Key concepts in Density Functional Theory (II)

Kohn-Sham scheme, band structure and optical spectra

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Outline

1. From Kohn-Sham equations to band structures
   - An example: Si band structure
2. Optical absorption
   - An example: independent-particle Si absorption spectrum
3. Summary

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Can we calculate spectra within static DFT?

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

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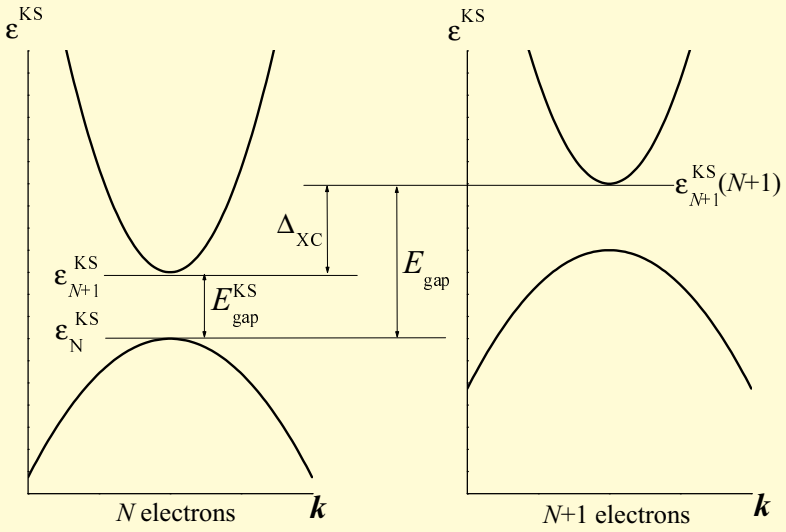
Kohn-Sham band structure: some facts

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}



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

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

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

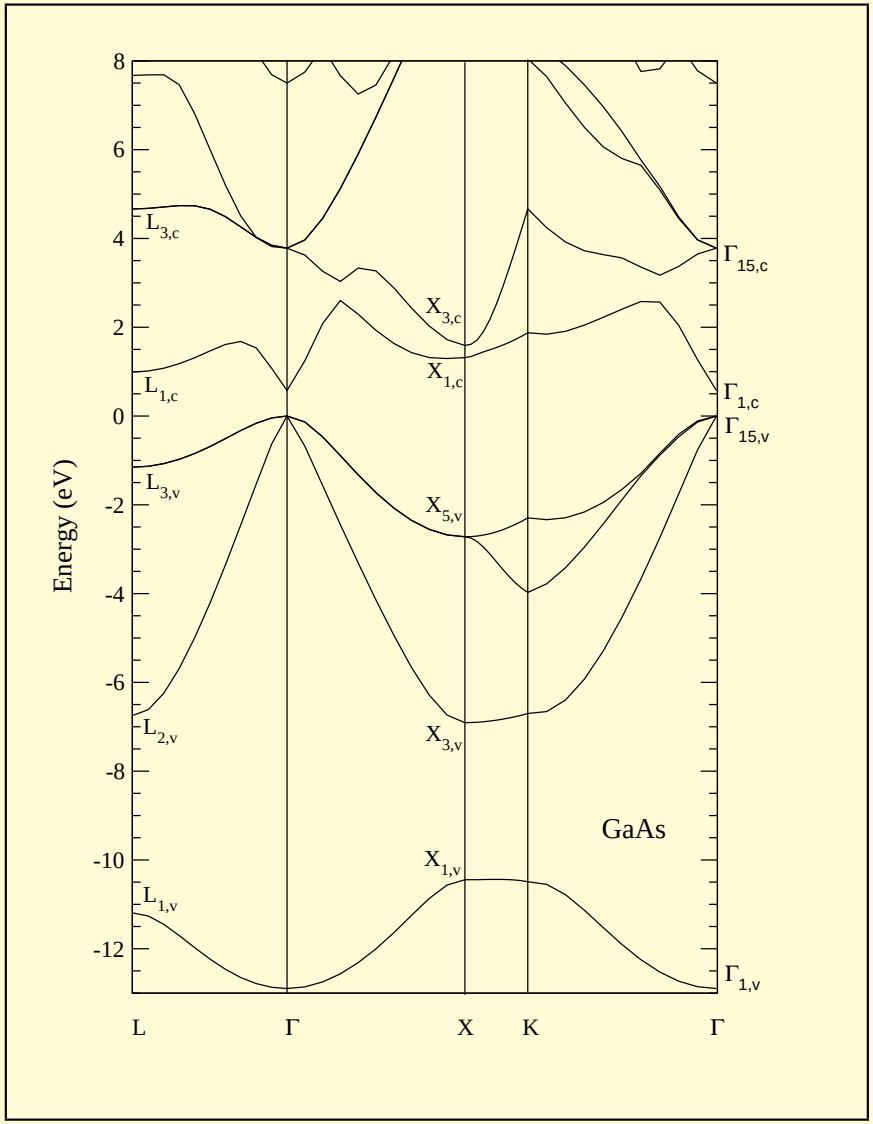
Band gap error not due to LDA, but to the discontinuity in the exact V_{xc}.

