

Post DFT Methods

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Outline

- DFT and XC definition
- Hartree-Fock and exact exchange
- Hybrid Functionals
- DFT+U
- GW

XC: definition 1

Many body Hamiltonian – many body wavefunction

$$H = -\frac{1}{2}\nabla^2 - \sum_{i,j} \frac{eZ_j}{|r_i - R_j|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|R_i - R_j|}$$

DFT Hamiltonian – single particle wavefunction

$$H = -\frac{1}{2}\nabla^2 - \sum_i \int \frac{Z_i n(r) dr}{|R_i - r|} + \frac{1}{2} \int \frac{n(r')}{|r - r'|} dr' + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|R_i - R_j|} + \mu_{xc}[n(r)]$$

By definition: these both produce the same electron density

XC: Definition 2

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 at r and the value of its XC hole $n_{xc}(r, r')$ at r' .

The zoo of XC Methods

LDA RPBE B3LYP WDA
WC Meta-GGA SDA
PW91 PBE0 EXX
Semi-Empirical HF OEP CI MP4
PBE MP2 CC

Some properties of E_{xc}

- However we fit the XC contribution, there are some properties that should hold: if we scale the density

$$n_l(x, y, z) = l^3 n(lx, ly, lz)$$

Then, for example

$$\lim_{l \rightarrow \infty} E_{xc}[n_l] > -\infty$$

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

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

...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.

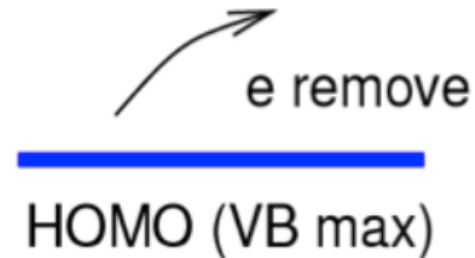
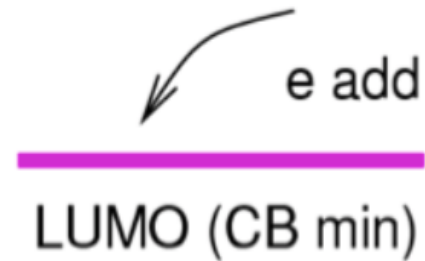
So what's the problem?

$$E_g = -A + I = [E(N+1) - E(N)] - [E(N) - E(N-1)]$$

Large errors in:

- LDA
- GGA
- Hartree-Fock

Particle number discontinuity



Single particle theories

- Density functional theory

$$\left(-\frac{\hbar^2}{2m_e} \Delta + V^{\text{ion}}(\mathbf{r}) + V^{\text{el}}(\mathbf{r}) + V^{\text{xc}}(\mathbf{r}) \right) \phi_n(\mathbf{r}) = E_n \phi_n(\mathbf{r})$$

