DFT: Exchange-Correlation

Local functionals, exact exchange and other
post-DFT methods

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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, OEP
  - Empirical non-local (hybrids): B3LYP, HSE
  - DFT+U
  - DFT+D
  - Beyond DFT: GW
- Appropriate Use
- Closing statements

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Density Functional Theory

- Foundation is Hohenberg-Kohn-Sham approach

  N-electron system $\quad\quad\Longrightarrow\quad\quad$ auxiliary KS system

  $n(\boldsymbol{r})$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $n(\boldsymbol{r})$

- Auxiliary system has *same* electronic density as N-electron system

- Auxiliary system particles are *non-interacting*

  $\quad\quad\Longrightarrow\quad$ Kohn-Sham equations

$$\left(-\hbar^2/2m\nabla^2 + v_{ext}(r) + v_{Hartree}(r) + v_{xc}(r)\right)\varphi_i(r) = \varepsilon_i\varphi_i(r)$$

$$n(r) = \sum_i \varphi_i^*(r)\varphi_i(r)$$

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Density Functional Theory

- Hohenberg-Kohn-Sham approach turns an intractable N-body problem into N coupled one-body problems

- This is tractable!

- QM exchange-correlation effects in $v_{xc}(r)$

- This is the great unknown in DFT – we must approximate

- Commonly used approximations: LDA, GGA, BLYP, B3LYP …..
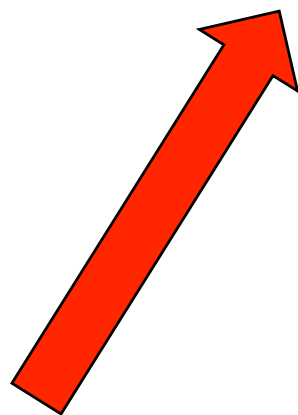
A Formal Definition

We can formally define the XC energy through:

$$E_{xc}\big[n(\vec{r})\big] = T\big[n(\vec{r})\big] - T_s\big[n(\vec{r})\big] + E_{ee}\big[n(\vec{r})\big] - E_H\big[n(\vec{r})\big]$$

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A Formal Definition

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Exact kinetic energy

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Exact kinetic energy

KS kinetic energy

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A Formal Definition

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Exact kinetic energy

KS kinetic energy

Exact e-e interaction

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A Formal Definition

We can formally define the XC energy through:

$$E_{xc}[n(\vec{r})] = T[n(\vec{r})] - T_s[n(\vec{r})] + E_{ee}[n(\vec{r})] - E_H[n(\vec{r})]$$

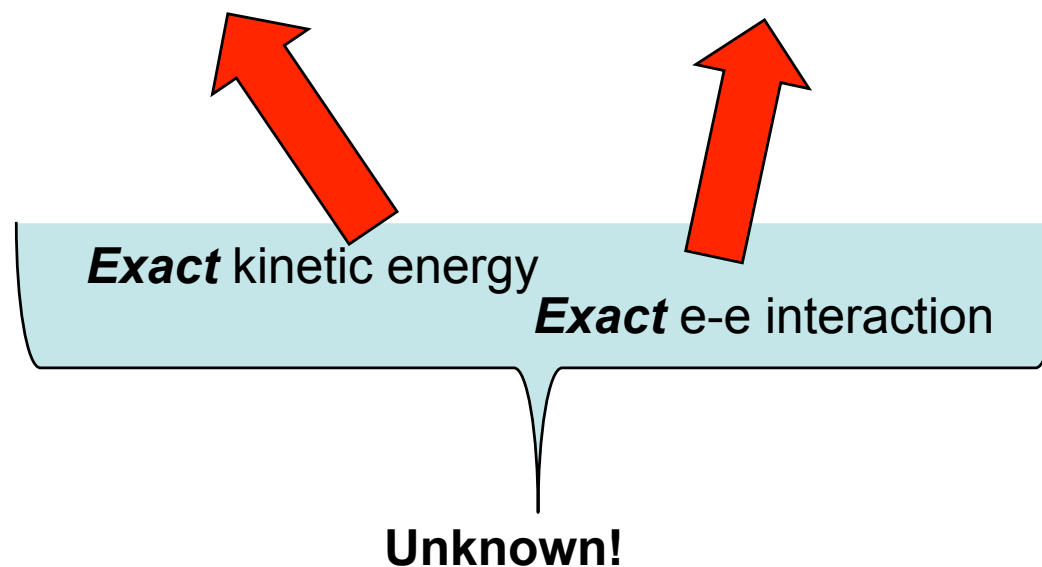*Exact* kinetic energy

KS kinetic energy

Exact e-e interaction

Hartree energy

A Formal Definition

We can formally define the XC energy through:

$$E_{xc}[n(\vec{r})] = T[n(\vec{r})] - T_s[n(\vec{r})] + E_{ee}[n(\vec{r})] - E_H[n(\vec{r})]$$

***Exact* kinetic energy**

***Exact* e-e interaction**

Unknown!

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Alternative Exact Definition

Exact XC interaction is unknown

Within DFT we can write the exact 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'.

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Properties of XC functional

- Although exact form of XC functional unknown, it must satisfy certain properties

Property	LDA	GGA	HF
Sum rule for XC hole.	✔	✔	✔
Self-interaction correction.	✗	✗	✔*
Derivative discontinuity.	✗	✗	✔
Correct 1/r potential decay.	✗	✗	✔*

- *Only for occupied orbitals.

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Properties of XC functional

Property	LDA	GG	HF
Sum rule for XC hole.			✔
Self-interaction correction.			*
Derivative discontinuity.			✔
Correct 1/r potential decay.	✗	✗	✔*

- XC hole is the displaced charge that forms round a point test charge.

- Sum of displaced charge should be the negative of the charge on the test charge.

- *Only for occupied orbitals.

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Properties of XC functional

Property		LDA	GG	HF
Sum rule for XC hole.				
Self-interaction correction.				
Derivative discontinuity.				
Correct 1/r potential decay.		✗	✗	✔^

- Hartree energy is coulomb interaction of classical charge.

- Contains interactions between electron and itself which are unphysical.

- XC functional should correct this.

- *Only for occupied orbitals.

