Introduction to Spectroscopy

Matteo Gatti and you all present online

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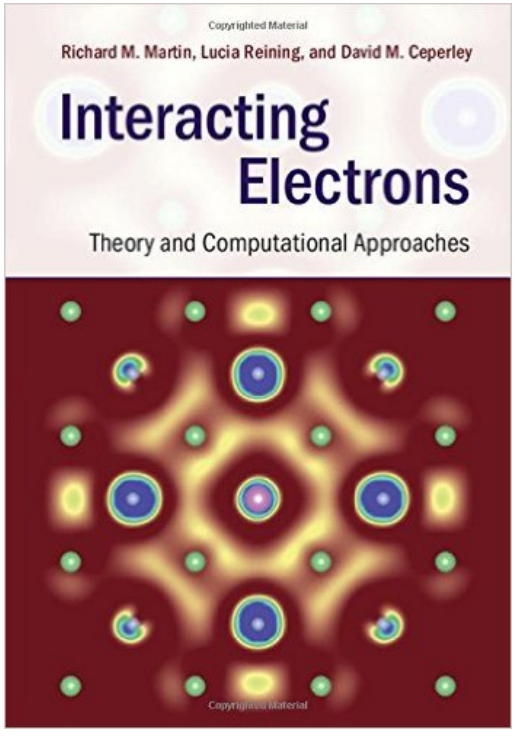
Online ASESMA 2021

Books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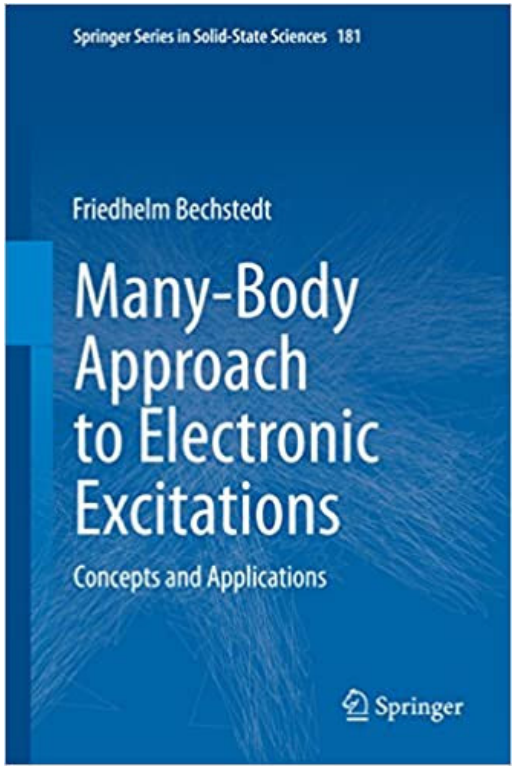
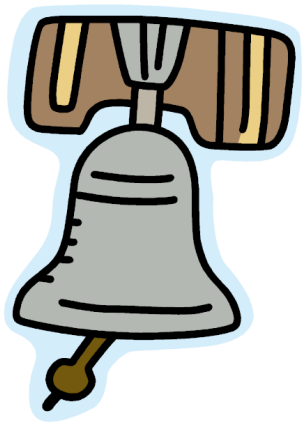

Springer Series in Solid-State Sciences 181
Friedhelm Bechstedt
Many-Body Approach to Electronic Excitations
Concepts and Applications
Springer

Outline

1. Introduction to spectroscopy
2. Photoemission: Why more than independent electrons?
3. Absorption: Why more than the band structure?
4. Summary

Spectroscopy

A first example

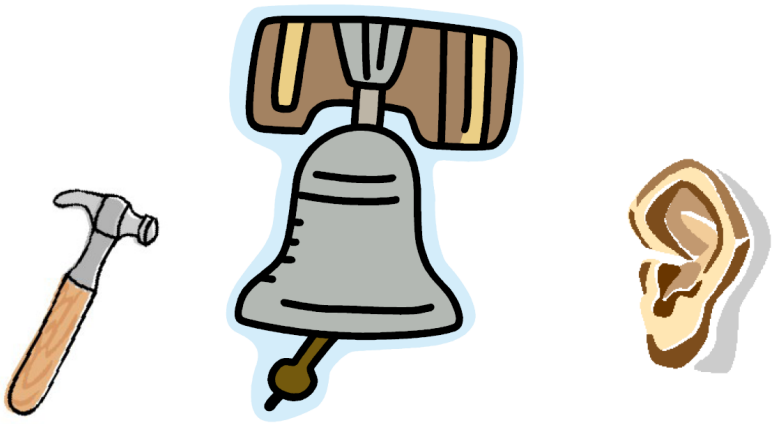


Spectroscopy

A first example

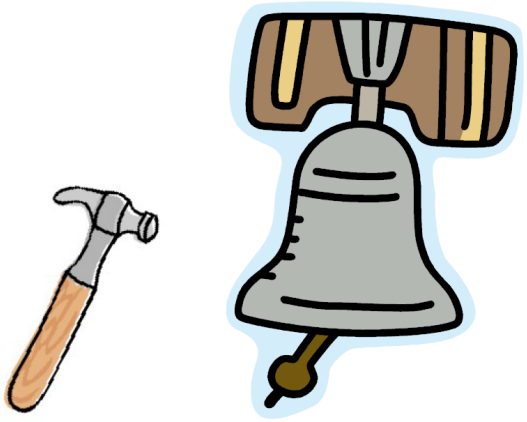
Spectroscopy

A first example



Spectroscopy

A first example

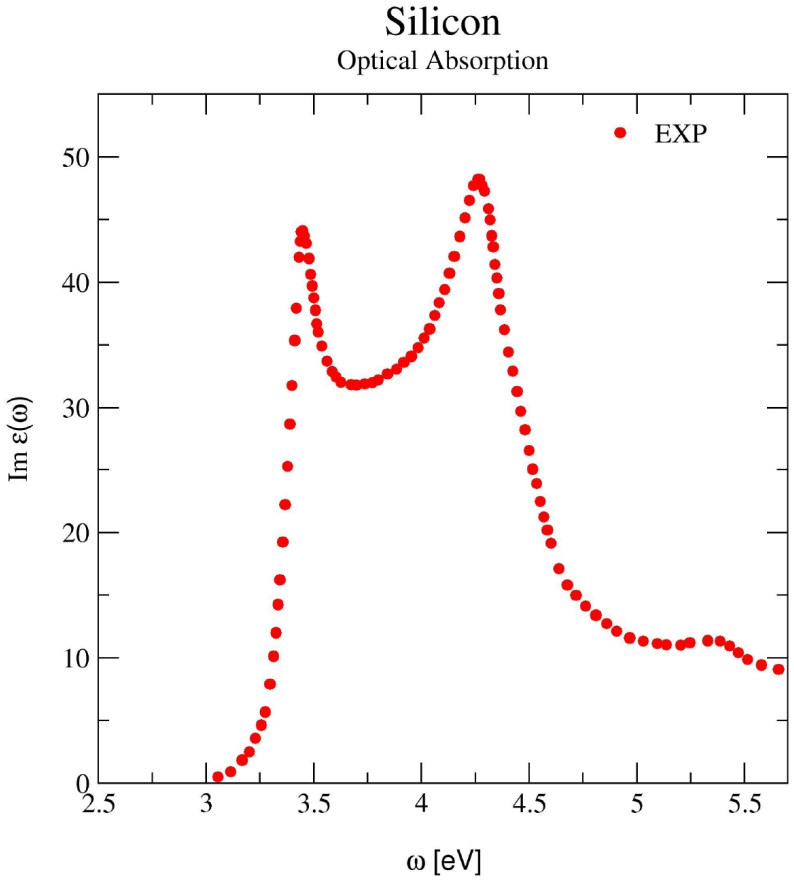


Perturbation

Excitation

Response

Theoretical spectroscopy



Exp. at 30 K from: P. Lautenschlager *et al.*, Phys. Rev. B **36**, 4821 (1987).

Theoretical spectroscopy

- Calculate and reproduce
- Understand and explain
- Predict

Theoretical Spectroscopy

- Which kind of spectra?
- Which kind of tools?

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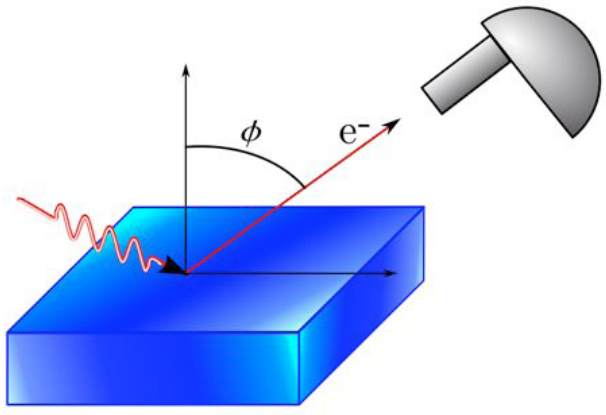
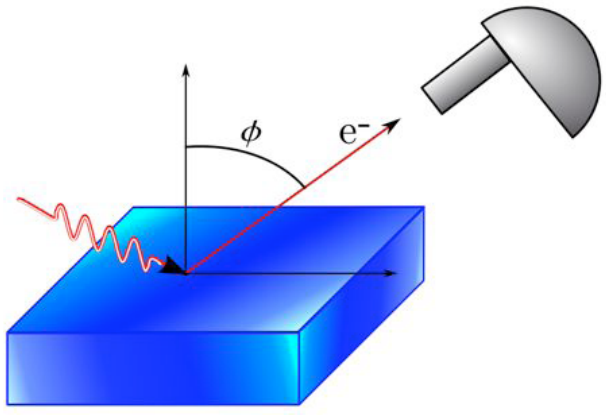
Direct Photoemission



