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Exchange and Correlation – cause and effects

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Overview of lecture

- What is Exchange? And correlation?
- LDA and GGA
- Van der Waals bonding
- Beyond GGA
- CASTEP details
- Examples

The problem with DFT

- Difficulty comes from mapping the N-body QM problem onto Nx 1-body QM problem
  - Mapping interacting electrons onto quasi-p
- "DFT cannot do..." :
  - This statement is usually wrong
- Should instead say:
  - "DFT using the ??? XC-functional can be used to calculate ???, but that particular functional introduces an error of ??? because of ???

XC introduction

- In KS-DFT we put all the unknown physics into the XC functional.
- Hence: $E_{xc} = T - T_{KS} + E_{ee} - E_H$
- T = exact many-body KE
- T_{KS}= Kohn-Sham KE of KS orbitals
- E_{ee}= exact electron-electron interaction
- E_H = Hartree electron-electron interaction

What is Exchange?

Exchange

- Electrons are Fermions and hence obey Pauli Exclusion Principle
  - If exchange the coordinates of 2 identical particles then total wavefunction (space*spin) changes sign = antisymmetric
  - This gives rise to the Exchange Energy:

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

Exchange in DFT

- In DFT we want to eliminate wavefunctions
  - Can we derive a suitable approximation from something we can solve analytically?
  - Preferably using a density?
- Homogenous Electron Gas (HEG)
  - Put N electrons into a volume V with a uniform positive background charge
  - No PE, just KE and exchange-correlation
  - Exchange energy density $\varepsilon_{xc}[n](\mathbf{r}) \sim n^{1/3}$

HEG results

- Analytic result for exchange in HEG

$$E_x^{LDA}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int n(\mathbf{r})^{4/3}\,d\mathbf{r}$$

- Can then use this as an approximation for the exchange energy in any system of the same density – the Local Density Approximation (LDA)
- But not for correlation …

What is Correlation?

Correlation

- Much harder to define!
- Usually defined as difference between exact many-body QM and Hartree-Fock answer:

$$E_x = E_{tot}^{HF} - T^{HF} - E_{ee}^{HF} - E_{eN}^{HF}$$

- Cannot derive analytically even for HEG except in certain limits
- Use of QMC (Ceperly-Alder 1981) to derive values of E_{xc} for varying densities
  - Different authors then fit to produce LDA

XC in DFT

- Formally, we can write

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

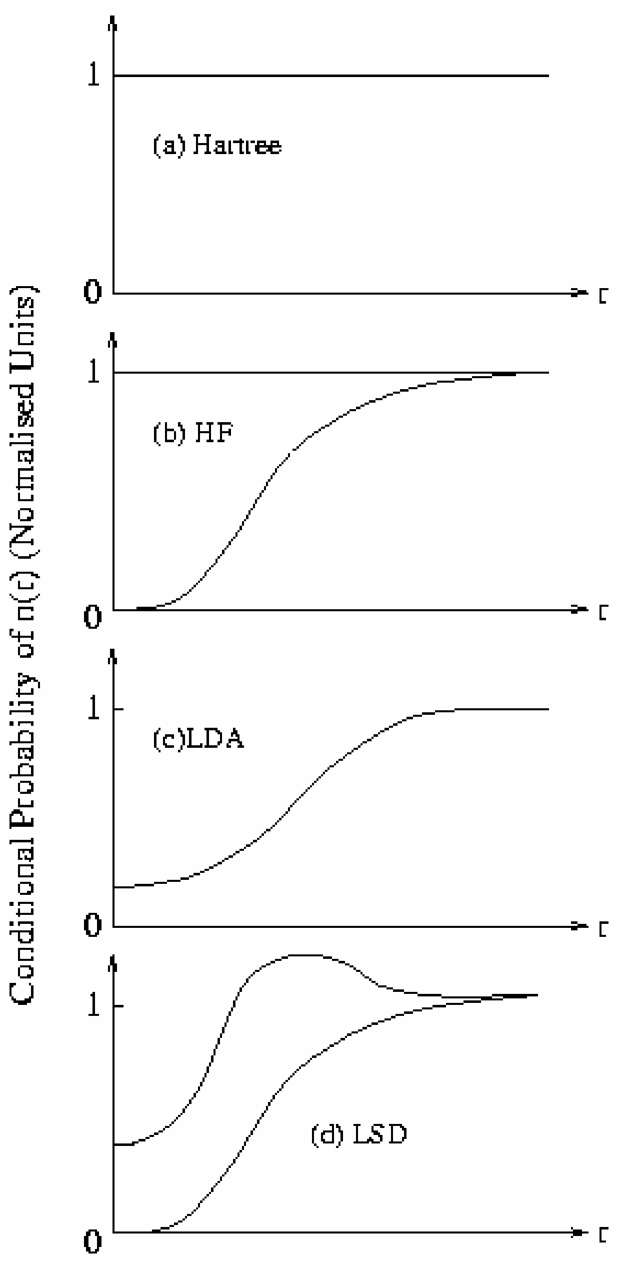
- But we do not know n_{xc}!
- This is the Coulomb energy of an electron at ***r*** interacting with its XC hole at ***r'***
  - The XC hole is the displaced charge around an electron – should integrate to 1 e^-

XC hole

- We know from the Pauli Exclusion Principle that

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

- This is known as the *sum rule*
- But we do not know the shape of the hole!