- Hartree Fock theory

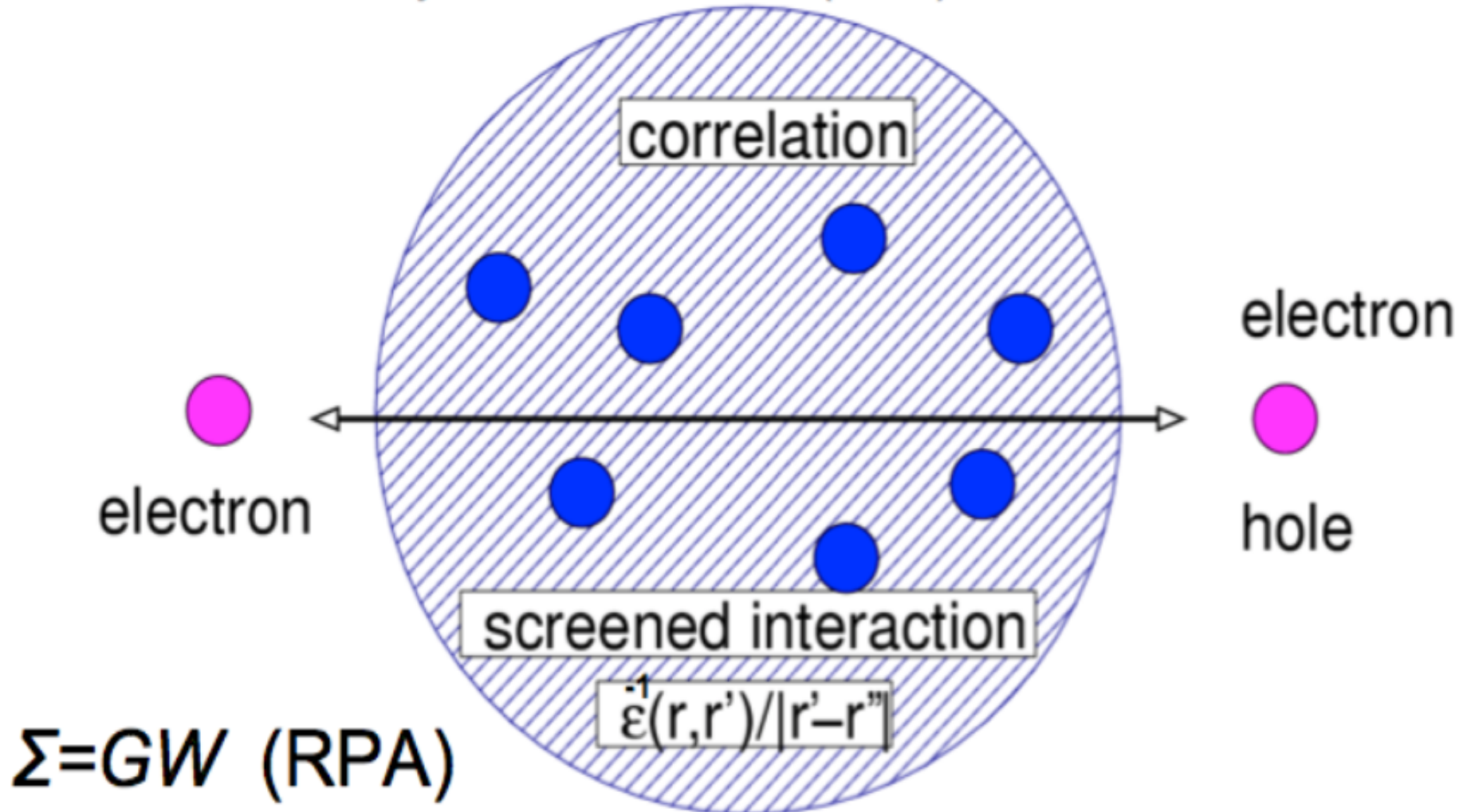
$$\left(-\frac{\hbar^2}{2m_e} \Delta + V^{\text{ion}}(\mathbf{r}) + V^{\text{el}}(\mathbf{r}) \right) \phi_n(\mathbf{r}) + \int V^x(\mathbf{r}, \mathbf{r}') \phi_n(\mathbf{r}') d^3 \mathbf{r}' = E_n \phi_n(\mathbf{r})$$

- Green function based methods such as GW (RPA)

$$\left(-\frac{\hbar^2}{2m_e} \Delta + V^{\text{ion}}(\mathbf{r}) + V^{\text{el}}(\mathbf{r}) \right) \phi_n(\mathbf{r}) + \int \Sigma^{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) \phi_n(\mathbf{r}') d^3 \mathbf{r}' d\omega = E_n \phi_n(\mathbf{r})$$

Correlation

L. Hedin, Phys. Rev. **139**, A796 (1965)



Non-local XC Functionals

Exact XC expression involves an integration over the XC hole $n_{xc}(\mathbf{r}, \mathbf{r}')$ surrounding an electron:

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

Where the XC hole is determined from the pair correlation function:

$$n_{xc}(r, r') = n(r') [g_{xc}(r, r') - 1]$$

Subject to the condition that n_{xc} contains one electron

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

Non-local KS Equation

$$-\frac{1}{2}\nabla^2\phi_i(\mathbf{r}) + \mu^{loc}(\mathbf{r})\phi_i(\mathbf{r}) + \int d\mathbf{r}'V^{NL}(\mathbf{r},\mathbf{r}')\phi_i(\mathbf{r}') = \varepsilon_i\phi_i(\mathbf{r}),$$

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

What is exchange?

- The exchange symmetry in quantum mechanics refers to the invariance of a quantum system when two identical particles exchange positions.
- For electronic systems, this symmetry leads to Pauli's exclusion principle that makes necessary the use of antisymmetric, or fermionic, wave functions.

Some notation

$$H = T + V_{en} + V_{ee} , \quad H \Psi = E \Psi$$

H : Hamiltonian of interacting system of N electrons.

Ψ : gs of H .

E : gs energy of H .

Φ : Slater determinant.

$$H_V = T + V_{en} + V , \quad H_V \Phi_V = E_V \Phi_V$$

H_V : Hamiltonian of N electrons in local potential, $V = \sum V(\mathbf{r}_i)$.