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. Why?

DFT in practise

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

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The code ABINIT

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).

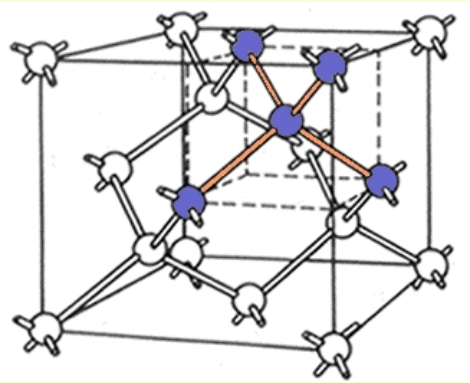
"A brief introduction to the ABINIT software package."
X. Gonze *et al*, Zeit. Kristallogr. 220, 558-562 (2005).

Exercise I

Ground state geometry and band structure of bulk silicon

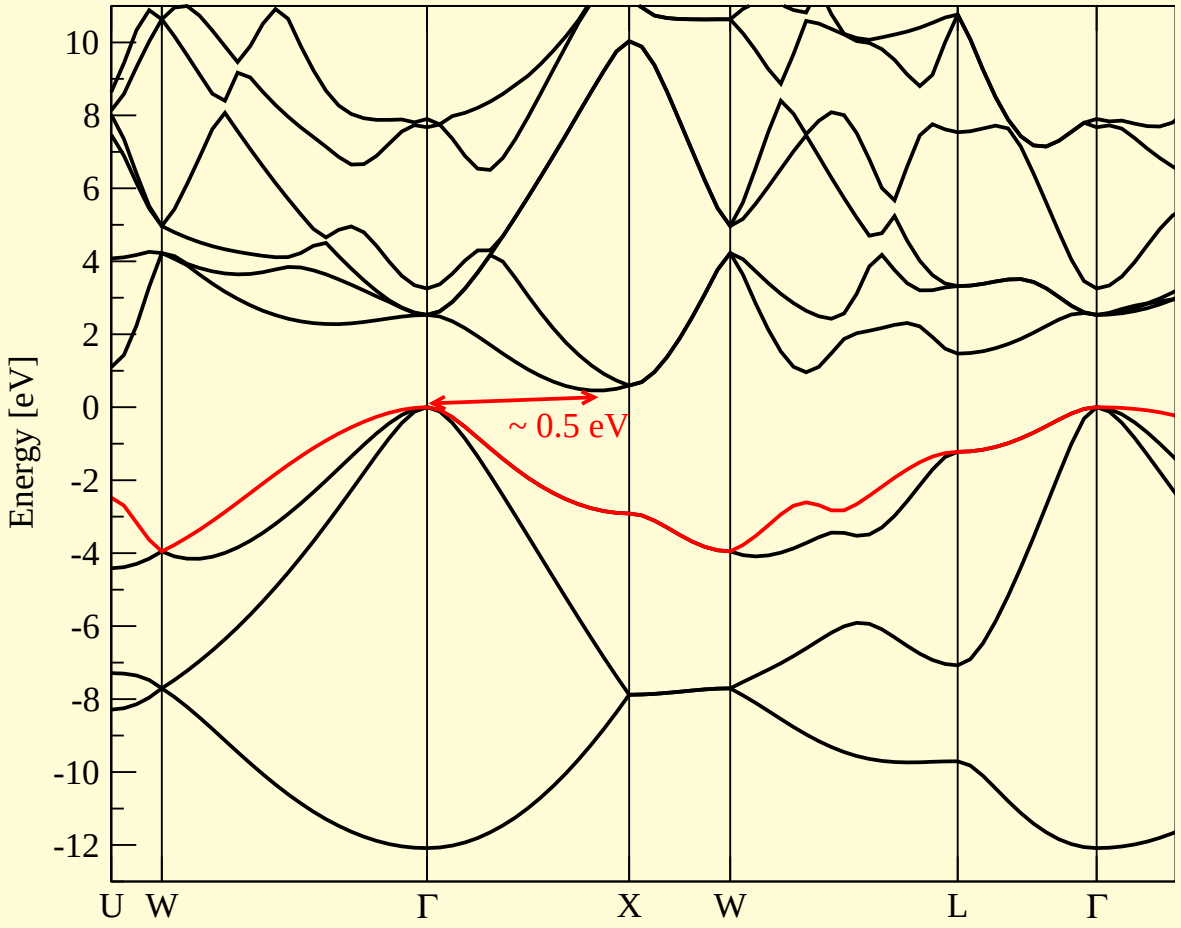
1. Determination of the lattice parameter a
2. Computation of the Kohn-Sham band structure