photon in - electron out

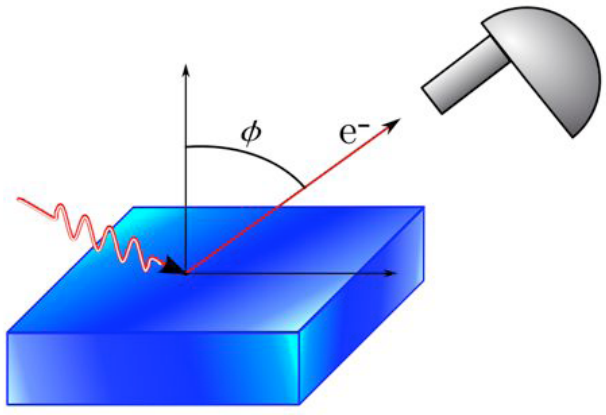
Direct Photoemission



photon in - electron out

$$E(N) + h\nu = E(N-1, i) + E_{kin}$$

Direct Photoemission

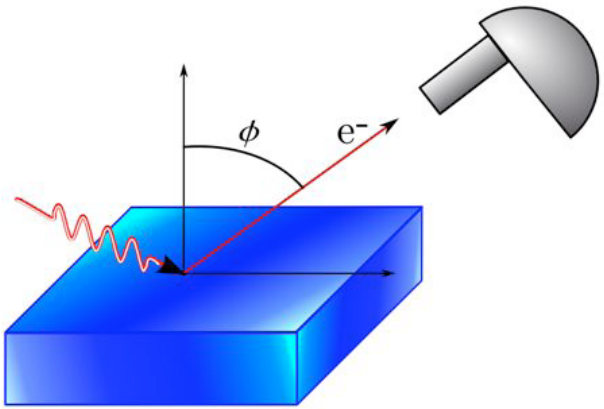


photon in - electron out

$$E(N) + h\nu = E(N-1, i) + E_{kin}$$

$$E_i = E(N) - E(N-1, i) = E_{kin} - h\nu$$

Direct Photoemission



photon in - electron out

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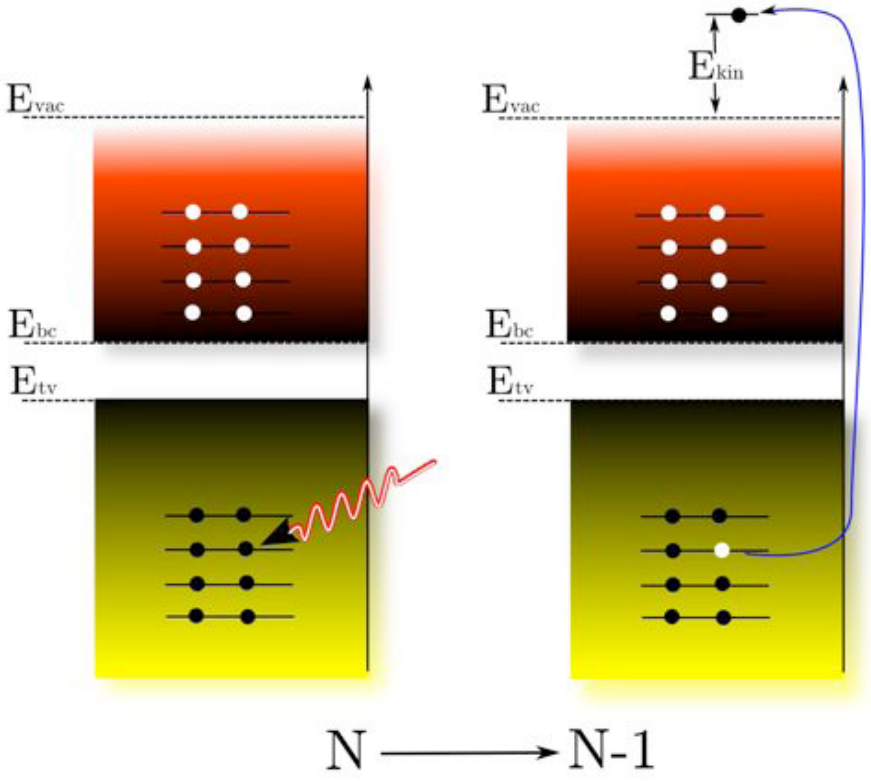
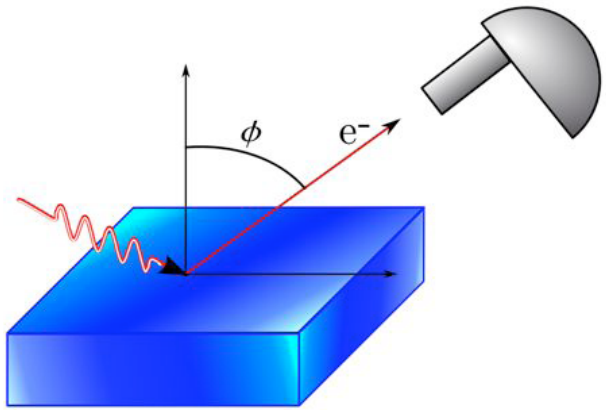


occupied states

S. Hüfner, Photoelectron spectroscopy

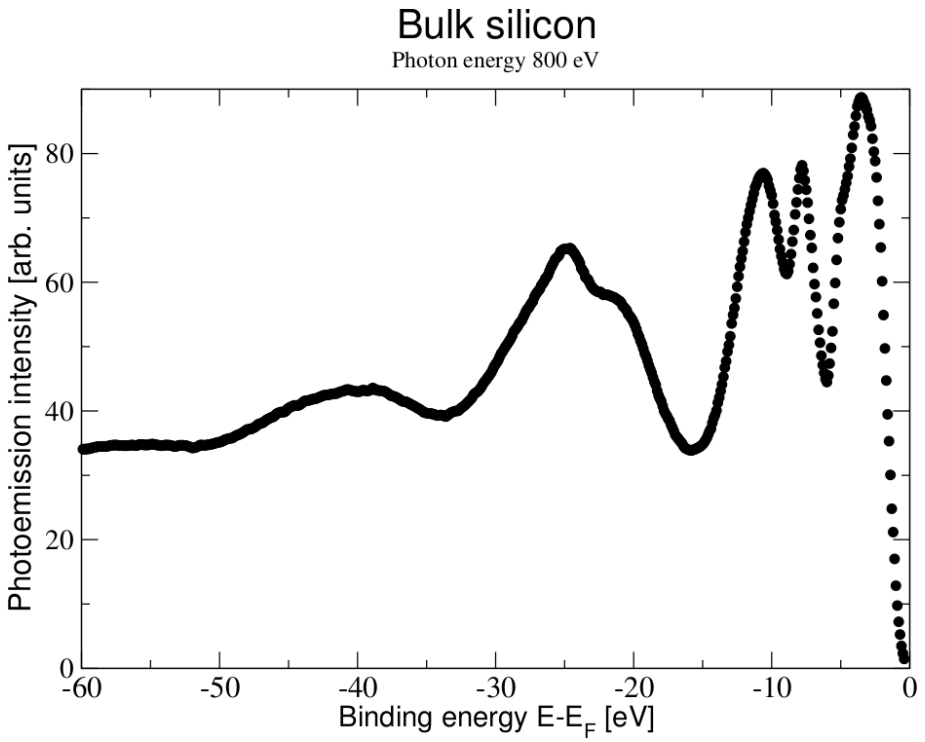
Direct Photoemission



photon in - electron out

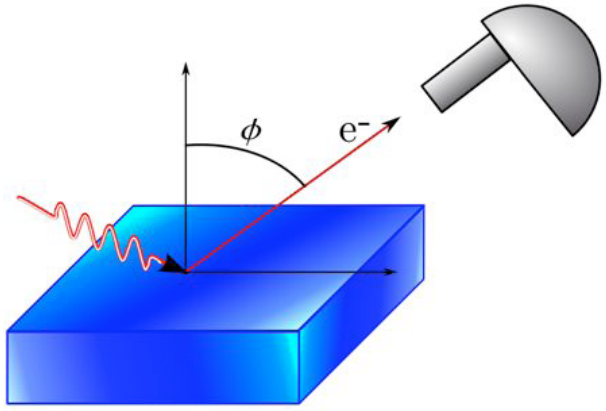
$$E(N) + h\nu = E(N-1, i) + E_{kin}$$

$$E_i = E(N) - E(N-1, i) = E_{kin} - h\nu$$



M. Guzzo *et al.*, PRL 107 (2011).

Angle-resolved photoemission (ARPES)

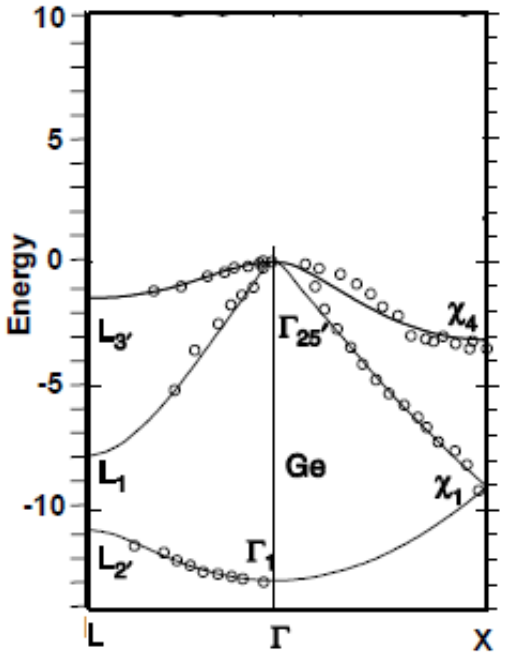


photon in - electron out

$$E(N) + h\nu = E(N-1, i) + E_{kin}$$

$$E_i = E(N) - E(N-1, i) = E_{kin} - h\nu$$

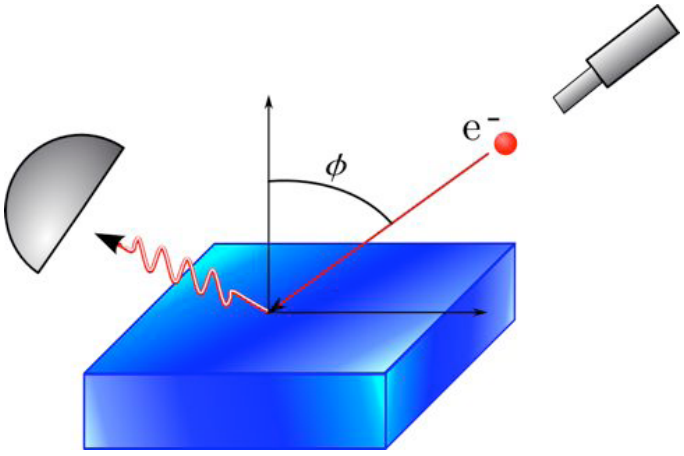
...plus momentum conservation $\Rightarrow$ ARPES



Germanium:

PRB **32** 2326 (1985); PRB **47** 2130 (1993).