Φ_V, E_V : gs and energy of H_V .

$$\left[-\frac{\nabla^2}{2} + V_{en}(\mathbf{r}) + V(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

3 different exchanges!

$$\Phi_{HF} \text{ minimises : } \langle \Phi | H | \Phi \rangle - E > 0$$

$$V_{xOEP} \text{ minimises : } \langle \Phi_V | H | \Phi_V \rangle - E > 0$$

$$V_{KS} \text{ minimises : } \langle \Psi | H_V | \Psi \rangle - E_V > 0$$

HF Exchange

- Exchange energy is defined as

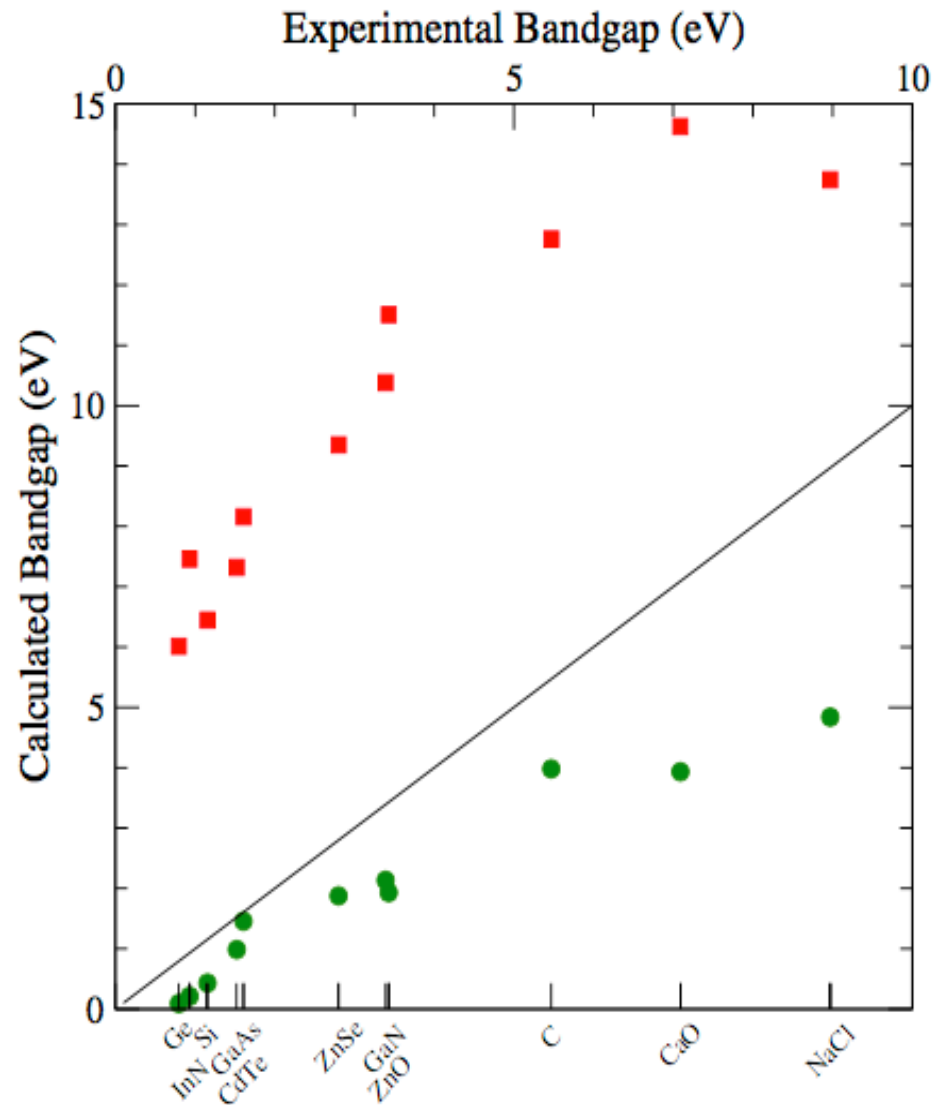
$$E_X = -\iint \psi_i^*(r_1)\psi_j^*(r_2)\frac{1}{r_{12}}\psi_i(r_2)\psi_j(r_1)dr_1dr_2$$

- Hartree-Fock energy is

$$E_{HF} = KE_{HF} + EE_{HF} + EN_{HF} + E_X$$

Correlation energy is defined as the difference between the exact energy and the Hartree-Fock energy

KS-HF versus KS-LDA



HF and LDA bandgaps
from
Hollins Clark Refson NIG
PRB **85**, 235126 (2012).