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

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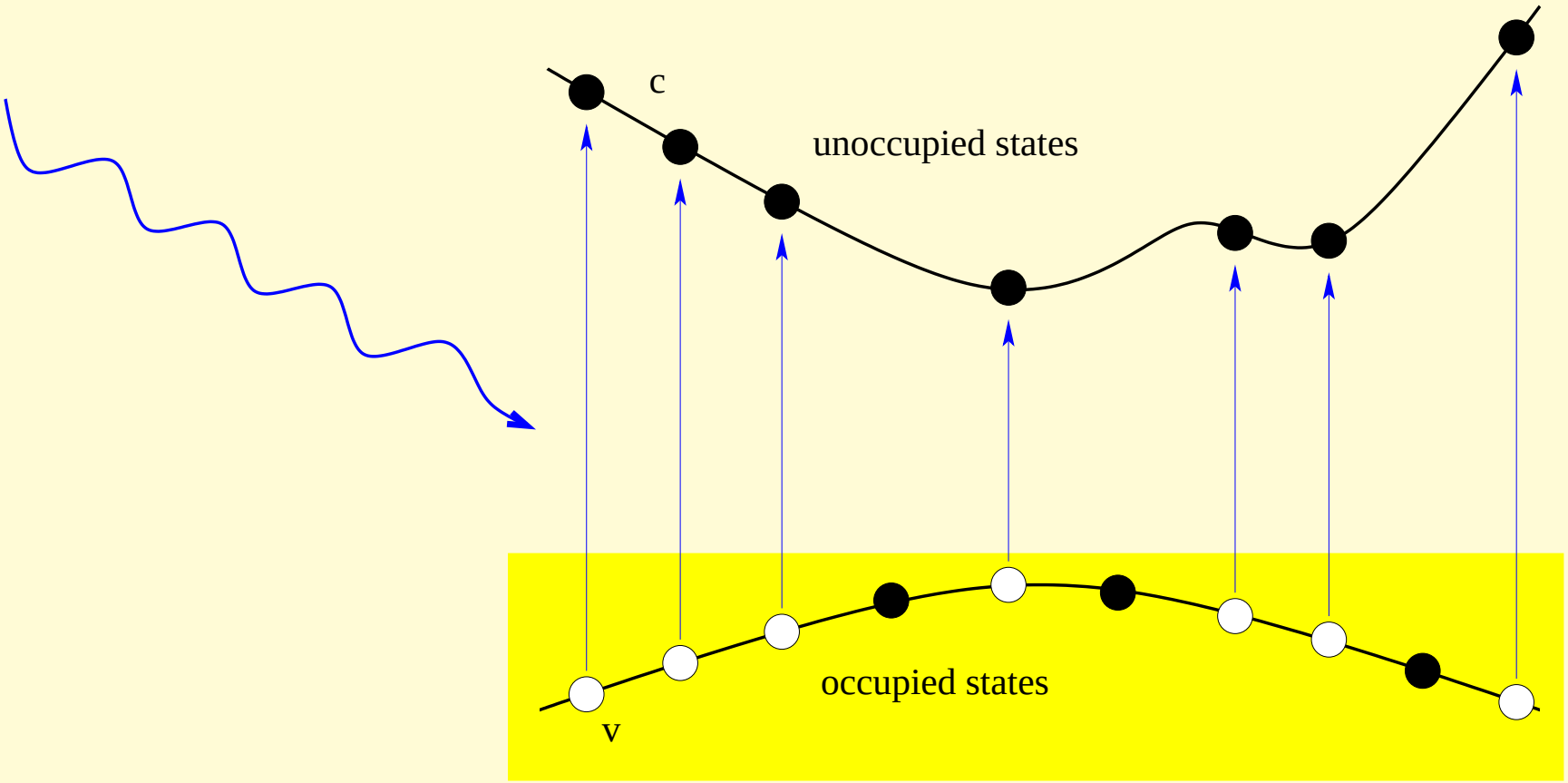
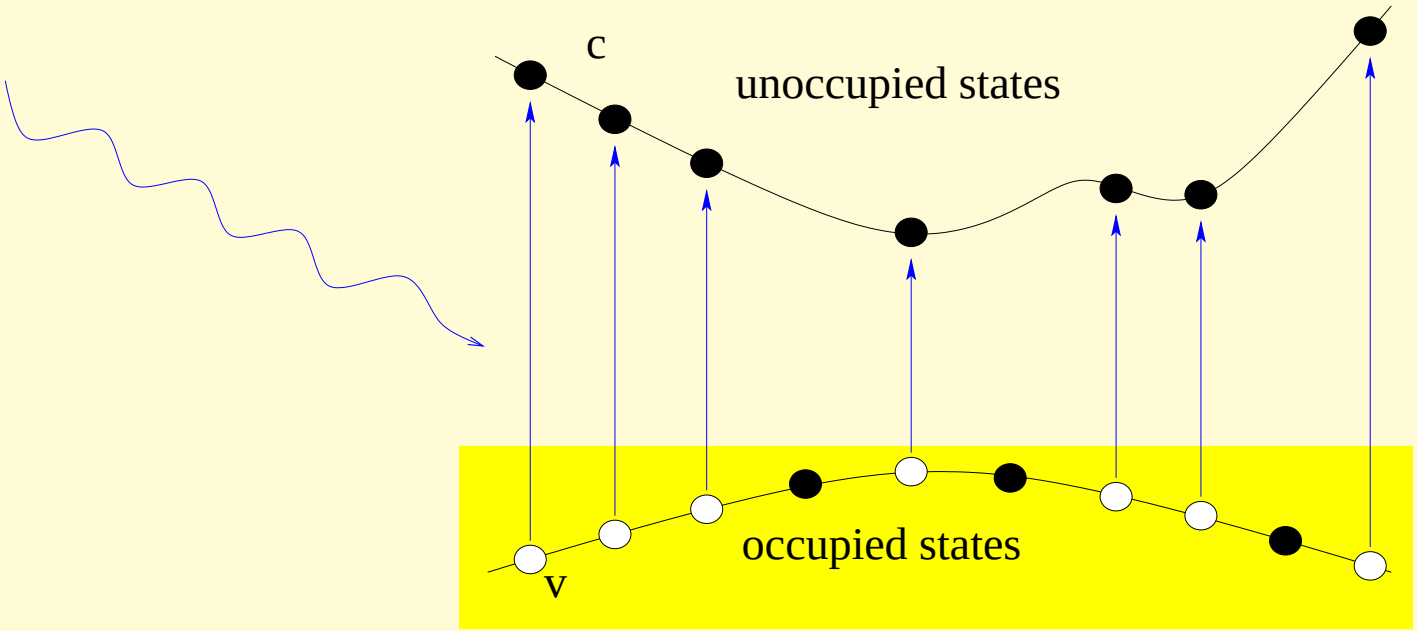
An intuitive picture for absorption