Inverse Photoemission

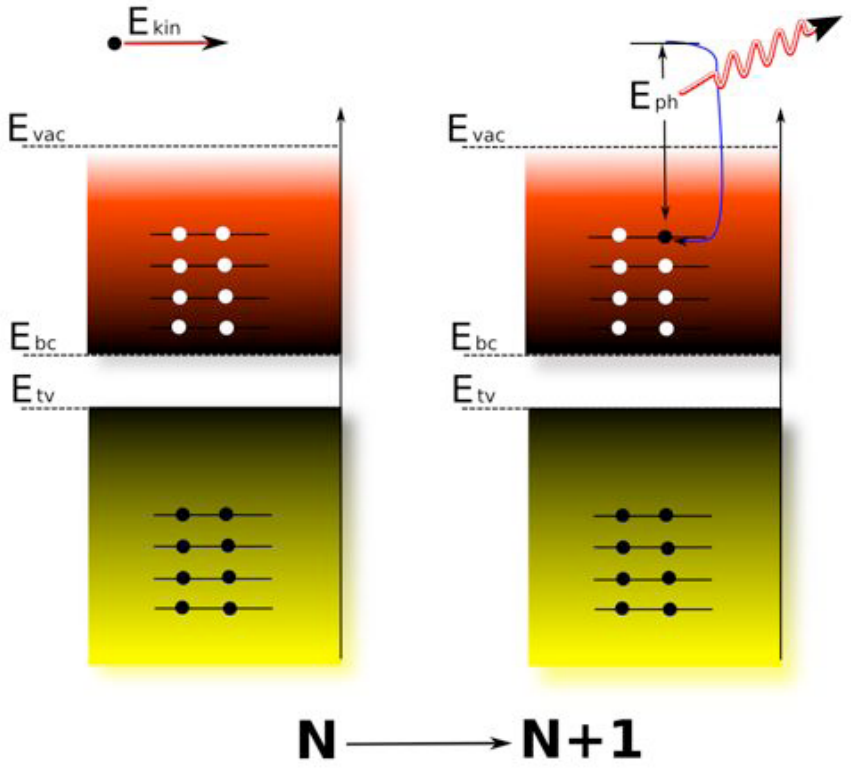


electron in - photon out

$$E(N) + E_{kin} = E(N+1, i) + h\nu$$

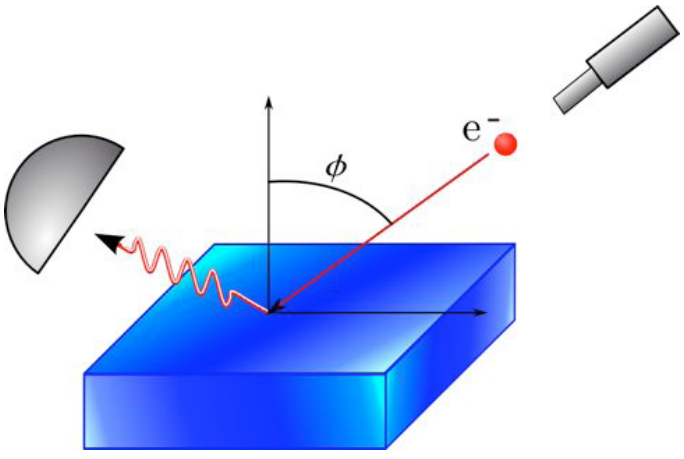
$$E_i = E(N+1, i) - E(N) = E_{kin} - h\nu$$

aka Bremsstrahlung
isochromat spectroscopy (BIS)

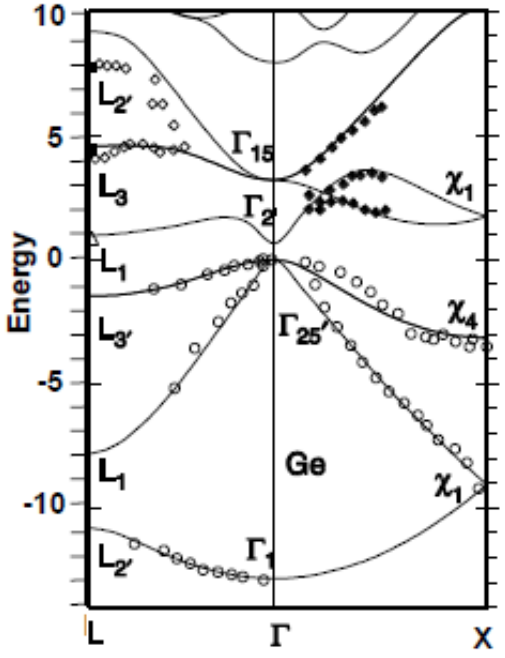


empty states

Inverse Photoemission



electron in - photon out



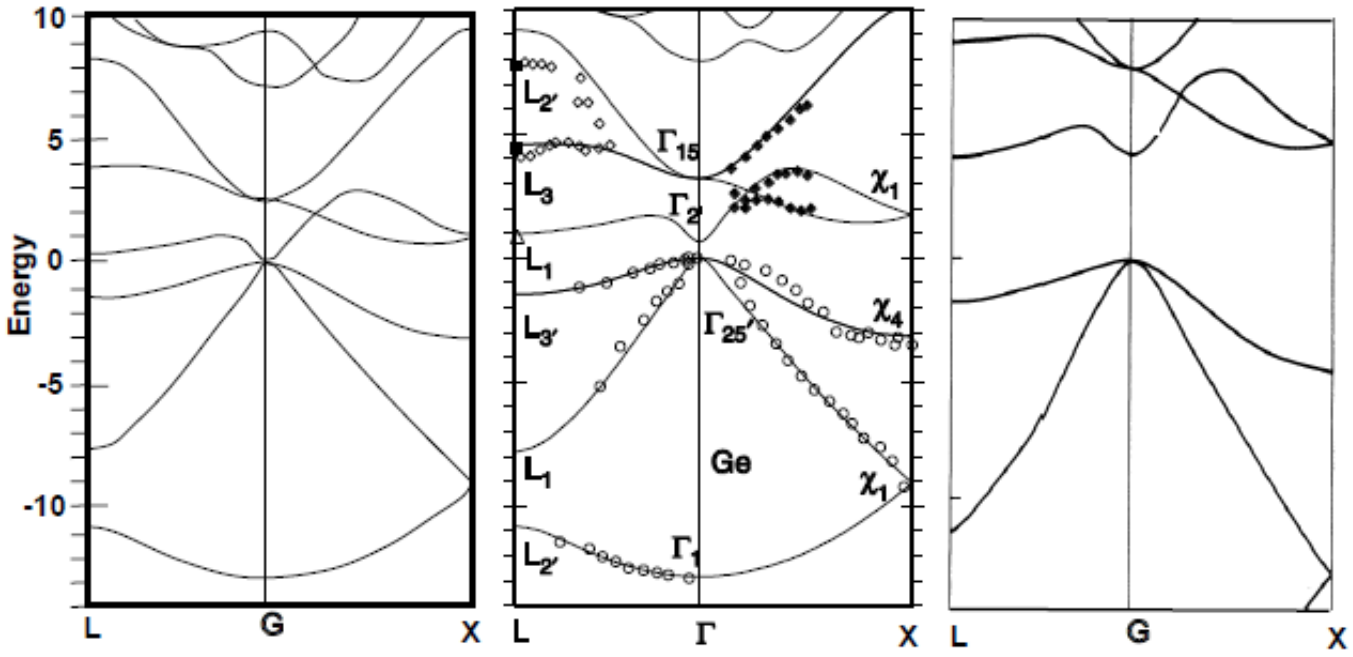
Germanium:

PRB **32** 2326 (1985); PRB **47** 2130 (1993)

$$E_g = \min_{c,v}\{E_c - E_v\} = \min_{c,v}\{[E(N+1,c) - E(N)] - [E(N) - E(N-1,v)]\}$$

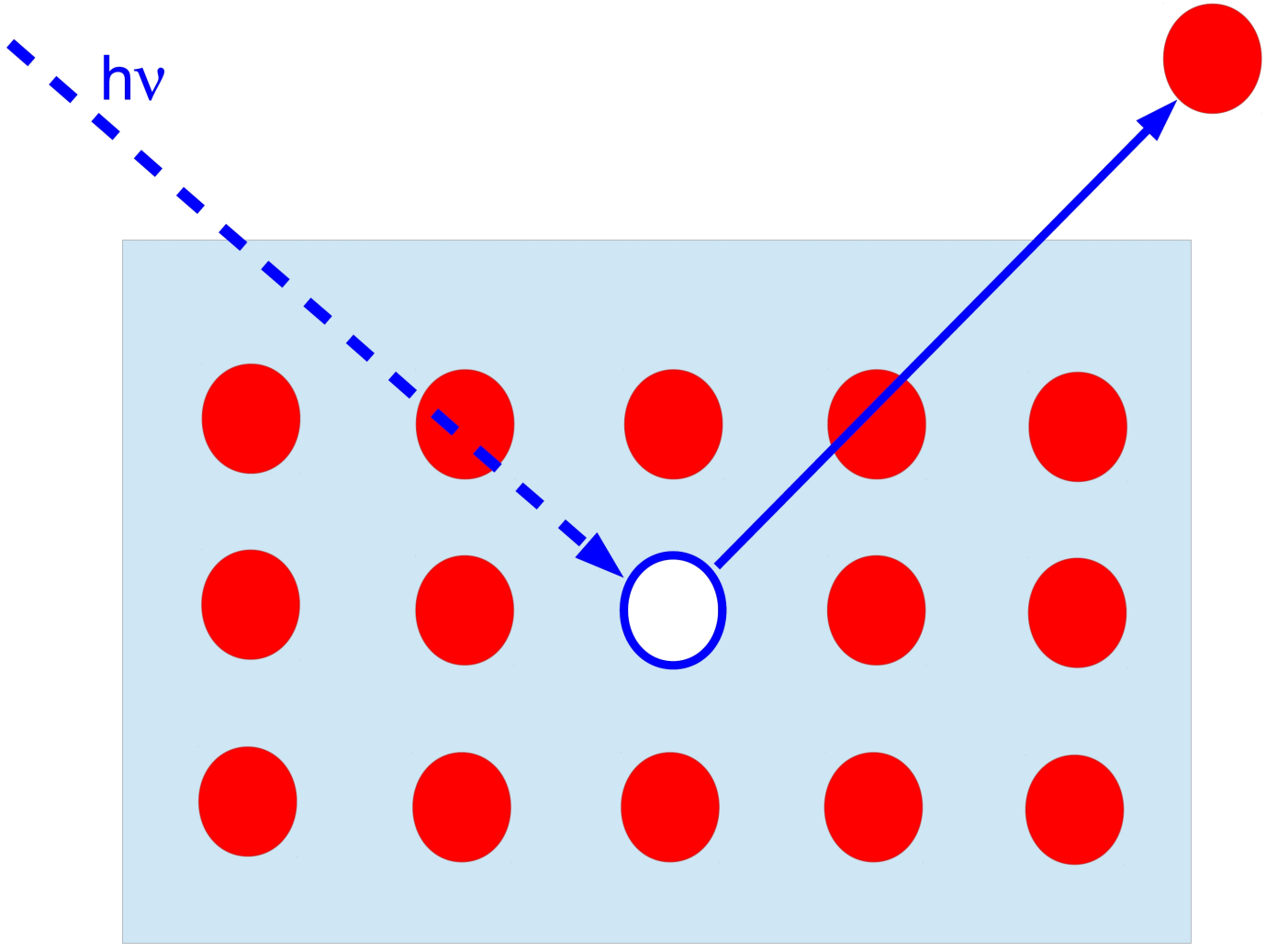
Why more than independent electrons?