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Properties of XC functional

Property
Sum rule for XC hole.
Self-interaction correction.
Derivative discontinuity.
Correct 1/r potential decay.

- XC potential should jump discontinuously when infinitesimal amount of charge added to system with integer electrons.
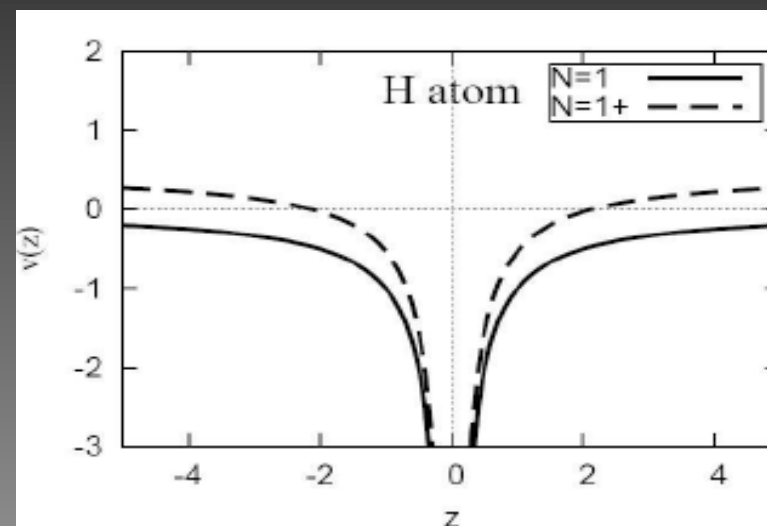
- *Only for occupied orbitals.

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Properties of XC functional

Property	LDA	GG	HF
Sum rule for XC hole.			
Self-interaction correction.			
Derivative discontinuity.			
Correct 1/r potential decay.			

- For finite systems, XC potential should decay as 1/r at long ranges.

- Orbitals should decay with individual exponents. This is not the case with LDA and GGA.

- *Only for occupied orbitals.

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Generalities

- **All functionals are approximations**
  Reports of 'Failures of DFT' are actually reports 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

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Ladder of functionals (LDA)

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

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

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)
- Underestimates lattice parameters
- Phase stability incorrect order
- Energetics of magnetic materials in error

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Ladder of functionals (GGA)

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

Why the GGA?

- LDA depends only on one variable (the density).

- GGAs 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.*

Ladder of functionals (meta-GGA)

Next come the meta-GGAs

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

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

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

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Various breeds of functionals

Non-empirical functionals

- Such as LDA

- Some 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

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Some GGAs

<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 ε_x in the limits where s tend to infinity.

- WC is newer - re-parameterisation of PBE.

Charge Differences (LDA-PW91)
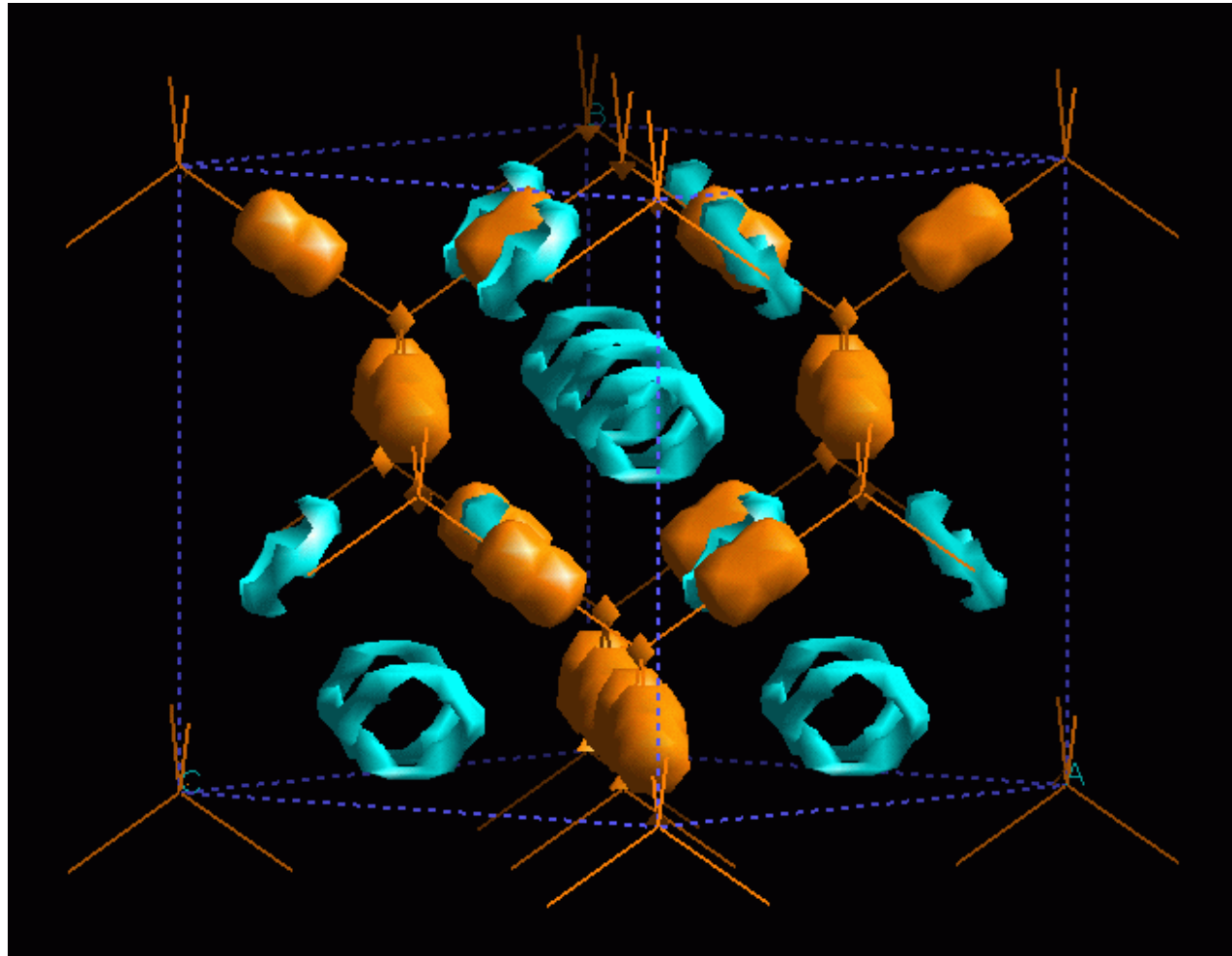
Empirical XC functionals

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

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Various breeds of functionals

Over-fitted functionals

- Contain many fitted parameters – usually from a few dozen to hundreds of parameters

- 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

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Hartree-Fock

Exchange is essentially the Pauli exclusion principle

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

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

which after some generalisation we find the energy is

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

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

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Moving off the ladder: Hybrid Functionals

- If one 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*)

- Leads to a 'zoo' of functionals: aesthetically and conceptually unappealing

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

Hybrid 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 a is around 20-25%. E_c^{local} usually contains parameters

Good answers provided one works with systems 'close' to the set of systems for which the functional was fitted.