Kohn-Sham (KS) energy states

An intuitive picture for absorption

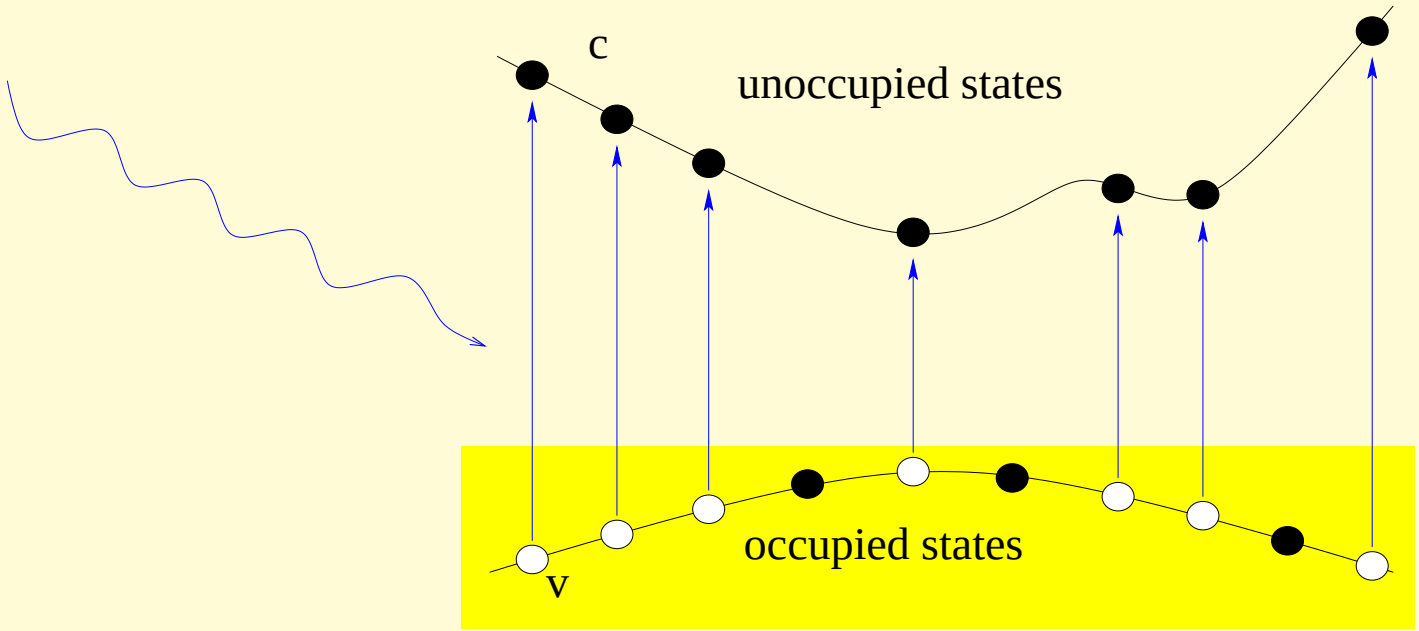


Independent particle transitions between KS states

$$\chi_{\mathrm{KS}} \sim \sum_{v,c} |\langle c|D|v\rangle|^2 \, \delta(\epsilon_c - \epsilon_v - \omega)$$

Very common approximation: Fermi's golden rule!

