Photoelectron Spectroscopy

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SOLEIL Theory Day, Gif-sur-Yvette
May 6th, 2014

Methods: Starting from First Principles

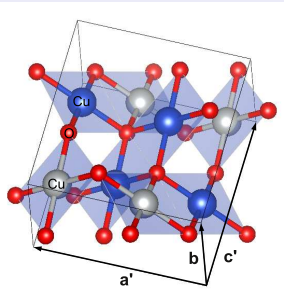
First-principles calculations

Density-functional theory (DFT)

Many-body perturbation theory (MBPT)

Ground state

- structural properties
- total energies
- charge densities



One-particle excitations

- band gaps
- band structures
- densities of states

Two-particle excitations:

- optical absorption
- excitonic states
- loss spectra

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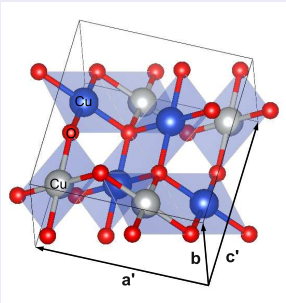

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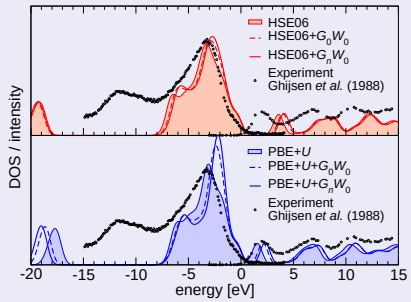

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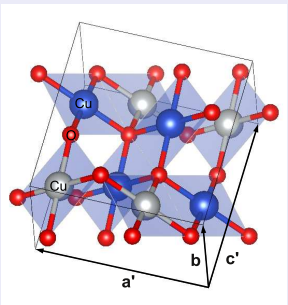

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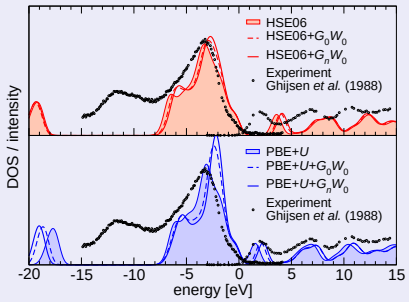

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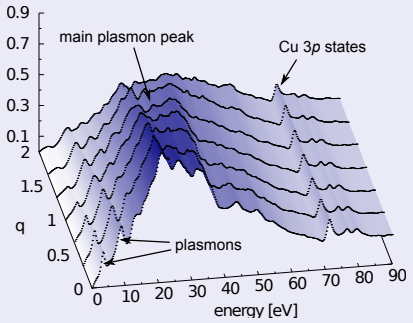
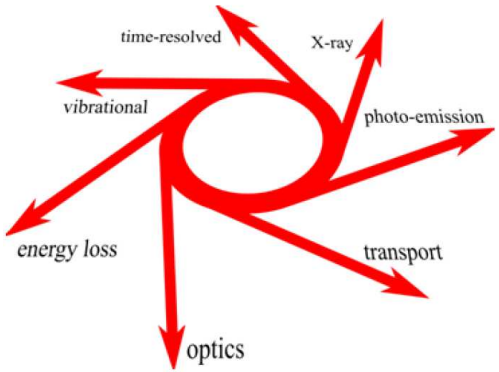


ETSF Photoemission Beamline

Systems:

- insulators
- semiconductors
- metals
- correlated oxides



ETSF

Codes:

VASP: b-initio ienna ackage imulation

www.flapw.de fleur SPEX

abinit

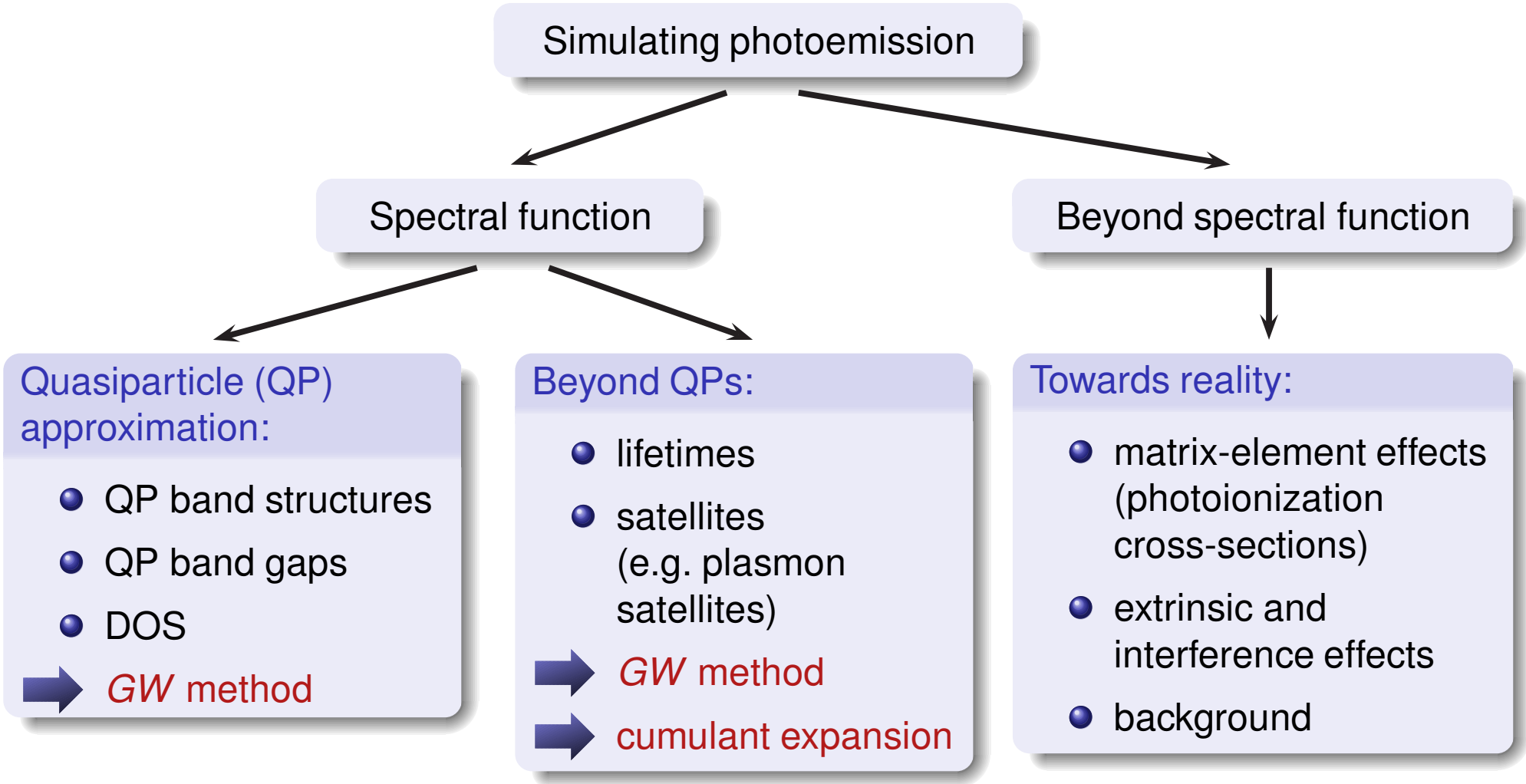
Yambo

Dimensions:

- bulk
- surfaces
- molecules
- nanosystems

➡ up to $\sim$ 100 atoms

ETSF Photoemission Beamline

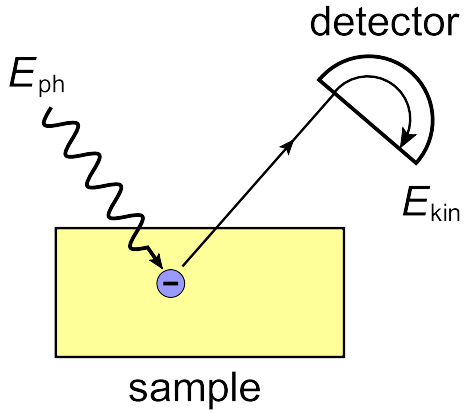


Photoemission and the Many-Body Problem

➡ probe the electronic structure

$$E_0^{(N)} + E_{\text{ph}} = E_n^{(N-1)} + E_{\text{kin}} + \Phi$$

$$E_{\text{ph}} = \underbrace{E_n^{(N-1)} - E_0^{(N)}}_{E_{\text{B}}} + E_{\text{kin}} + \Phi$$



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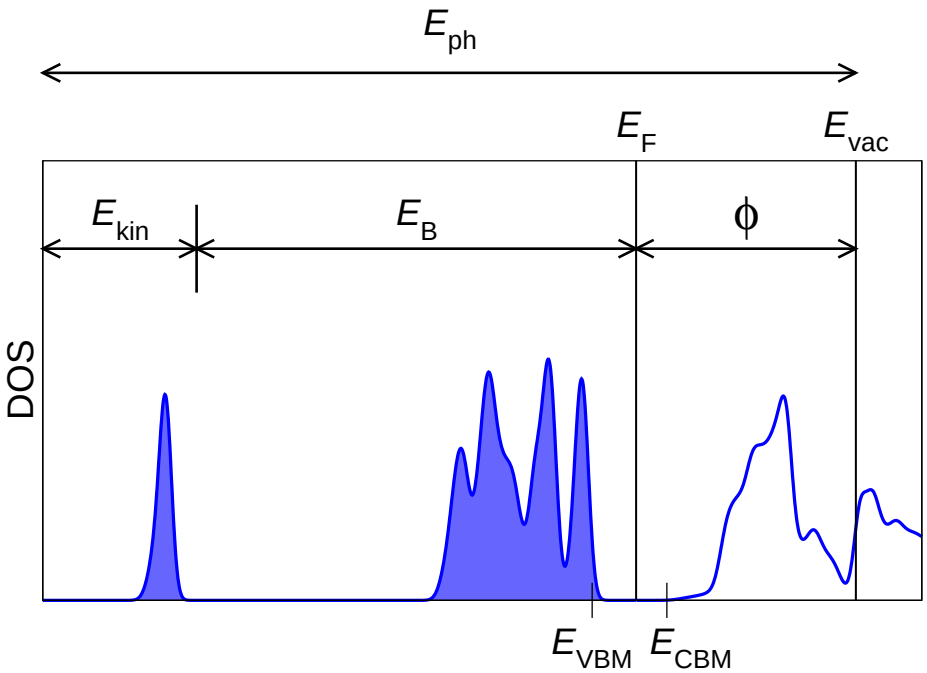

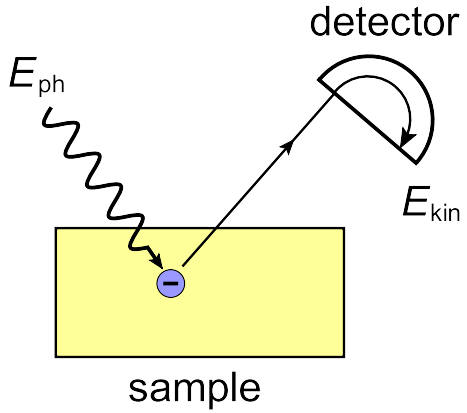

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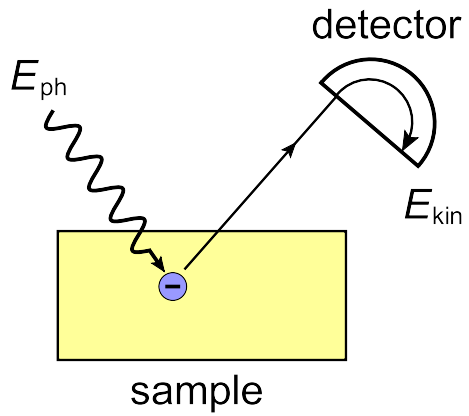

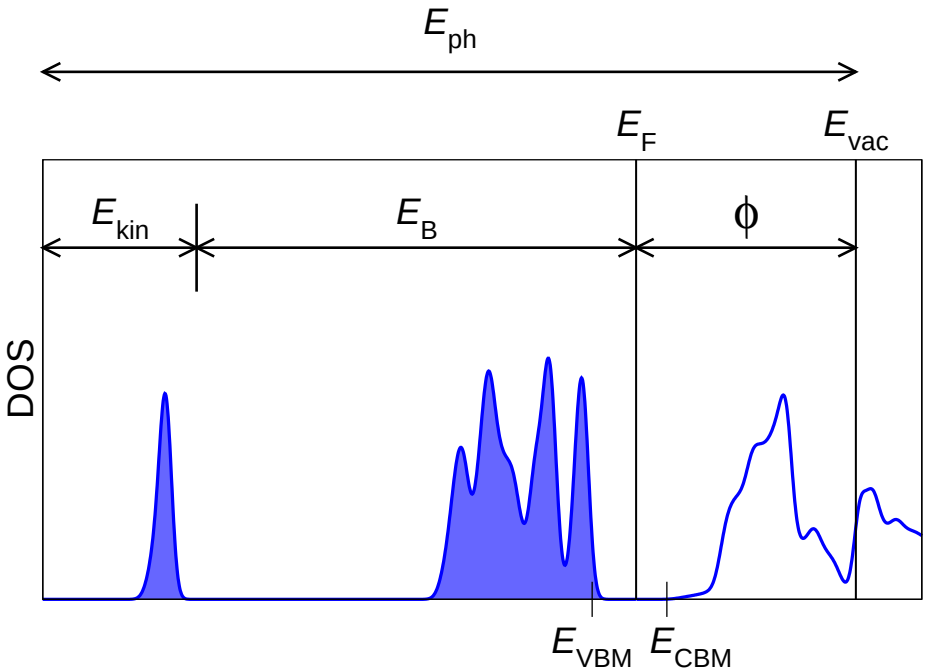

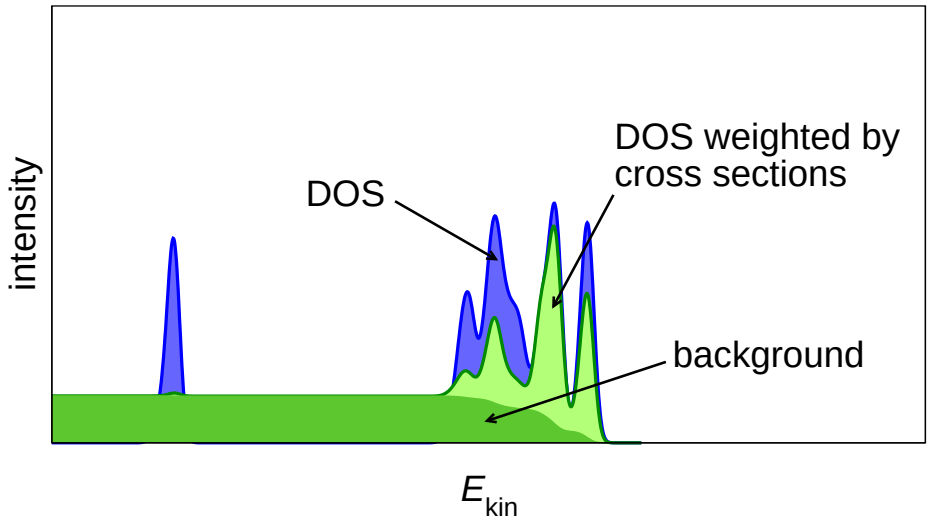

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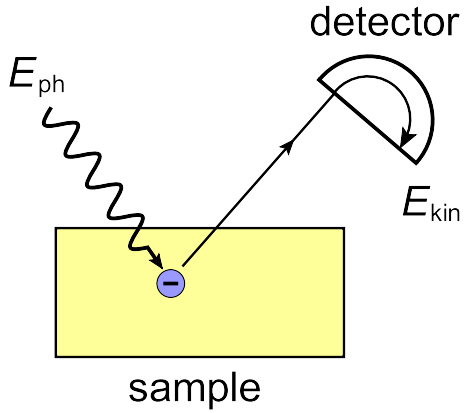

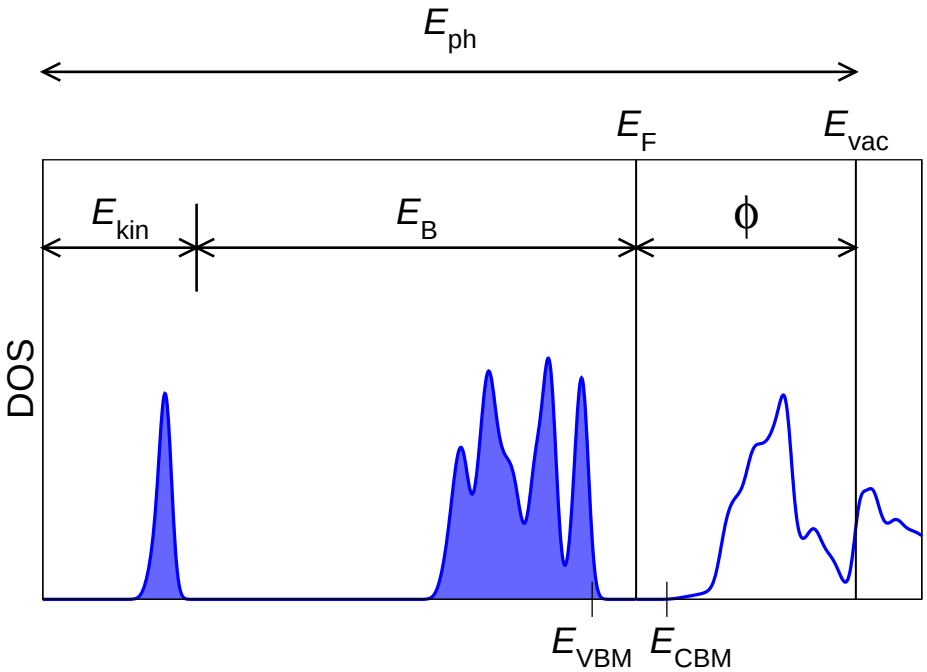

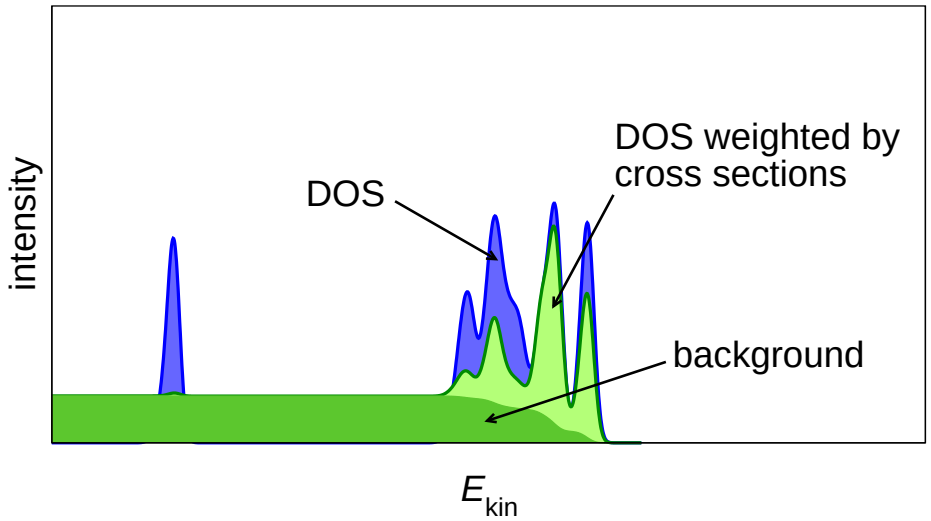

- requires full solution of the interacting many-body problem: $E_0^{(N)}$, $E_n^{(N-1)}$