LDA and GGA

Shape of XC hole

- The simplest approximation, the LDA, assumes that the hole is spherical
  - DOES obey the sum rule
  - Reasonably effective
  - Good for many simple systems
  - Tends to over-bind atoms – makes the bonds too short and strong, lattice parameters too small, etc.

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

Improving the LDA

- Generalized Gradient Approximation
  - Include value of density AND its derivative
  - A *semi-local* approximation so still very quick to calculate
  - Parameterized from QMC calculations of HEG + cosine perturbation
  - Tends to under-bind – makes bonds too weak – but better for surfaces etc.

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

How good is the GGA?

- Which GGA?
  - There are many! Different ways of parameterizing the same data
  - Not possible to obey all the known analytical limits with any given functional form
  - Discretion in choosing which rules to obey and which functional form to choose
  - NOT a silver bullet – does NOT improve all the things that LDA does not do well – and does some things worse!

Common GGAs

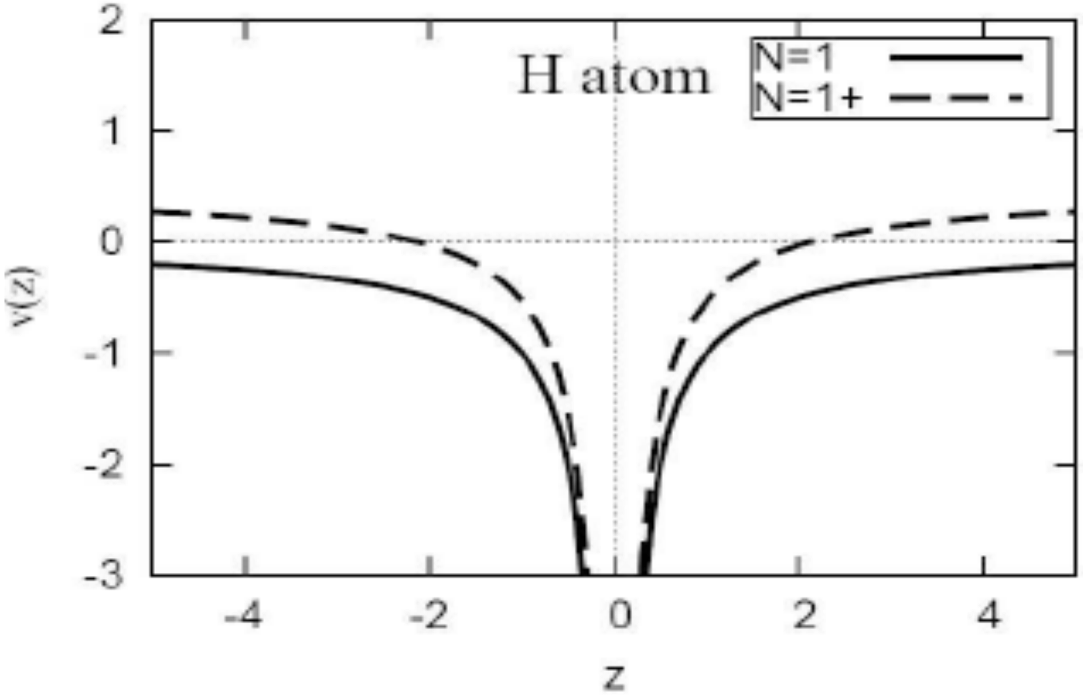
- PW91: J P Perdew & Y Wang, “*Accurate and simple analytic representation of the electron-gas correlation energy*”, *Phys. Rev. B* **45** 13244 (1992).
- PBE: JP Perdew, K Burke & M Ernzerhof, “*Generalised gradient approximation made simple*”, *Phys. Rev. Lett.* **77** 3865 (1996).
- RPBE: B Hammer,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

Properties of true XC functional

- Although exact form of XC functional is not known, we DO know certain rules/limits:
  - Sum rule: hole integrates to -1
  - Self-interaction correction:
    - The Hartree energy is Coulomb interaction of classical charge and so contains interactions between electron and itself!
    - True XC functional should correct this.
  - Long-range decay:
    - Should decay as r^{-1} at long distances

More properties

- And it is non-analytic:
  - There should be a discontinuous jump when add an infinitesimal charge to an integer number of electrons



Comparison

- How well do the LDA, GGA and HF do?