An intuitive picture for absorption



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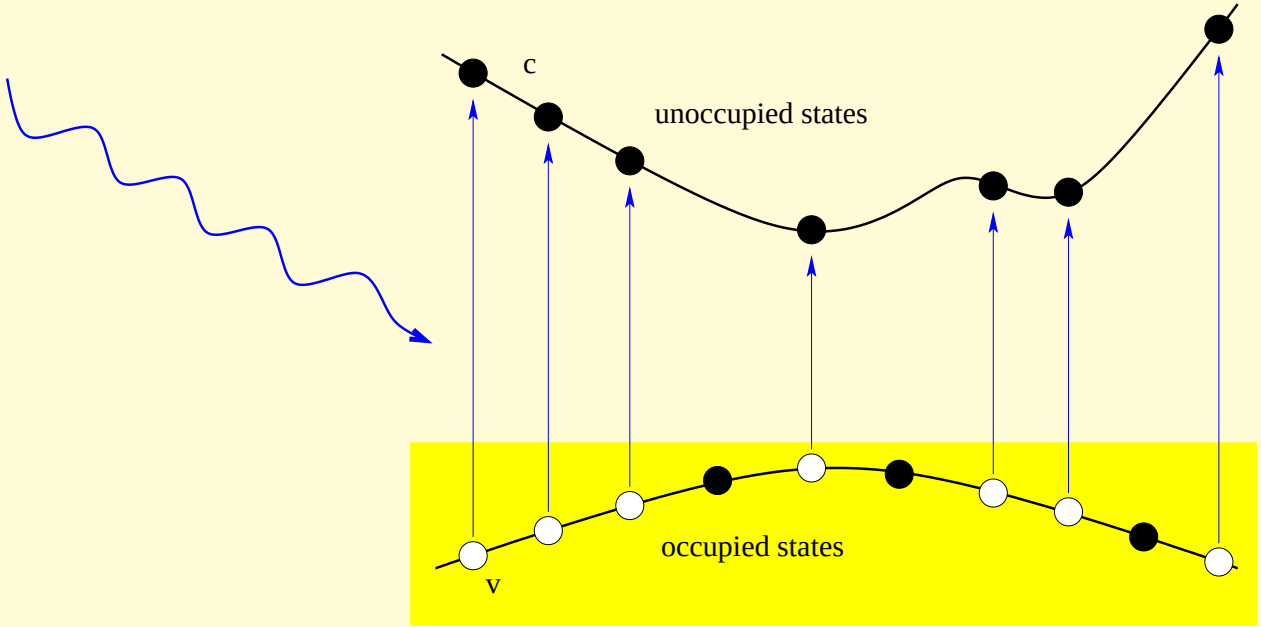
Optical absorption: dielectric function



$$\epsilon_2(\omega) = 2\frac{4\pi^2}{\Omega N_{\mathbf{k}}\omega^2}\lim_{q\to 0}\frac{1}{\mathbf{q}^2}\sum_{v,c,\mathbf{k}}|m_{v,c,\mathbf{k}}|^2\,\delta(\epsilon_{c\mathbf{k}}-\epsilon_{v\mathbf{k}}-\omega)$$

$m_{v,c,\mathbf{k}} = \langle c\,|\mathbf{q}\cdot\mathbf{v}|\,v\rangle$ velocity matrix elements

Joint density of states

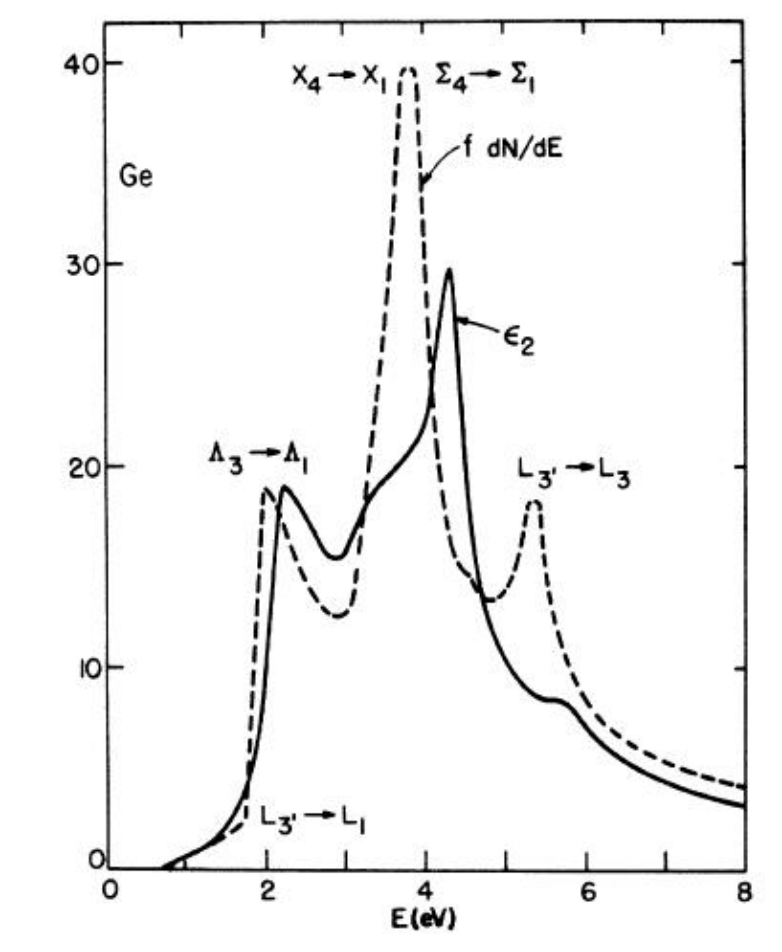
In the independent-particle approximation the dielectric function is determined by two contributions: optical matrix elements and energy levels.