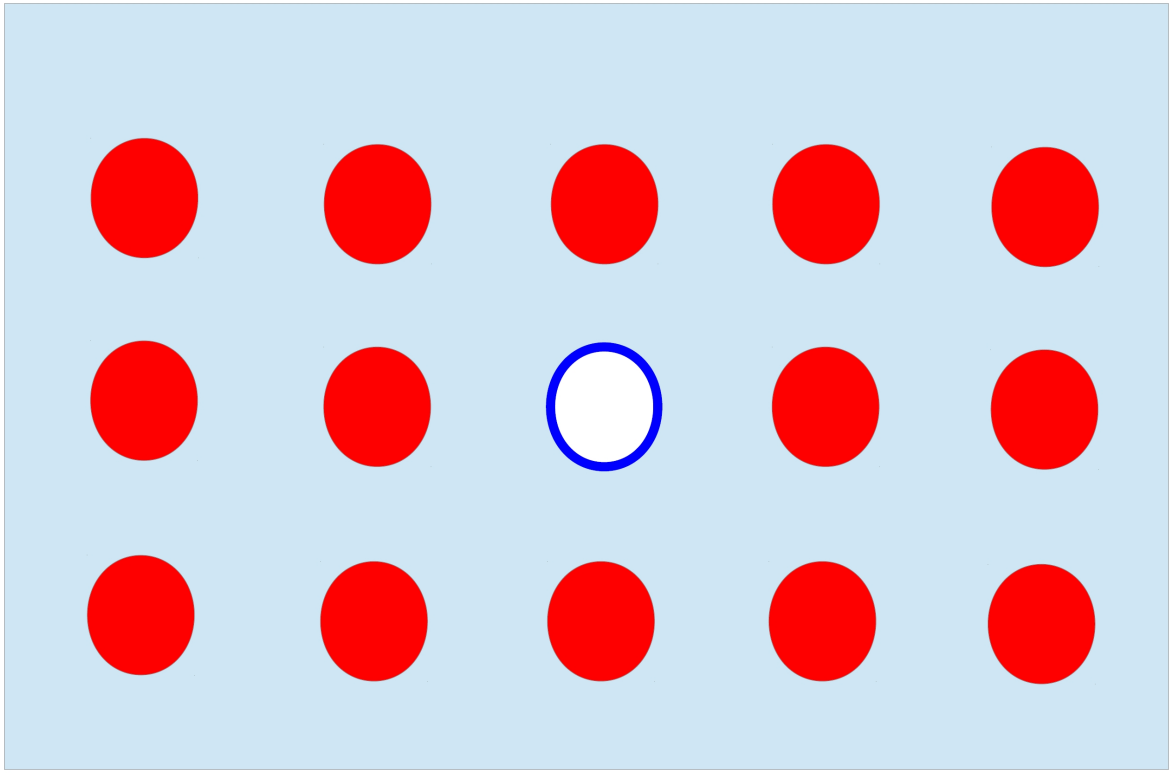
LDA Hartree-Fock



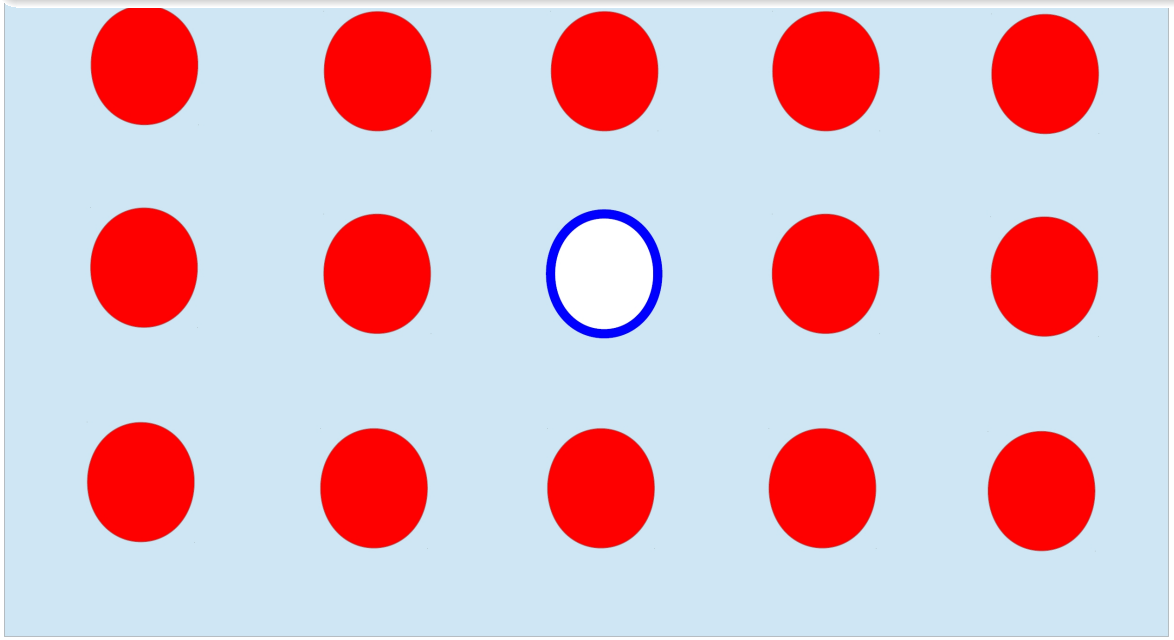
Germanium band structure

Exp. from PRB **32** (1985); PRB **47** (1993);
GW from PRB **48** (1993); Hartree-Fock from PRB **35** (1987)