Key Quantity: Green's Function

Green's function: $G(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \frac{1}{i\hbar} \langle N | \mathcal{T} \psi(\mathbf{r}_1 t_1) \psi^+(\mathbf{r}_2 t_2) | N \rangle$

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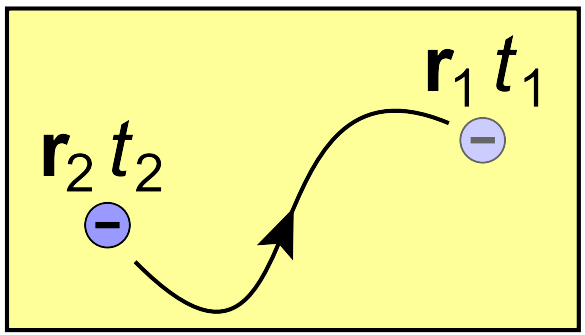
Electron propagator:

$\langle N | \psi(\mathbf{r}_1 t_1)\, \psi^+(\mathbf{r}_2 t_2) | N \rangle$



electron addition

➡ inverse photoemission

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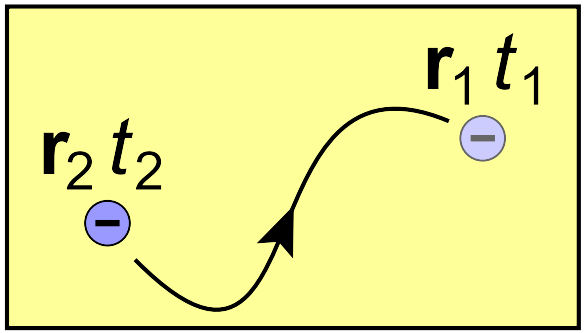

electron addition

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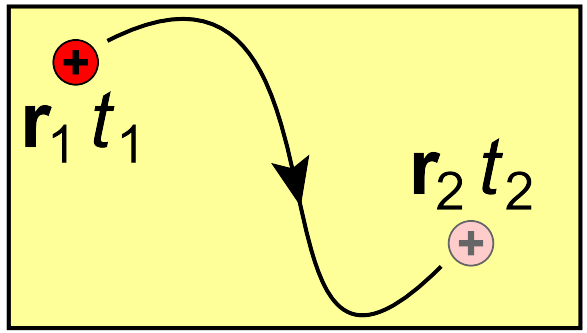
Hole propagator:

$\langle N | \psi^+(\mathbf{r}_2 t_2)\, \psi(\mathbf{r}_1 t_1) | N \rangle$

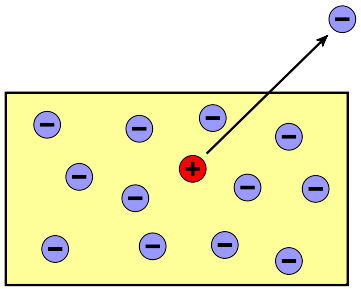


electron removal

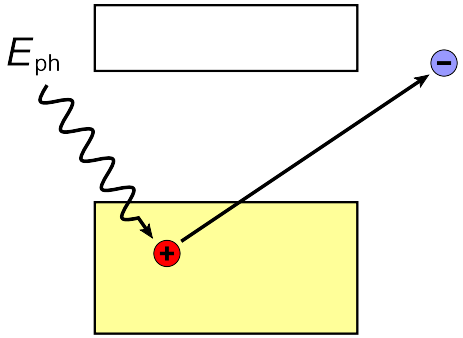
➡ photoemission

Spectral Function and Quasiparticles

real space

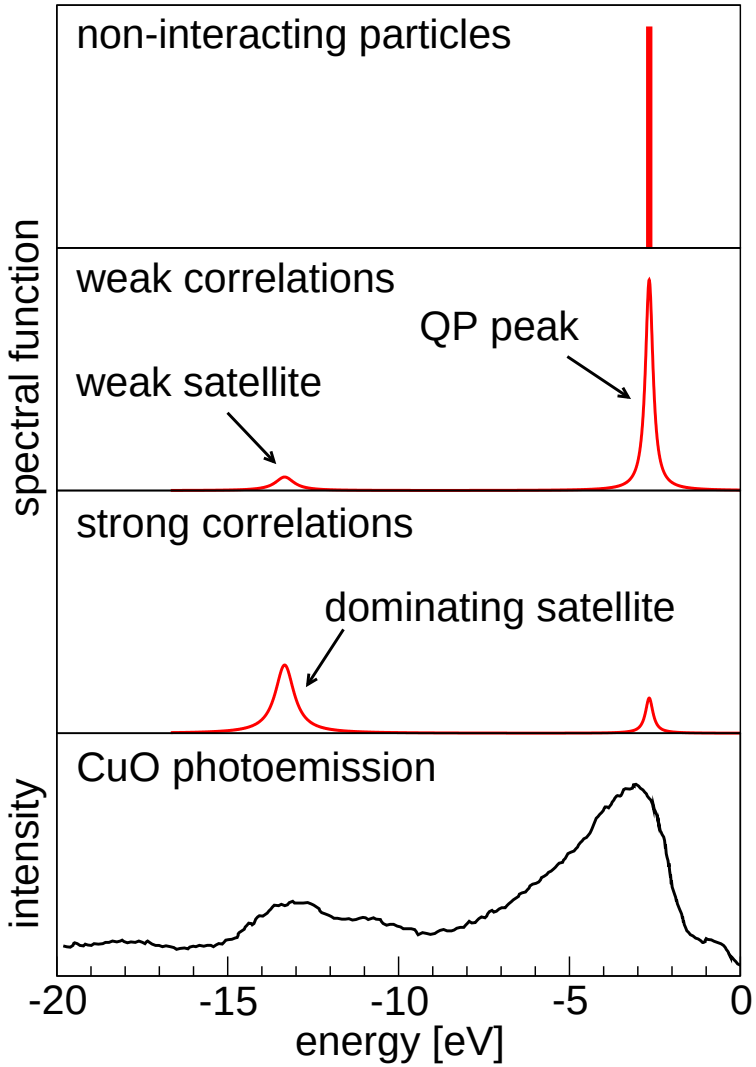


reciprocal space



Spectral function: $A(\omega) = \mathrm{Tr}\ |\mathrm{Im}\ G(\omega)|$

Density of states: $\mathrm{DOS}(\omega) \sim A(\omega)$



Experimental data:
Ghijsen *et al.*, PRB **38**, 11322 (1988)

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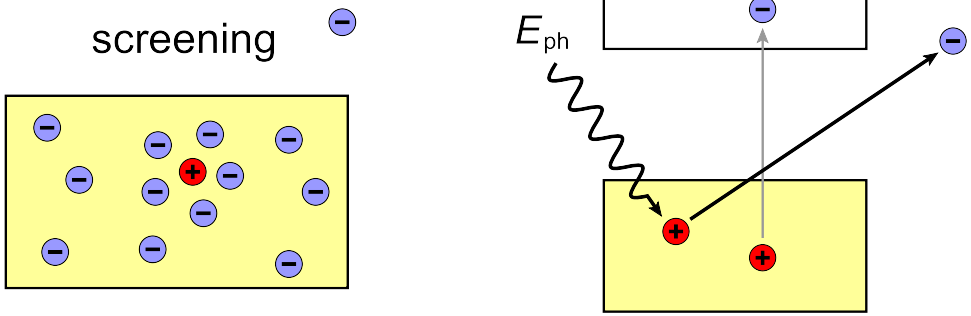

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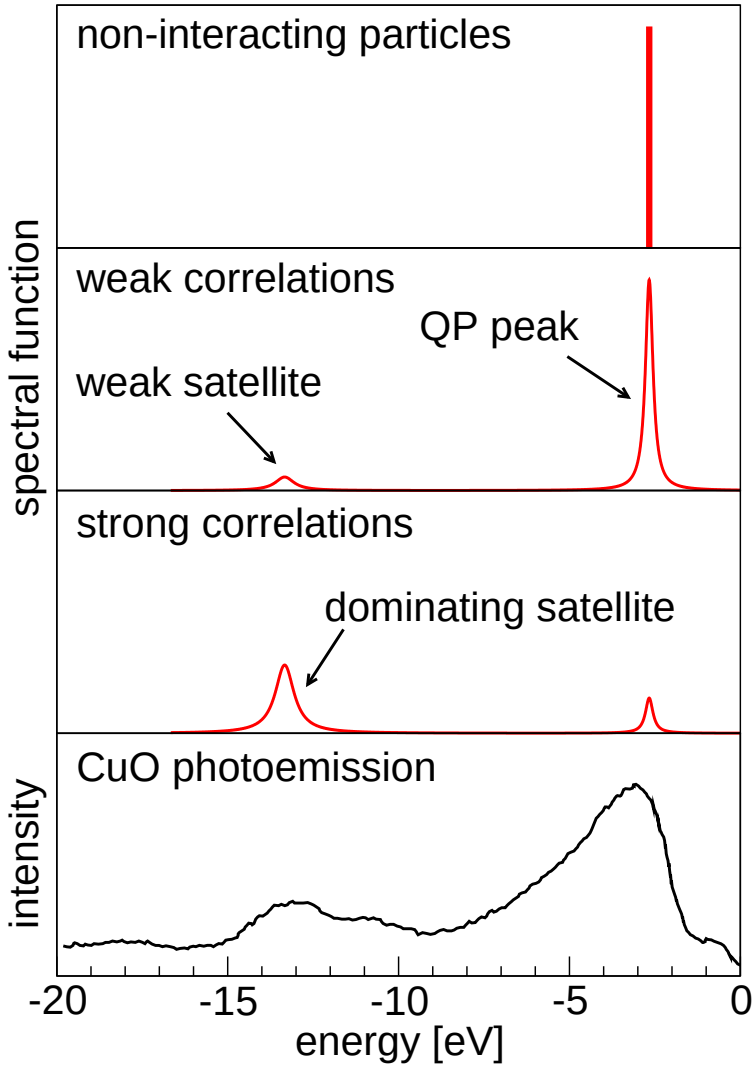

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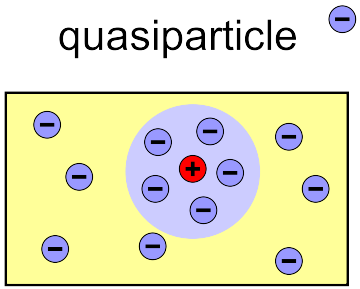
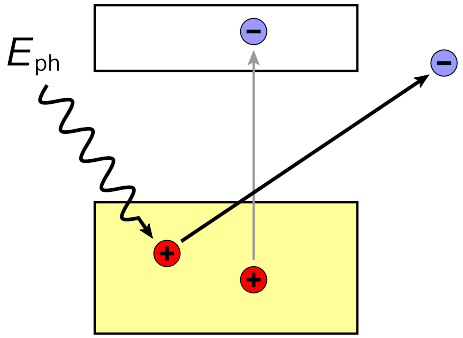
reciprocal space

quasiparticle





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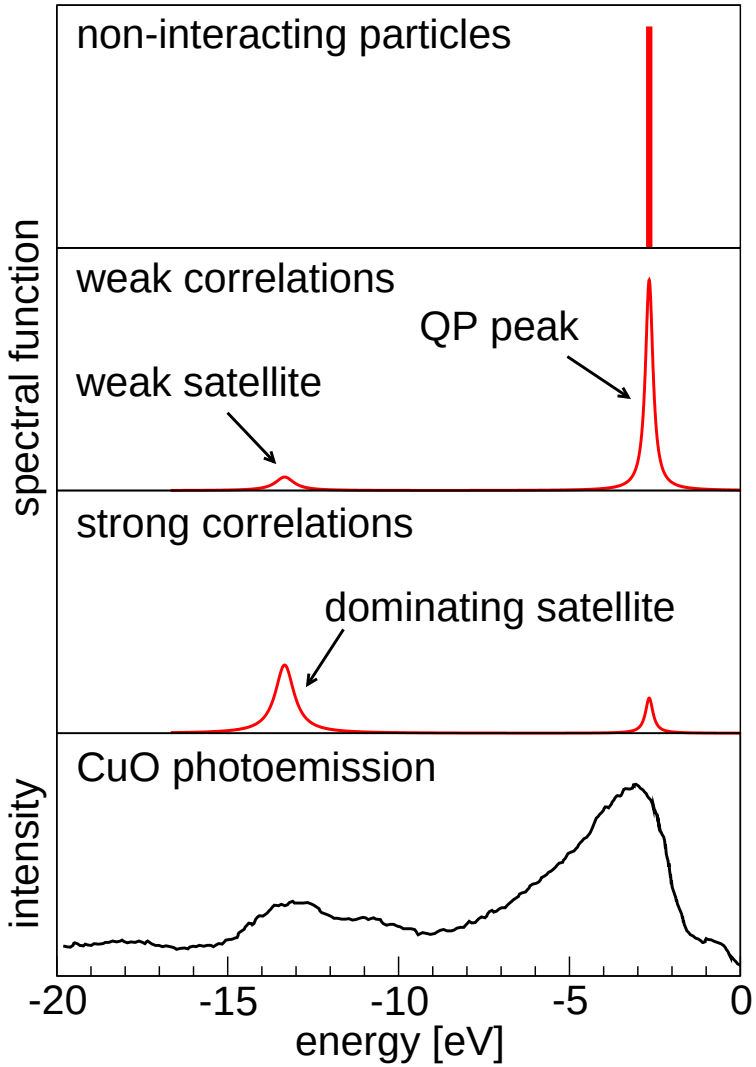

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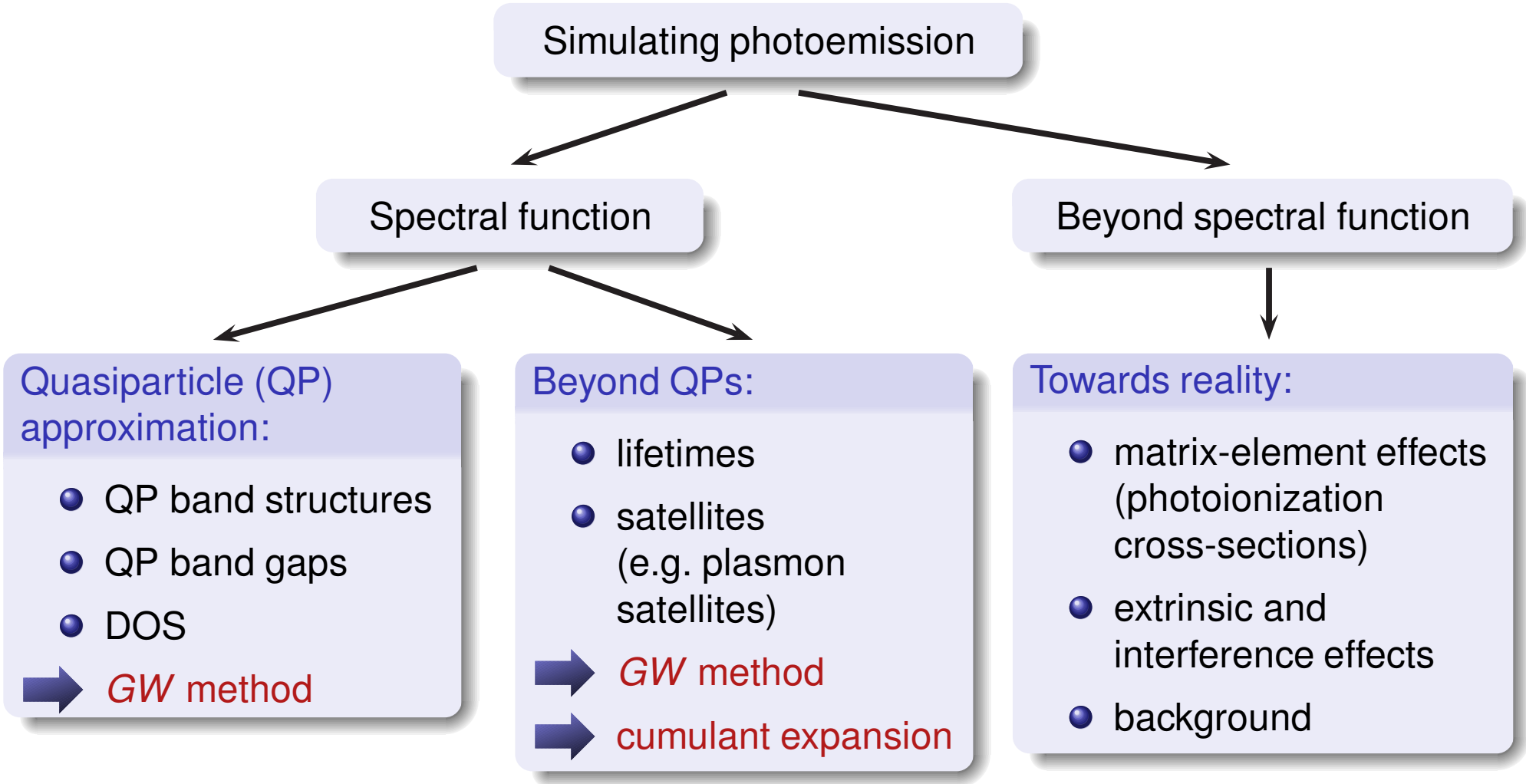
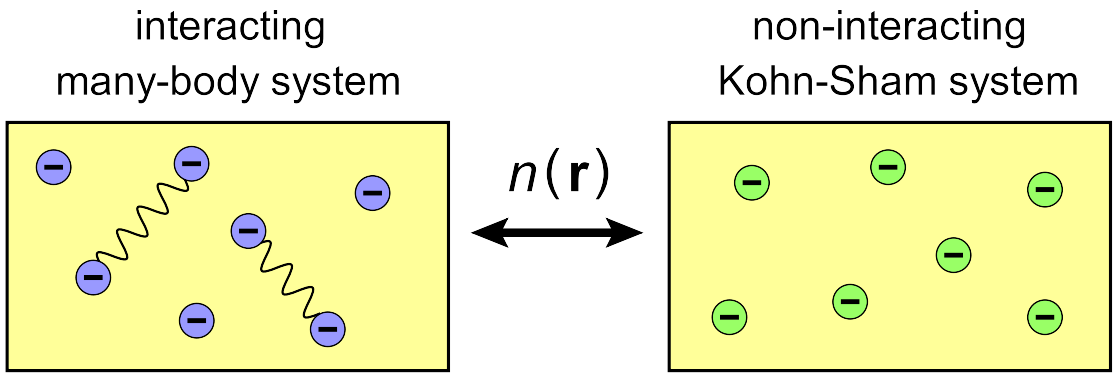


Density-Functional Theory (DFT)



Kohn-Sham equations:

Kohn, Sham, Phys. Rev. **140**, A1133 (1965)

$$\left[-\frac{\hbar^2}{2m_0}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r},[n]) + V_{\text{XC}}(\mathbf{r},[n])\right]\varphi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}\,\varphi_{n\mathbf{k}}(\mathbf{r})$$

density: $n(\mathbf{r}) = \sum_{n\mathbf{k}}^{\text{occ}} |\varphi_{n\mathbf{k}}(\mathbf{r})|^2$ ➡ self-consistent solution

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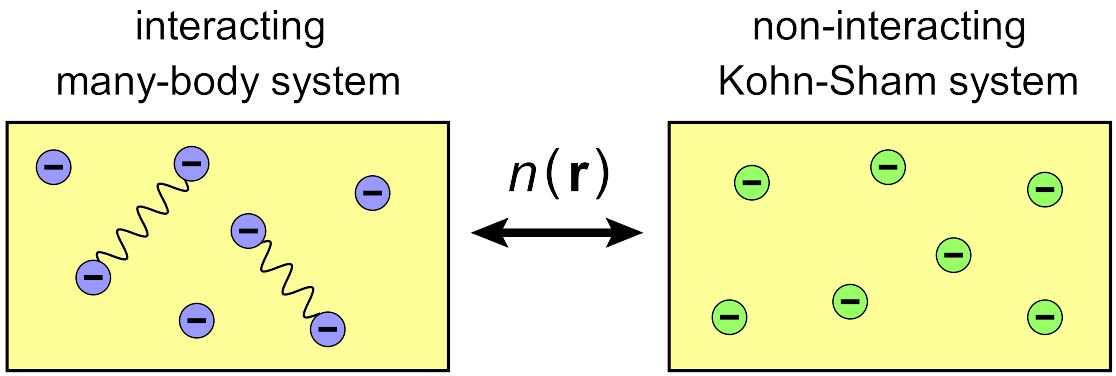

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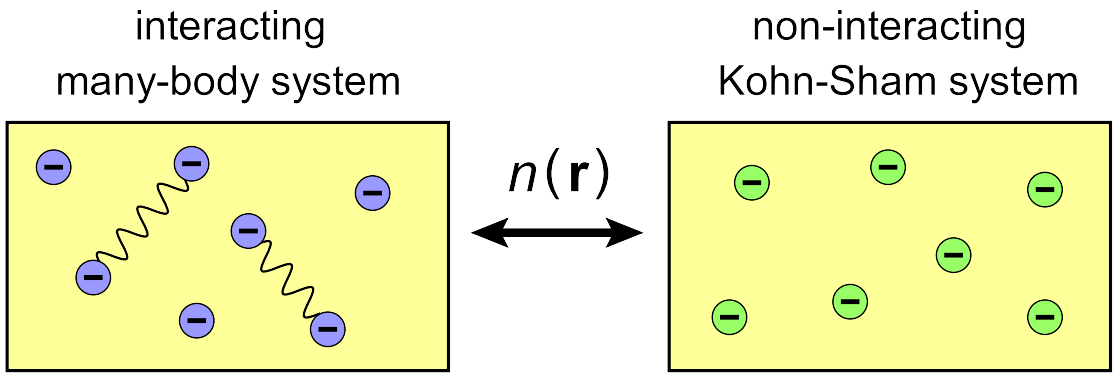
Exchange-correlation potential V_{XC}?

