Key concepts in Density Functional Theory (II)

Kohn-Sham scheme and band structures

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Outline

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Can we calculate excited states within static DFT?

Density functional theory in the Kohn-Sham scheme

- gives an efficient and accurate description of GROUND STATE properties (total energy, lattice constants, atomic structure, elastic constants, phonon spectra ...)
- is not designed to access EXCITED STATES
- however ...

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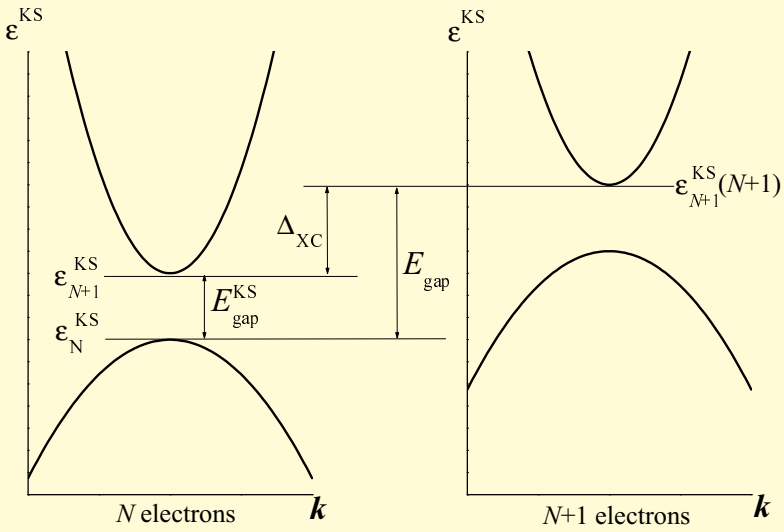
Kohn-Sham band structure: some facts

One-electron band structure

is the dispersion of the energy levels n as a function of $\mathbf{k}$ in the Brillouin zone.

- The Kohn-Sham eigenvalues and eigenstates are not one-electron energy states for the electron in the solid.
- However, *it is common to interpret the solutions of Kohn-Sham equations as one-electron states*: the result is often a good representation, especially concerning band dispersion.
- Gap problem: the KS band structure underestimates systematically the band gap (often by more than 50%)

Discontinuity in V_{xc}



$$E_g = (E_{(N+1)} - E_{(N)}) - (E_{(N)} - E_{(N-1)})$$

$$E_g^{\mathrm{DFT}} = \varepsilon_{N+1}^{\mathrm{KS}} - \varepsilon_N^{\mathrm{KS}}$$

$$\Delta_{xc} = E_g - E_g^{\mathrm{DFT}} = V_{xc}^{(N+1)}(\mathbf{r}) - V_{xc}^{(N)}(\mathbf{r})$$

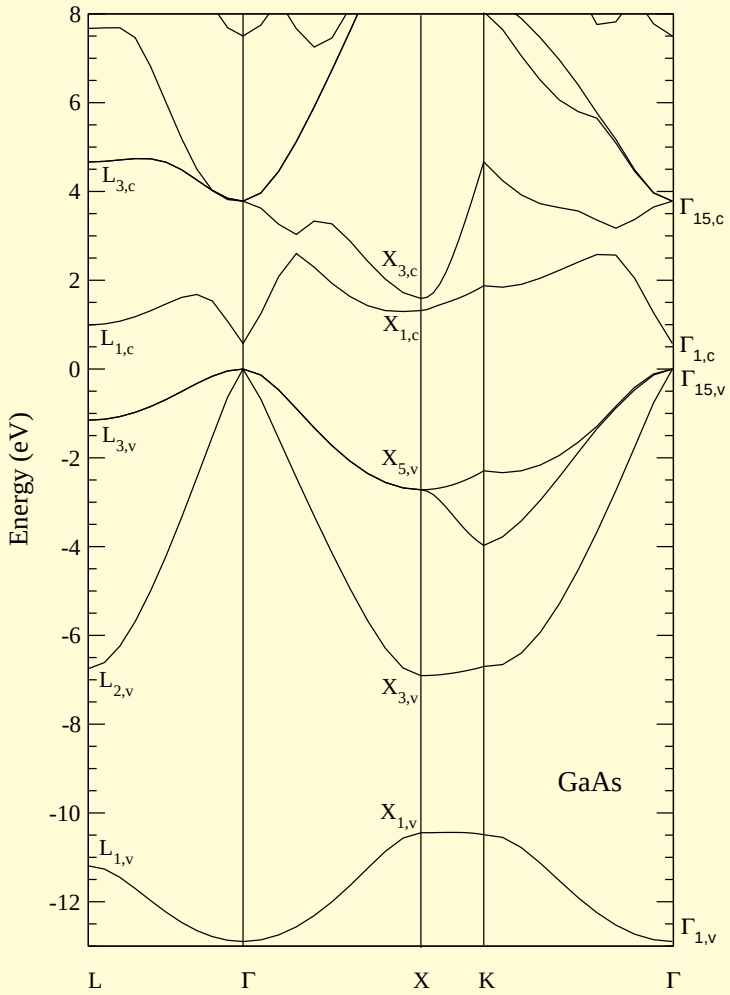
Band gap error not due to LDA, but to the discontinuity in the exact V_{xc}.