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Functionals with Hubbard U

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

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DFT+U

- A brief digression – the Hubbard model:

$$\hat{H} = -t \sum_{\langle ij \rangle} a_{i\sigma}^{+} a_{j\sigma} + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

- 2 limits:

  $t \gg U$:   conventional band solid. Total energy minimised by minimising kinetic energy. Delocalised Bloch states.

  $U \gg t$:   energy minised by minimising potential energy. Avoid double occupancy of sites – localised states.

- At half-filling, each site has one electron – Mott insulator

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DFT+U

- How does this relate to DFT?

$$\hat{H}_{KS-DFT} = -\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(\vec{r}) + v_{Hartree}(\vec{r}) + v_{xc}(\vec{r}) \rightarrow \sum_{ij} h_{ij}\hat{a}_i^+\hat{a}_j$$

- With v_{xc} from LDA/GGA, we have a mean-field solution

- This is the same for occupied *and* unoccupied states

- LDA/GGA **will not** be able to predict a Mott insulator

- LDA/GGA suffers from self-interaction error
      -excessive electron delocalisation

- On-site repulsion U not well-treated: important correlations neglected

- Particularly important for highly localised *d* and *f* electrons

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DFT+U

- In DFT+U split electrons into two subsystems:

  - localised *d* or *f* electrons described by $\dfrac{1}{2} U \sum_{i \neq j} n_i n_j$

  - delocalised *s* and *p* electrons described by LDA/GGA

- Introduce new functional:

$$E^{LDA+U}[n] = E^{LDA}[n] + E^{U}[n_i^{\sigma}] - E^{dc}[n_i^{\sigma}]$$

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DFT+U

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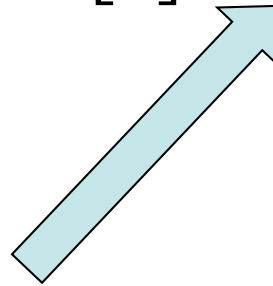
Hubbard U term: describes
localised electrons

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DFT+U

- In DFT+U split electrons into two subsystems:

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$$E^{LDA+U}\left[n\right] = E^{LDA}\left[n\right] + E^{U}\left[n_i^{\sigma}\right] - E^{dc}\left[n_i^{\sigma}\right]$$
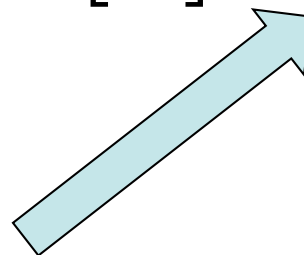
Double counting correction: removes contribution from localised orbitals in LDA/GGA functional

DFT+U

$$E^{LDA+U}[n] = E^{LDA}[n] + E^{U}[n_i^{\sigma}] - E^{dc}[n_i^{\sigma}]$$
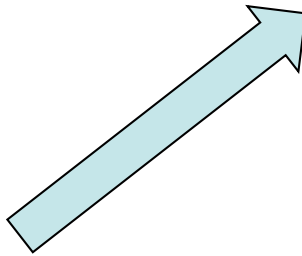
Specifying a *U* parameter in units of energy completely specifies this interaction

•Can compute from first principles (various schemes)

•Or treat as an empirical parameter - Typical value is 4-5 eV.

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

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DFT+U

$$E^{LDA+U}[n] = E^{LDA}[n] + E^{U}[n_i^{\sigma}] - E^{dc}[n_i^{\sigma}]$$
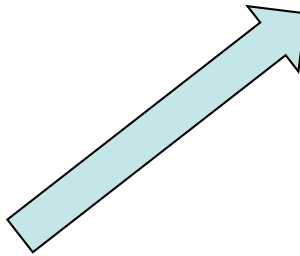
Specifying a *U* parameter in units of energy completely specifies this interaction

- In CASTEP specify in .cell file:

```
%block HUBBARD
Cu 1 d:  2.5
%endblock HUBBARD
```

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Back to non-local functionals

- For non-local functionals solve a *generalised* Kohn-Sham problem:

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

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

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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 (orbital-dependent) potential is:

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

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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
- Computationally painful