- local potential $V_{\text{XC}}(\mathbf{r},[n])$: LDA, PBE, ...
- non-local potential $V_{\text{XC}}(\mathbf{r}\mathbf{r}',[n])$:
  - hybrid functionals (PBE0, HSE06, ...)
  - on-site term U for localized orbitals (LDA+U, ...)

Density-Functional Theory (DFT)



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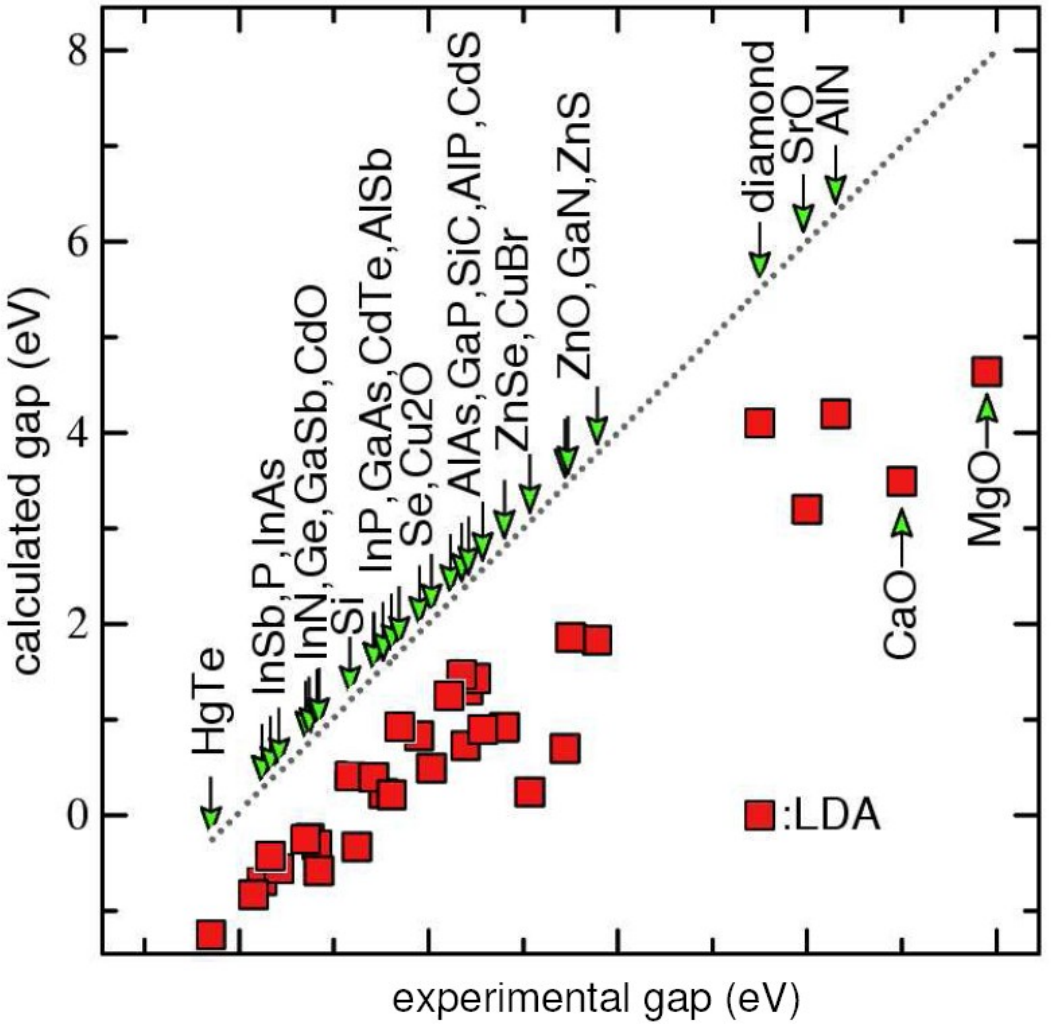
Problems:

- Kohn-Sham band structure has no physical meaning (strictly speaking)
- band-gap problem: strong underestimation of band gaps

➡ electron addition and removal properties wrong

Why more than DFT?



adapted from M. van Schilfgaarde et al., PRL 96 (2006)

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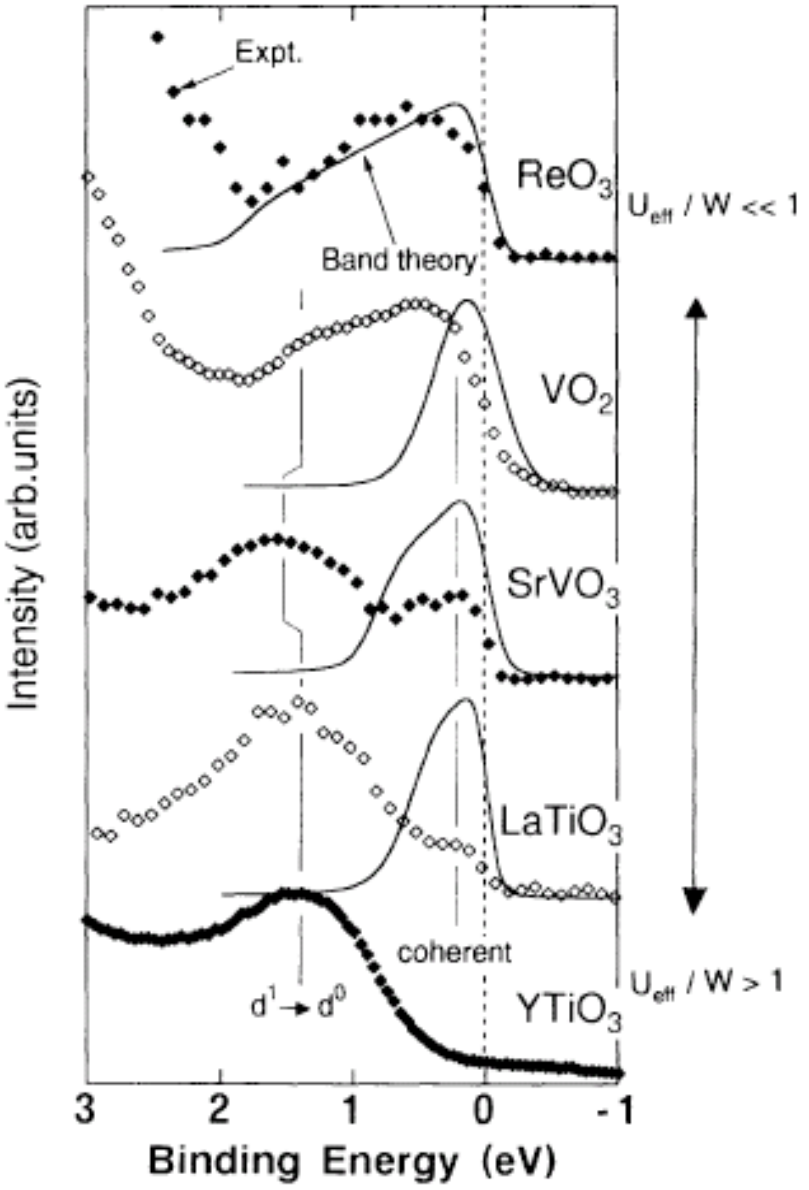
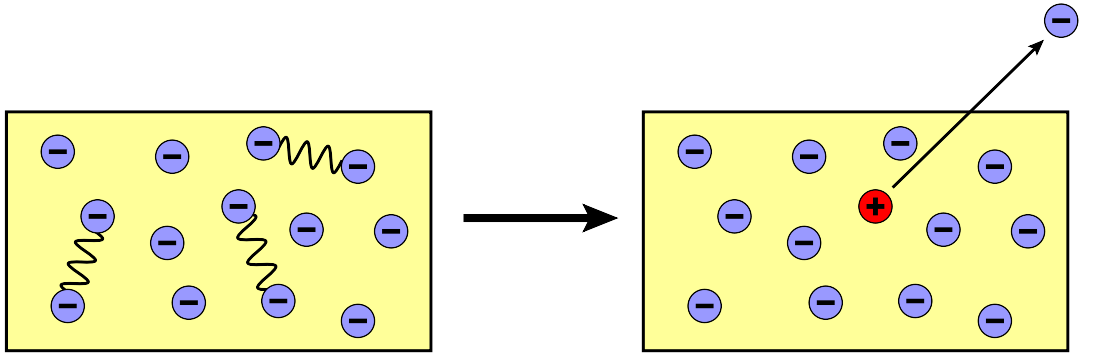


LDA = "band theory" ?

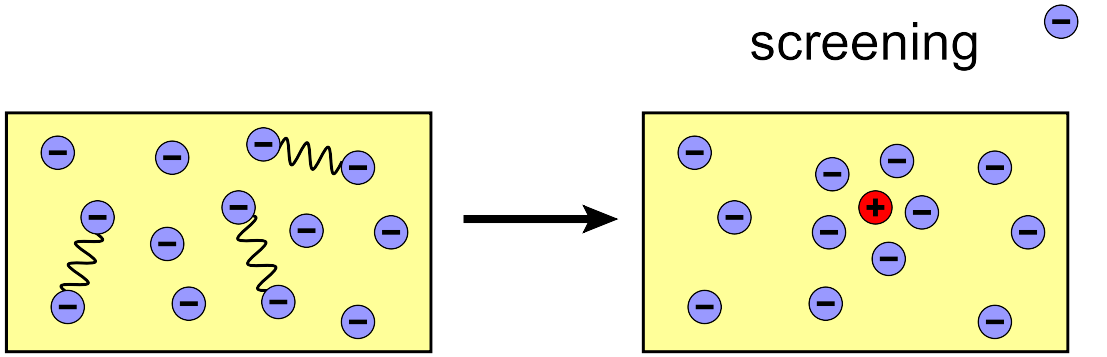
Fujimori et al, PRL 69 (1992)

Quasiparticle Excitations



N-particle system (*N*-1)-particle system

Quasiparticle Excitations



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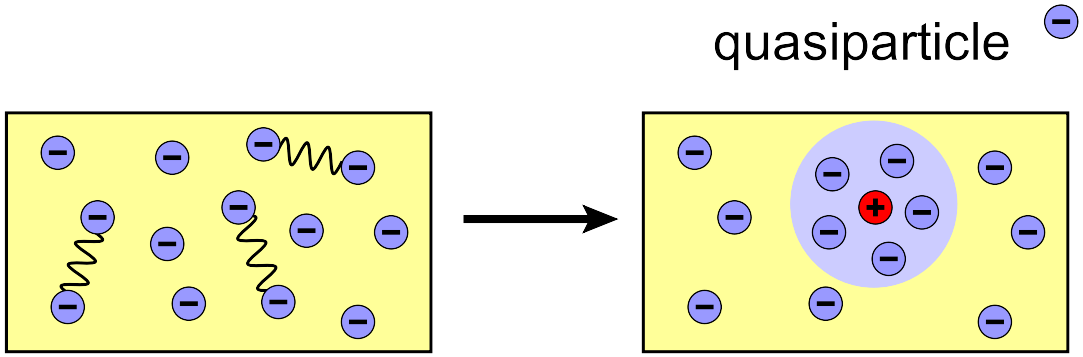

Quasiparticle equation:

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Problems:

- exchange and correlation: non-local and frequency-dependent self-energy Σ
- self-consistent solution
- no explicit expression for the self-energy

Hedin's *GW* Approximation

Self-energy: $\Sigma \approx i\hbar\, G\, W$

Green's function $G(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2)$

Dynamically screened Coulomb interaction $W(\mathbf{r}_1 \mathbf{r}_2, \omega)$

Hedin, Phys. Rev. **139**, A796 (1965)

Hedin, Lundqvist, Solid State Phys. **23**, 1 (1969)

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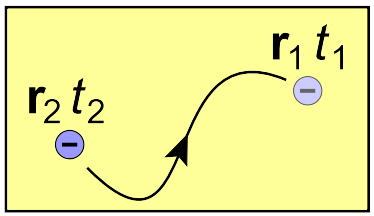

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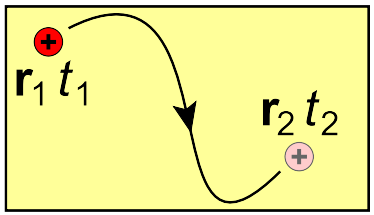

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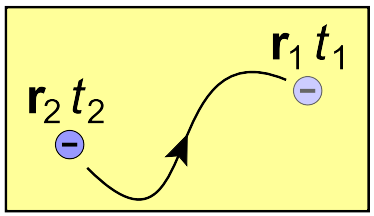
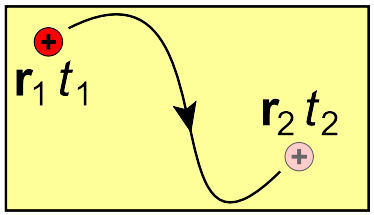
Electron propag.: $\langle N|\, \psi(\mathbf{r}_1 t_1)\, \psi^+(\mathbf{r}_2 t_2)\, |N\rangle$

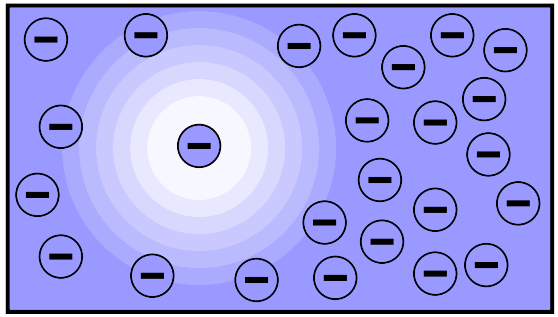


Hole propag.: $\langle N|\, \psi^+(\mathbf{r}_2 t_2)\, \psi(\mathbf{r}_1 t_1)\, |N\rangle$



Dynamically screened Coulomb interaction $W(\mathbf{r}_1 \mathbf{r}_2, \omega)$

$$W(\mathbf{r}_1 \mathbf{r}_2, \omega) = \int d\mathbf{r}_3\, \varepsilon^{-1}(\mathbf{r}_1 \mathbf{r}_3, \omega)\, v(\mathbf{r}_3 - \mathbf{r}_2)$$



Hedin, Phys. Rev. **139**, A796 (1965)

Hedin, Lundqvist, Solid State Phys. **23**, 1 (1969)

Hedin's *GW* Approximation

Self-energy: $\Sigma \approx i\hbar\, G\, W$

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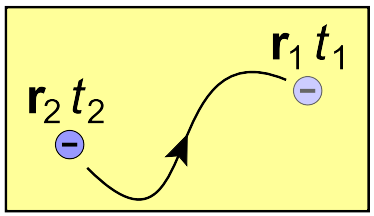

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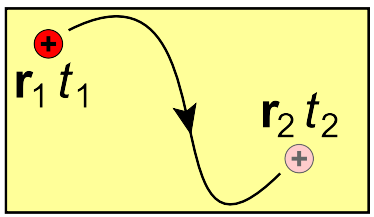