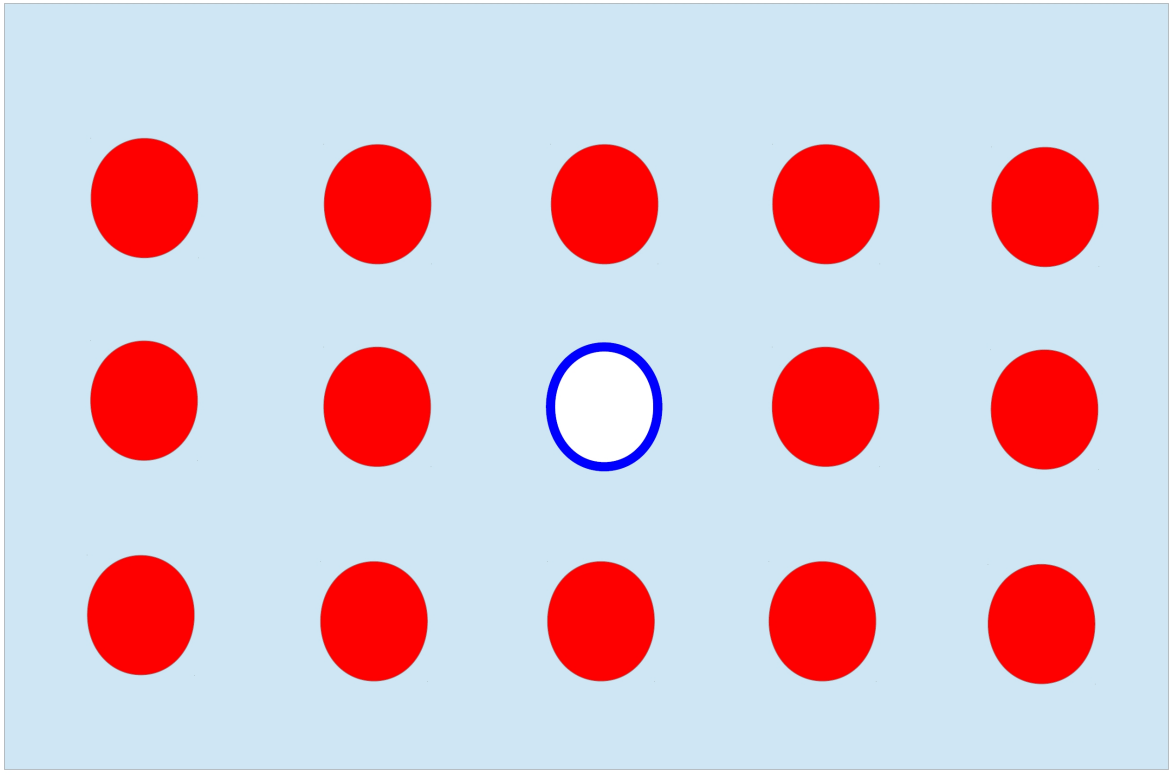

hν



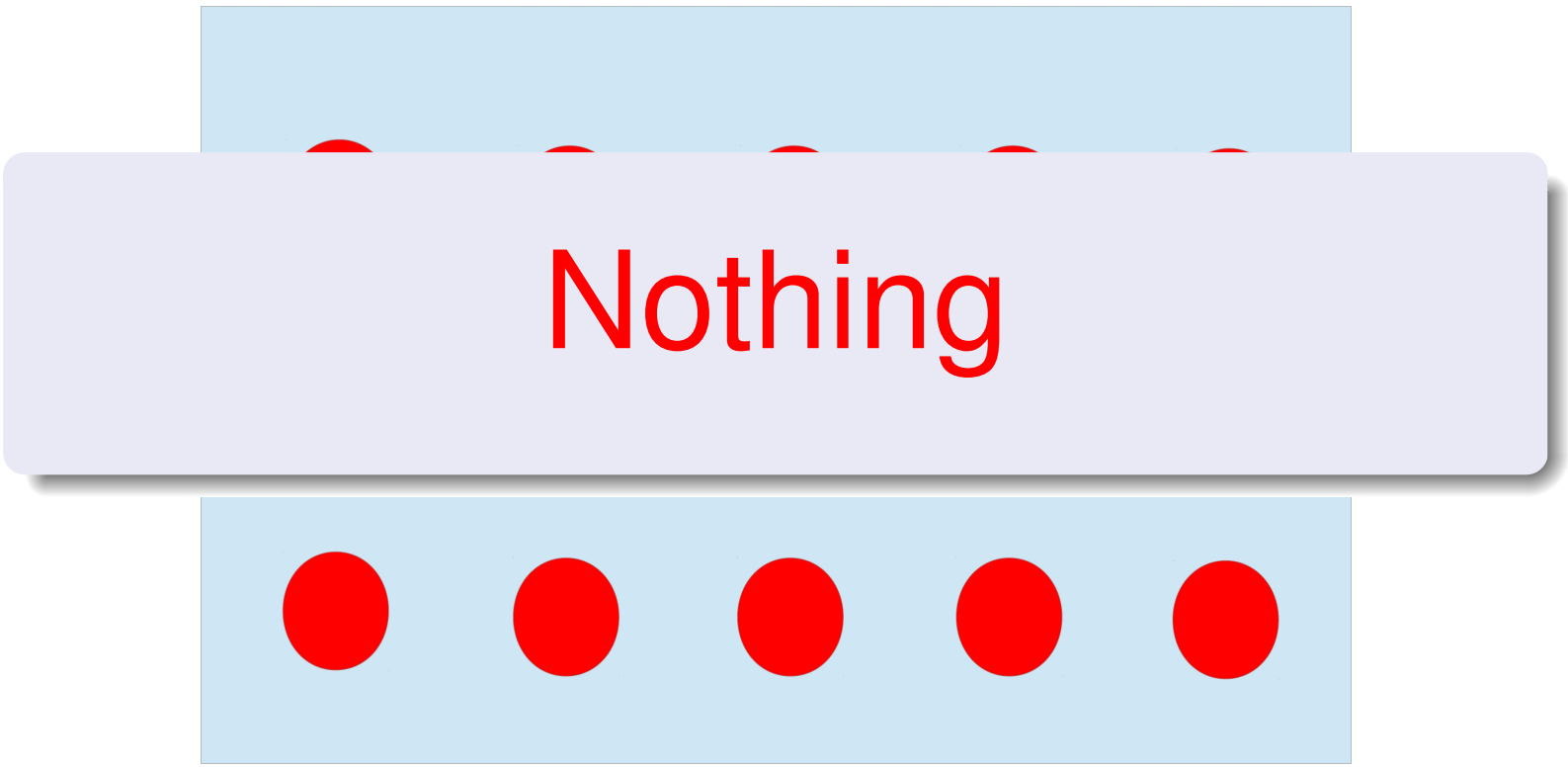
What happens?



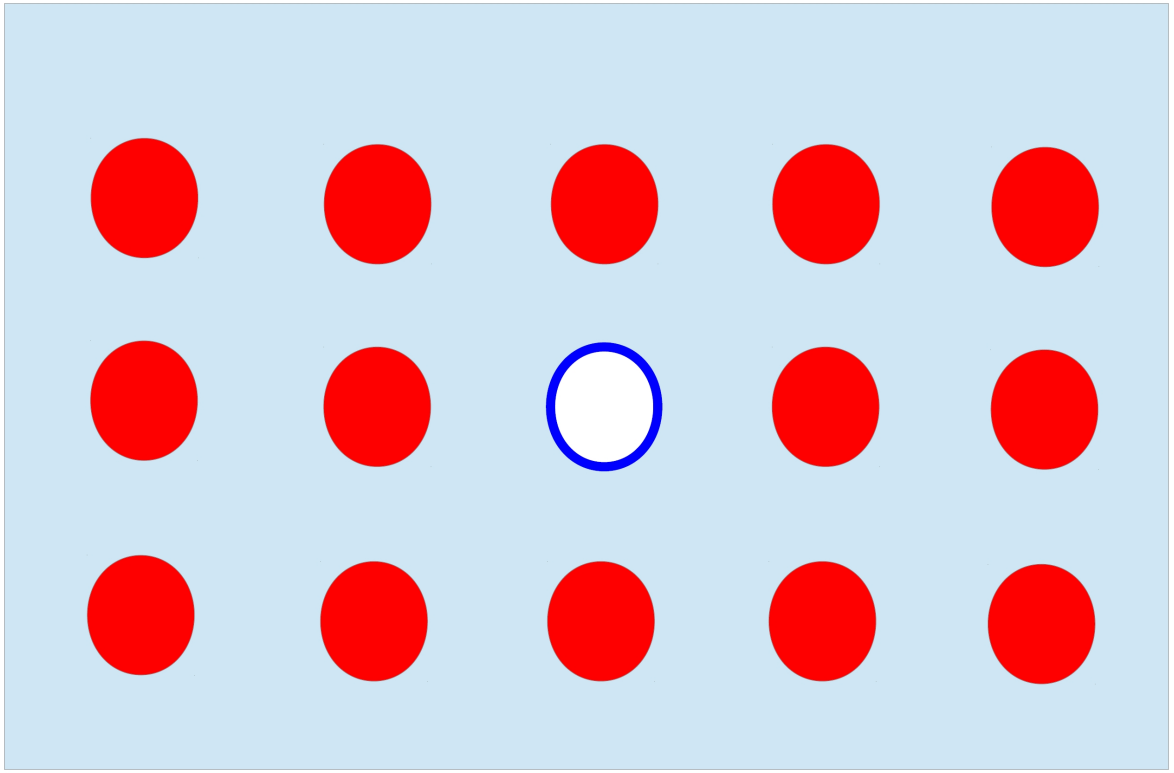
Non-interacting particles



Non-interacting particles



Interacting particles



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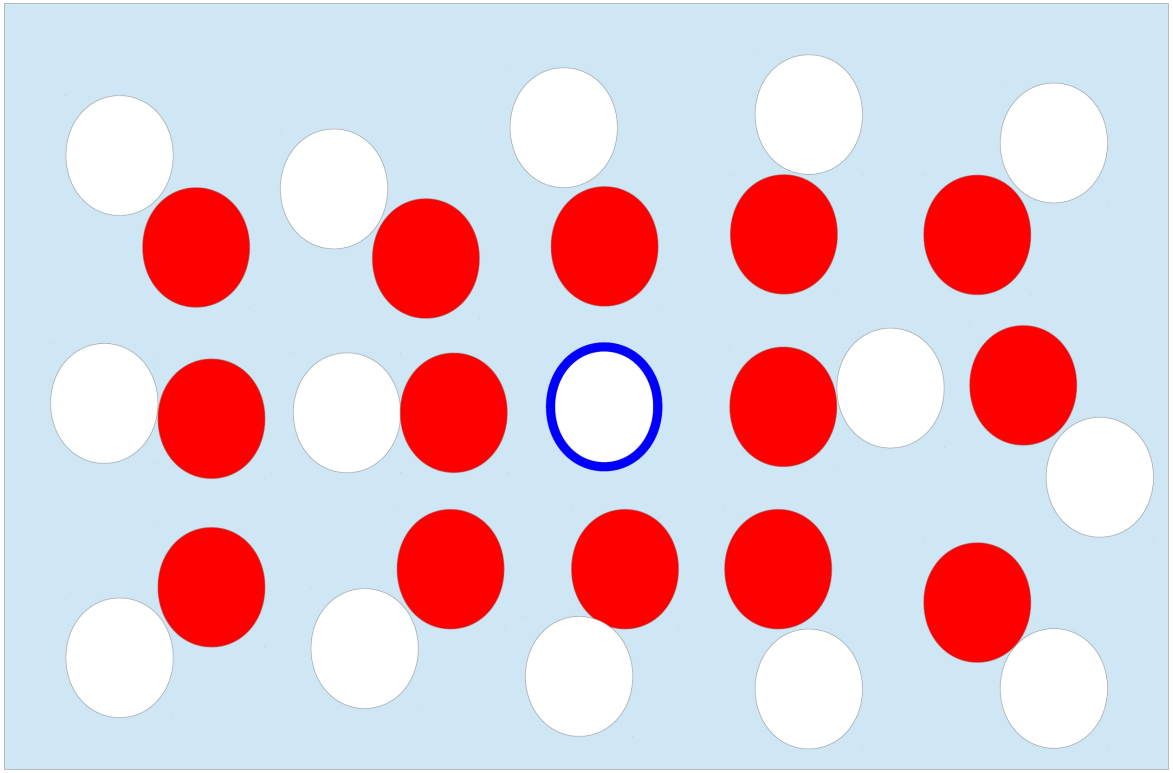