• Fortunately there's a clever FFT method that reduces this to
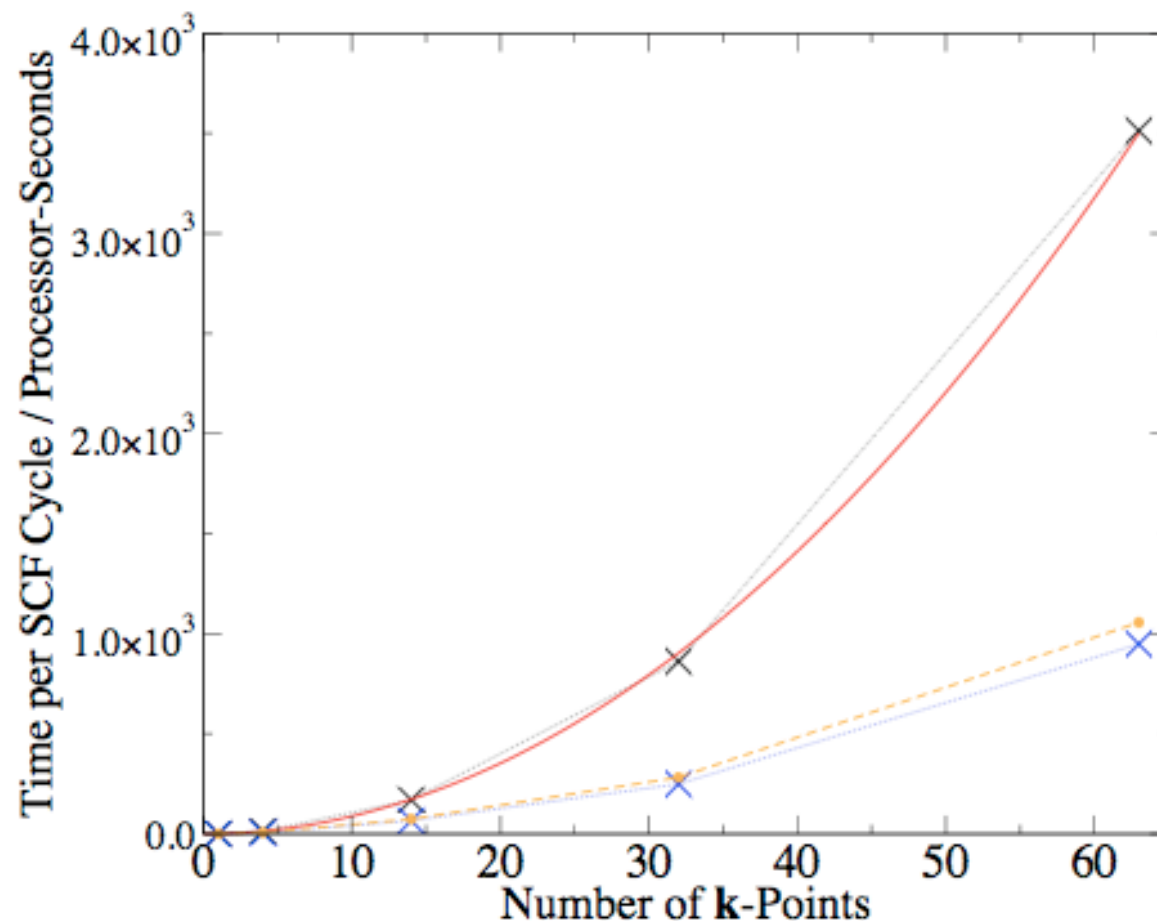
$$N_{plwv} \log(N_{plwv}) N_{bands}^2 N_{kpts}^2$$

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Non-local: how expensive?
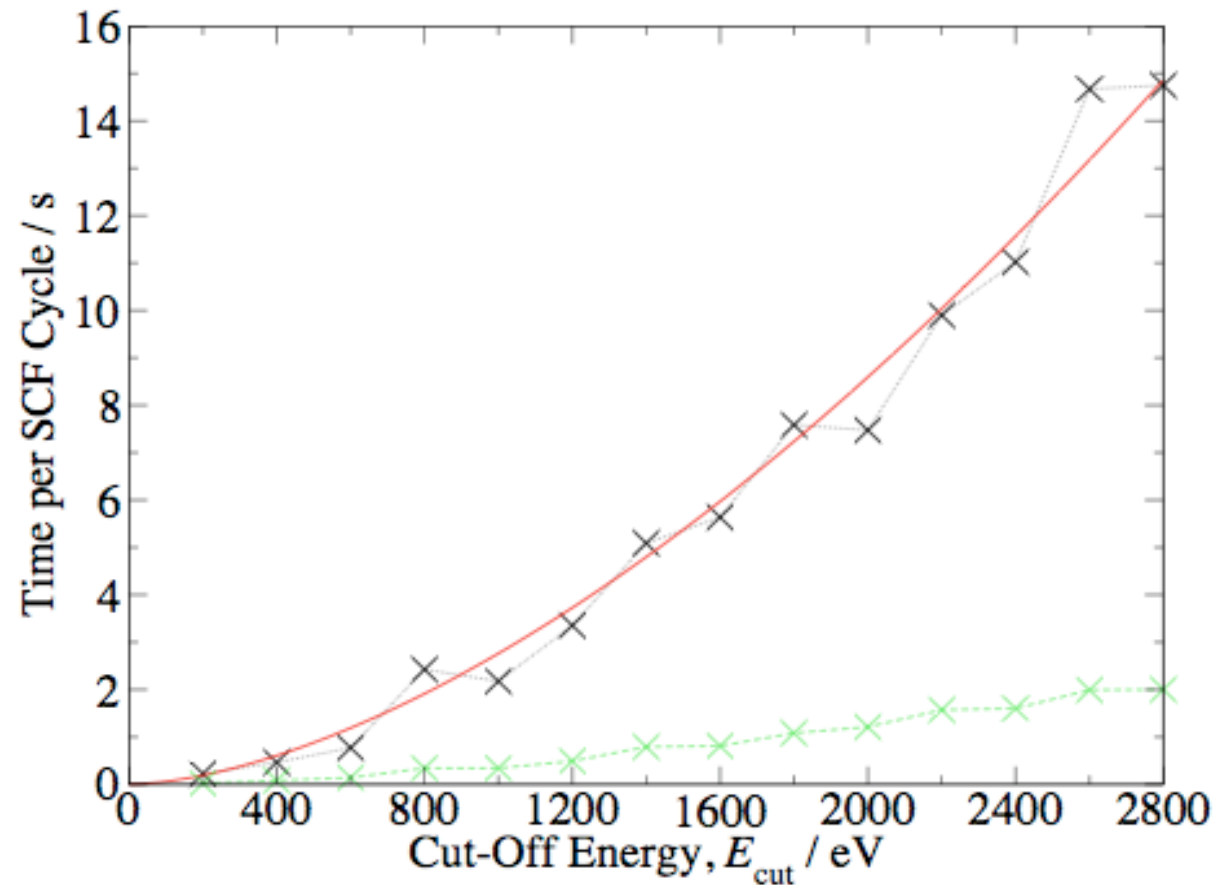
Non-local scales with cut-off as:

$$\sim E_{cut}^{\frac{3}{2}} \log(E_{cut})$$

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Scaling with *k*-points

Scales as:

$$\sim N_k^2$$

LDA is linear with k-points
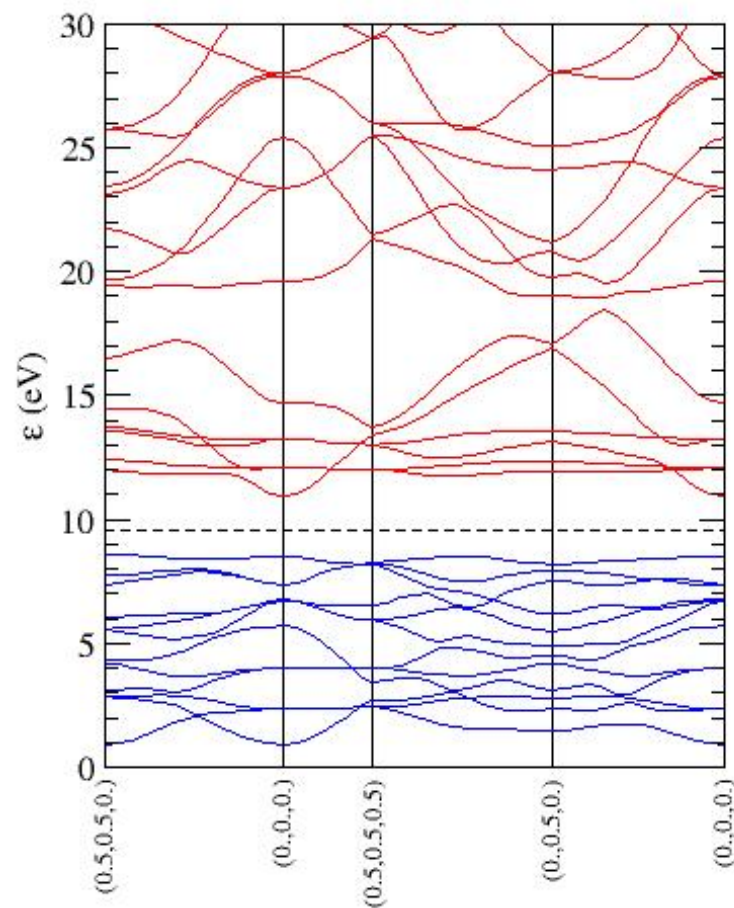
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Why bother with this expense?
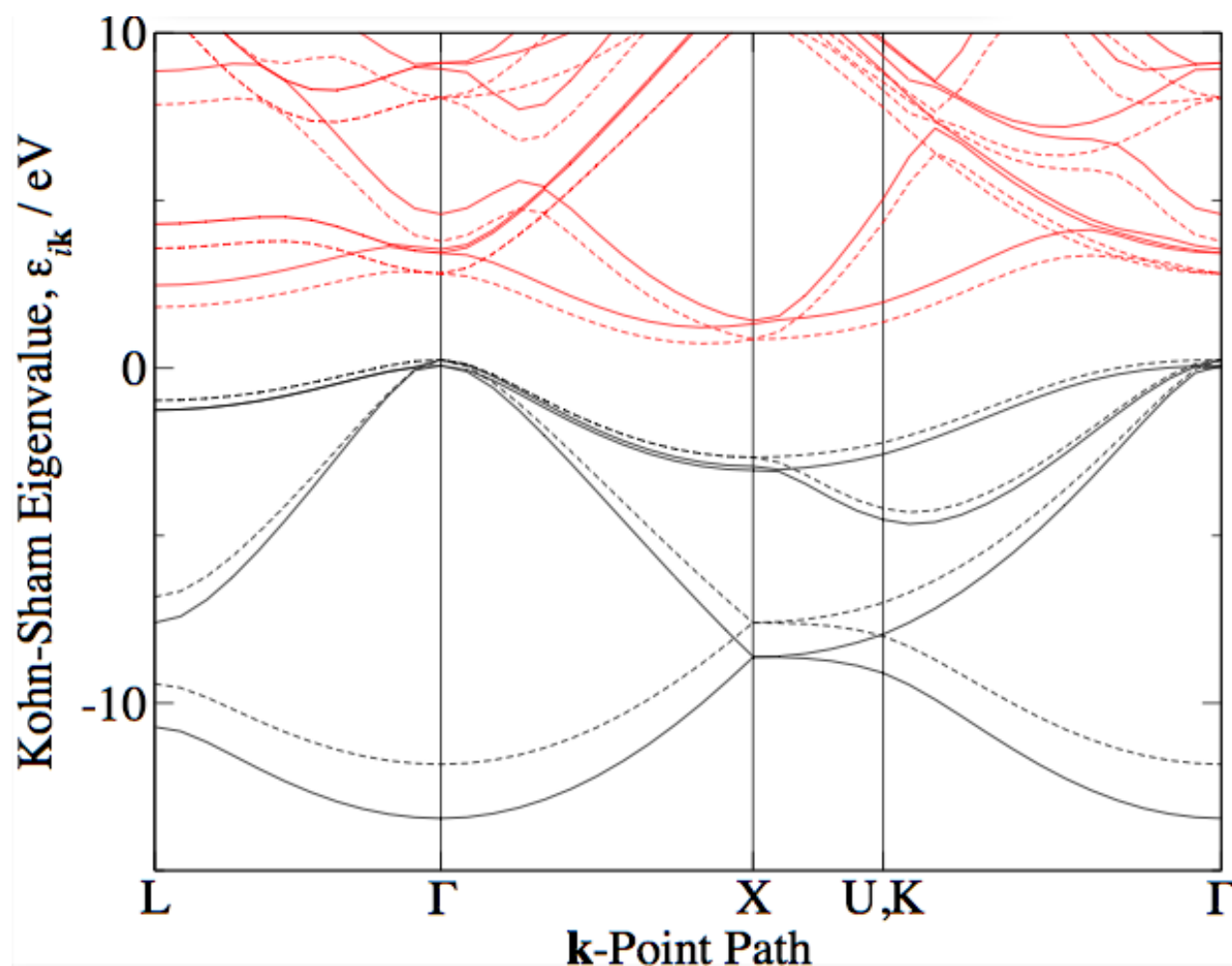
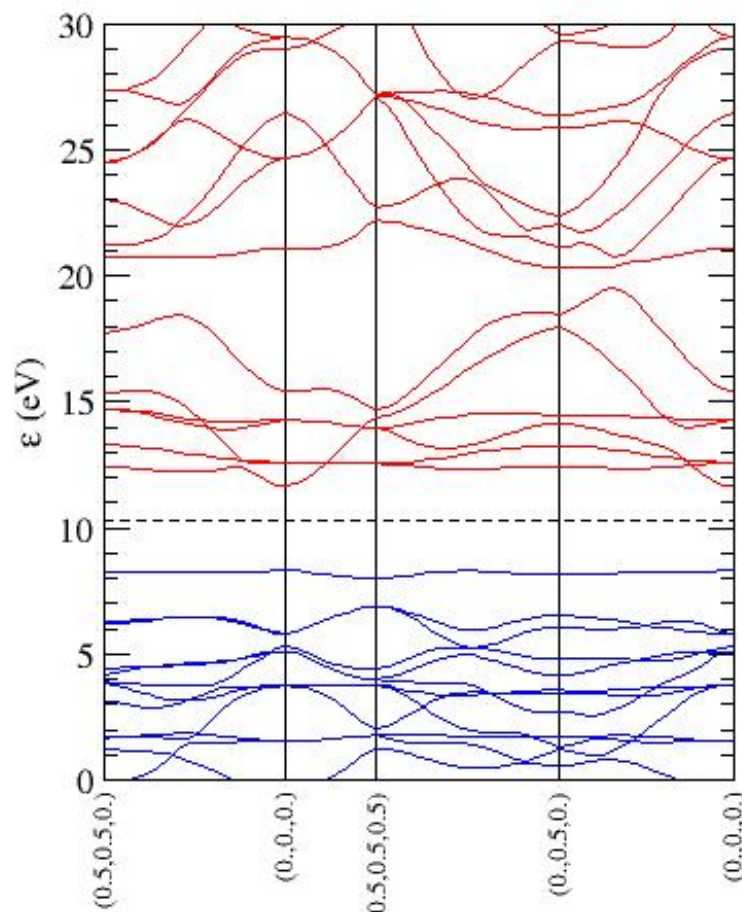