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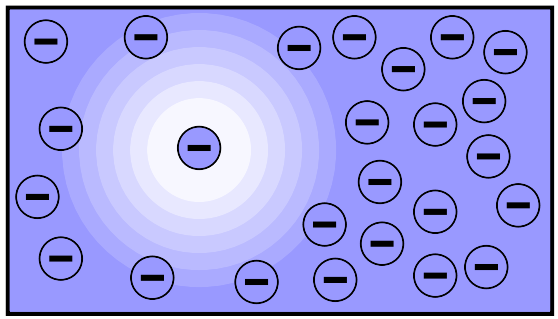
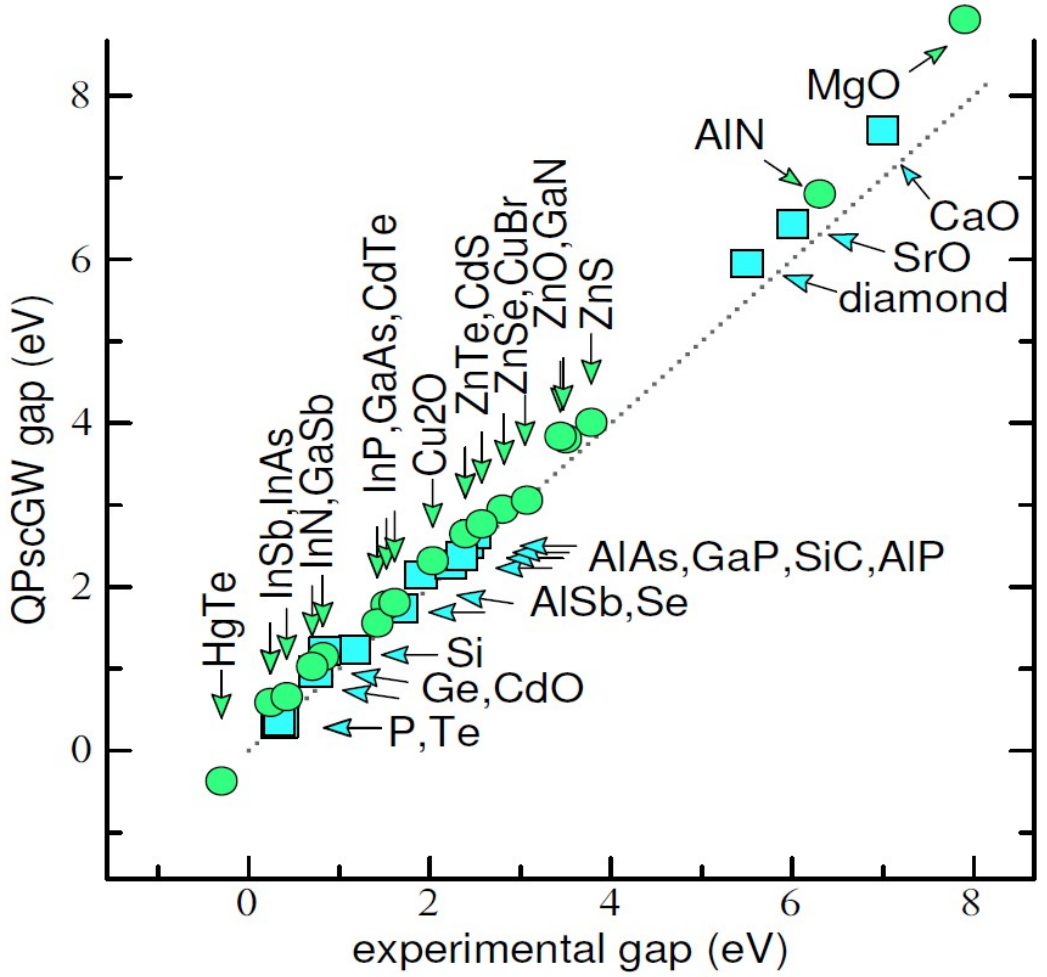
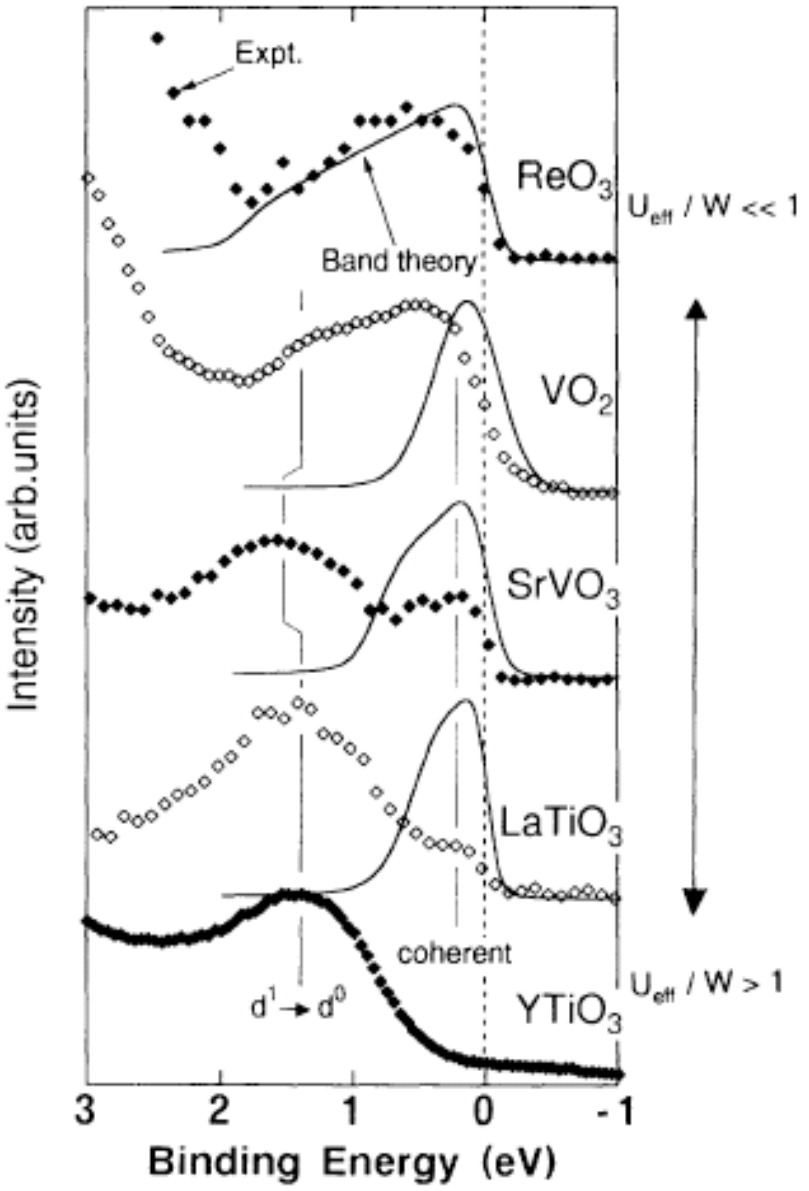


➡ main contribution:
dynamical screened exchange
(Hartree-Fock: $\varepsilon^{-1}(\mathbf{r}_1 \mathbf{r}_3, \omega) \equiv 1$)

Why more than DFT?



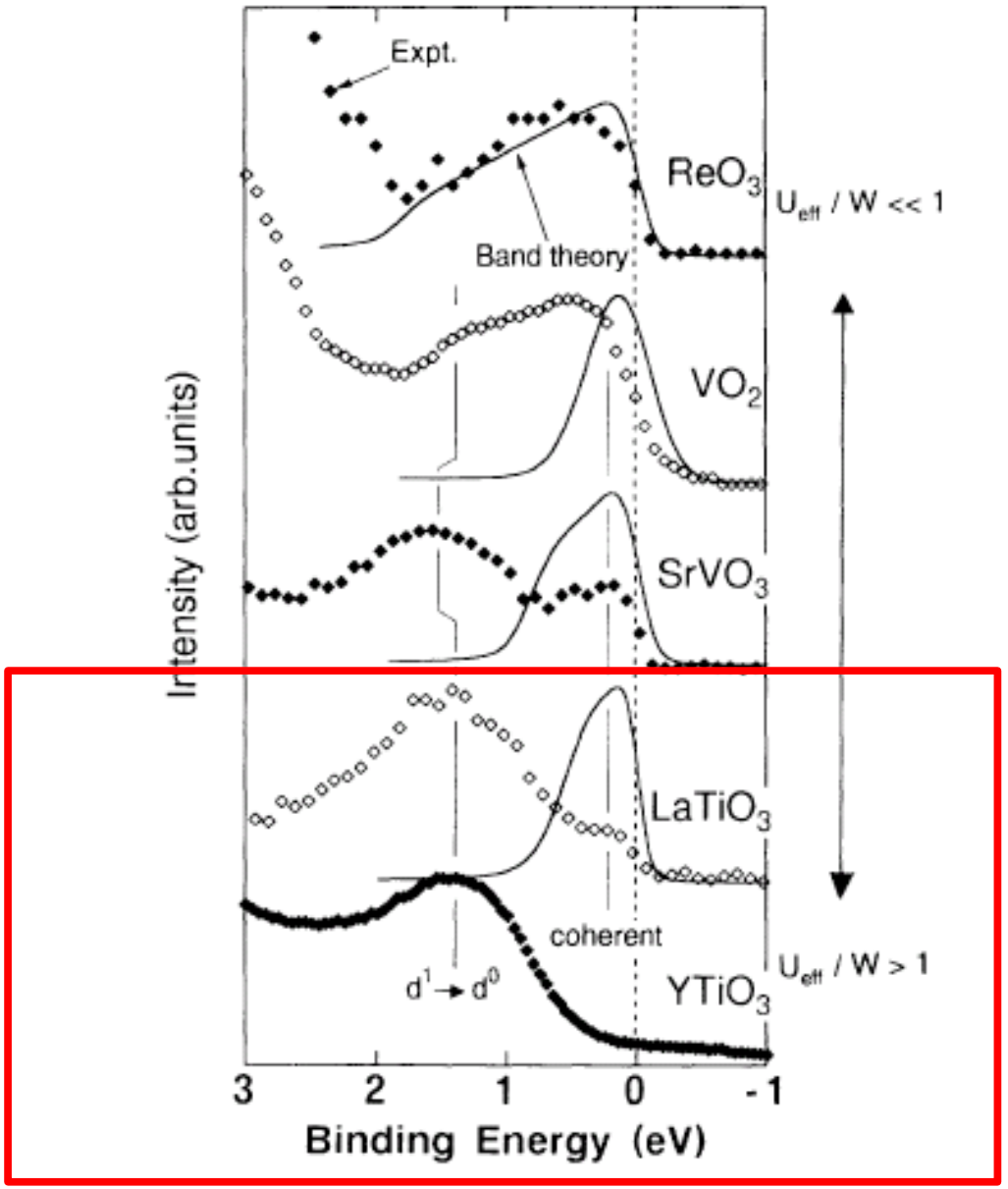
adapted from M. van Schilfgaarde et al., PRL 96 (2006)



Fujimori et al, PRL 69 (1992)

LDA = "band theory" ?

Also missing physics!



Fujimori et al, PRL 69 (1992)

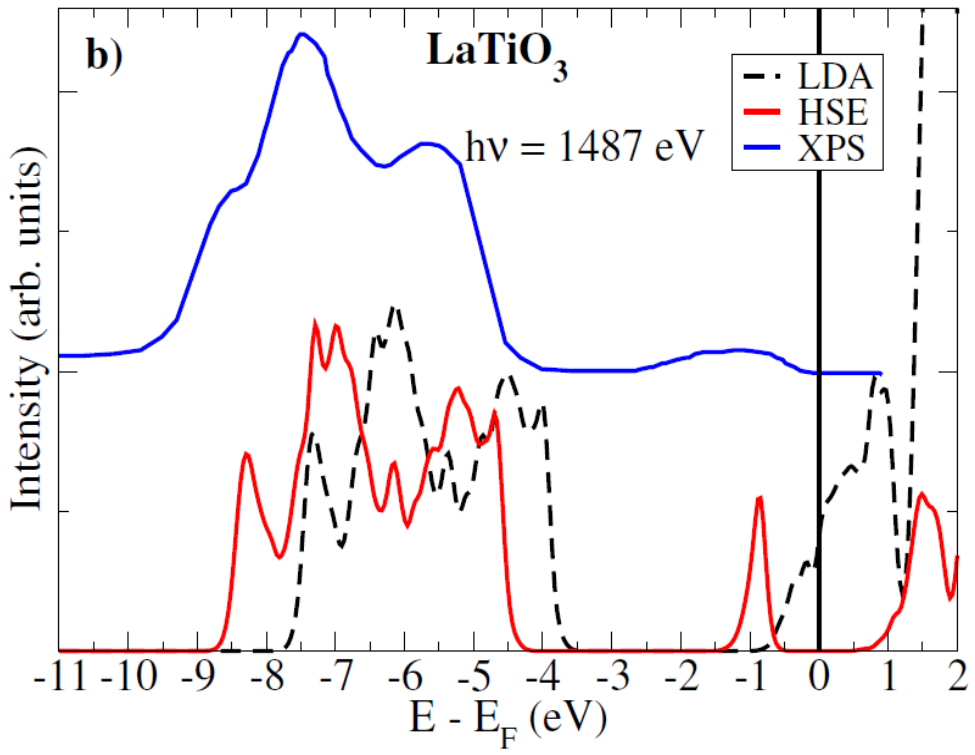
LDA = "band theory" ?

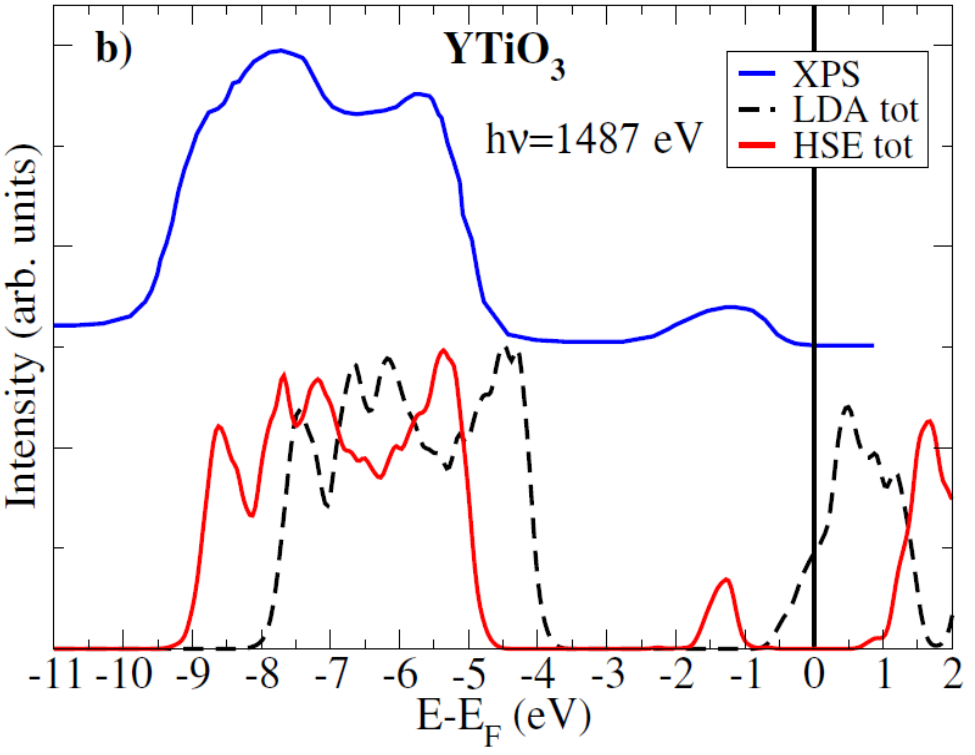
Also missing physics!

Exchange + Correlation

Mott insulators?

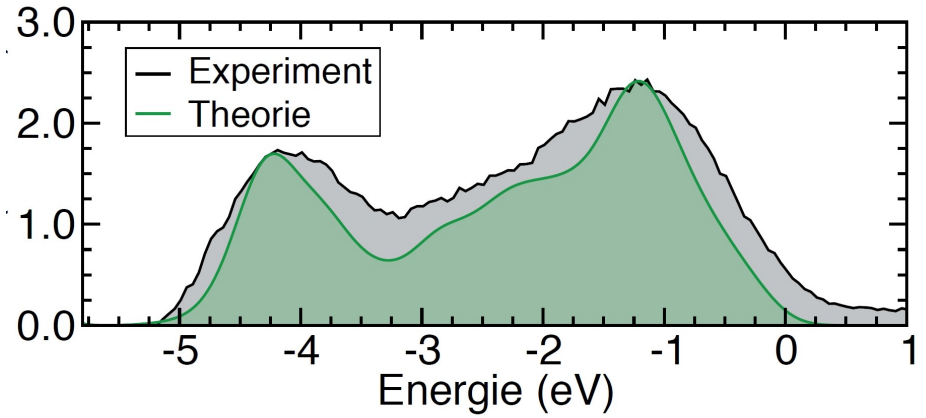
The role of nonlocal exchange

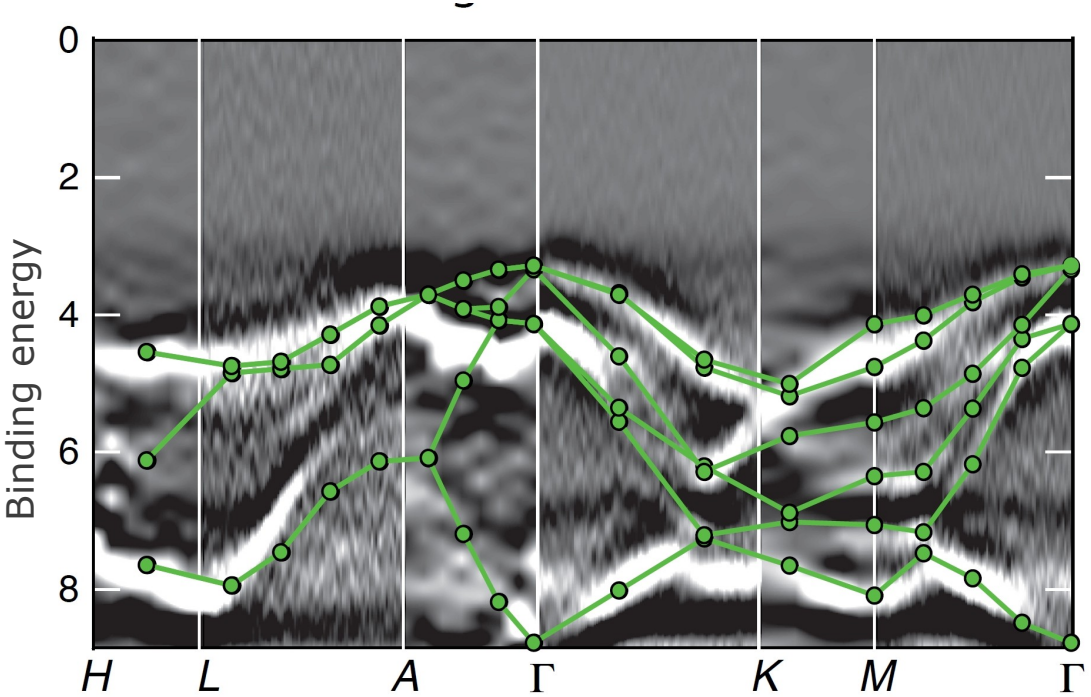




F. Iori, M. Gatti and A. Rubio, PRB 85 (2012)
Exp. from H. Roth PhD thesis – Köln 2008

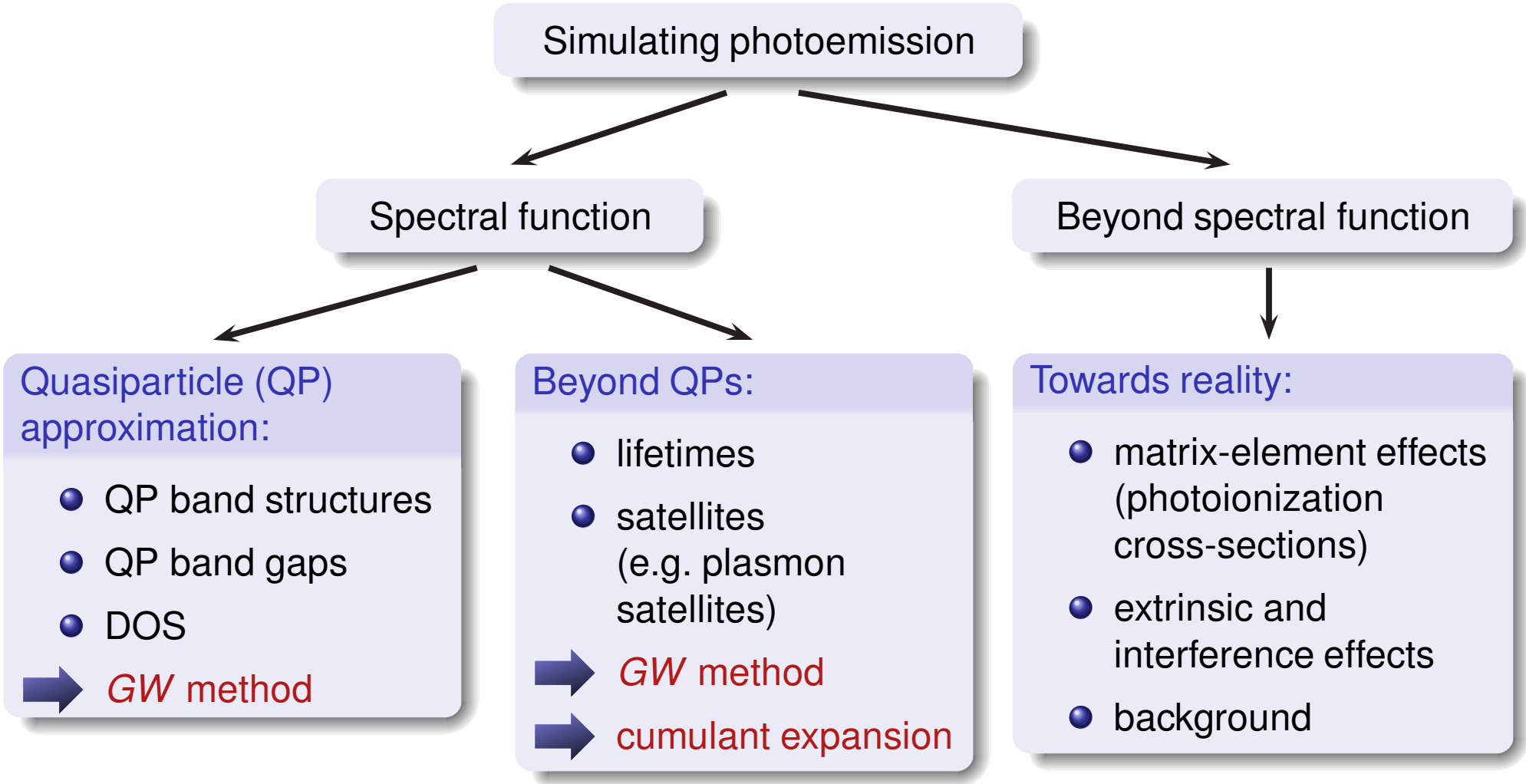
ARPES vs. band structure: ZnO



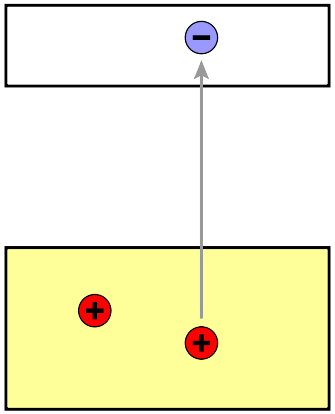


Exp from M. Kobayashi, et al. Proceedings of the 29th International Conference on the Physics of Semiconductors (2008)
André Schleife PhD thesis, University of Jena (2010)