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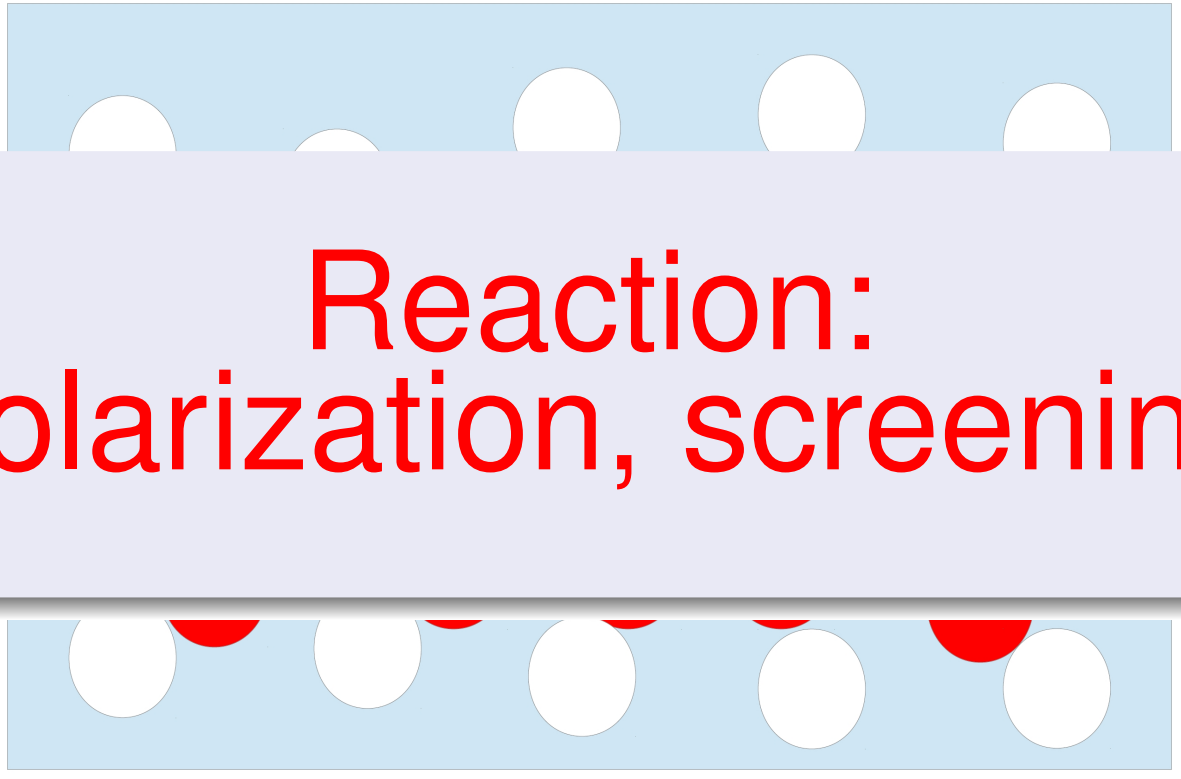
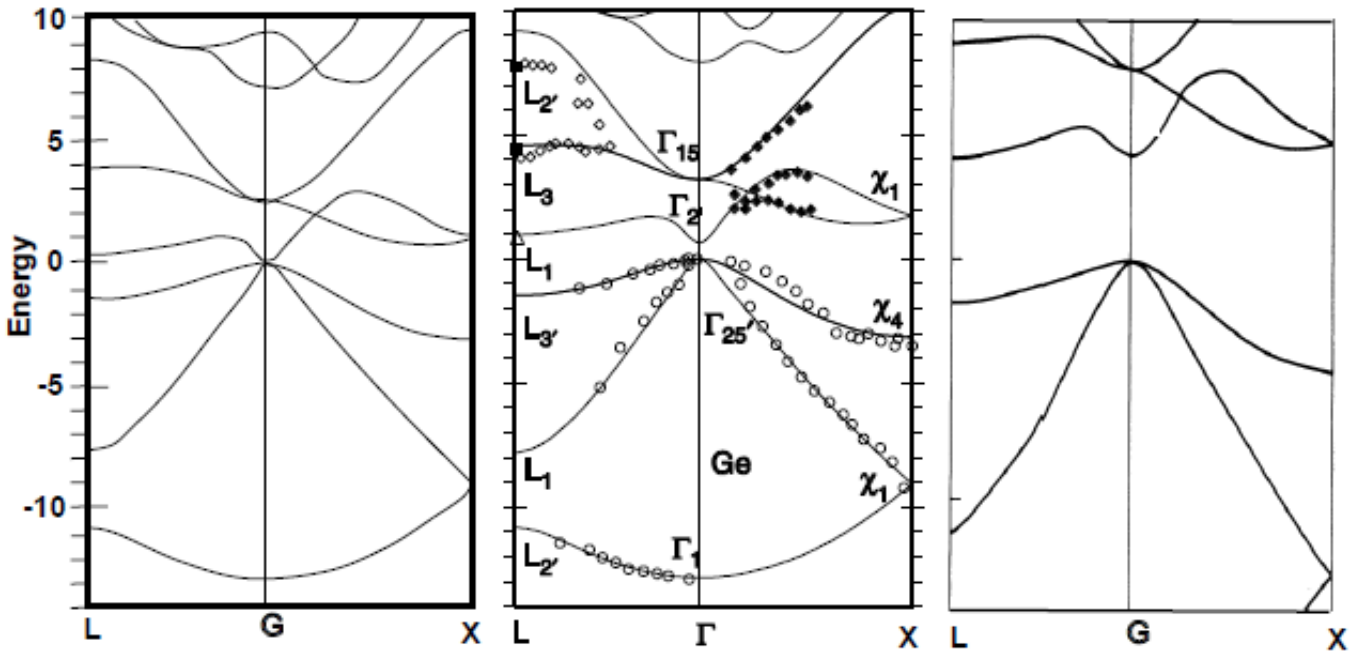


Reaction: polarization, screening

Why more than independent electrons?

LDA GW Hartree-Fock



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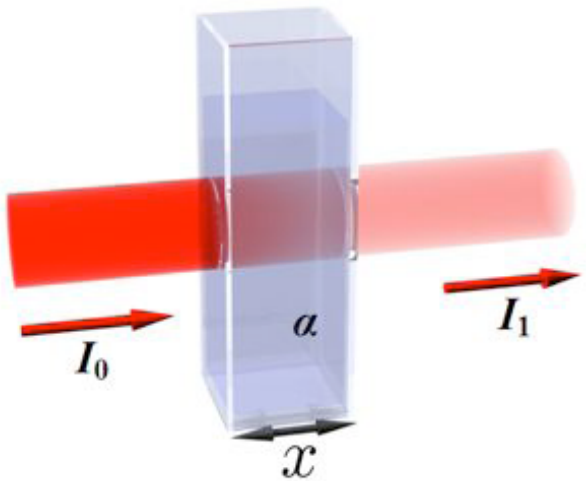
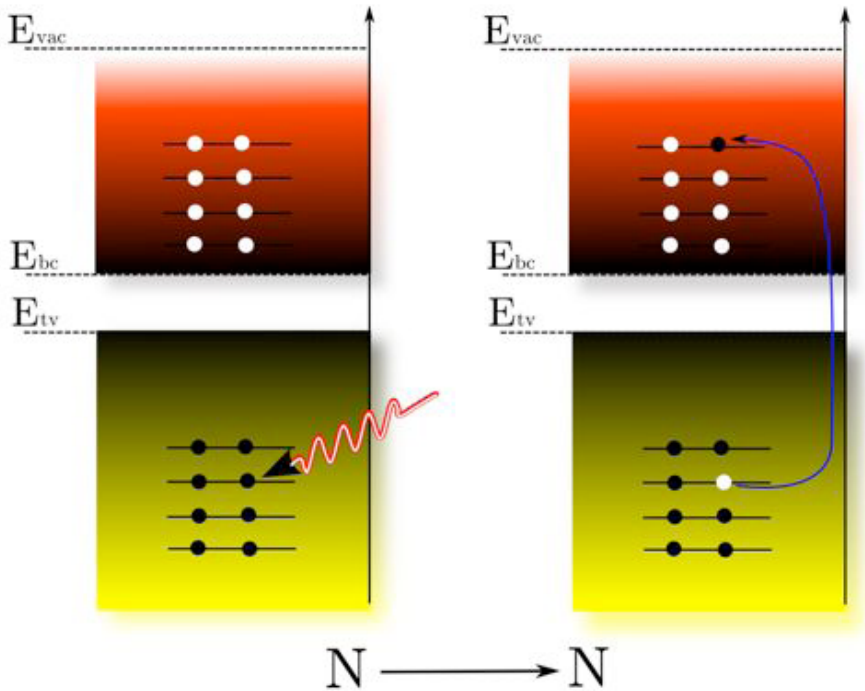
Absorption



Beer-Lambert law: $I = I_0 e^{-\alpha x}$



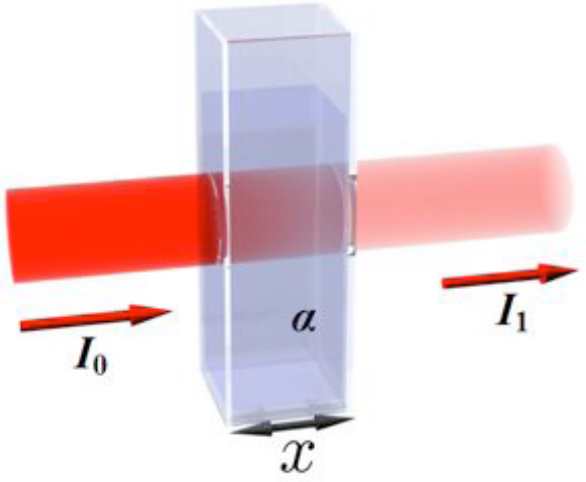
$\alpha(\omega) \propto \mathrm{Im}\epsilon_M(\mathbf{q} \to 0, \omega) \quad \Rightarrow \quad$ (extended system) absorption coefficient

$\sigma(\omega) \propto \mathrm{Im}\epsilon_M(\mathbf{q} \to 0, \omega) \quad \Rightarrow \quad$ (finite system) photoabsorption cross section

$$E(x,t) = E_0 e^{i\frac{\omega\tilde{n}}{c}x} e^{-i\omega t} \qquad \tilde{n} = \sqrt{\epsilon_M} = n + ik \qquad \epsilon_M = \epsilon_1 + i\epsilon_2$$

J. D. Jackson, Classical Electrodynamics

Absorption



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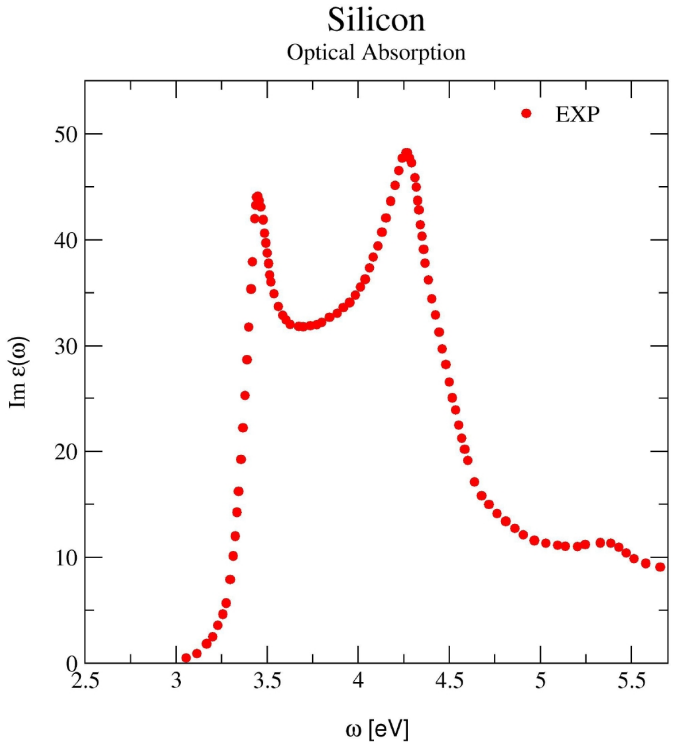