Property	***LDA***	***GGA***	***HF***
Sum rule	Y	Y	Y
Self-interaction correction	N	N	Y*
r^{-1} long-range decay	N	N	Y*
Derivative discontinuity	N	N	Y

* Only for occupied orbitals

- Why not use HF? VERY poor band gaps and vibrational properties, more expensive

Lattice Parameters

- Semiconductor lattice parameters (in Å)

	LDA	PW91	PBE	RPBE	Expt.
C	3.53	3.57	3.54	3.54	3.57
Si	5.38	5.46	5.47	5.47	5.43
Ge	5.54	5.71	5.72	5.72	5.66
SiC	4.3	4.36	4.36	4.36	4.35
AlN	4.31	4.39	4.4	4.4	4.37
AlP	5.41	5.49	5.5	5.5	5.45
AlAs	5.6	5.69	5.71	5.71	5.66
GaN	4.46	4.55	4.55	4.55	4.5
GaP	5.38	5.49	5.5	5.5	5.45
GaAs	5.57	5.7	5.71	5.71	5.65

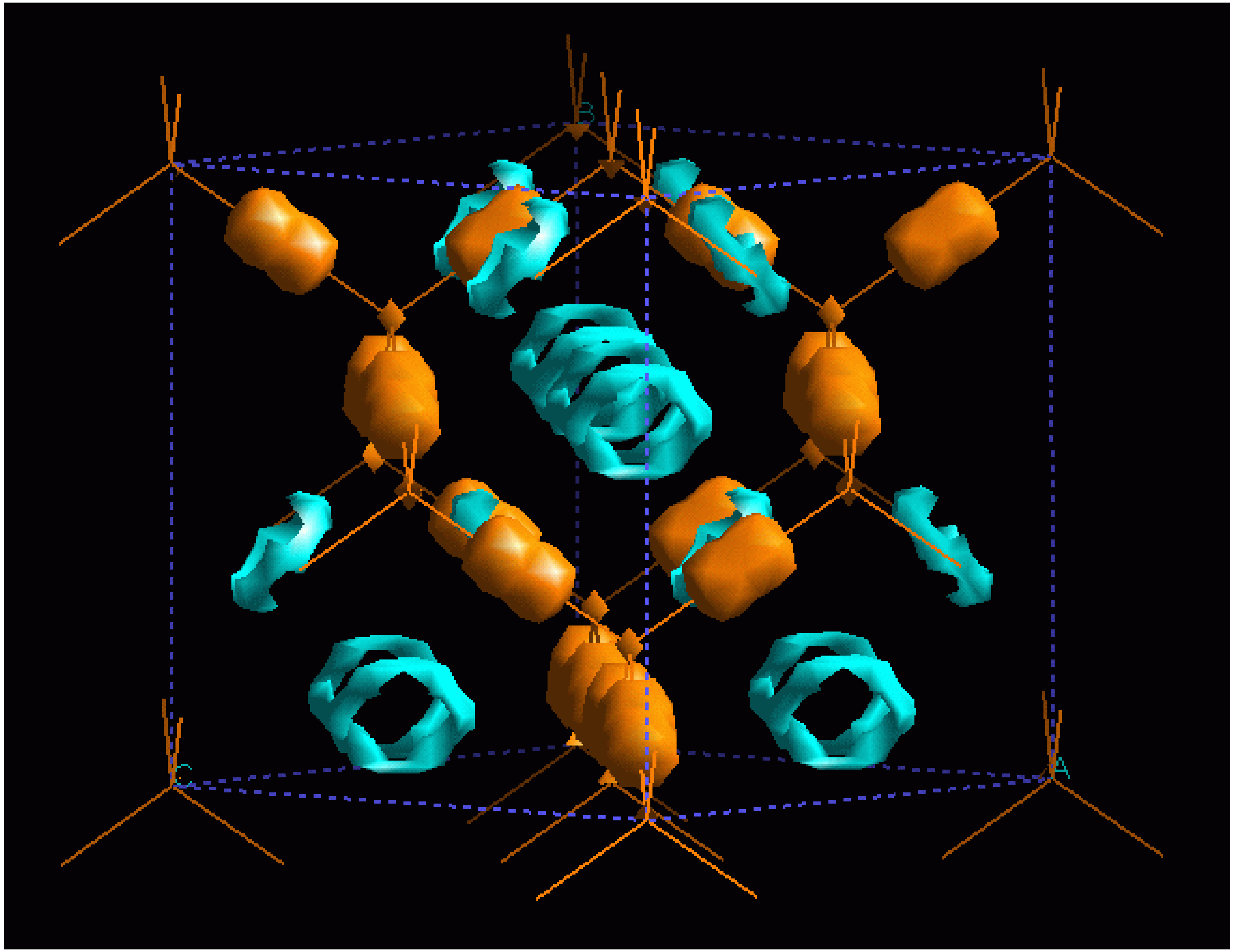
Bulk Modulus

- Bulk modulus (in GPa)

	LDA	PW91	PBE	RPBE	Expt
C	457	425	426	425	442
Si	97	88	84	84	98.8
Ge	78	62	63	62	76.8
SiC	227	215	211	210	-
AlN	206	192	189	187	202
AlP	89	82	81	80	-
AlAs	75	71	69	69	-
GaN	199	173	171	170	190
GaP	89	77	76	75	88.7
GaAs	75	65	63	63	74.8

Charge Difference

- Bulk Si: ρ(LDA)-ρ(GGA)



General comments

- LDA
  - Nice covalent systems & simple metals
- GGA:
  - Molecules, surfaces, H-bonded materials
  - Highly varying densities (d and f states)
  - Some nasty metals
  - Most magnetic systems
- Missing?
  - Van der Waals bonded materials, localized electrons, strongly correlated materials …