ETSF Photoemission Beamline

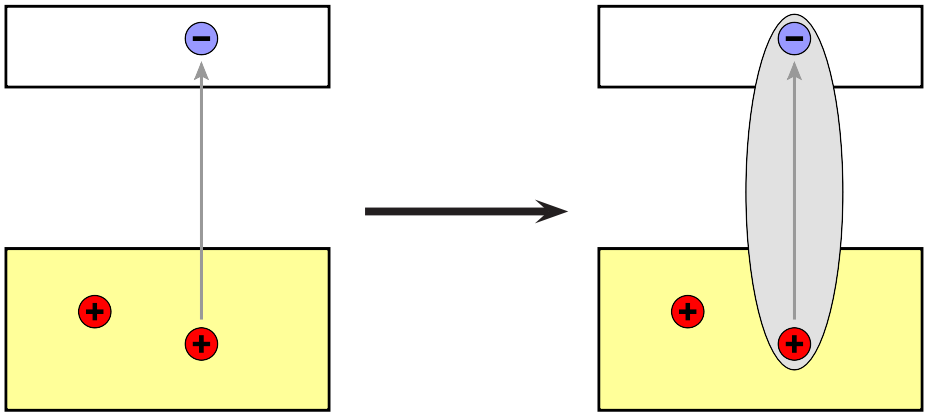


Electron Correlation ... 3-Particle Problem



Romaniello *et al.*, PRB **85**, 155131 (2012)

Electron Correlation ... 3-Particle Problem



- $\Sigma = i\hbar GW$
- plasmon satellite series

  Langreth, PRB **1**, 471 (1970)

  Aryasetiawan *et al.*,

  PRL **77**, 2268 (1996)

  Guzzo *et al.*,

  PRL **107**, 166401 (2011)

Romaniello *et al.*, PRB **85**, 155131 (2012)

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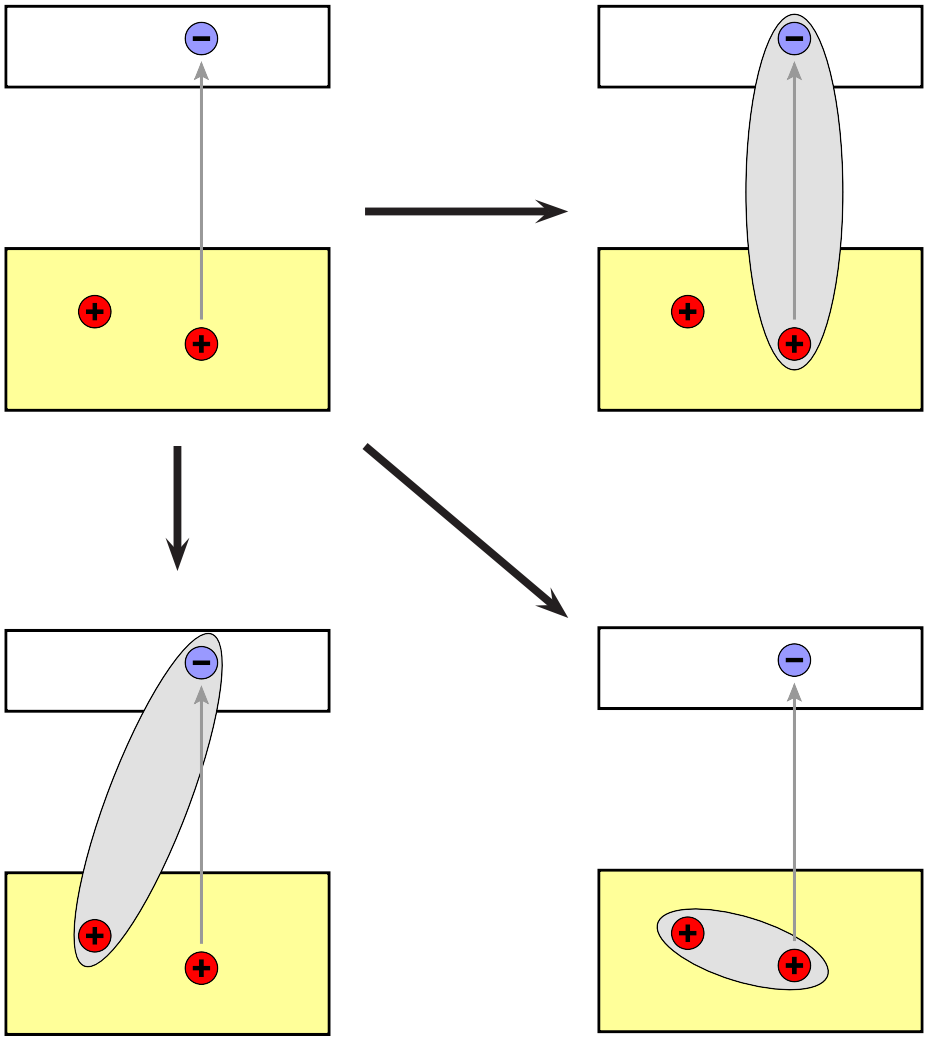

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  PRL **77**, 2268 (1996)

  Guzzo *et al.*,

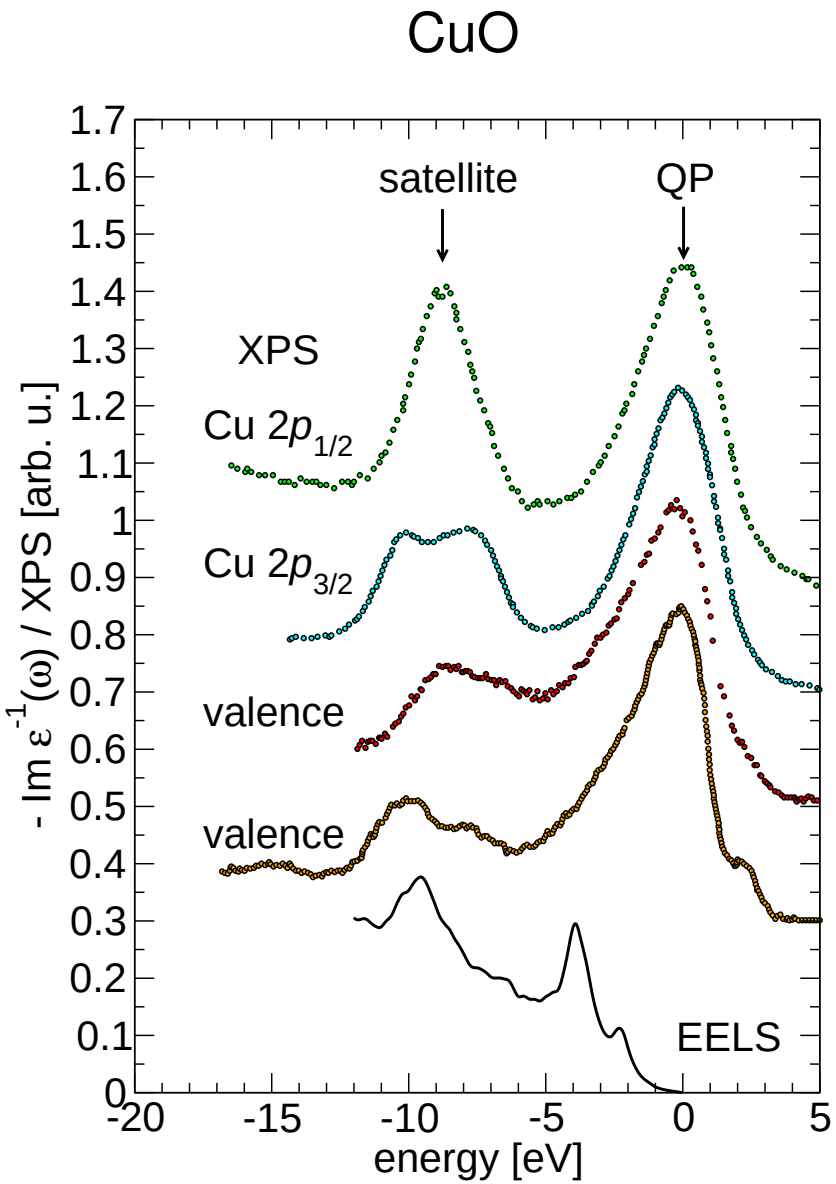
  PRL **107**, 166401 (2011)

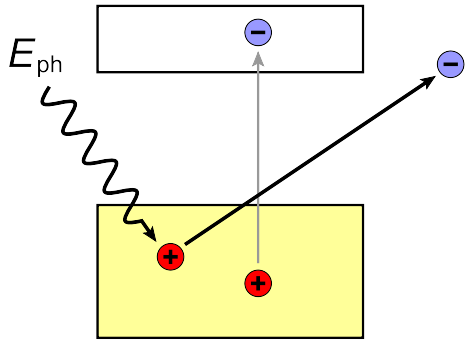
- $\Sigma = i\hbar GT$
- hole-hole or electron-hole T matrix
- 6 eV satellite in Ni

  Springer *et al.*, PRL **80**, 2389 (1998)

Romaniello *et al.*, PRB **85**, 155131 (2012)

Spectral Function ... Plasmon Satellites



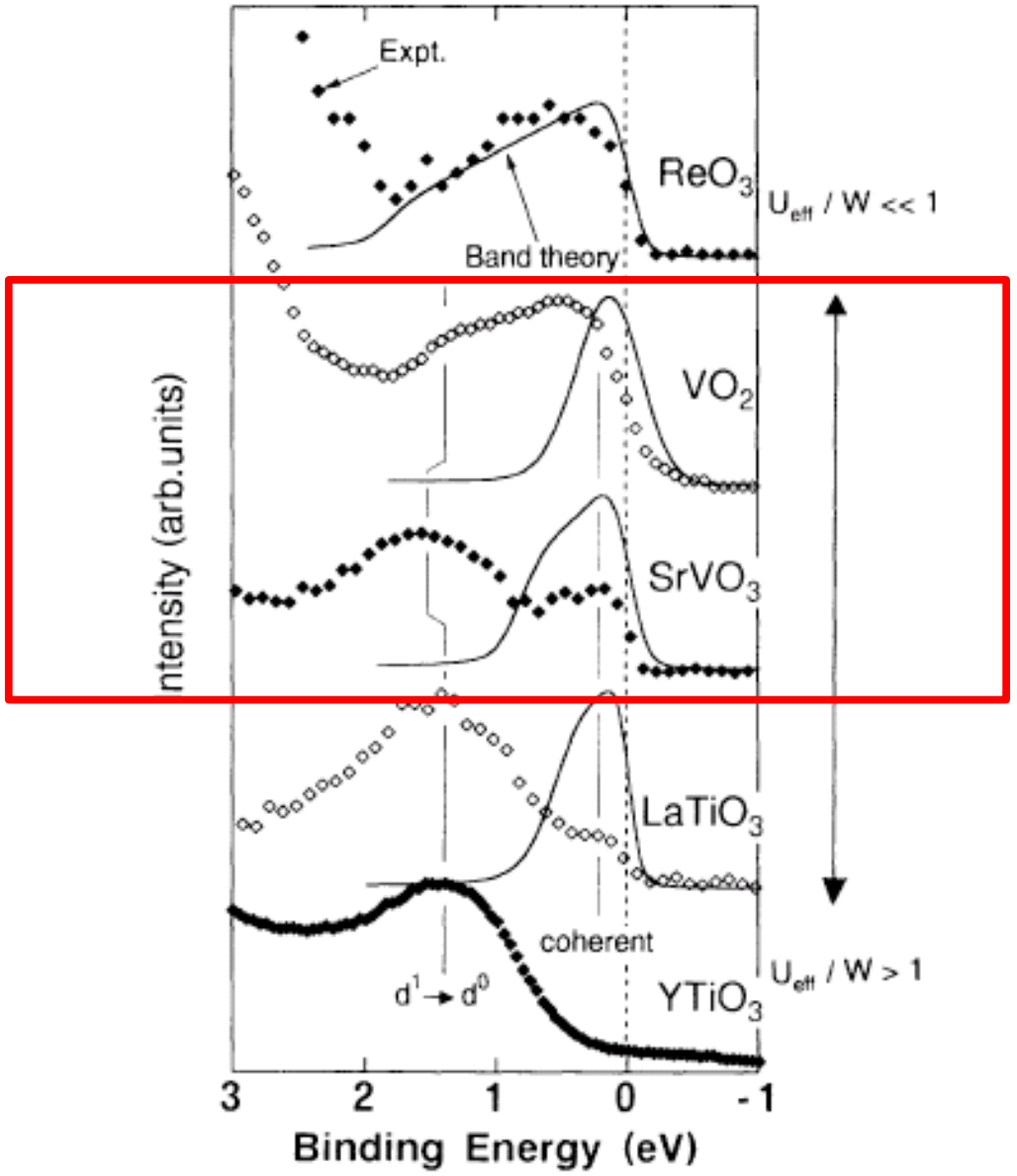


- satellite: response of the material to the photoemission hole remaining in the system

➡ plasmon excitations

- prominent loss peaks should appear in satellite structure

Experimental data:
Siemons, PhD thesis (2008)
Ghijsen *et al.*, PRB **38**, 11322 (1988)
Shen *et al.*, PRB **42**, 8081 (1990)

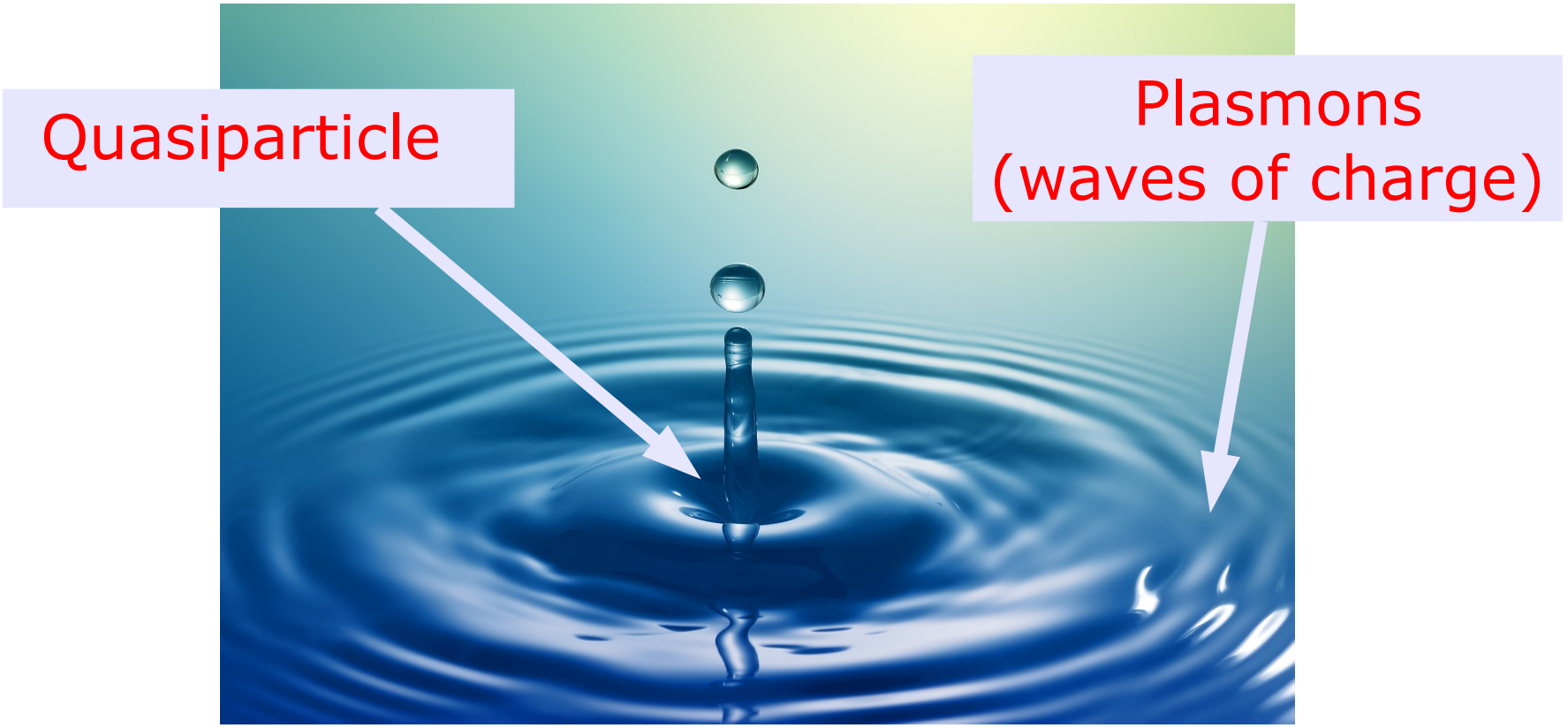


Fujimori et al, PRL 69 (1992)

Correlated metals:
Satellites?