$$\epsilon_2(\omega) = 2\frac{4\pi^2}{\Omega N_{\mathbf{k}}\omega^2} \lim_{q\to 0} \frac{1}{\mathbf{q}^2} \sum_{v,c,\mathbf{k}} |m_{v,c,\mathbf{k}}|^2 \, \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega)$$

If $m_{v,c,\mathbf{k}}$ can be considered constant then the spectrum is essentially given by the joint density of states:

$$\epsilon_2 \propto JDOS/\omega^2 = \frac{1}{N_{\mathbf{k}}\omega^2} \sum_{v,c,\mathbf{k}} \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega)$$

A textbook example: Ge optical absorption



- In common semiconductors the JODS is a good approximation to the independent-particle spectrum
- *Another example in the seminar this afternoon.*

D. Brust *et al.*, Phys. Rev. Lett. *9*, 94 (1962).

Absorption spectra

Question

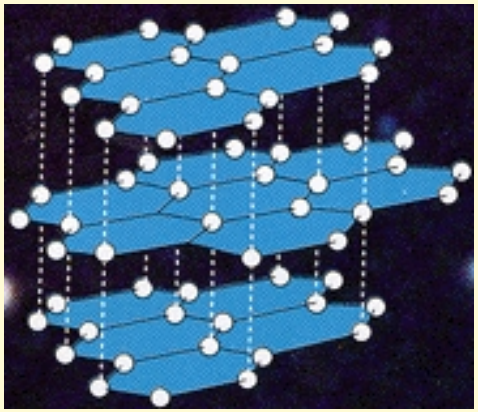
Which level of approximation should I use if I am interested in comparing to experiments?

Answer

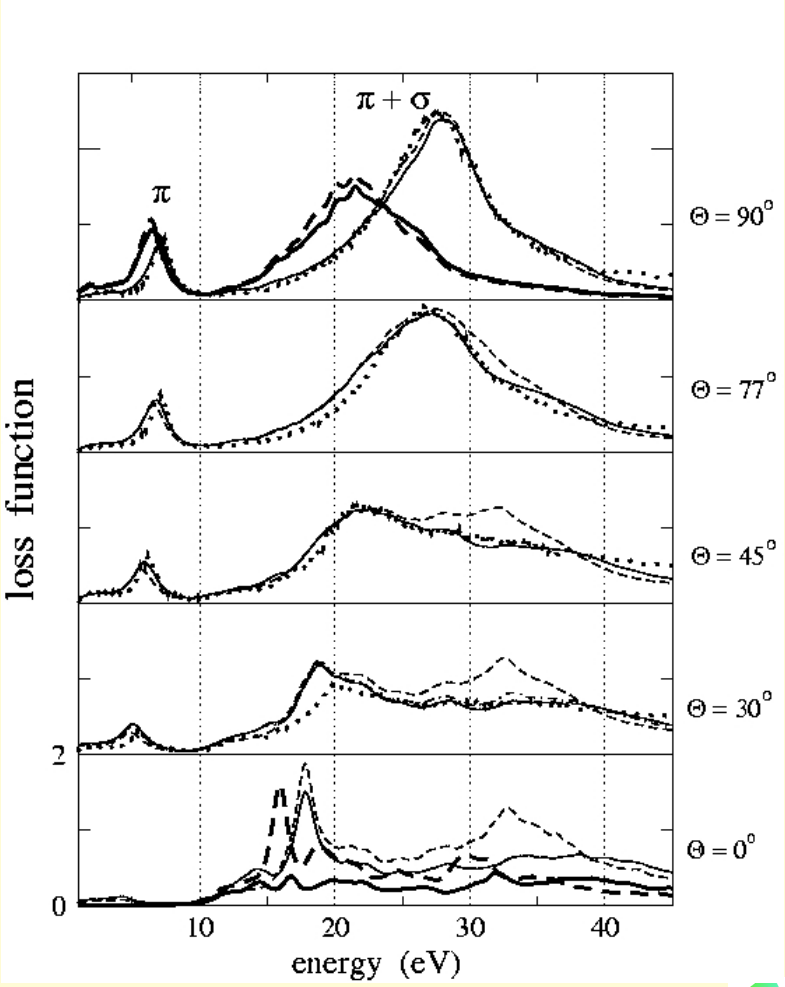
There is not a unique answer.
It depends on the system and on the kind of spectroscopy.

