow E_{xc}^{LDA}[n]; \nabla n \rightarrow 0$$

...and many more. However we fit E_{xc} , we don't want to break what we know is correct. There are many GGA's that don't obey known rules.

Exchange-Correlation Functionals

Non-empirical functionals

Such as LDASome GGAs (PW91, PBE, rPBE, WC, PBEsol,...)

Not fitted to any empirical results
These come from known exact conditions
If these conditions are important to your physical value of interest then you should get a reliable result
These functionals often have systematic failures (and successes!) so their reliability can usually be predicted

Some GGA's

- <u>PW91</u>: J. P. Perdew and Y. Wang, "Accurate and simple analytic representation of the electron-gas correlation energy", *Phys. Rev. B* **45** 13244 (1992).
- <u>PBE</u>: J. P. Perdew, K. Burke and M Ernzerhof, "Generalised gradient approximation made simple", *Phys. Rev. Lett.* **77** 3865 (1996).
- <u>RPBE</u>: B. Hammer, L. B. Hansen and J. K. Norskov, "Improved adsorption energies within DFT using revised PBE functionals", *Phys. Rev. B* 59 7413 (1999).
- <u>WC</u>: Z. Wu and R. E. Cohen, "More accurate gradient approximation for solids", Phys. Rev. B 73, 235116 (2006)

Different fits for ab initio GGAs

- PW91 is the first *reasonable* GGA that can be reliably used over a very wide range of materials.
- PW91 contains much of the known *correct* physics of the exchange and correlation interactions.
- PBE is based on PW91 containing the correct features of LDA but the correct (but *hopefully* not important!) features of PW91 that are **ignored** are:
- (1) Correct 2nd order gradient coefficients of e_x and E_c in the slowly varying limit.
- (2) Correct non-uniform scaling of \mathcal{E}_x in the limits where *s* tend to infinity.
- WC is newer re-parameterisation of PBE.

GGA's (Continued)

- The revised PBE (known as RPBE) only differs from PBE functional in the choice of mathematical form for $\epsilon_{\rm x}.$
- It was chosen only for its simplicity (a simpler F(s) than stated previously).
- PBE and RPBE contain the same essential physics and also leave out the same (non-essential?) Physics.
- WC, PBEsol, recently introduced. Somebody will probably get a PhD if they test them thoroughly.

Charge Differences (LDA-PW91)



Exchange-Correlation Functionals

Hybrid Functionals: a few empirical parameters

These include B3LYP, HSE, B88, (PBE0)

$$E_{xc} = \alpha E_x^{exact} + (1 - \alpha) E_x^{local} + E_c^{local}$$

Generally α is around 20-25%. E_c^{local} usually contains parameters

You will get good answers so long as your system is 'close' to the systems where functional was fitted

Exchange-Correlation Functionals

Good(!) empirical (and non-empirical) functionals are widely applicable

None are good at everything, but they are all reasonable for most properties

e.g. PBE is not the best functional for any particular property but is probably the best, on average for all properties.

Good empirical functionals are usually best for the particular property that they were designed for

Over-fitted functionals

Contains many fitted parameters – usually from a few dozen to hundreds of paramters

Usually fitted to a particular set of properties of hundreds of molecules made from atoms of low atomic number

There are many of these in the literature. Beware: every one of these (so far) only works for systems for which they are fitted

The academic/Accelrys version of Castep does not contain any of these

Exchange-Correlation Functionals

Various breeds of functionals: 4 DFT+U

What this is not:

A general method to get the band gap correct for any material

What this is:

Fixes a very specific problem that LDA/GGA can get wrong in highly correlated materials

DFT+U

Standard band theory: in a periodic potential a periodic potential leads to a periodic density

The electronic structure conforms to the same symmetry as the crystal

$$V(r)=V(r+L) \rightarrow n(r)=n(r+L)$$

(appears to be a sensible conclusion!)