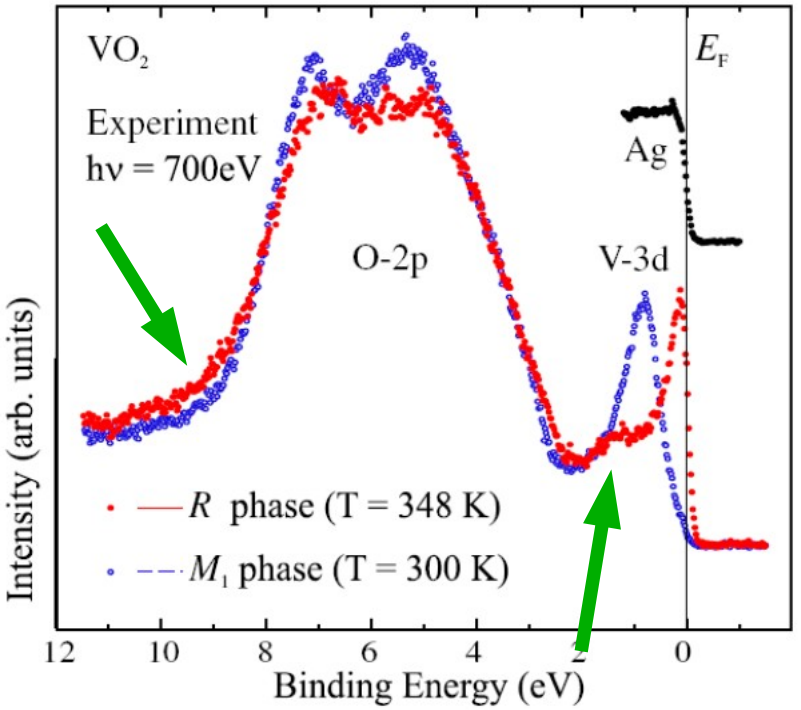
Correlation = coupling of excitations

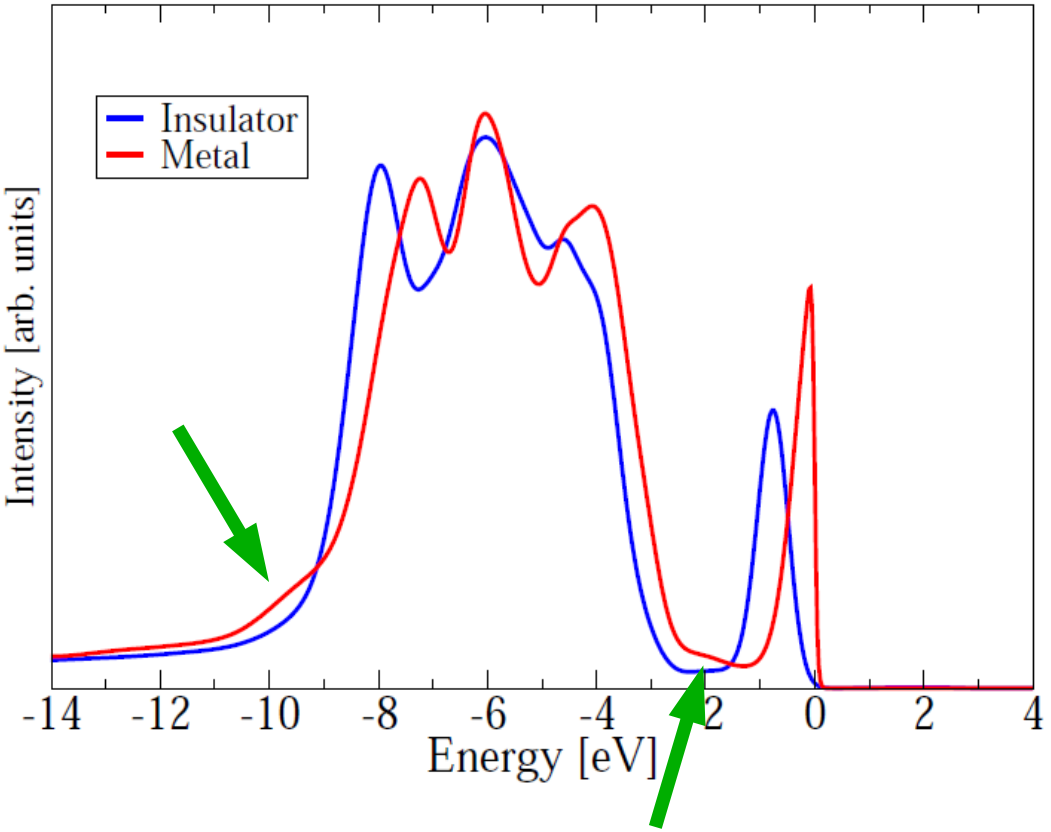
Adding/removing electrons: reaction of all the others



Dynamical correlation: VO_2

Metal-Insulator transition in VO_2



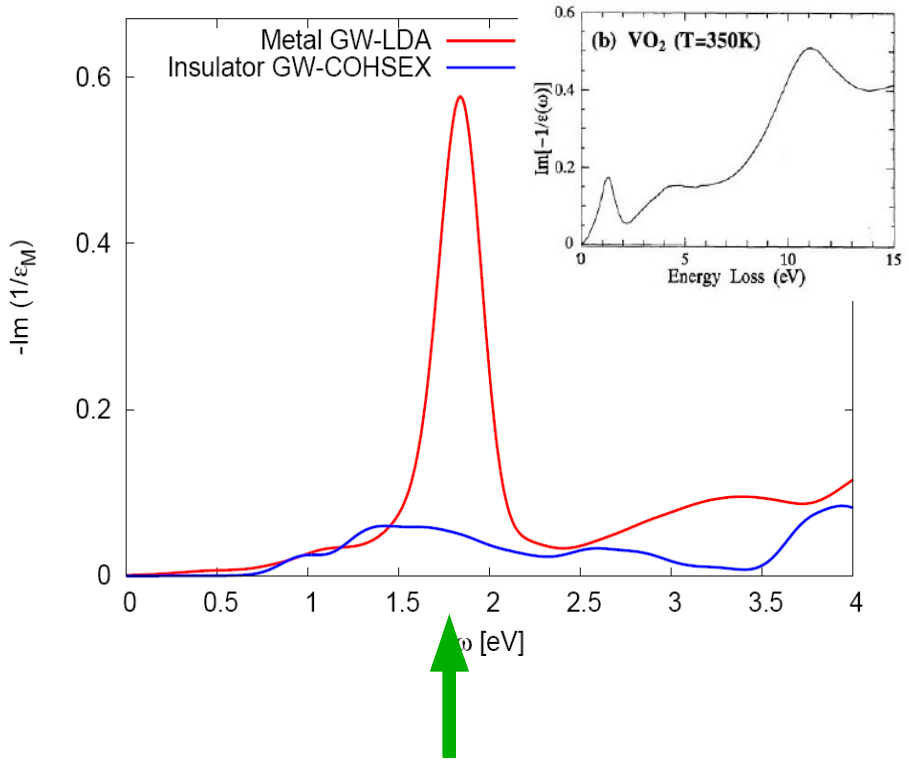


Spectral function

M. Gatti, G. Panaccione, and L. Reining (submitted)

Dynamical correlation: VO_2

$-\mathrm{Im}\,\varepsilon^{-1}(q,\omega)$ **IXS/EELS**



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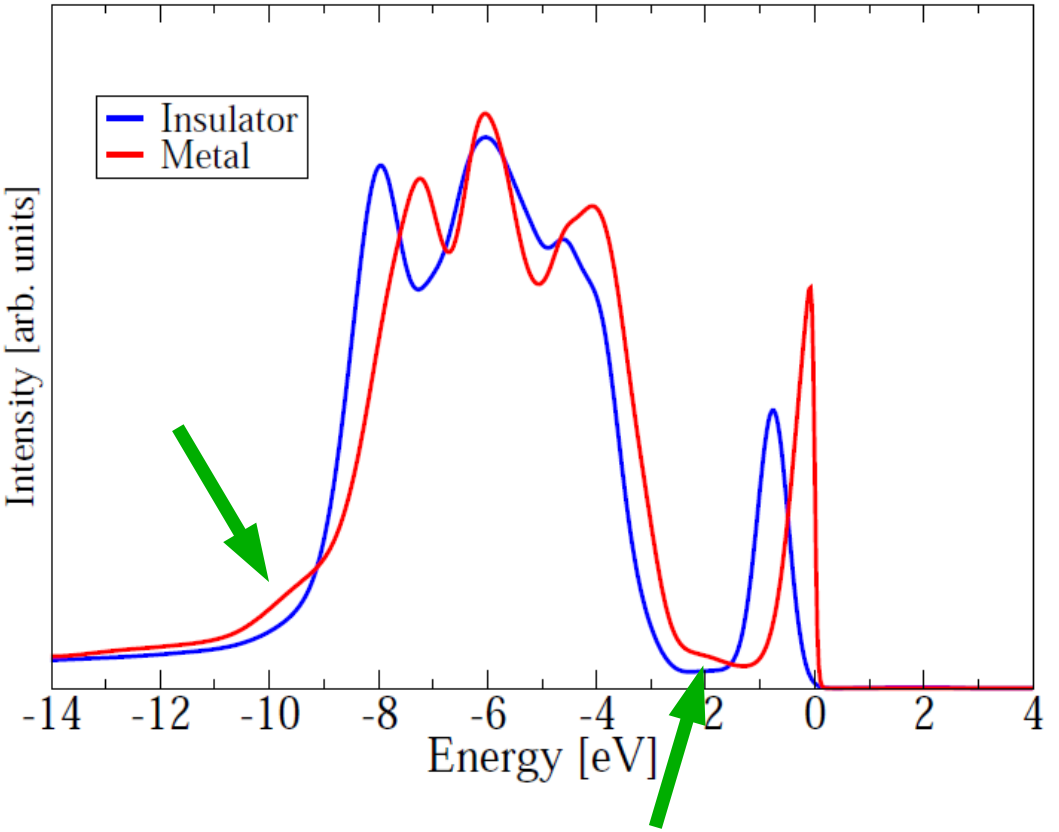

$W(r,r',\omega) = \varepsilon^{-1}(r,r',\omega)v(|r-r'|)$

Spectral function

Dynamical correlation: VO_2

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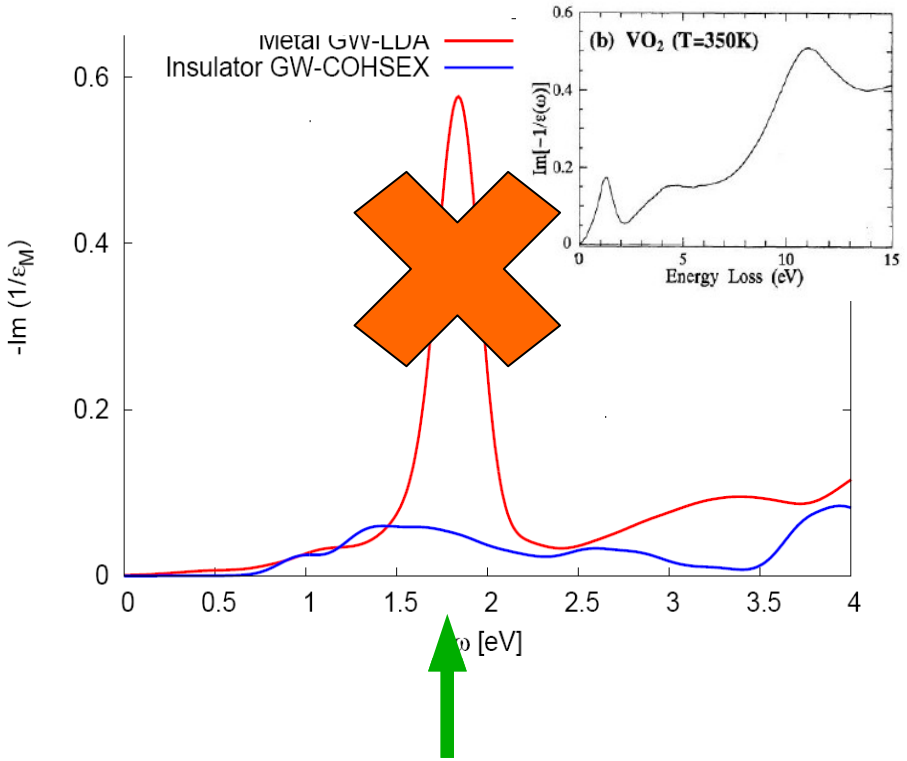

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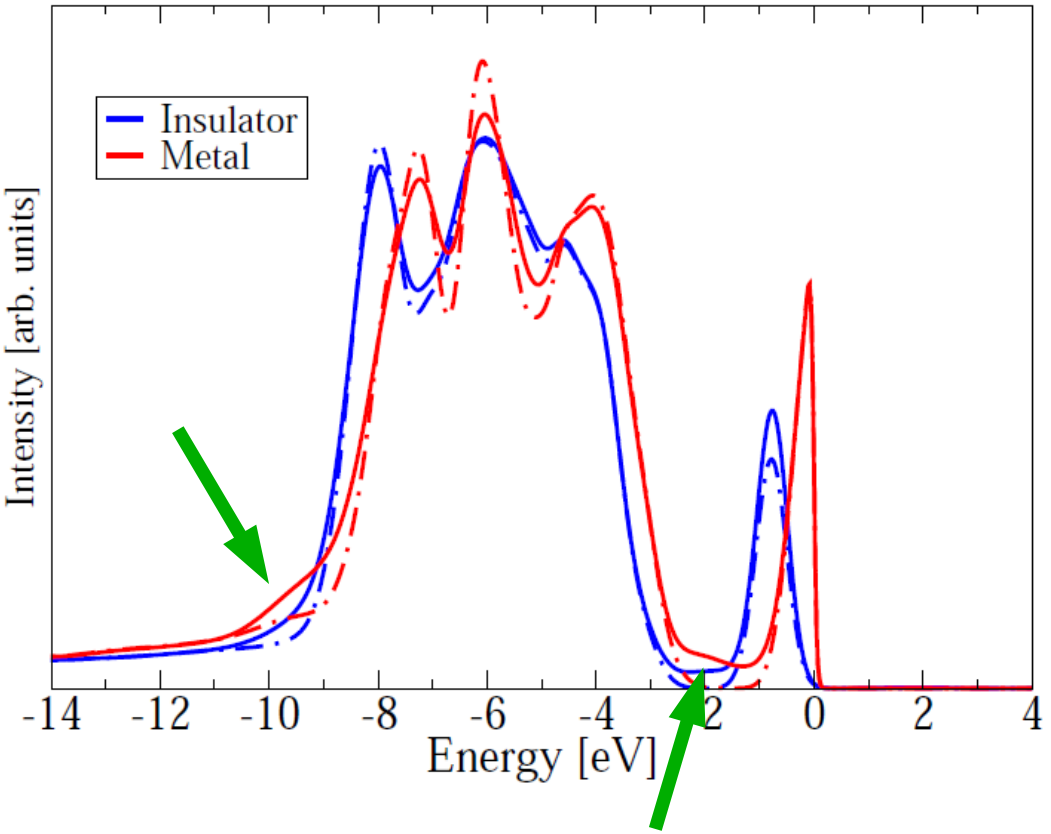

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Spectral function

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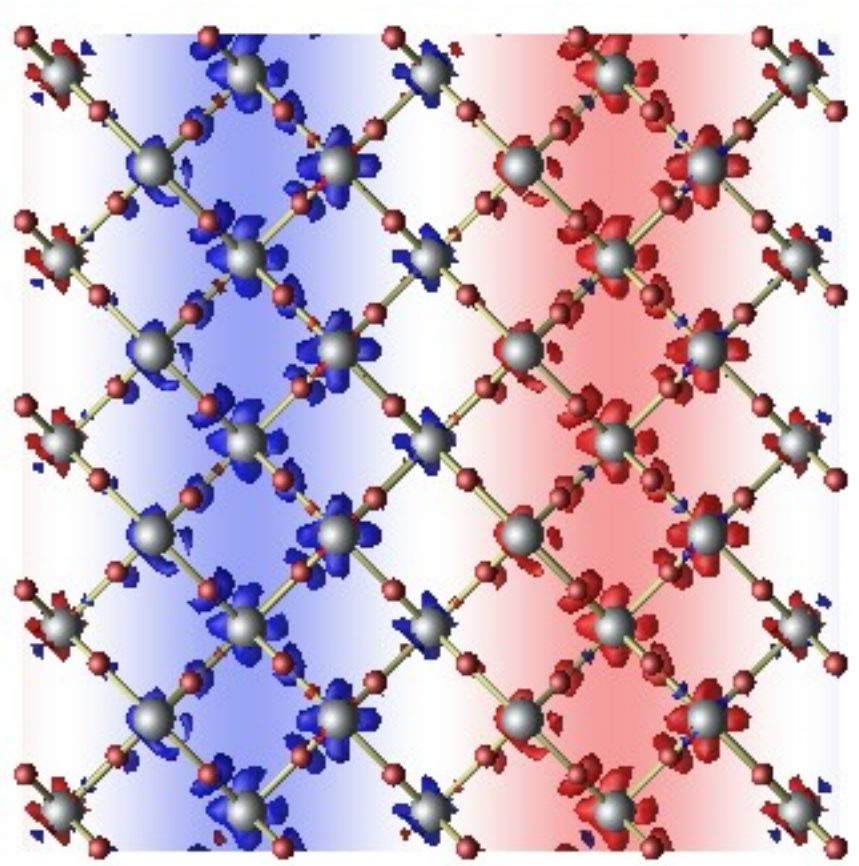
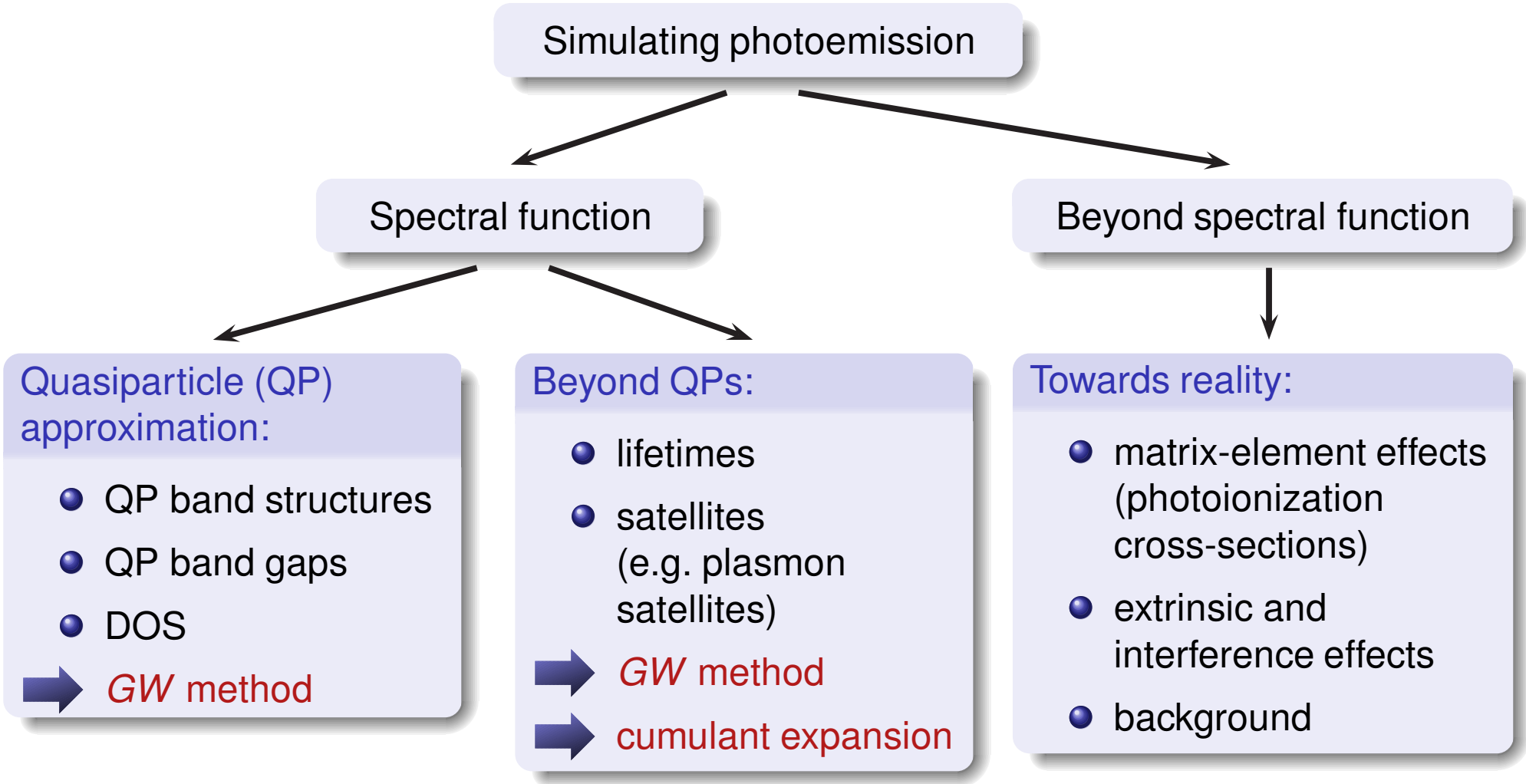
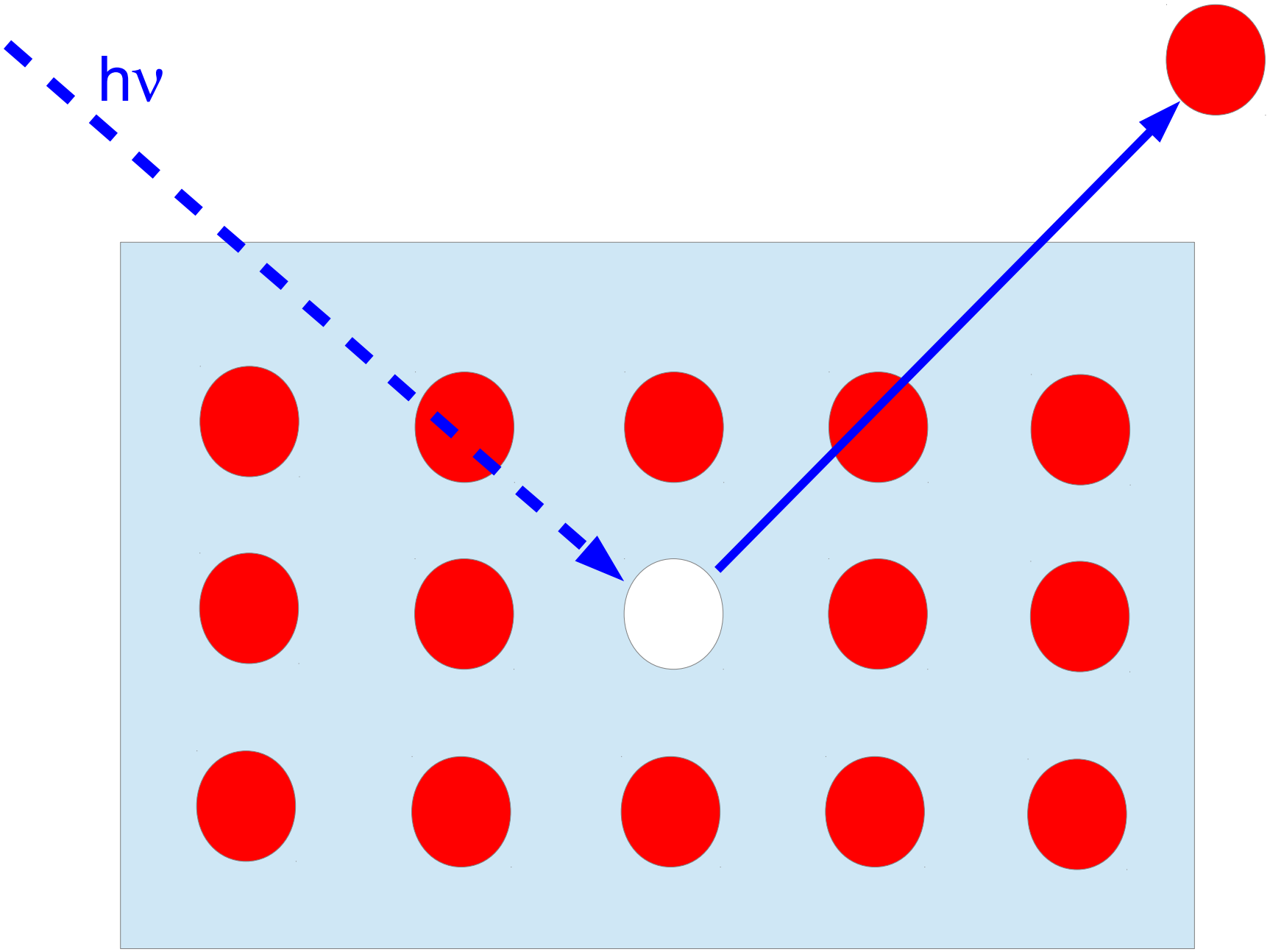