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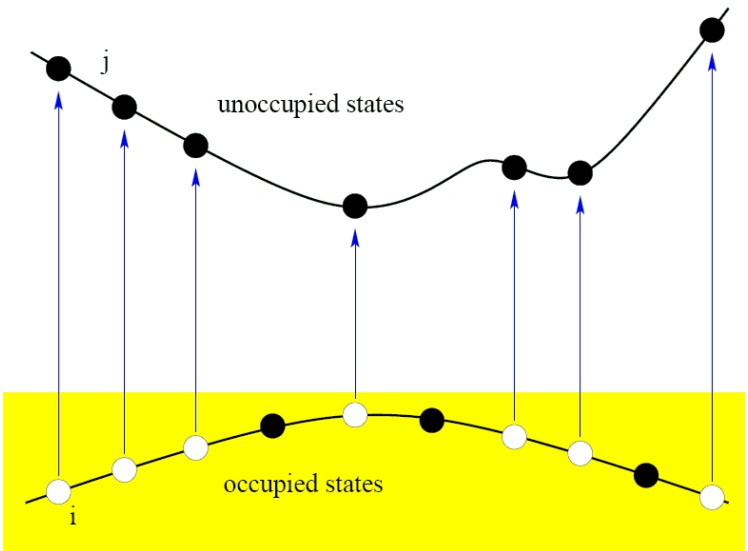
$\sigma(\omega) \propto \mathrm{Im}\epsilon_M(\mathbf{q} \to 0, \omega) \quad \Rightarrow \quad$ (finite system) photoabsorption cross section

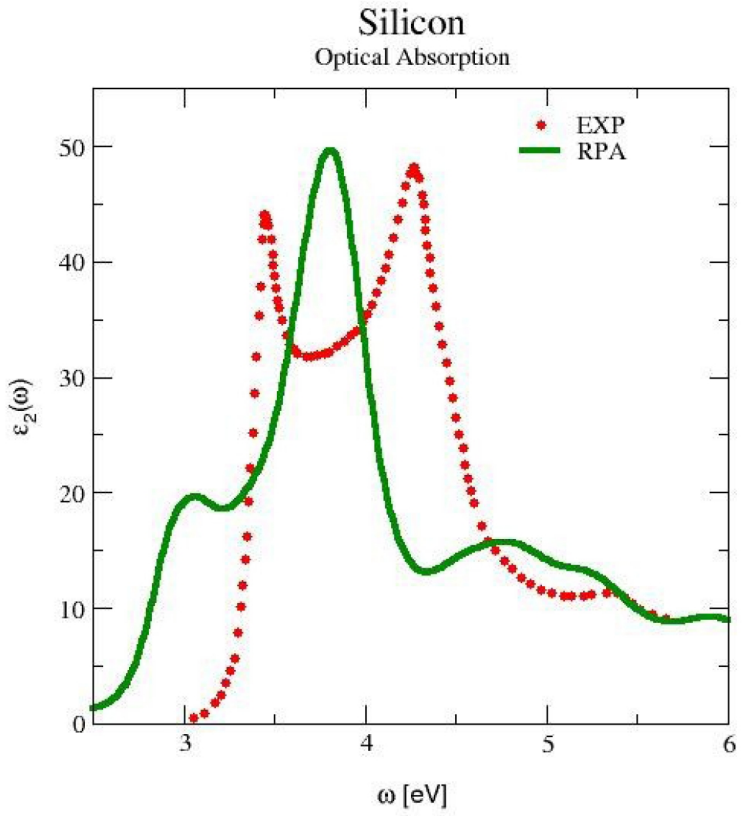
$$\mathrm{Im}\epsilon_M(\omega) \equiv \epsilon_2(\omega)$$

More than LDA band structure

Independent transitions:

$$\epsilon_2(\omega) = \frac{8\pi^2}{\Omega\omega^2} \sum_{ij} |\langle\varphi_j|\mathbf{e}\cdot\mathbf{v}|\varphi_i\rangle|^2 \delta(\varepsilon_j - \varepsilon_i - \omega)$$





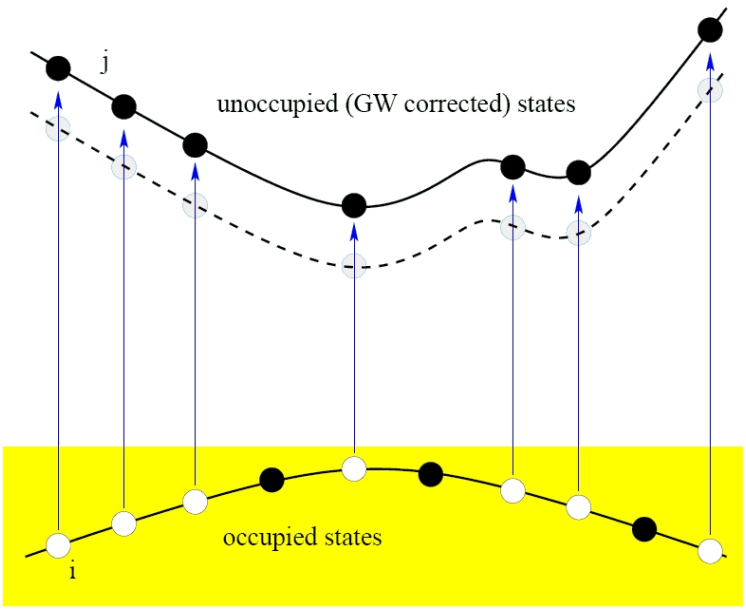
What is wrong?

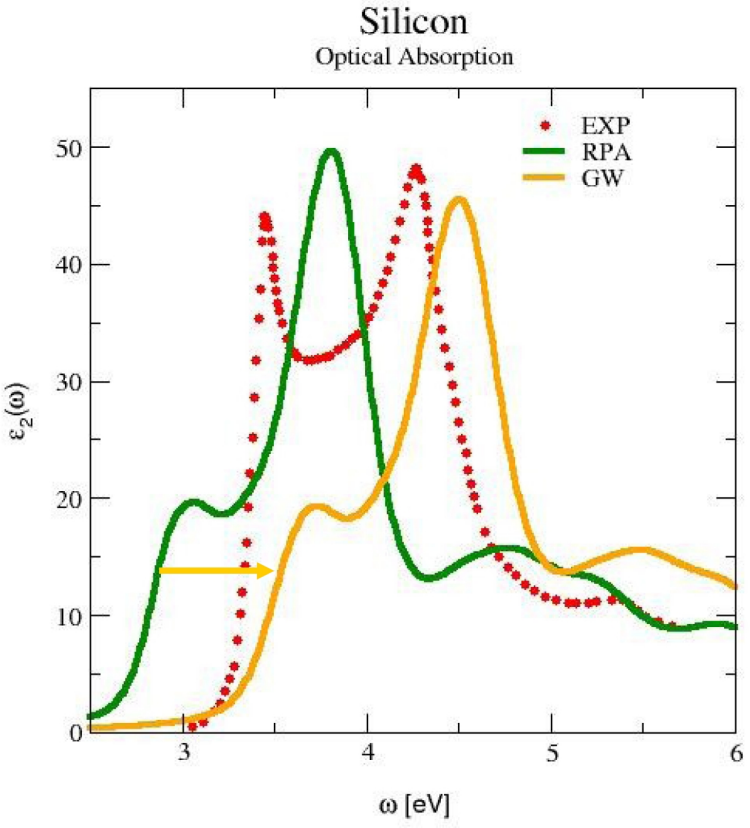
What is missing?

More than GW band structure

Independent transitions:

$$\epsilon_2(\omega) = \frac{8\pi^2}{\Omega\omega^2} \sum_{ij} |\langle\varphi_j|\mathbf{e}\cdot\mathbf{v}|\varphi_i\rangle|^2 \delta(E_j - E_i - \omega)$$

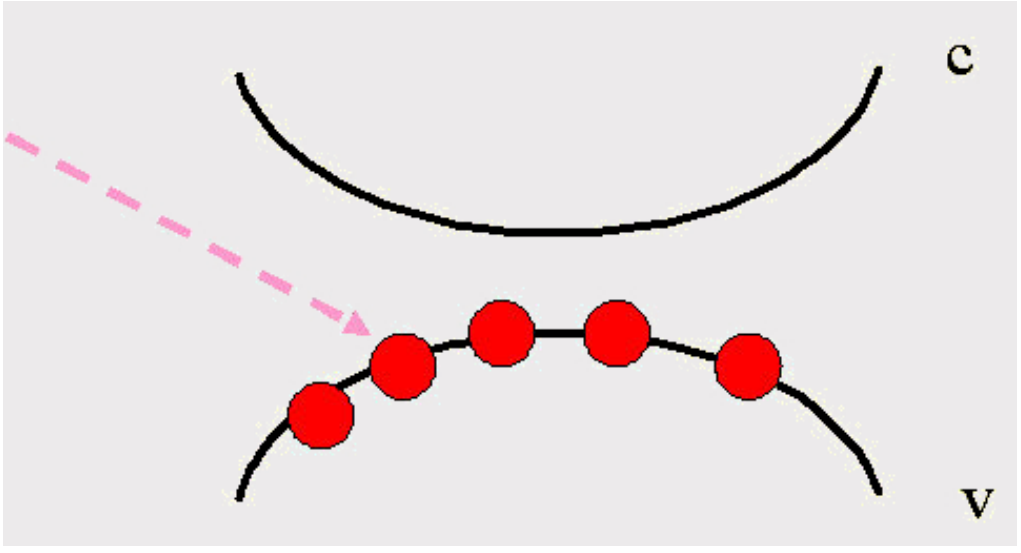




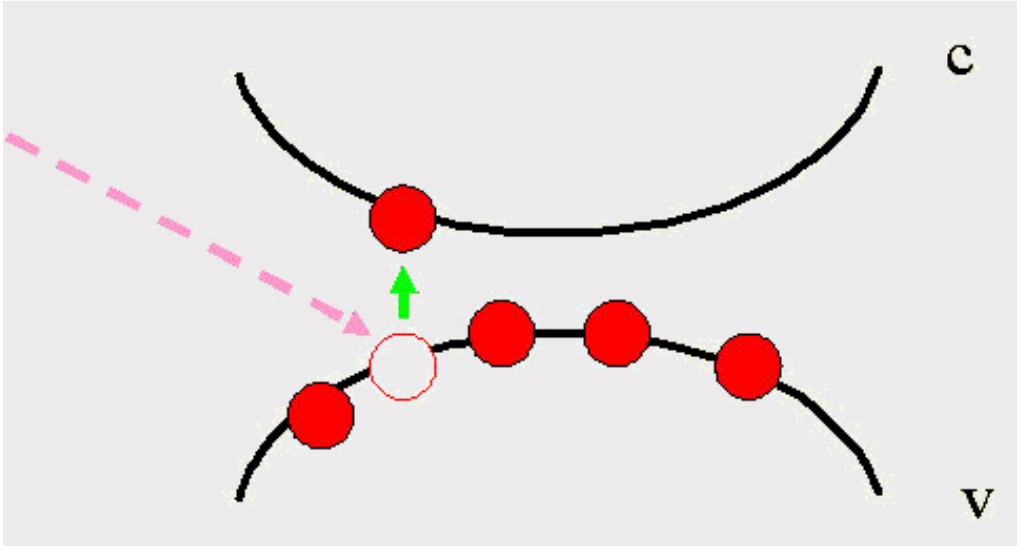
What is wrong?

