

# Key concepts in Density Functional Theory (II)

Kohn-Sham scheme, band structure and optical spectra

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June 27, 2007 – Queen's University, Belfast



# 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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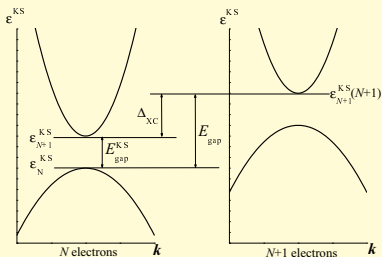
# Kohn-Sham band structure: some facts

## 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 $V_{XC}$



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

$$E_g^{\text{DFT}} = \epsilon_{N+1}^{\text{KS}} - \epsilon_N^{\text{KS}}$$

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

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



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).

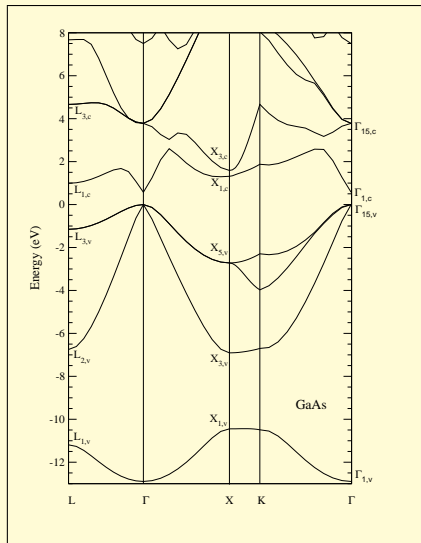


R. W. Godby, M. Schlüter and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986).





# 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](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."

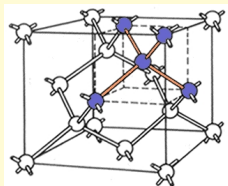
X. Gonze *et al*, Zeit. Kristallogr. 220, 558-562 (2005).

# Exercise I

## Ground state geometry and band structure of bulk silicon

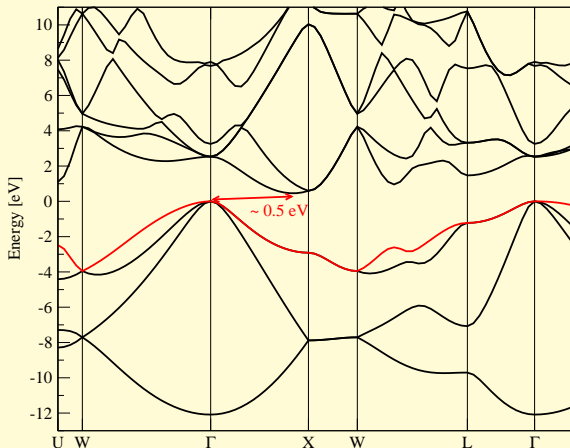
- 1 Determination of the lattice parameter  $a$
- 2 Computation of the Kohn-Sham band structure

# Equilibrium geometry of silicon



- Our DFT-LDA lattice parameter:  
 $a = 10.217 \text{ Bohr} = 5.407 \text{ \AA}$
- Exp. value:  $a = 5.431 \text{ \AA}$  at  $25^\circ$ .

# Kohn-Sham band structure of silicon



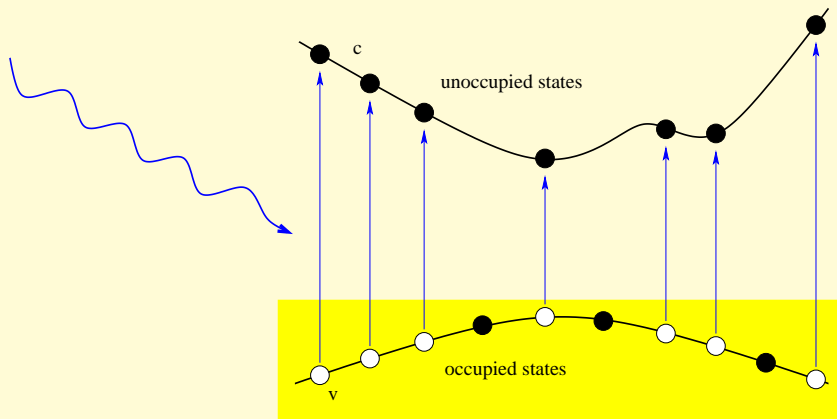
- Indirect gap
- Good dispersion of bands close to the gap
- Exp. gap = 1.17 eV
- Scissor operator = 0.65 – 0.7 eV



# Outline

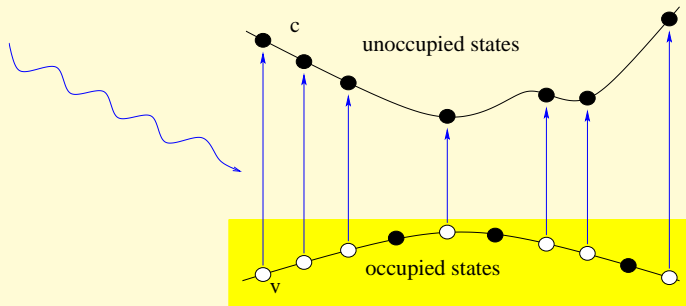
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# An intuitive picture for absorption



Kohn-Sham (KS) energy states

# An intuitive picture for absorption

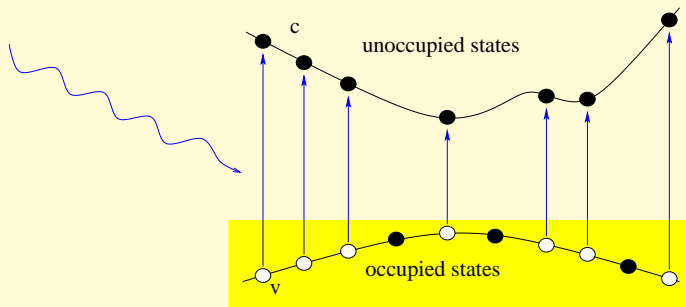


Independent particle transitions between KS states

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

Very common approximation: Fermi's golden rule!