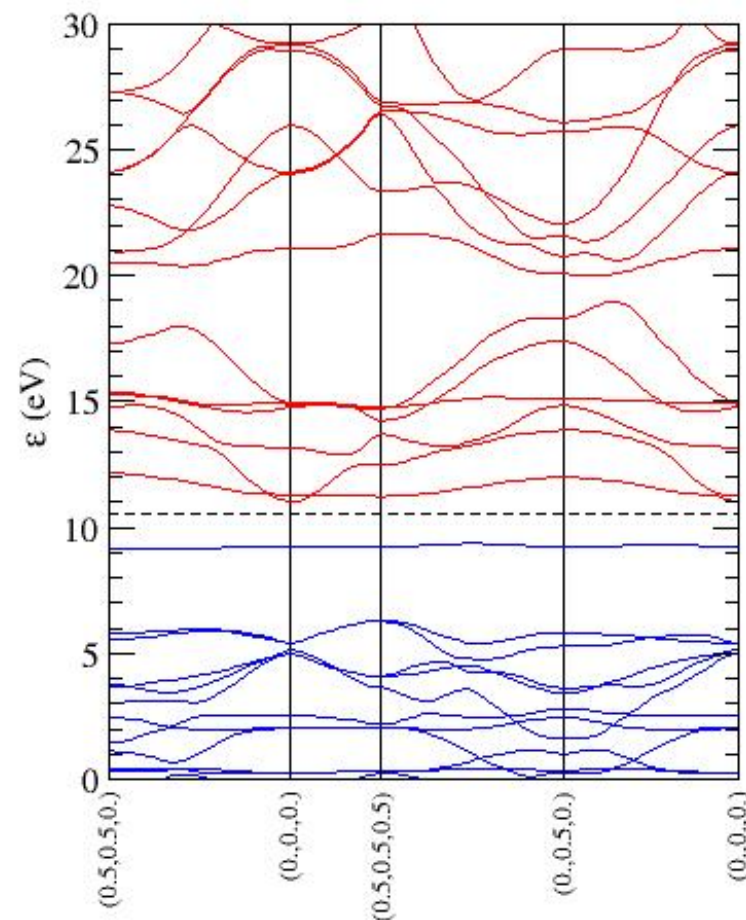# Example of non-local functionals: Antiferromagnetic FeO
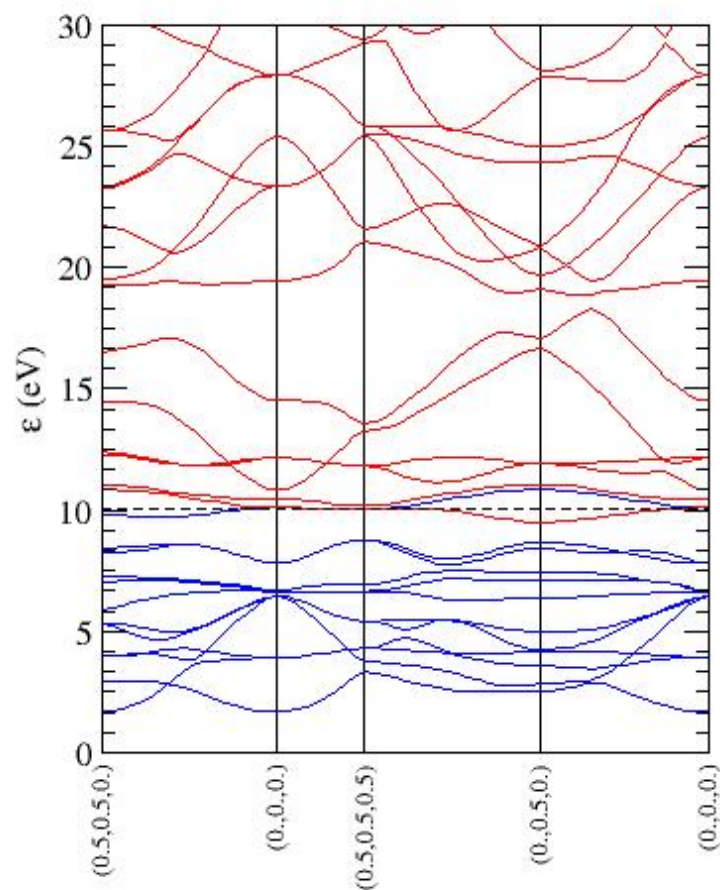
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Example of non-local functionals: Antiferromagnetic FeO