Van der Waals bonding

VdW

- VdW (or dispersion bonding) is a non-local effect
    - A fluctuation in the electron density on atom 1 causes a temporary electric dipole
    - This dipole causes an electric field which decays as r^{-3}
    - E-field induces dipole on atom 2
    - Dipole on atom 2 causes interaction with atom 1 as r^{-6}
    - Long range, non-local, NOT in any local or semi-local XC functional

VdW in practice

- A special-purpose functional
  - E.g. Dion functional – lacking theoretical foundation and not very good in practice
- Semi-empirical dispersion correction (SEDC)
  - All based on simple r^{-6} form with pair-wise interaction:

$$E_{vdW} = C_{ij} \frac{f_{damp}(r_{ij})}{r_{ij}^6}$$

  - Different schemes have different forms for interaction strength C_{ij} and short-range damping

Beyond GGA

Jacob's Ladder

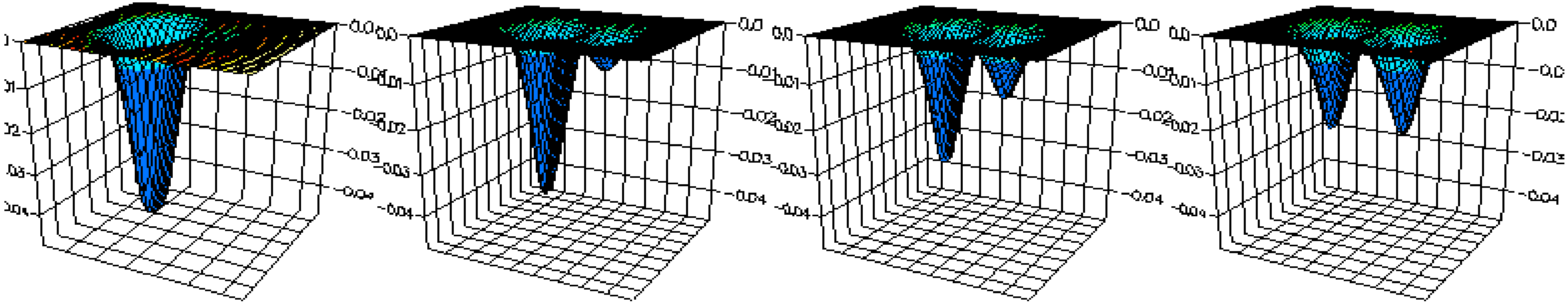
- LDA – only depends on $n\left(\mathbf{r}\right)$
- GGA – depends on $n\left(\mathbf{r}\right),\ \boldsymbol{\nabla} n\left(\mathbf{r}\right)$
- Meta-GGA – depends on $n\left(\mathbf{r}\right),\ \boldsymbol{\nabla} n\left(\mathbf{r}\right),\ \nabla^2 n\left(\mathbf{r}\right)$
- … could continue to higher derivatives BUT always semi-local and more expensive and diminishing returns

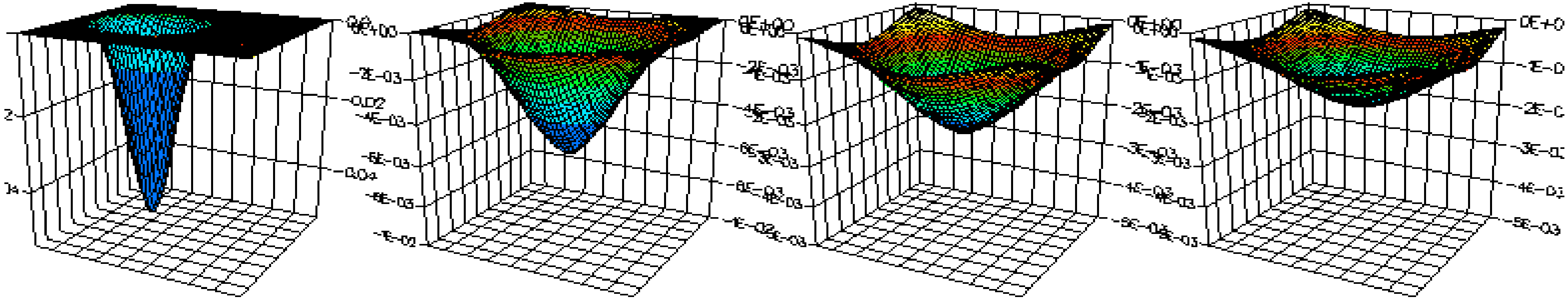
- Alternative – go non-local …

LDA vs QMC?