Hybrids

- LDA/GGA band gap is too small
- HF band gap is too large
- Mix them up:

$$E = \alpha E_{HF} - \alpha E_{X^{local}} + E_{XC^{local}}$$

Common Hybrids

- PBEh (previously PBE0)

$$E_{xc}^{\text{PBE0}} = \frac{1}{4} E_x^{\text{HF}} + \frac{3}{4} E_x^{\text{PBE}} + E_c^{\text{PBE}}$$

- HSE

$$E_x^{\text{HSE03}} = \frac{1}{4} E_x^{\text{HF,SR}}(\mu) + \frac{3}{4} E_x^{\text{PBE,SR}}(\mu) + E_x^{\text{PBE,LR}}(\mu)$$

$$\frac{1}{r} = S_\mu(r) + L_\mu(r) = \frac{\text{erfc}(\mu r)}{r} + \frac{\text{erf}(\mu r)}{r}$$

A Non-local Functional

$$E_{XC}^{NL} = -\frac{1}{2} \sum_{ikjq} \int \int d\mathbf{r} d\mathbf{r}' \frac{\phi_{ik}^*(\mathbf{r}) \phi_{ik}(\mathbf{r}') \phi_{jq}^*(\mathbf{r}') \phi_{jq}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} e^{-k_s |\mathbf{r} - \mathbf{r}'|}.$$

- Based on Hartree-Fock
- Non-local correlation included via screening term

The potential is:

$$V_{XC}^{NL}(\mathbf{r}, \mathbf{r}') = -\frac{1}{2} \sum_{jq} \frac{\phi_{jq}(\mathbf{r}) \phi_{jq}^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} e^{-k_s |\mathbf{r} - \mathbf{r}'|}.$$