What is missing?

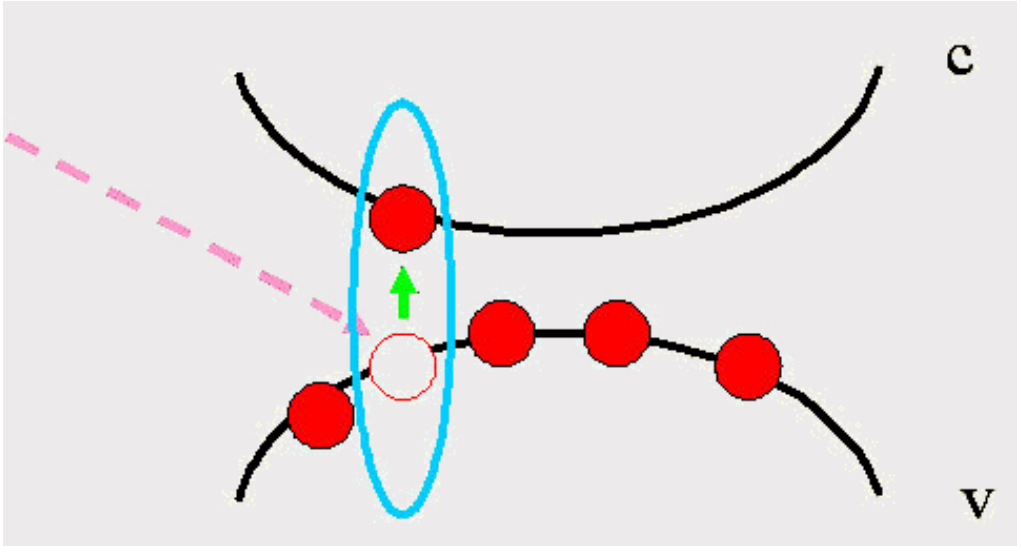
Absorption



Absorption



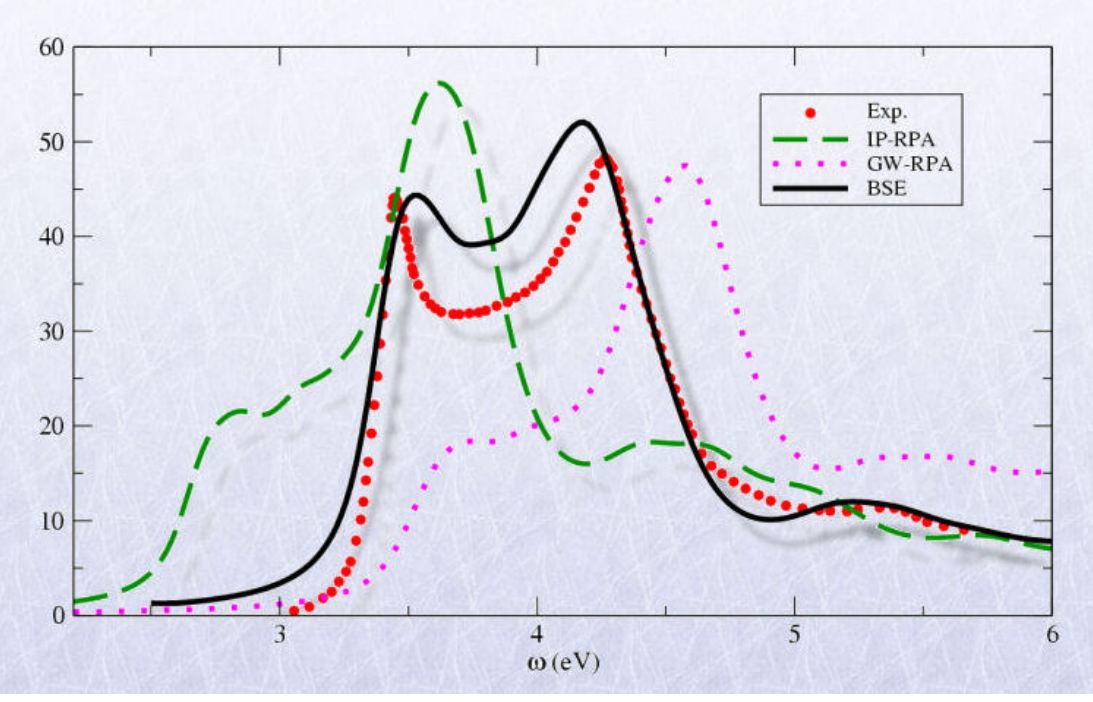
Absorption



Excitonic effects = electron - hole interaction

Absorption spectrum

Bulk silicon

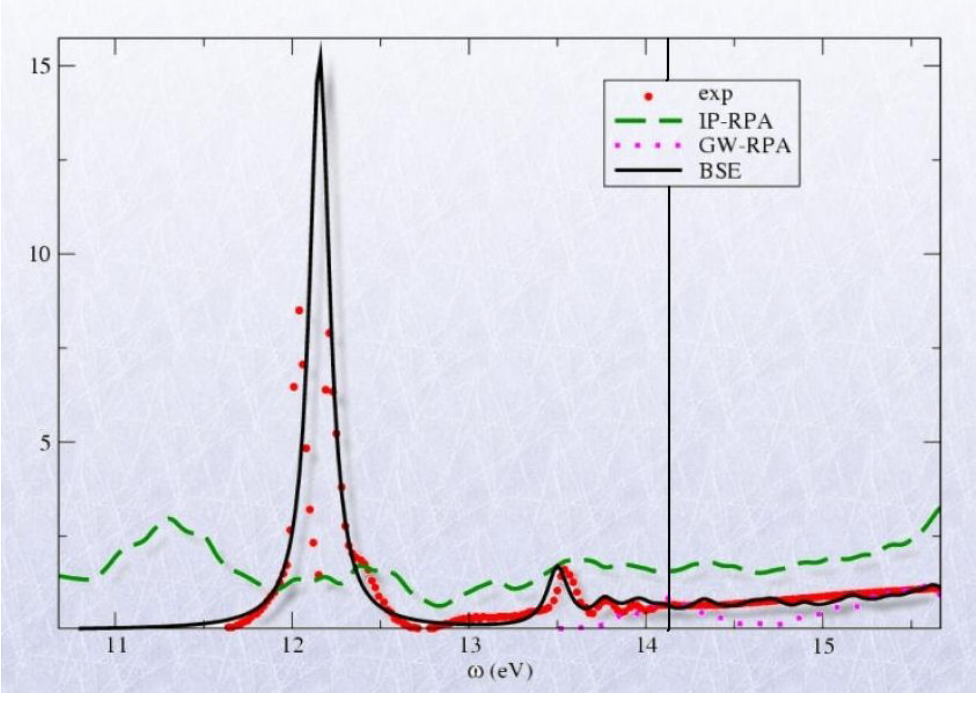


G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74** (2002).

Bound excitons

E_{abs} = Optical gap $<$ Photoemission (fundamental) gap = E_{pes}

Binding energy = $E_{\text{pes}} - E_{\text{abs}}$



Solid argon: F. Sottile *et al.* PRB **76** (2007).

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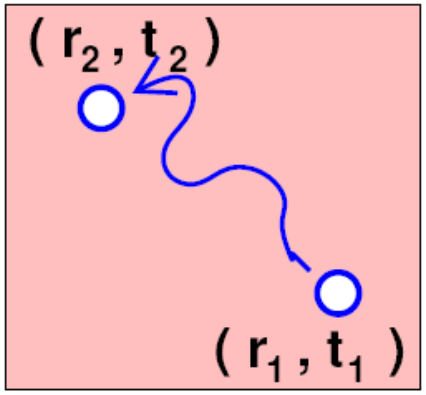
Characters in the many-body world

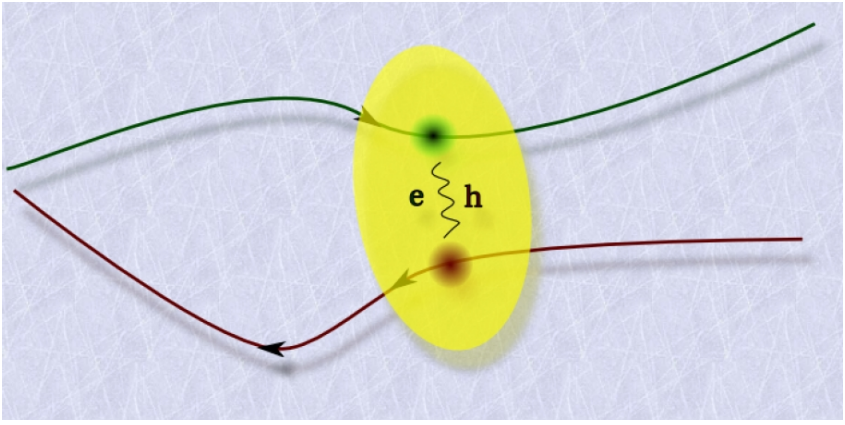
Photoemission (band structure)



One-particle Green's function *G*

GW approximation

Optical absorption (excitons)



Two-particle correlation function *L*

Bethe-Salpeter equation

(TD)DFT vs. MBPT: different worlds, same physics

(TD)DFT

- based on the density: a many-body theory of a collective variable
- moves density around
- response function χ: neutral excitations
- is efficient (simple)

MBPT

- based on Green's functions
- moves (quasi)particles around
- one-particle G: electron addition and removal - GW
  two-particle L: electron-hole excitation - BSE
- is intuitive (easy)

Spectroscopy is exciting!!!

Many thanks!

For more info: matteo.gatti@polytechnique.fr