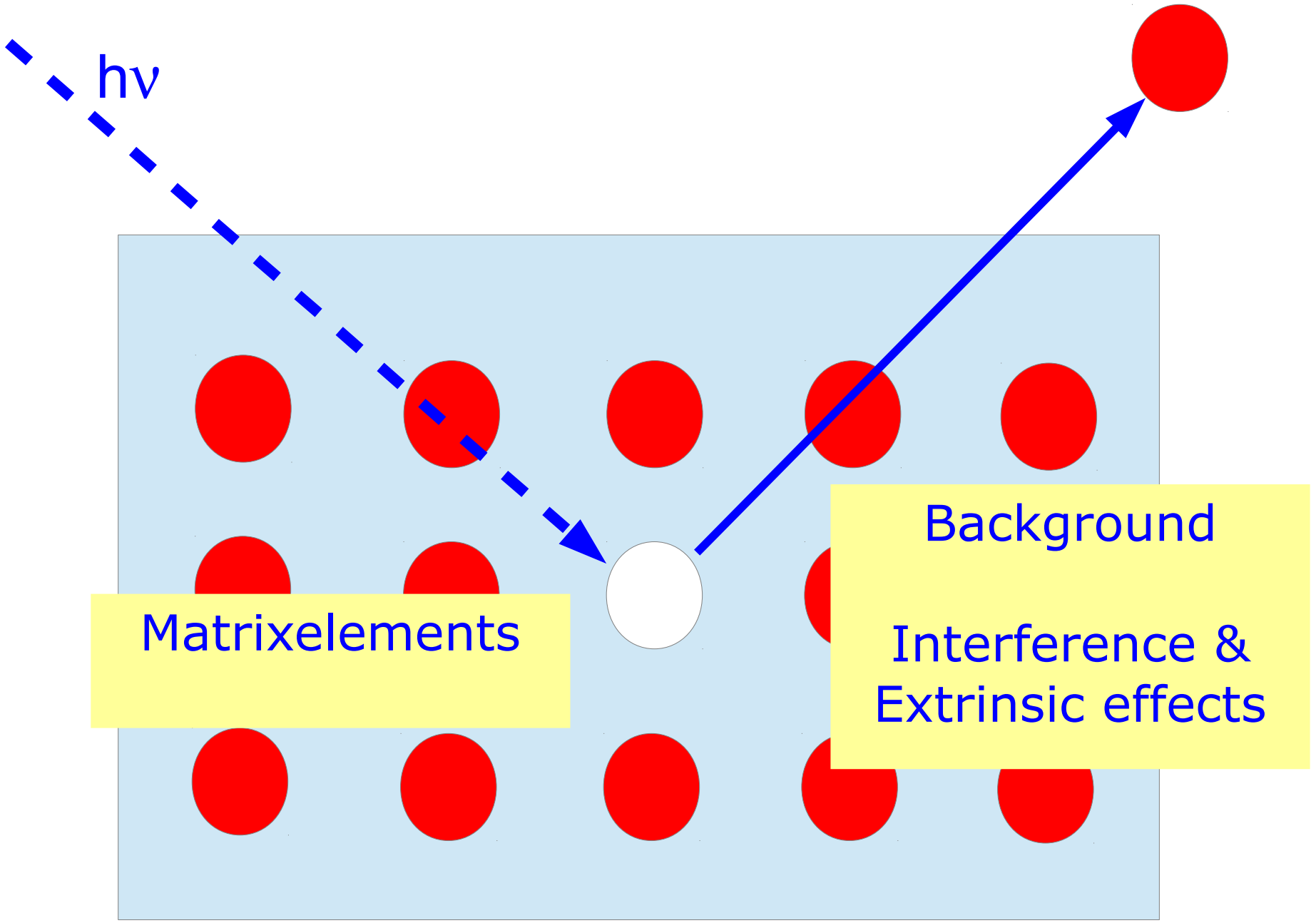
See Francesco's talk

Ralf Hambach, PhD thesis, Ecole Polytechnique (2010)

ETSF Photoemission Beamline

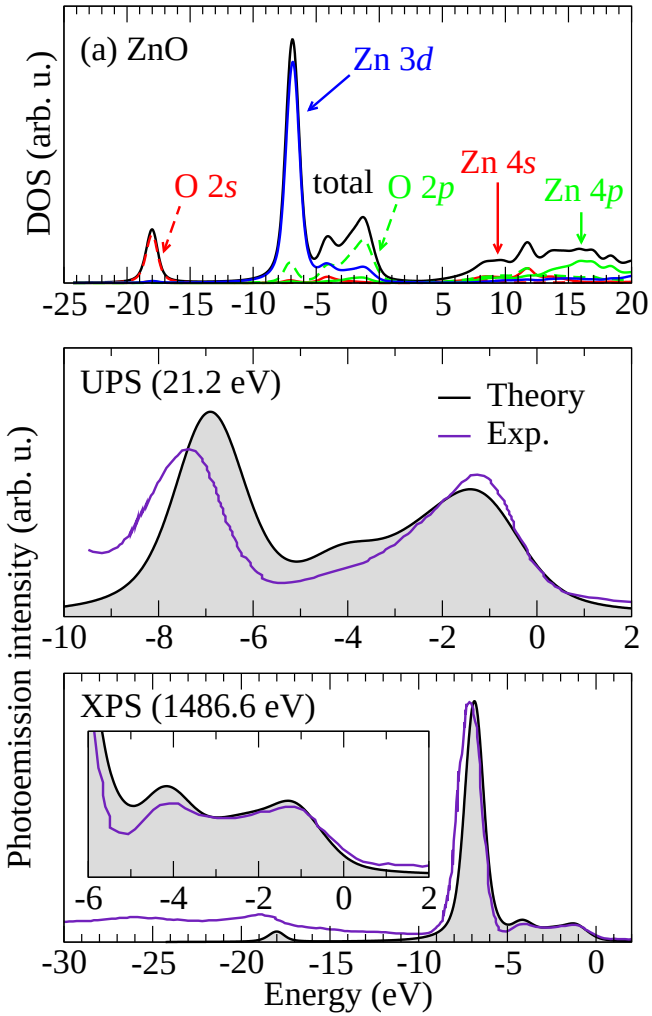



hν

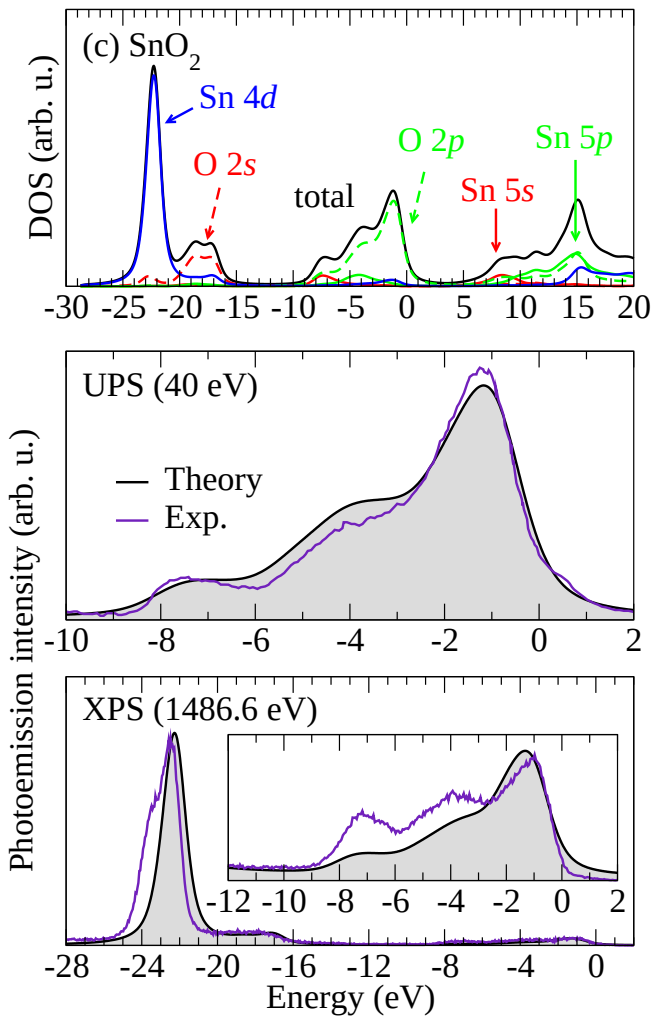

hν
Matrixelements
Background
Interference &
Extrinsic effects

TCOs: Including Photoionization Cross-Sections

ZnO

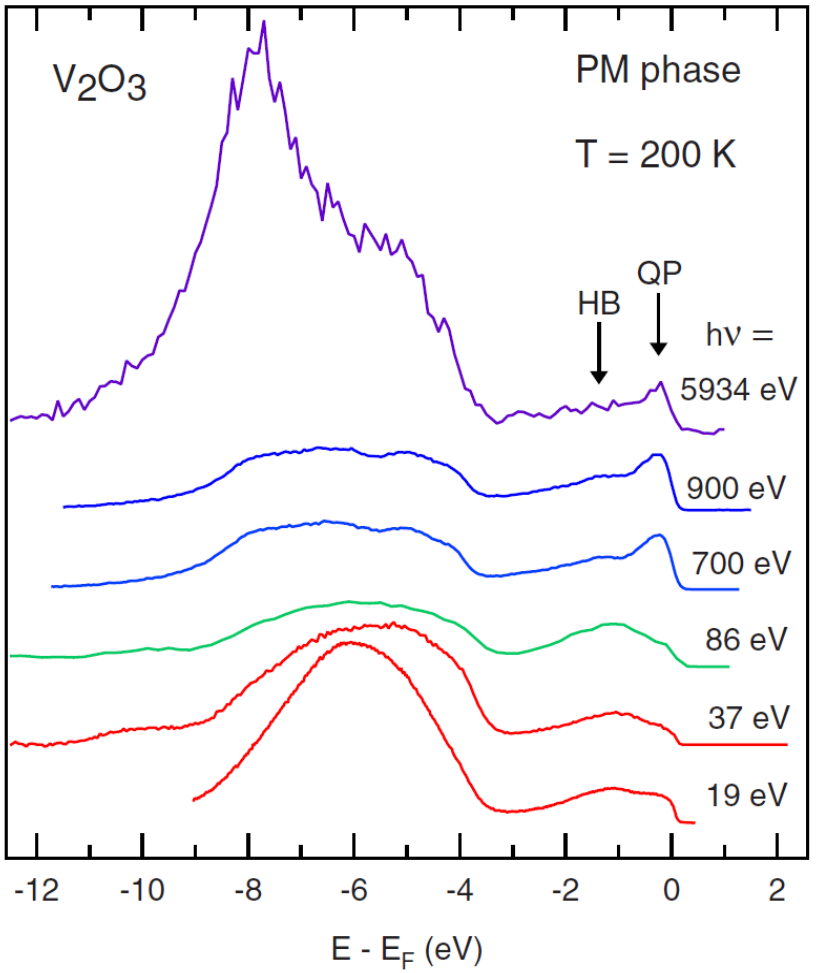


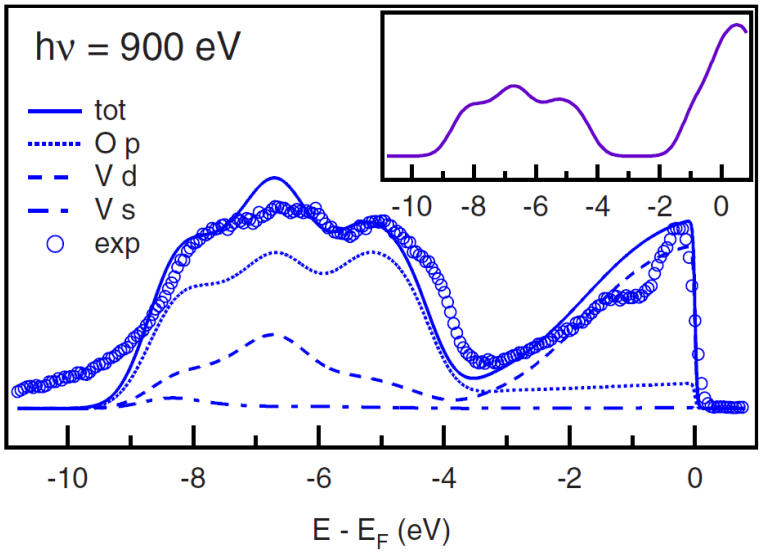
SnO_2

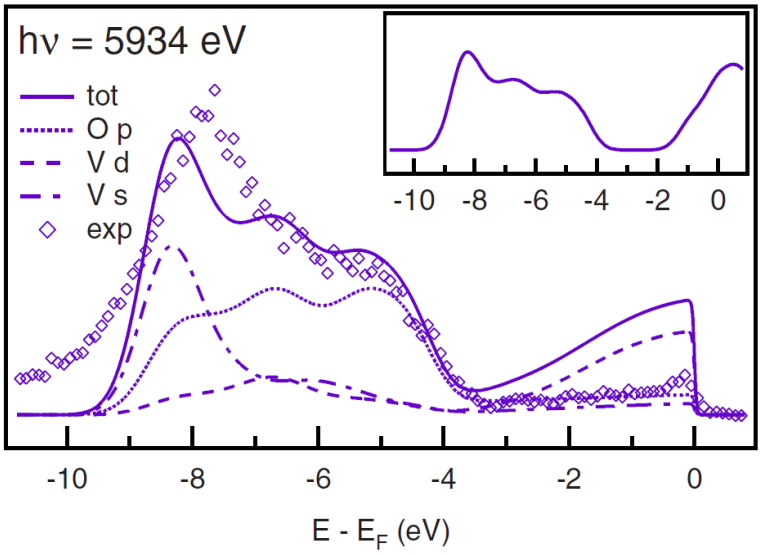


Rödl *et al.*, Phys. Stat. Solidi A **211**, 74 (2014)