L. J. Sham and M. Schlter, Phys. Rev. Lett. **51**, 1888 (1983); L. J. Sham and M. Schlter, Phys. Rev. B **32**, 3883 (1985).

J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).

R. W. Godby, M. Schlüter and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986).

GaAs band structure



Experimental gap: 1.53 eV
DFT-LDA gap: 0.57 eV

Applying a scissor operator (0.8 eV) we can correct the band structure.

DFT in practice

1. Pseudopotential or all-electron?
2. Represent Kohn-Sham orbitals on a basis (plane waves, atomic orbitals, gaussians, LAPW, real space grid,..)
3. Calculate the total energy for trial orbitals. For plane waves:
   1. kinetic energy, Hartree potential in reciprocal space,
   2. xc potential, external potential in real space
   3. FFTs!
4. Sum over states = BZ integration for solids: special k-points
5. Iterate or minimize to self-consistency

Software supporting DFT

- Abinit
- ADF
- AIMPRO
- Atomistix Toolkit
- CADPAC
- CASTEP
- CPMD
- CRYSTAL06
- DACAPO
- DALTON
- deMon2K
- DFT++
- DMol3
- EXCITING
- Fireball
- FSatom - list of codes
- GAMESS (UK)
- GAMESS (US)
- GAUSSIAN
- JAGUAR
- MOLCAS
- MOLPRO
- MPQC
- NRLMOL
- NWChem
- OCTOPUS
- OpenMX
- ORCA
- ParaGauss
- PLATO
- PWscf (Quantum-ESPRESSO)
- Q-Chem
- SIESTA
- Spartan
- S/PHI/nX
- TURBOMOLE
- VASP
- WIEN2k

`http://en.wikipedia.org/wiki/Density_functional_theory`

Outline

The code ABINIT

abinit.org

http://www.abinit.org

"First-principles computation of material properties : the ABINIT software project."
X. Gonze *et al*, Computational Materials Science 25, 478-492 (2002).

"A brief introduction to the ABINIT software package."
X. Gonze *et al*, Zeit. Kristallogr. 220, 558-562 (2005).

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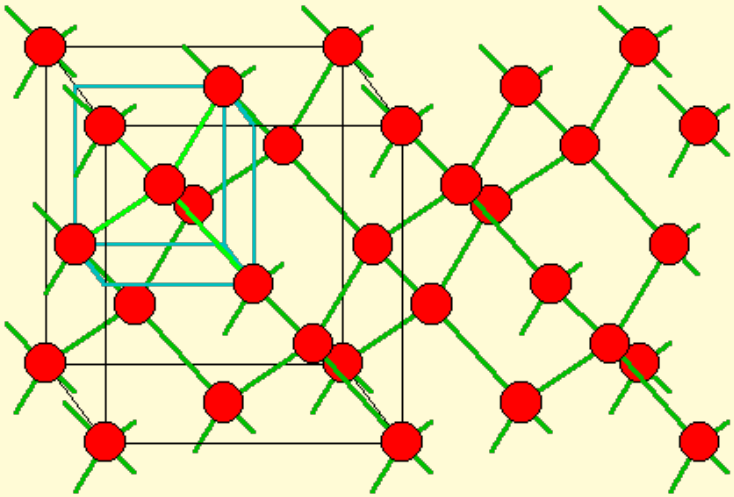
Coming soon: Tutorial III