# An intuitive picture for absorption

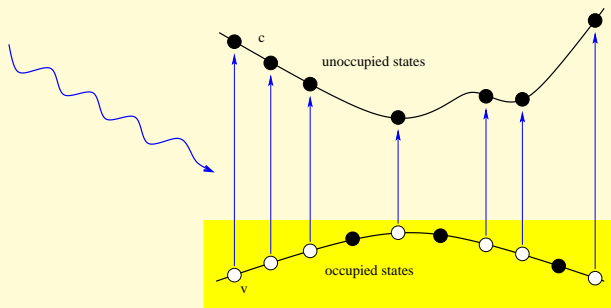


Independent particle transitions between KS states

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

Very common approximation: **Fermi's golden rule!**

# Optical absorption: dielectric function



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

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

## Joint density of states

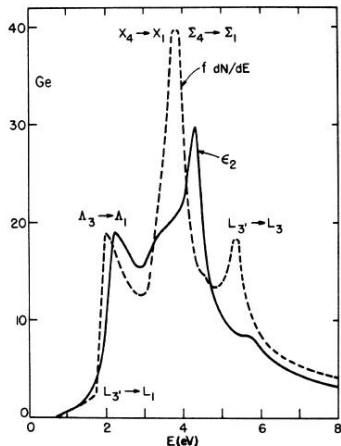
In the independent-particle approximation the dielectric function is determined by two contributions: **optical matrix elements** and **energy levels**.

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


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

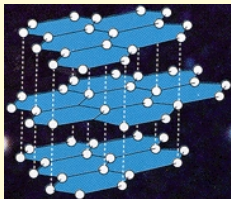
There is **not** a unique answer.

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!*

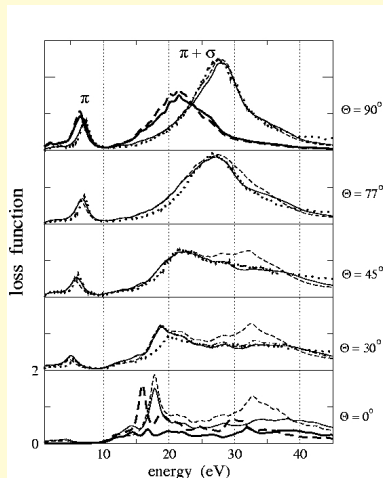


# EELS of graphite



For a  $\mathbf{q}$  in the plane the independent-particle approximation agrees with experiment.

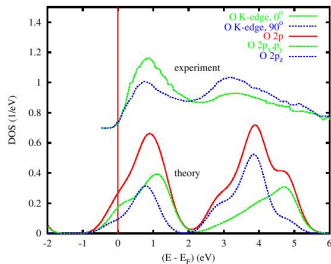
What happens when  $\mathbf{q} \neq 90^\circ$ ?




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<sub>2</sub> 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. [4], [5]; 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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Contributors: Fabien Bruneval, L. Caramella, Andrea Cucca, Nathalie Vast, Margherita Marsili

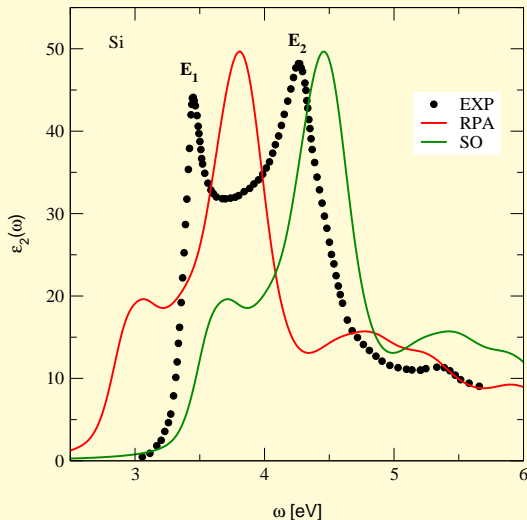


# Exercise II

## Optical absorption of bulk silicon

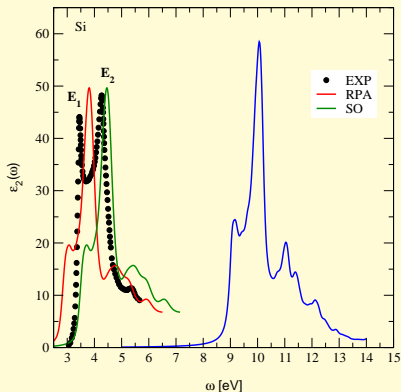
- 1 Starting point: the Kohn-Sham band structure (output from ABINIT)
- 2 Calculation of the optical absorption spectrum of silicon within the independent-particle approximation

# 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: blue-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.