- XC hole in simple cosine potential

Accurate XC hole

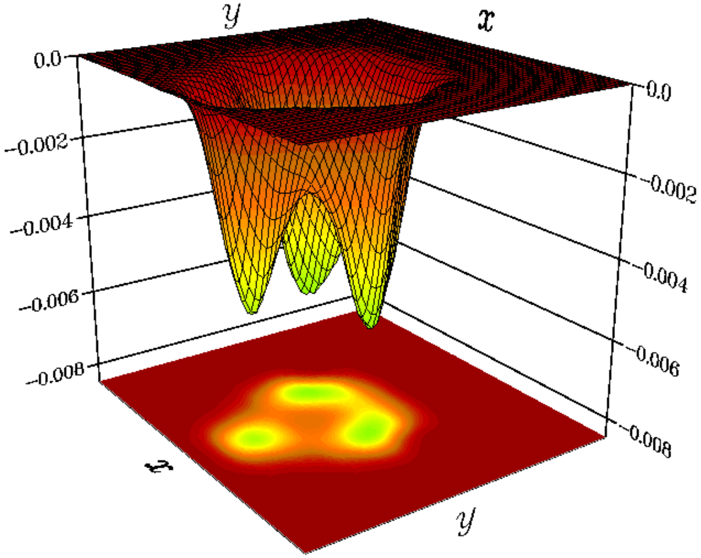


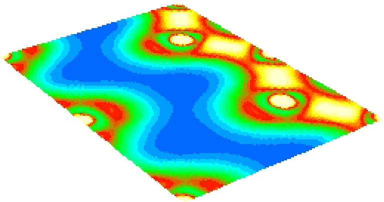


LDA

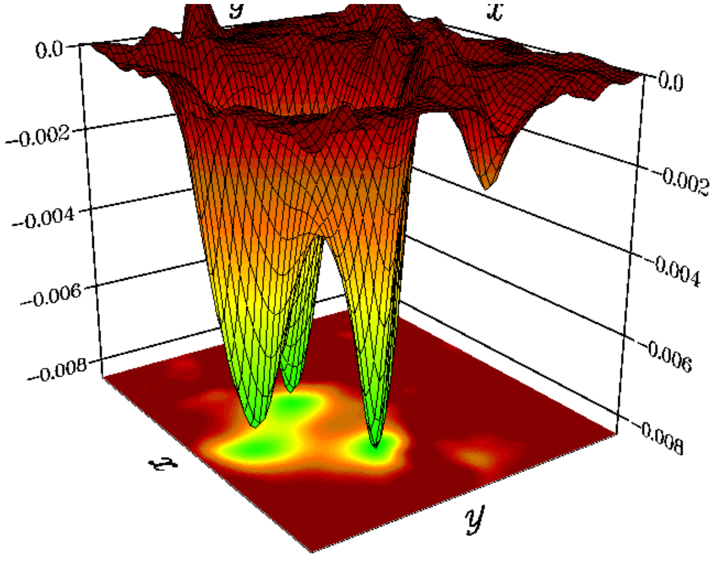
LDA vs QMC?

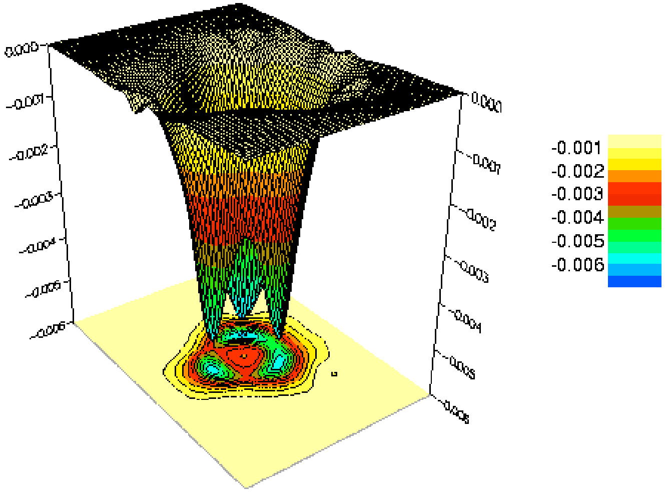
- XC hole in silicon





Charge density of Si in the [110] plane.





The XC-hole associated with an electron at the interstitial site.

More?

- Non-local functionals
  - Screened exchange, WDA etc
- Can go beyond DFT:
  - DFT+U
    - A way of treating very localized (e.g. f electrons) with a Hubbard U parameter
  - Hybrid functionals – mix HF and DFT
  - GW theory, RPA, etc.

  - See advanced course for more details!