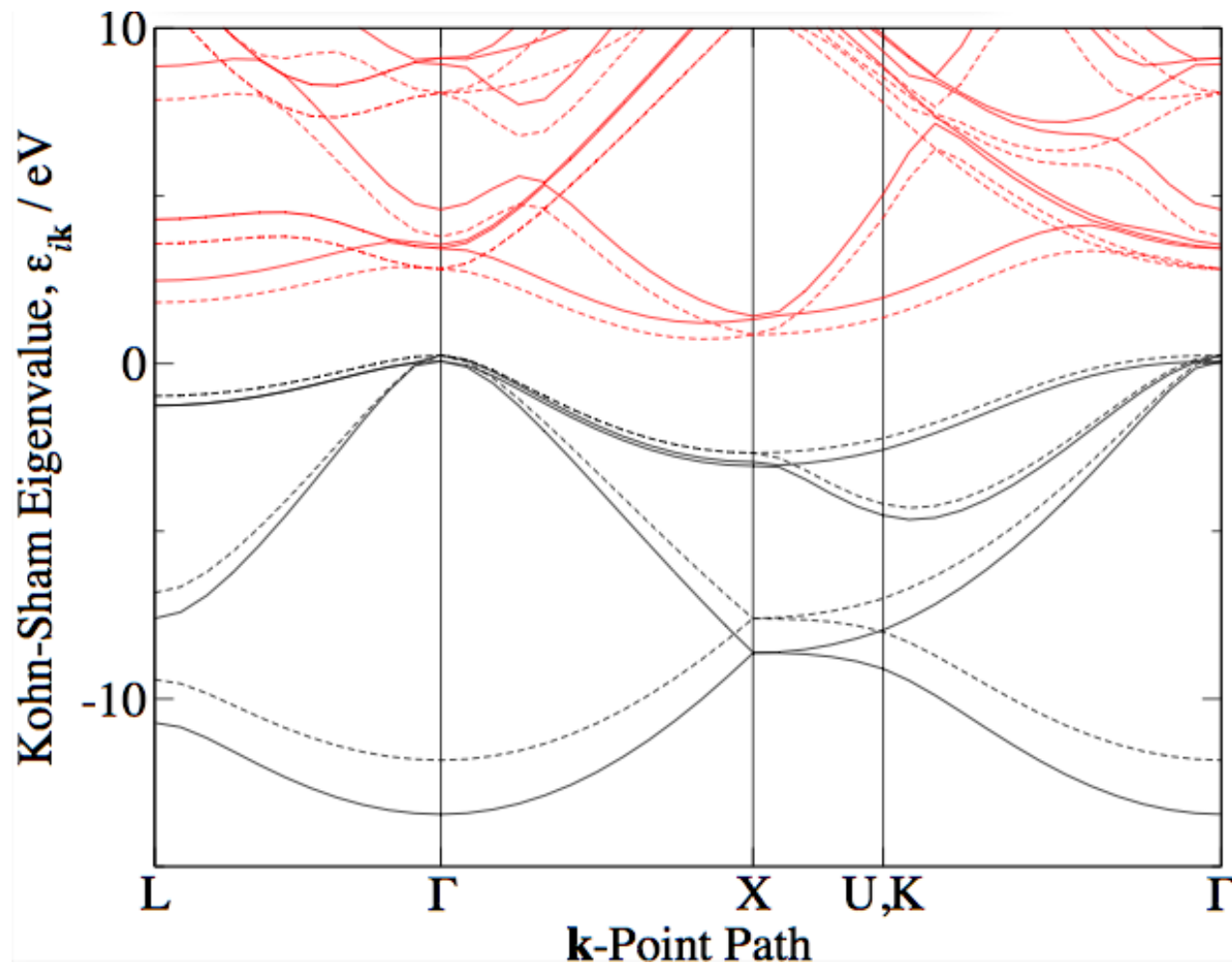
Plane wave representation

$$E_{XC}^{NL} = -\frac{2\pi}{\Omega} \sum_{ikjq} \sum_{GG'G''} \frac{c_{ik}^*(\mathbf{G}) c_{ik}(\mathbf{G}') c_{jq}^*(\mathbf{G}' + \mathbf{G}'') c_{jq}(\mathbf{G} + \mathbf{G}'')}{|\mathbf{q} - \mathbf{k} + \mathbf{G}''|^2 + k_s^2},$$

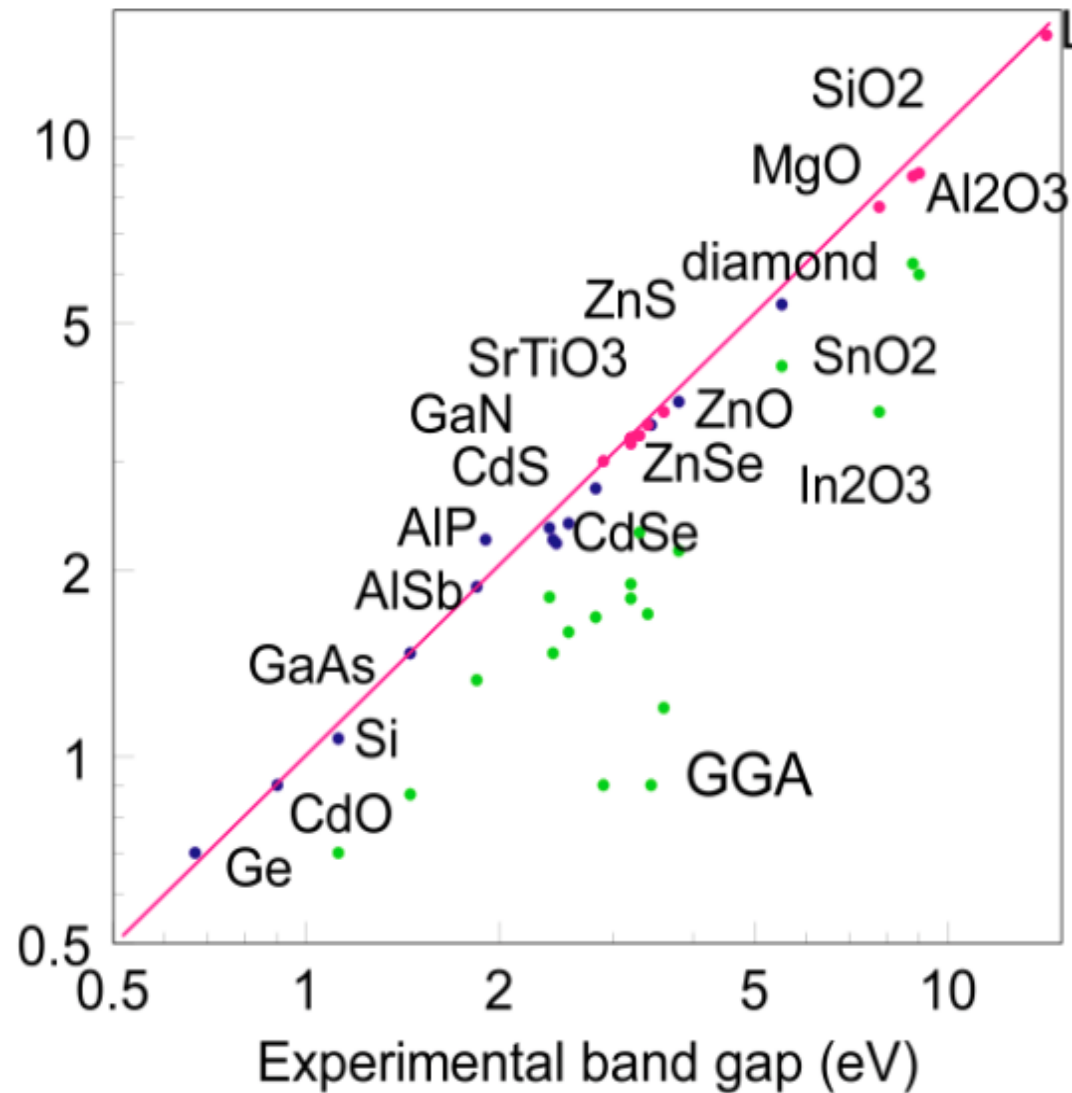
- Note:
 - Double sum over bands
 - Double sum over k-points
 - Triple sum over plane waves (aargghh!)
- Fortunately there's a clever FFT method that reduced this to

$$N_p \log(N_p) N_b^2 N_k^2$$

Why bother with this expense?