- In some cases, the independent-particle approximation already gives results good enough.
- It is often necessary to go beyond the independent particle approximation.
- *Many more examples in the next days!*

EELS of graphite



For a **q** in the plane the independent-particle approximation agrees with experiment.
What happens when $\mathbf{q} \neq 90^\circ$?



A. G. Marinopoulos *et al.*, Phys. Rev. Lett. **89**, 076402 (2002).

XAS of Vanadium Oxide

- Partial DOS calculation within independent-particle picture
- Overall good agreement between theory and experiment

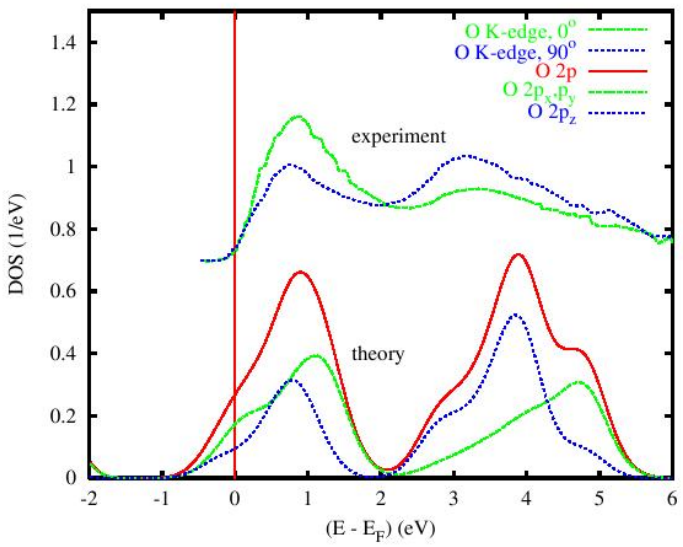


Fig. 15 Partial O $2p$ densities of states (DOS) of rutile VO_2 folded with a 0.5 eV wide Gaussian (lower set of curves) and XAS O K edge spectra (upper set of curves; note the offset introduced in order to distinguish experimental and theoretical results; from Ref. [90, 48]; data shifted by 529.5 eV).

V. Eyert, Ann. Phys. (Leipzig) **11**, 9 (2002).

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The code DP

Dielectric Properties

http://theory.polytechnique.fr/codes/dp/dp.html

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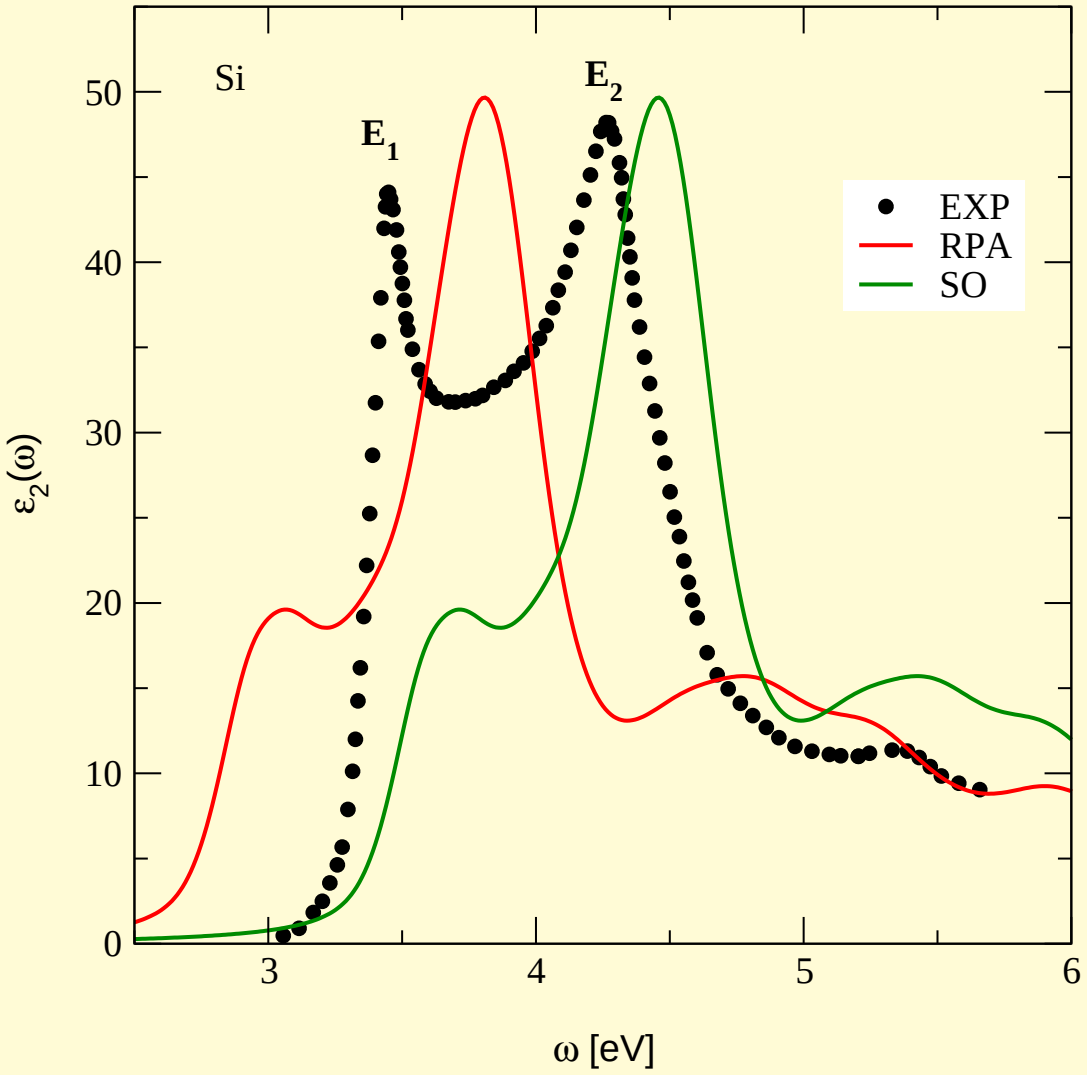
Authors: Valerio Olevano, Lucia Reining, Francesco Sottile.
Contributors: Fabien Bruneval, L. Caramella, Andrea Cucca, Nathalie Vast, Margherita Marsili