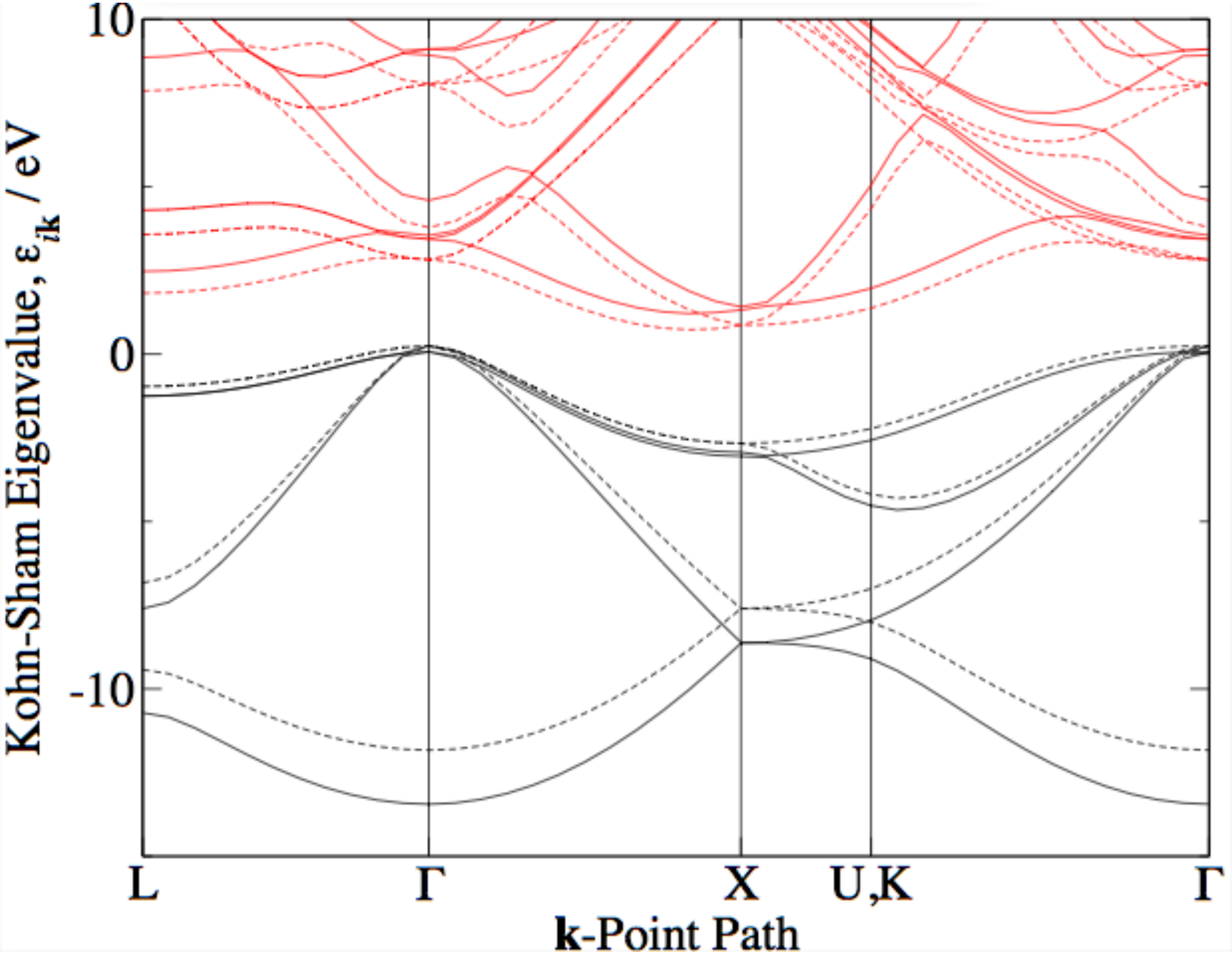
CASTEP details

CASTEP

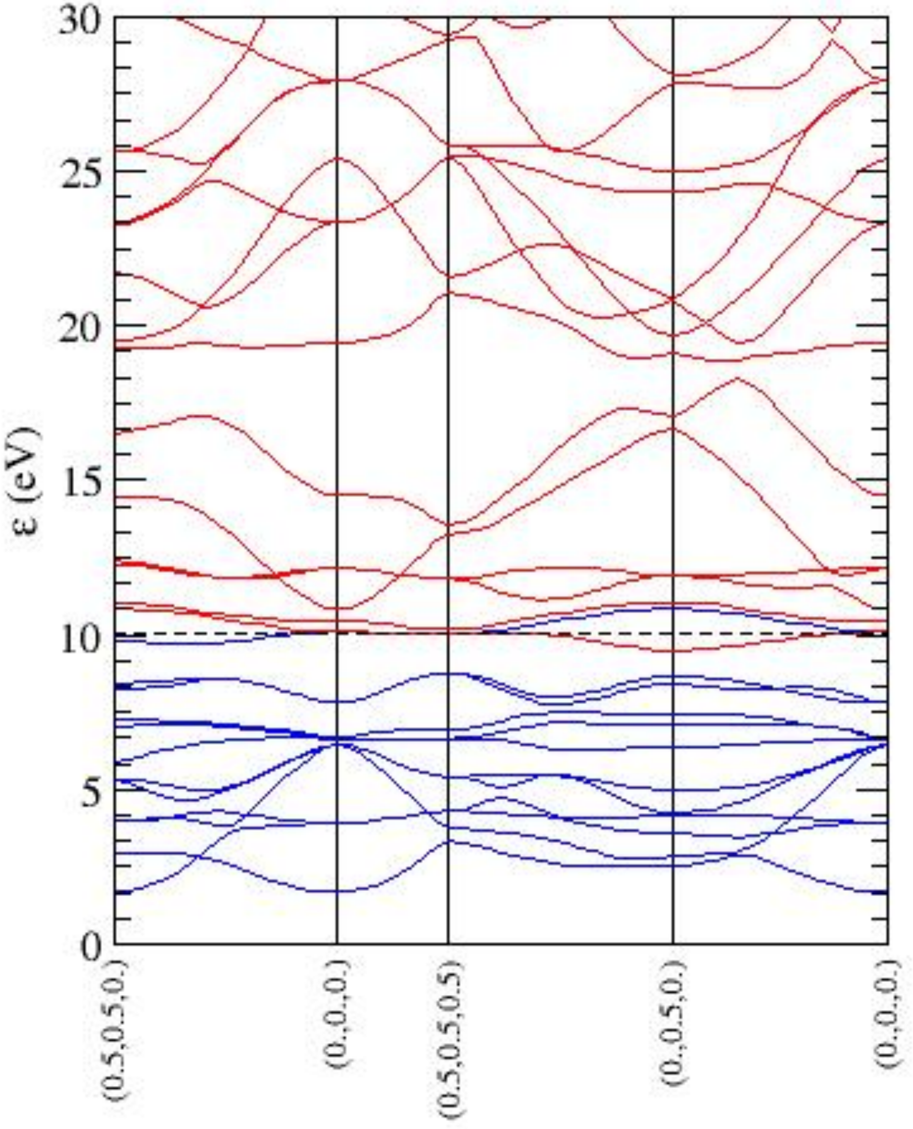
- LDA: `xc_functional = LDA`
- GGA: `xc_functional = PW91/ PBE/ RPBE/ WC/ PBEsol` …
  - All functionality supported by LDA and GGA
- SEDC: `sedc_scheme = G06/ OBS/ JCHS/ TS/ MBD` …
  - Not all elements supported and not all GGA
- MetaGGA: `xc_functional = RSCAN` …
- Non-local: `xc_functional = sX/ PBE0/ B3LYP/ HSE03/ HSE06` …