Ground state geometry and band structure of bulk silicon

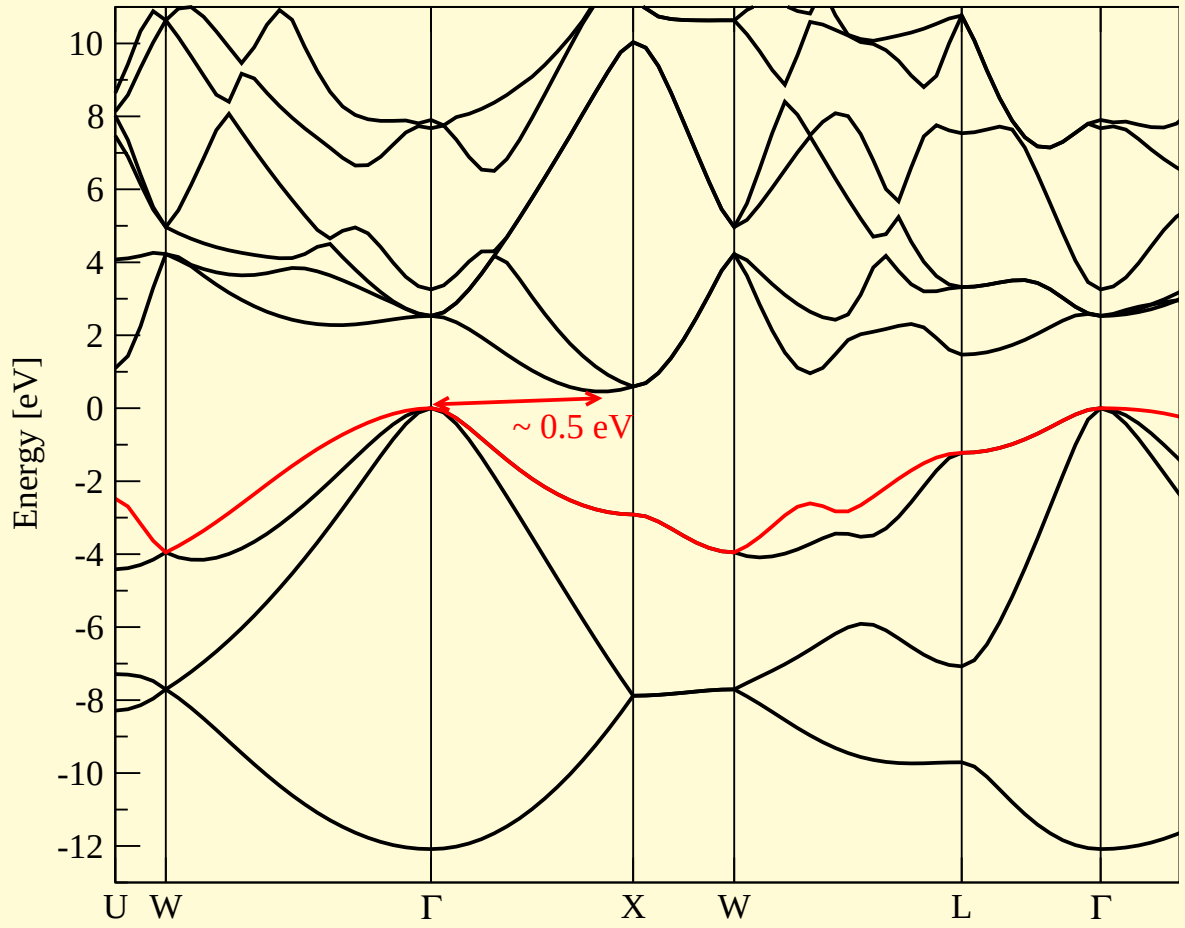
1. Determination of the total energy.
2. Determination of the lattice parameter a.
3. Computation of the Kohn-Sham band structure.

Equilibrium geometry of silicon



- Our DFT-LDA lattice parameter: $a = 10.217$ Bohr $= 5.407$ Å
- Exp. value: $a = 5.431$ Å at 25°.

Kohn-Sham band structure of silicon



- Indirect gap
- Good dispersion of bands close to the gap
- Exp. gap = 1.17 eV
- Scissor operator = 0.65 – 0.7 eV

Outline

Summary

- Application of standard DFT to solids:
  - band structure calculations (Kohn-Sham bands)
- We know that the Kohn-Sham bands are not quasiparticle states.
- However they turn out to give a qualitative picture in many cases.
- When they are completely wrong we need to go beyond standard DFT.

Coming next: All you need to know to make a DFT calculation in practice!

Suggestion of essential bibliography

Some additional items:

- R. M. Martin, *Electronic structure: Basic Theory and Practical Methods*, Cambridge University Press (2004).
- `http://www.abinit.org` and references there.