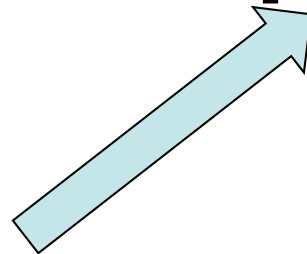# Optimised Effective Potential (OEP)

- Recall exchange energy:

$$E_x = -\frac{1}{2}\sum_{ikjq}\iint drdr' \frac{\psi_{ik}^*(r)\psi_{ik}(r')\psi_{jq}^*(r')\psi_{jq}(r)}{|r-r'|}$$

- Hartree-Fock, sX : **non-local** potential

- OEP: find the optimum **local** potential arising from the non-local HF E_x (i.e. total energy variational w.r.t V)

- Optimised effective potential can be found from solution of

$$\sum_{i=1}^{N^\sigma}\int d\vec{r}'\psi_i^{\sigma *}(\vec{r}')\left[V_{xc}^{OEP}(\vec{r}') - V_{i,xc}^{\sigma,NL}(\vec{r}')\right]G_0^\sigma(\vec{r}',\vec{r})\psi_i^\sigma(\vec{r}) + cc = 0$$

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Optimised Effective Potential (OEP)

$$\sum_{i=1}^{N^\sigma} \int d\vec{r}' \psi_i^{\sigma*}(\vec{r}') \left[V_{xc}^{OEP}(\vec{r}') - V_{i,xc}^{\sigma,NL}(\vec{r}') \right] G_0^\sigma(\vec{r}',\vec{r}) \psi_i^\sigma(\vec{r}) + cc = 0$$

Requires sum over **all** bands
 - in principle infinite
 - computationally impractical
 - represents a serious convergence issue

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Optimised Effective Potential (OEP)

$$\sum_{i=1}^{N^\sigma} \int d\vec{r}' \psi_i^{\sigma*}(\vec{r}') \left[V_{xc}^{OEP}(\vec{r}') - V_{i,xc}^{\sigma,NL}(\vec{r}') \right] G_0^\sigma(\vec{r}',\vec{r}) \psi_i^\sigma(\vec{r}) + cc = 0$$

- In CASTEP we use DFPT to avoid calculation of unoccupied states (Hollins, Clark, Refson and Gidopoulos, PRB **85**, 235126 (2012)

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Optimised Effective Potential (OEP)

- OEP provides 'better' KS bandgaps than LDA/GGA

- Superior to HF
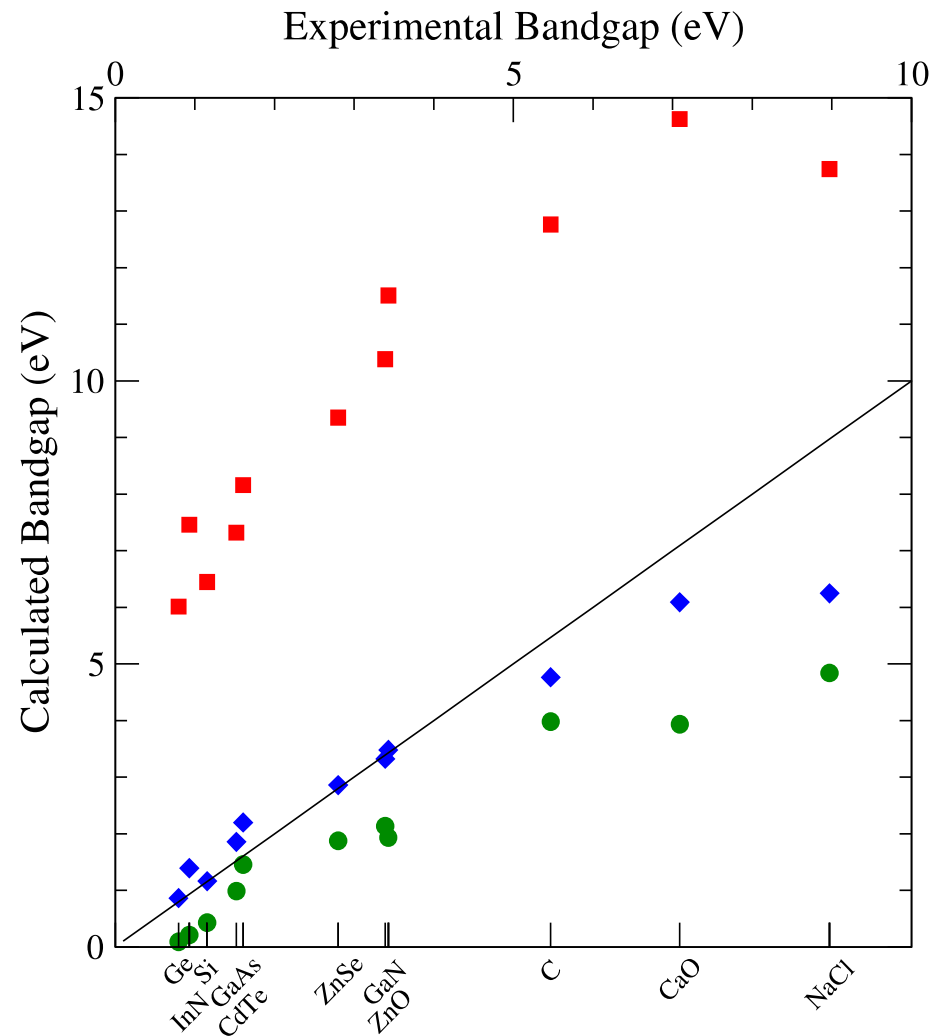
van der Waals

- Traditional functionals do not describe van der Waals interactions

- Recent developments now include semi-empirical dispersion corrections

- Known as DFT+D

- Options in Castep include:
    - OBS [Phys. Rev. B 73, 205101, (2006)]
    - G06 [J. Comput. Chem. 27, 1787, (2006)]
    - JCHS [J. Comput. Chem. 28, 555, (2007)]
    - TS [Phys. Rev. Lett.,102, 073005 (2009)]