Some more gaps



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

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

$$V(\mathbf{r})=V(\mathbf{r}+\mathbf{L}) \rightarrow n(\mathbf{r})=n(\mathbf{r}+\mathbf{L})$$

(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)

DFT+U

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

Consider



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

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)

DFT+U CasteP Input

```
%BLOCK LATTICE_CART
  1.768531594289455      0.0000000000000000      5.002162732258916
 -0.884265797144727      1.531593288050062      5.002162732258916
 -0.884265797144727     -1.531593288050061      5.002162732258916
%ENDBLOCK LATTICE_CART

%BLOCK POSITIONS_FRAC
  0 -1.2500000000000000      0.7499999999999998      0.7499999999999996
  0 -0.7499999999999998      1.2500000000000000     -0.7499999999999996
 Fe -0.0000000000000000      0.0000000000000000      0.0000000000000000 spin=-5
 Fe -0.4999999999999999     -0.4999999999999999      1.5000000000000000 spin=5
%ENDBLOCK POSITIONS_FRAC
```

```
kpoints_mp_grid 7 7 7
```

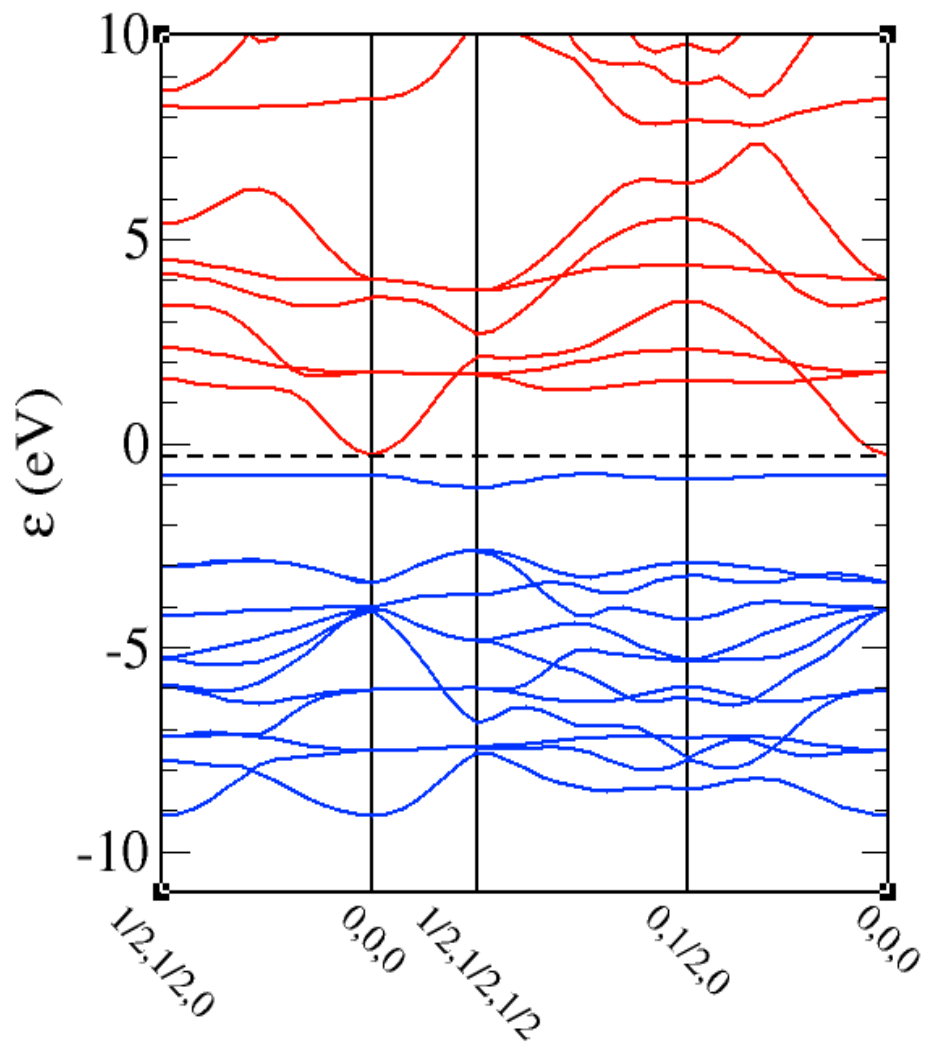
```
%block bs_kpoint_path
0.5 0.5 0.0
0.0 0.0 0.0
0.5 0.5 0.5
0.0 0.5 0.0
0.0 0.0 0.0
%endblock bs_kpoint_path
```

```
%block hubbard_u
Fe d:5.0
%endblock hubbard_u
```