Exercise II

Optical absorption of bulk silicon

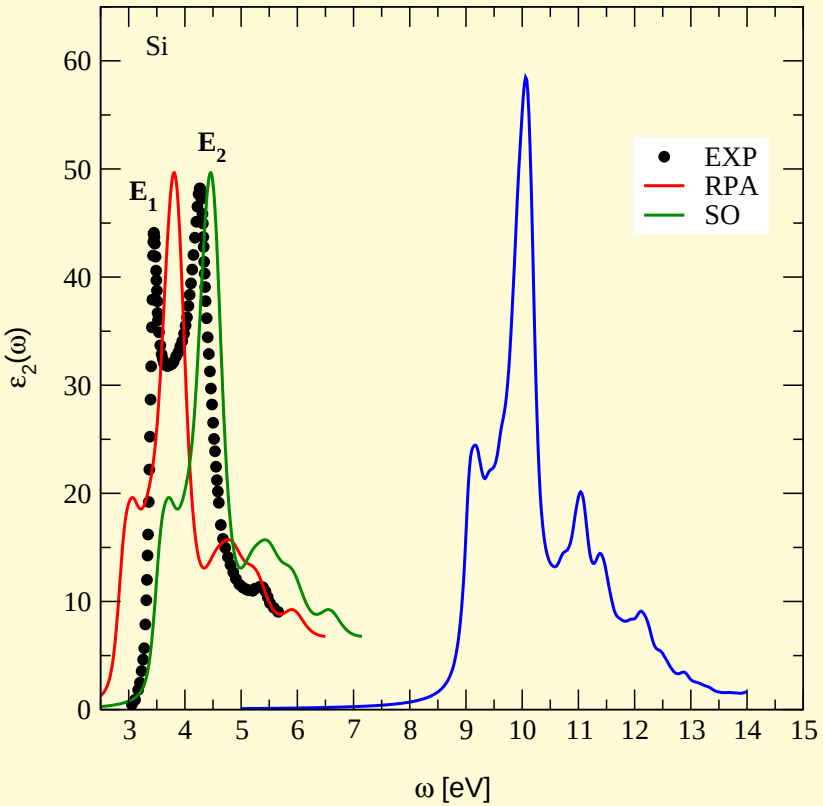
1. Starting point: the Kohn-Sham band structure (output from ABINIT)
2. Calculation of the optical absorption spectrum of silicon within the independent-particle approximation

Independent-particle absorption spectrum of silicon



- E_1 and E_2 peaks are red-shifted.
- excitonic effects on E_1 are missing.
- Scissor operator does not help: blu-shifted peaks.

Independent-particle absorption spectrum of silicon



- Comparison with Hartree-Fock calculation

F. Bruneval *et al.*, J. Chem. Phys. **124**, 144113 (2006)

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Summary

- Application of standard DFT to the calculation of
  - band structures (Kohn-Sham bands)
  - optical spectra within independent-particle approximation
- In the next days we will see how to go beyond standard DFT
- *Coming next: All the concepts we have just seen used to understand how rewritable DVDs work!*

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.