- Still open to research and validation tests

van der Waals Implementation

- Implemented for geometry optimisation:
  - Energies
  - Forces
  - Stresses

- Currently available for a subset of the periodic table

- Mainly first row elements

- Not implemented for all functionals

- Example:
  - Castep DFT+D on azobenzene on transition metal surface: Phys. Rev. B **80**, 035414 (2009)

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Beyond DFT: Quasiparticles

- Many-body perturbation theory: alternative and accurate means of describing electronic excitations

- Quasiparticle states and energies determined from

$$\left(-\hbar^2/2m\nabla^2 + v_{ext}(r) + v_{Hartree}(r)\right)\varphi_i(r) + \int d^3r' \Sigma(r,r';\varepsilon_i^{qp})\varphi_i(r') = \varepsilon_i^{qp}\varphi_i(r)$$

Beyond DFT: Quasiparticles

- Quasiparticle states and energies determined from

$$\left(-\hbar^2/2m\nabla^2 + v_{ext}(r) + v_{Hartree}(r)\right)\varphi_i(r) + \int d^3r' \Sigma(r,r';\varepsilon_i^{qp})\varphi_i(r') = \varepsilon_i^{qp}\varphi_i(r)$$

- $\Sigma(r,r';\varepsilon_i^{qp})$ - 'self-energy'

       - non-Hermitian

       - non-local, frequency dependent

       - incorporates exchange and correlation effects

- Formally, 'looks like' KS eqns **BUT** very different

- How do we solve this?

The GW Approximation

- Take self-energy to be:

$$\Sigma(r,r';\varepsilon) = i/2\pi \int_{-\infty}^{\infty} d\varepsilon' \, e^{i\varepsilon'\delta} \, G(r,r';\varepsilon+\varepsilon')W(r,r';\varepsilon')$$

The GW Approximation

- Take self-energy to be:

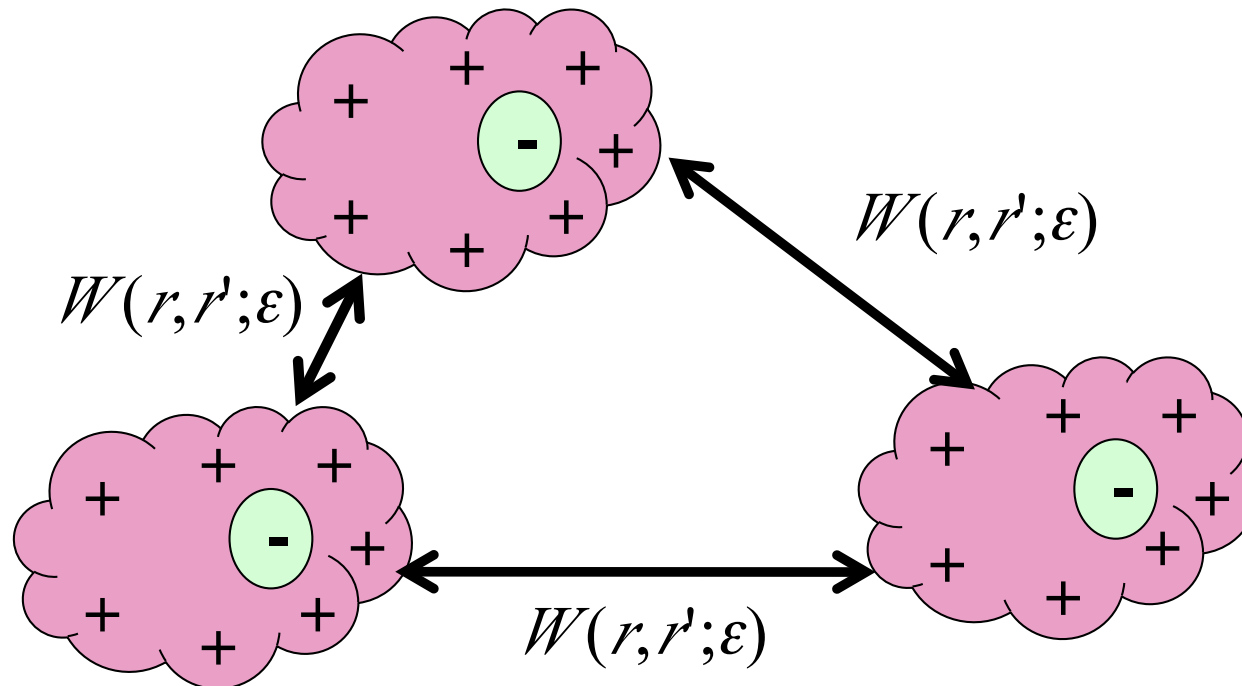$$\Sigma(r,r';\varepsilon) = i/2\pi \int_{-\infty}^{\infty} d\varepsilon' \, e^{i\varepsilon'\delta} \, G(r,r';\varepsilon+\varepsilon')W(r,r';\varepsilon')$$

- Where $\quad G(r,r';\varepsilon)$ - Green's function

$\quad W(r,r';\varepsilon)$ - screened Coulomb interaction

The GW Approximation

- What does this describe physically?

The GW Approximation

- Formally, GW is *dynamically screened* Hartree-Fock

- Replacing $W(r,r';\varepsilon)$ by $v(r,r')$ yields Hartree-Fock

- In practice, we calculate corrections to the Kohn-Sham eigenvalues:

$$\varepsilon_i^{QP} = \varepsilon_i^{KS} + \left\langle \varphi_i \left| \Sigma_{GW}\left(\varepsilon_i^{QP}\right) - v_{xc} \right| \varphi_i \right\rangle$$

- Currently being developed and implemented within CASTEP

Some suggestions

- LDA
  - Nice covalent systems
  - Simple metals
- DFT+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)
- van der Waals
  - Dispersion: DFT+D methods

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Conclusions

- Introduced notion of exchange and correlation

- Introduced various flavours of XC functional in CASTEP

- XC functional employed should be dictated by physics under consideration

- There is no 'golden bullet': all XC functionals have pros and cons

- New developments: OEP and GW

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