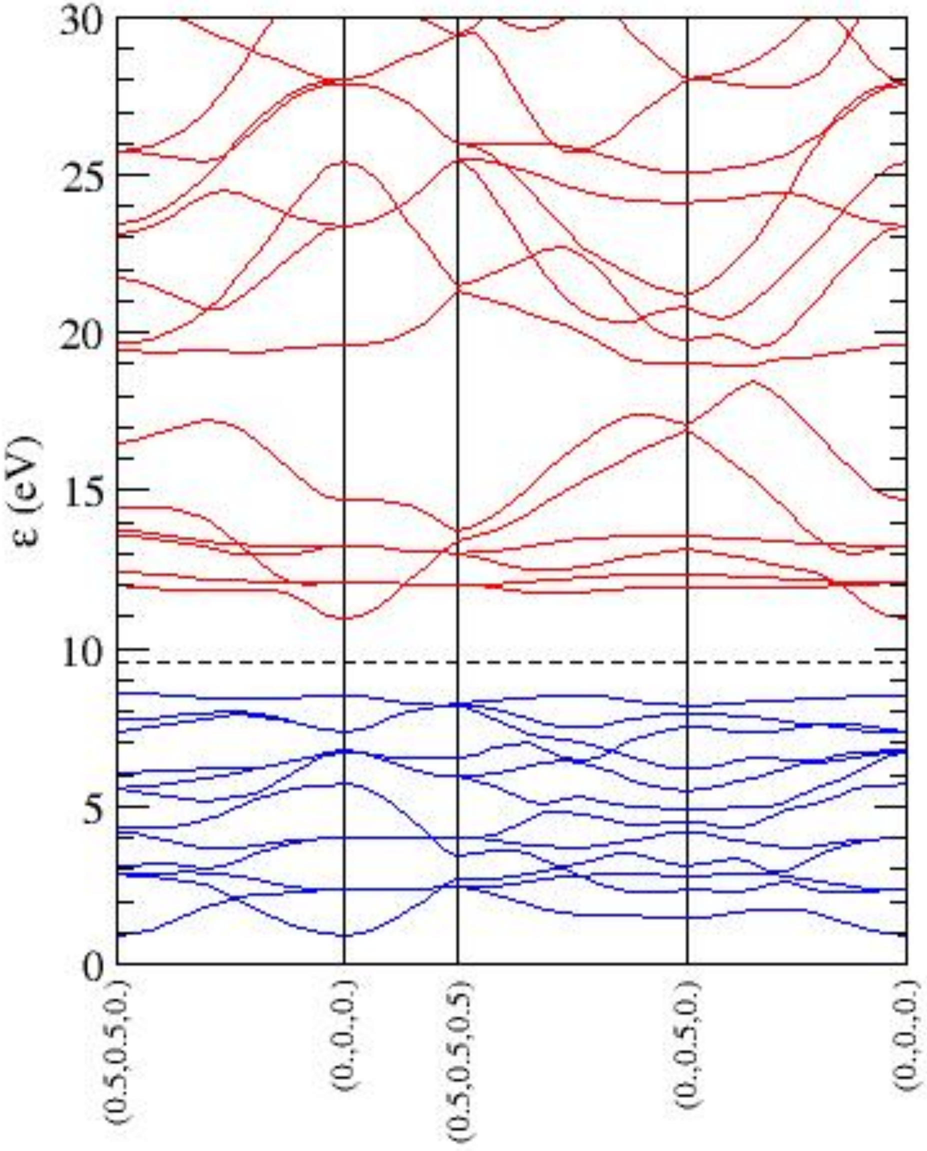
Examples

Silicon with LDA and sX

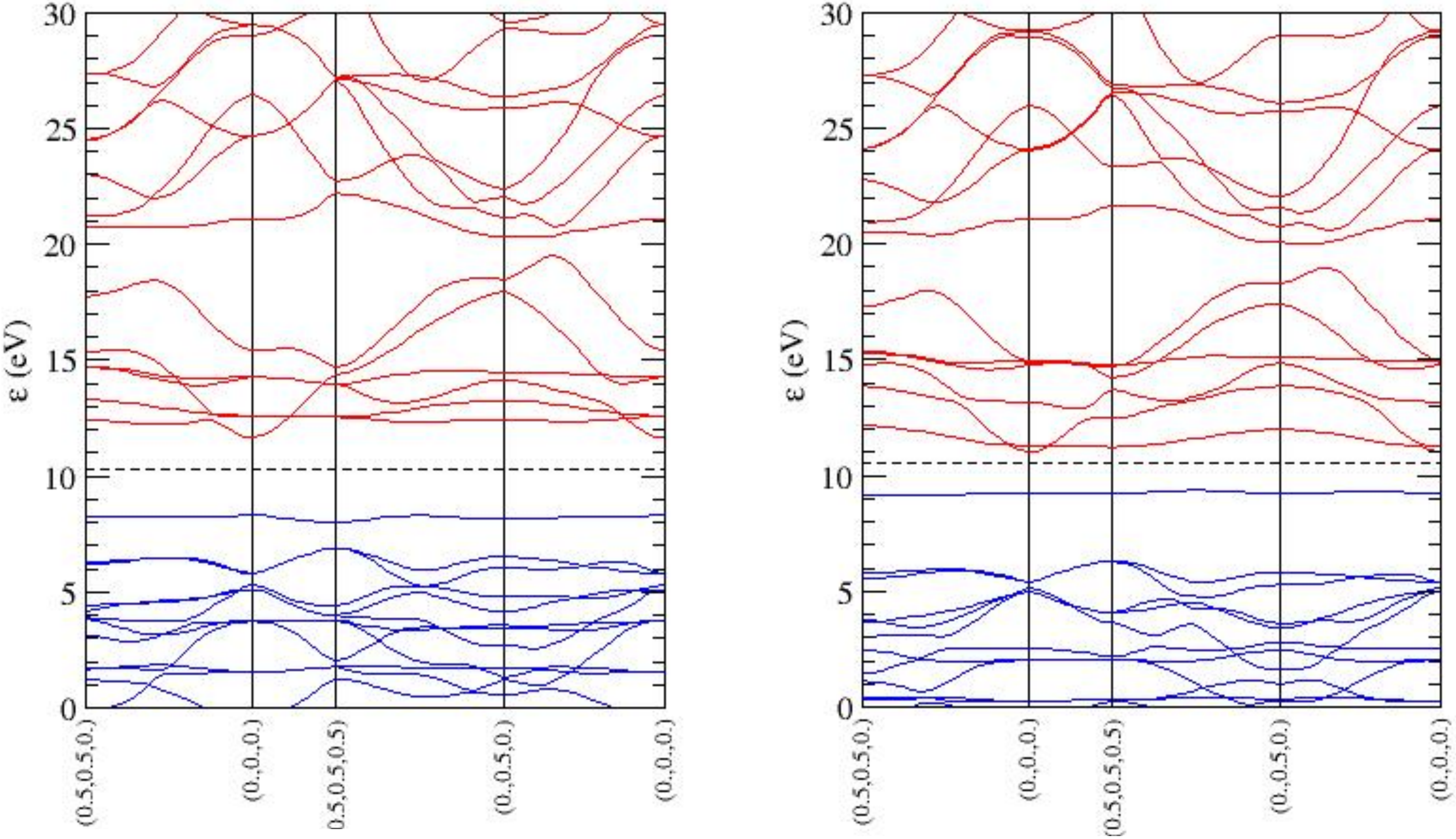


AFM FeO with PBE and LDA+U





AFM FeO with PBE0 and sX



Summary

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- DFT is formally exact but in practice has one key approximation – XC functional
  - LDA is quick & simple, tends to over-bind
  - GGA is almost as fast, tends to under-bind
- Both leave out vdW – a non-local interaction
  - SEDC is quick & simple fix for vdW BUT is empirical and not universal
- Non-local XC is expensive
  - See advanced course for sX and hybrids etc

References

- RG Parr and W Yang, *"Density functional theory of atoms and molecules"*, OUP (1989)
- JP Perdew and K Schmidt, *"Jacob's ladder of density functional approximations for the exchange-correlation energy"* AIP Conf. Proc. 577 1 (2001)
- RM Martin, *"Electronic Structure: basic theory and practical methods"*, Cambridge University Press (2004)

- K Burke *"The ABC of DFT"*, http://dft.uci.edu/doc/g1.pdf (2012)