If the material has an odd number of electrons per unit cell then it has to be a metal (highest band will be half filled, implying it must cut the Fermi level, i.e. metallic)

Exchange-Correlation Functionals

DFT+U

Materials such as CoO and NiO have an odd number of electrons per crystallographic unit cell but are insulators

Consider

$(Ni^{2+}O^{2-})_2 \rightarrow Ni^{3+}O^{2-} + Ni^{+}O^{2-})$

so that Ni atoms in neighbouring cells have different charges

This happens and opens a band gap (unit cell of electronic structure is twice the size of crystallographic cell)

LDA/GGA does not get this correct

'Highly-correlated' interaction between electrons in Ni atoms missing in LDA/GGA

Exchange-Correlation Functionals

DFT+U

We have (slightly simplified here) a new interaction:

$$E_{LDA+U}[n(r)] = E_{LDA}[n(r)] + E_{U}[\{n_{m}^{I\sigma}\}]$$

where E_U is an additional empirical interaction that mimics the interaction of the 'highly-correlated' *d* electrons

This interaction is fully specified by a U parameter in units of energy. Typical value is 4-5 eV.

Warning: this method is regularly mis-used (and results published)

Exchange-Correlation Functionals

DFT+U in Castep

In the .cell file, add the block:

%block hubbard_u <species> <orbital>:<U parameter, in eV> %endblock hubbard_u

For example

%block hubbard_u Ni d:5.0 %endblock hubbard_u

Exchange-Correlation Functionals

Back to non-local functionals

$$\left(-\frac{1}{2}\nabla^2\psi_i(r) + V^{loc}(r)\psi_i(r) + \int dr' V^{nl}(r,r')\psi_i(r') = \varepsilon_i\psi_i(r)\right)$$

- Note: Integral over all space adds to complexity of problem
- Calculations much more expensive than local methods

Another Non-local Functional: screened-exchange

$$E_{xc}^{nl} = -\frac{1}{2} \sum_{ikjq} \iint dr dr' \frac{\psi_{ik}^{*}(r)\psi_{ik}(r')\psi_{jq}^{*}(r')\psi_{jq}(r)}{|r-r'|} e^{-k_{s}|r-r'|}$$

- •Based on Hartree-Fock
- •Non-local correlation included via screening term
- The potential is:

$$V_{xc}^{nl} = -\frac{1}{2} \sum_{jq} \frac{\psi_{jq}(r)\psi_{jq}^{*}(r')}{|r-r'|} e^{-k_{s}|r-r'|}$$

Exchange-Correlation Functionals

Plane wave representation

$$E_{xc}^{nl} = -\frac{2\pi}{V} \sum_{ikjq} \sum_{G,G',G''} \frac{c_{ik}^{*}(G)c_{ik}(G')c_{jq}^{*}(G'+G'')c_{jq}(G+G')}{|q-k+G''|^{2}+k_{s}^{2}}$$

- Note:
 - Double sum over bands
 - Double sum over k-points
 - Triple sum over plane waves (aargghh!)

•Fortunately there's a clever FFT method that reduces this to

$$N_{plwv} \log(N_{plwv}) N_{bands}^2 N_{kpts}^2$$

Exchange-Correlation Functionals

Non-local: how expensive?





Parallel Performance



Why bother with this expense?



Exchange-Correlation Functionals

Example of non-local functionals: Antiferromagnetic FeO

PBE

LDA+U



Example of non-local functionals: Antiferromagnetic FeO

sX

PBE0



Some suggestions

- LDA
 - Nice covalent systems
 - Simple metals
- LDA+U
 - Mott insulators and highly correlated materials
- GGA:
 - Molecules
 - H-bonded materials
 - Highly varying densities (d and f states)
 - Some nasty metals
 - Most magnetic systems
- Non-local hybrids and sX:
 - Band gaps (with caution)
 - Some nasty magnetic systems (again, with caution)
- Note: VdW materials not on this list new functionals claiming vdW to be implemented soon