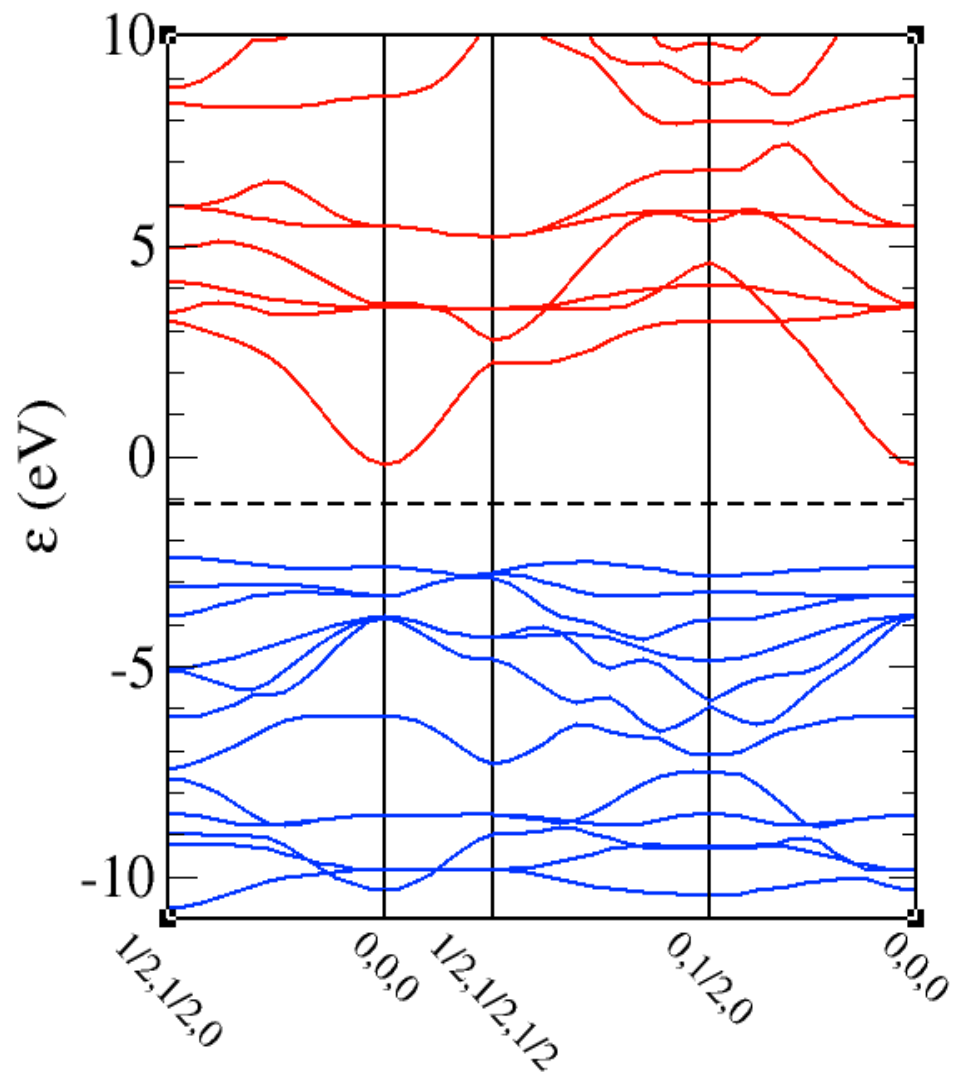
```
task : BandStructure
xc_functional : PBE
spin_polarized : true
opt_strategy : speed
cutoff_energy : 1000 eV
```

Band Structures

GGA



GGA+U



GW via Sternheimer equation

- 1st order variation in wavefunction determined through:

$$(\hat{H} - \varepsilon_v \pm \omega) \Delta \psi_{v[r,\omega]}^{\pm} = -(1 - \hat{P}_{\text{occ}}) \Delta V_{[r,\omega]} \psi_v,$$

- Self-consistent solution of these equations allows determination of screened Coulomb interaction, W
- Algorithm:
 - 1) Initialise W as bare Coulomb interaction v
 - 2) Calculate variation in wave functions
 - 3) Determine induced charge density
 - 4) Determine induced screening potential
 - 5) Determine W

GW via Sternheimer equation

- Similarly, Green's function may be determined through (non-self-consistent) solution of

$$(\hat{H} - \omega^+)G_{[\mathbf{r},\omega]}^A = -\delta_{[\mathbf{r}]}.$$

- where

$$G^A(\mathbf{r},\mathbf{r}';\omega) = \sum_n \frac{\psi_n^*(\mathbf{r})\psi_n(\mathbf{r}')}{\omega - \varepsilon_n^-},$$

$$G(\mathbf{r},\mathbf{r}';\omega) = G^A(\mathbf{r},\mathbf{r}';\omega) + G^N(\mathbf{r},\mathbf{r}';\omega),$$

$$G^N(\mathbf{r},\mathbf{r}';\omega) = 2\pi i \sum_v \delta(\omega - \varepsilon_v) \psi_v^*(\mathbf{r})\psi_v(\mathbf{r}').$$

GW via Sternheimer equation

- Self-energy may then be computed as

$$\Sigma(\mathbf{r}, \mathbf{r}'; \omega) = \Sigma^c(\mathbf{r}, \mathbf{r}'; \omega) + \Sigma^{\text{ex}}(\mathbf{r}, \mathbf{r}'),$$

- where

$$\Sigma^c(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i}{2\pi} \int_{-\omega_C}^{\omega_C} d\omega' G(\mathbf{r}, \mathbf{r}'; \omega + \omega') [W(\mathbf{r}, \mathbf{r}', \omega') - v(\mathbf{r}, \mathbf{r}')]$$

- and

$$\Sigma^{\text{ex}}(\mathbf{r}, \mathbf{r}') = - \sum_v \psi_v^*(\mathbf{r}) \psi_v(\mathbf{r}') v(\mathbf{r}, \mathbf{r}').$$

Plane wave implementation

- In plane waves, we can write

$$(\hat{H}_{\mathbf{k}+\mathbf{q}} - \varepsilon_{v\mathbf{k}} \pm \omega) \Delta u_{v\mathbf{k}[\mathbf{q},\mathbf{G},\omega]}^{\pm} = - (1 - \hat{P}_{\text{occ}}^{\mathbf{k}+\mathbf{q}}) \Delta v_{[\mathbf{q},\mathbf{G},\omega]} u_{v\mathbf{k}},$$

$$\Delta n_{[\mathbf{q},\mathbf{G},\omega]} = \frac{2}{N_{\mathbf{k}v\mathbf{k}\sigma}} \sum u_{v\mathbf{k}}^* \Delta u_{v\mathbf{k}[\mathbf{q},\mathbf{G},\omega]}^{\sigma}.$$

$$W_{\mathbf{G}\mathbf{G}'}(\mathbf{q}; \omega) = [\delta_{\mathbf{G}\mathbf{G}'} + \Delta n_{[\mathbf{q},\mathbf{G},\omega]}(\mathbf{G}')] v(\mathbf{q} + \mathbf{G}').$$

- Algorithm as before
- Must repeat calculation for each $[\mathbf{q}, \mathbf{G}, \omega]$ (\mathbf{q} is a Bloch wave vector)

Plane wave implementation

- Recall that

$$W_{\mathbf{G}\mathbf{G}'}(\mathbf{q}; \omega) = v(\mathbf{q} + \mathbf{G}) \epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q}; \omega).$$

- In long wave ($\mathbf{q} = \mathbf{0}$) limit, wings of inverse dielectric matrix diverge
- Similarly, long wave limit of Coulomb potential diverges

- Introduce syri interaction $W_{\mathbf{G}\mathbf{G}'}^t(\mathbf{q}; \omega) = 4\pi e^2 \frac{1 - \cos R_c |\mathbf{q} + \mathbf{G}|}{|\mathbf{q} + \mathbf{G}| |\mathbf{q} + \mathbf{G}'|} \tilde{\epsilon}_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q}; \omega).$ uncate Coulomb

Plane wave implementation

- For Green's functions we have:

$$(\hat{H}_{\mathbf{k}} - \omega^+)g_{[\mathbf{k}, \mathbf{G}, \omega]}^{\mathbf{A}}(\mathbf{G}') = -\delta_{\mathbf{G}\mathbf{G}'},$$

$$g_{[\mathbf{k}, \mathbf{G}, \omega]}^{\mathbf{N}}(\mathbf{G}') = 2\pi i \sum_{\dots} \delta(\omega - \varepsilon_{v\mathbf{k}}) u_{v\mathbf{k}}^*(\mathbf{G}) u_{v\mathbf{k}}(\mathbf{G}').$$

- Solve for each $[\mathbf{k}, \mathbf{G}, \omega]$
- Self-energy determined in real space (FFT G, W to real space for integration).
- FFT self-energy back to reciprocal space for evaluation of matrix elements