Matrix elements: V_2O_3

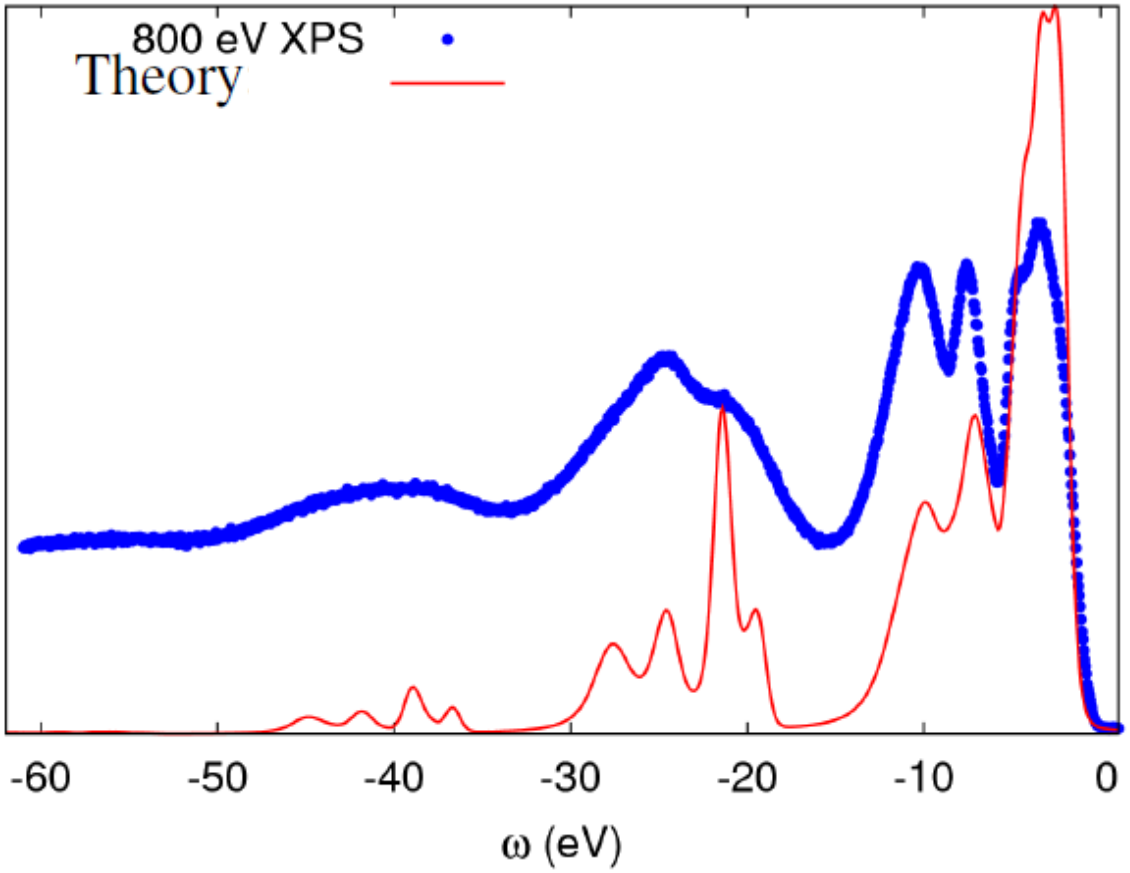






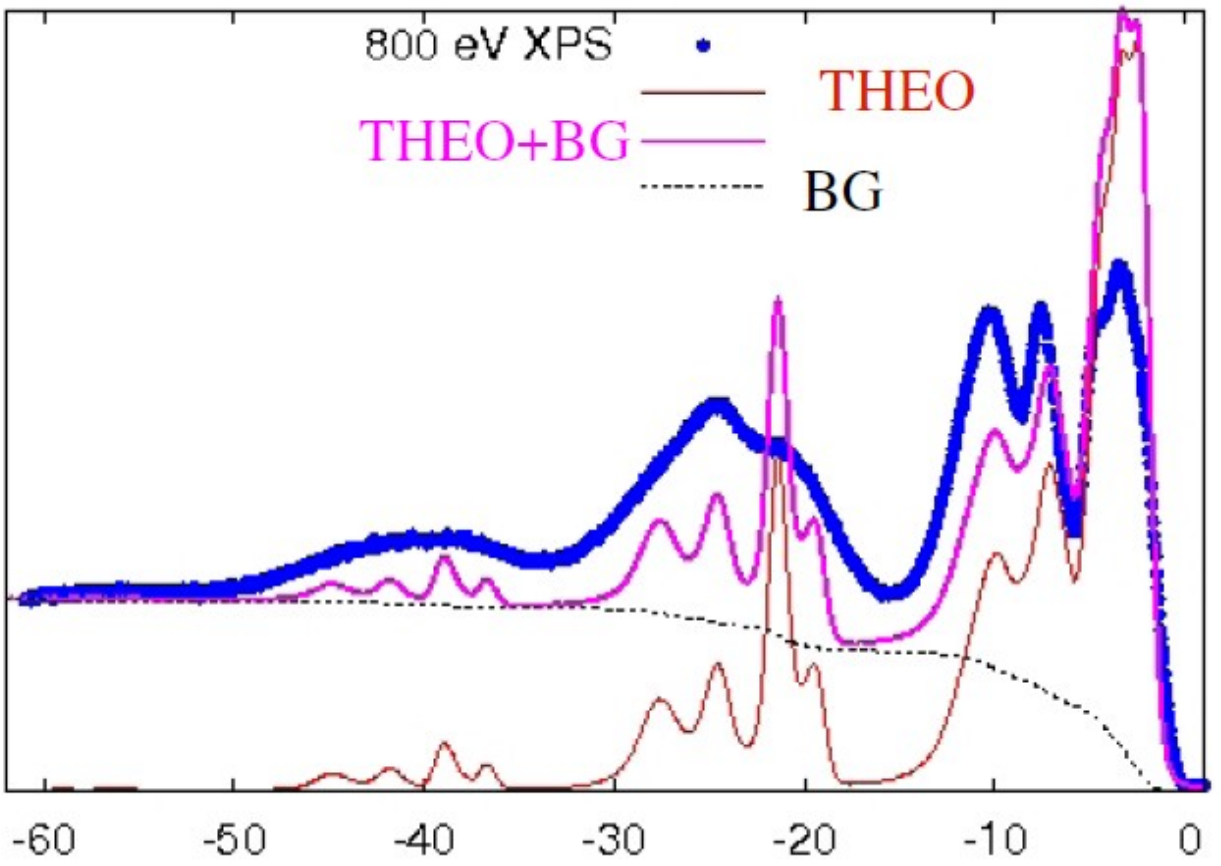
E. Papalazarou, et al., PRB 80 (2009)

Getting closer to what is really measured



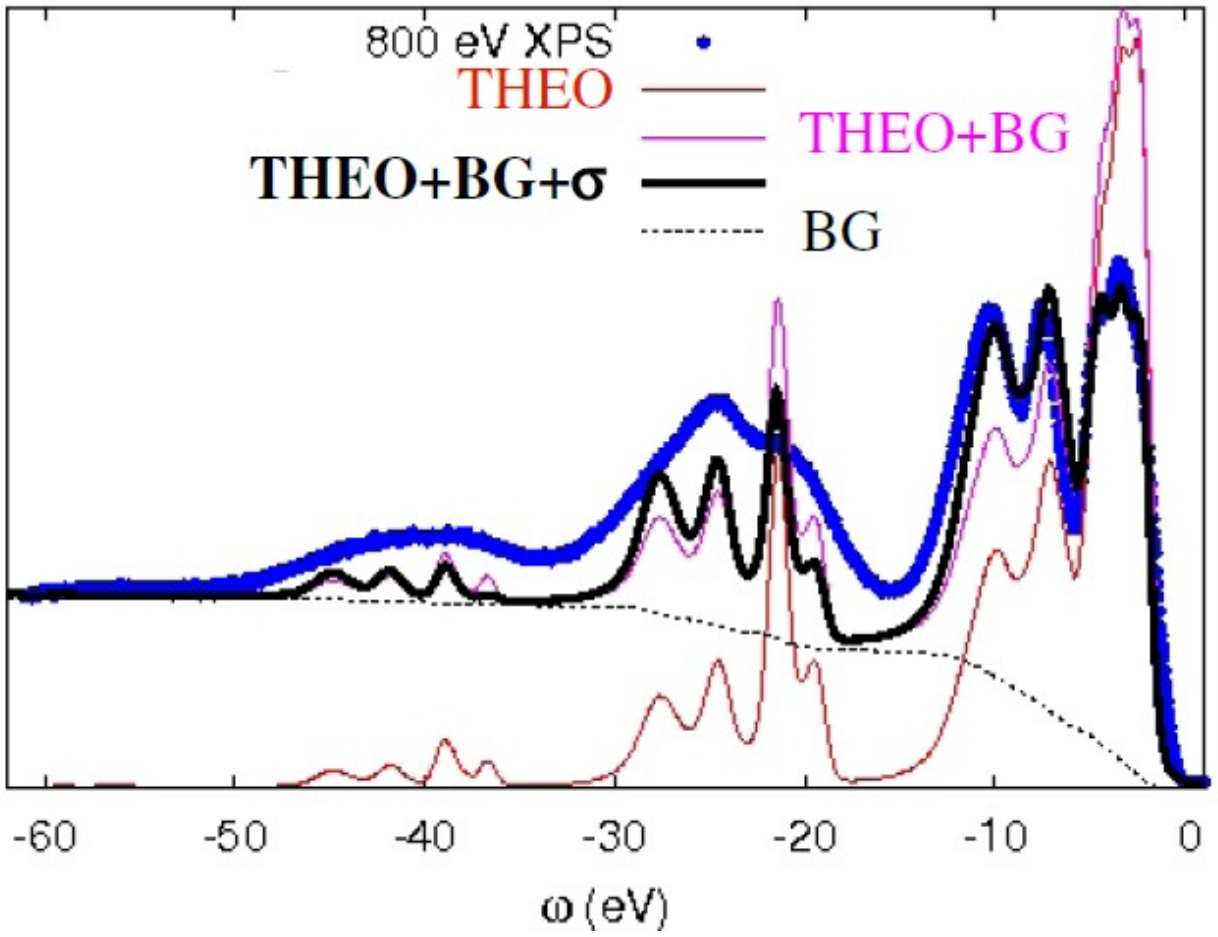
Spectral function

Getting closer to what is really measured



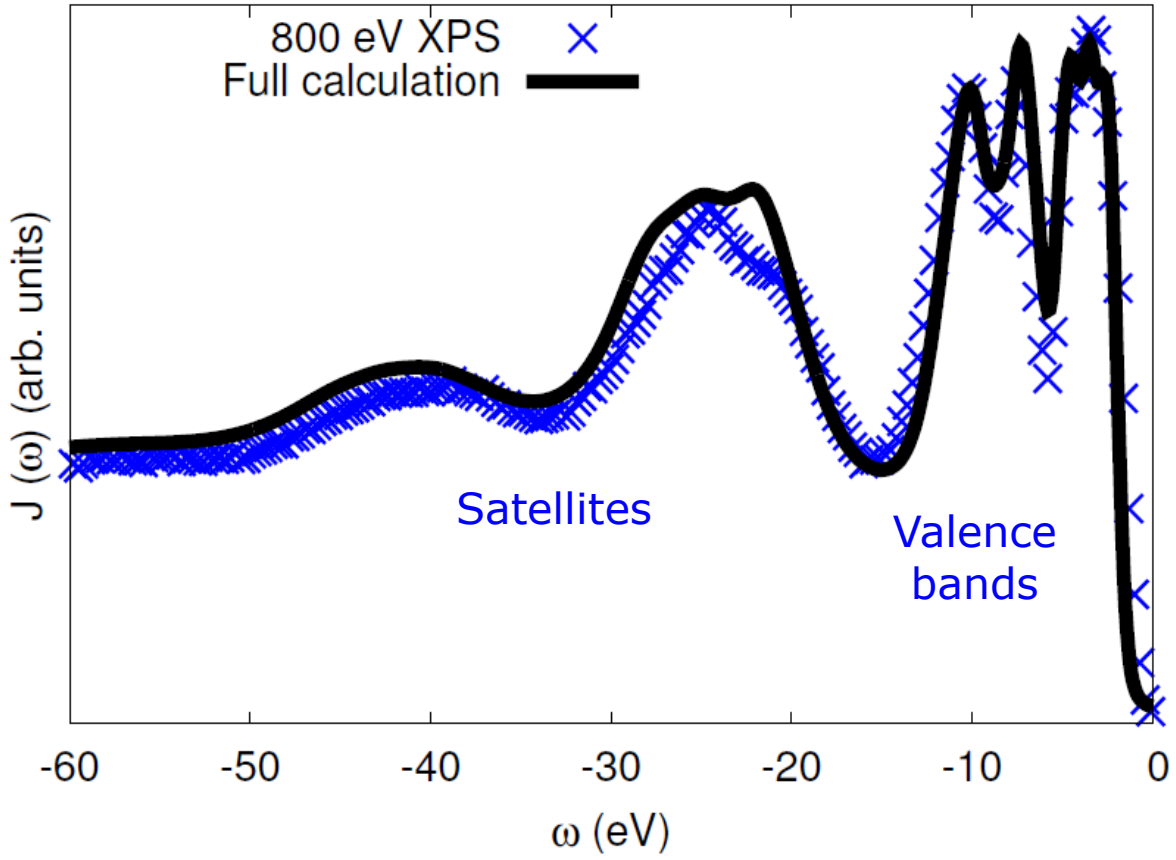
+ Background

Getting closer to what is really measured



+ Matrix elements

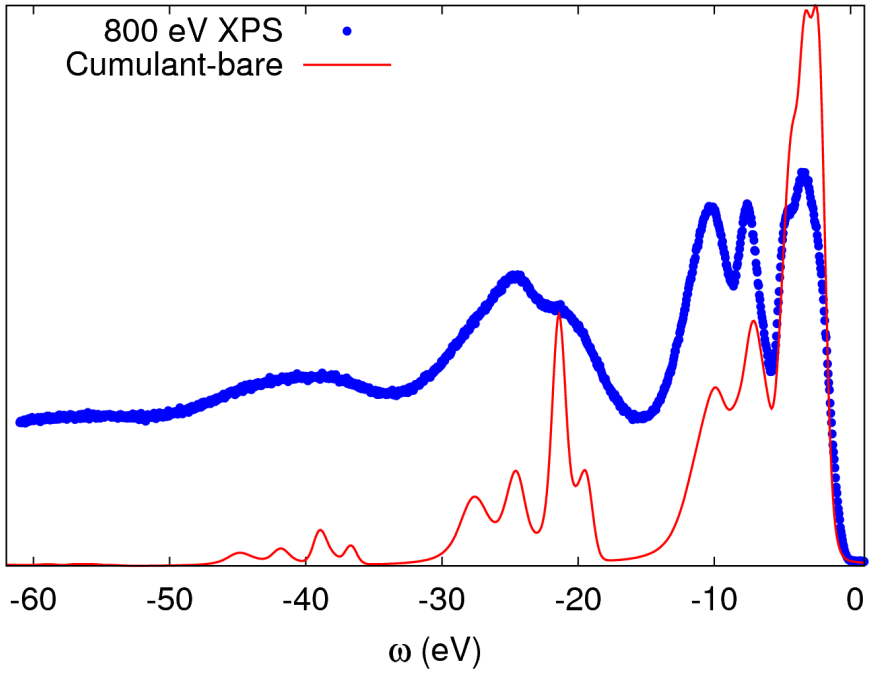
Getting closer to what is really measured



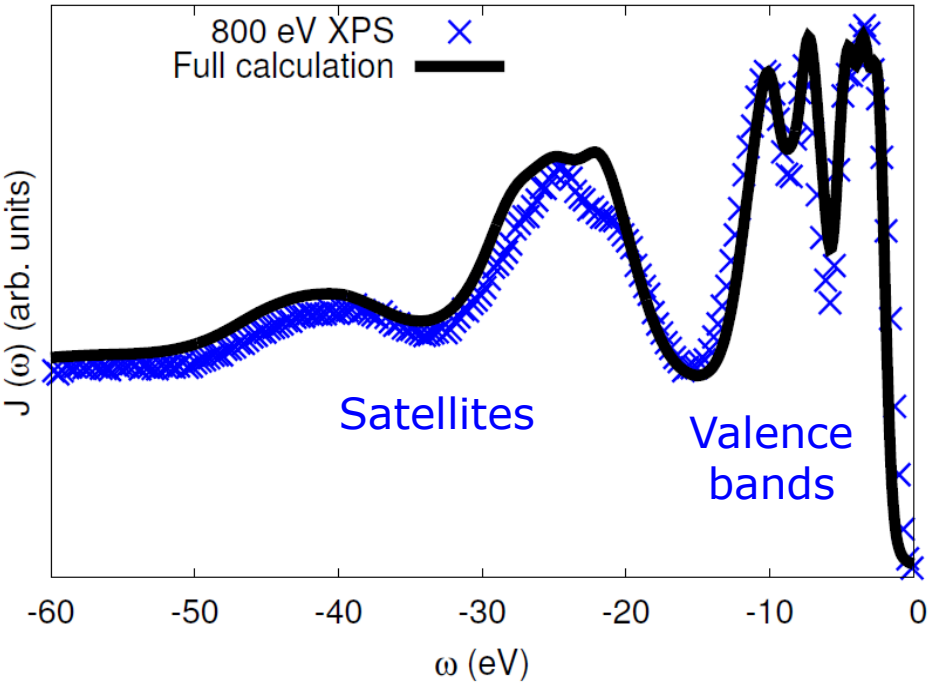
+ Interference/extrinsic effects

Getting closer to what is really measured

Spectral function



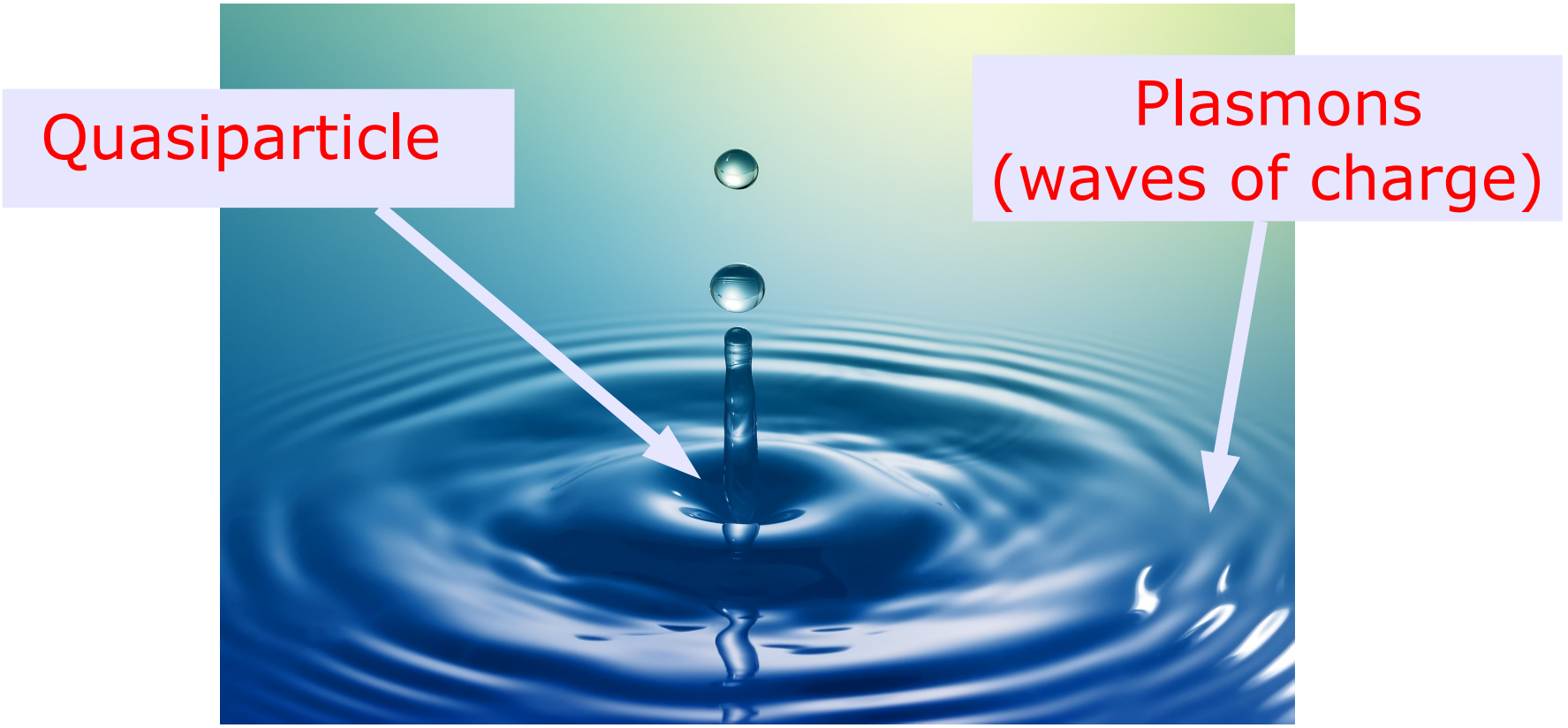
Photocurrent



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

Correlation = coupling of excitations

Adding/removing electrons: reaction of all the others



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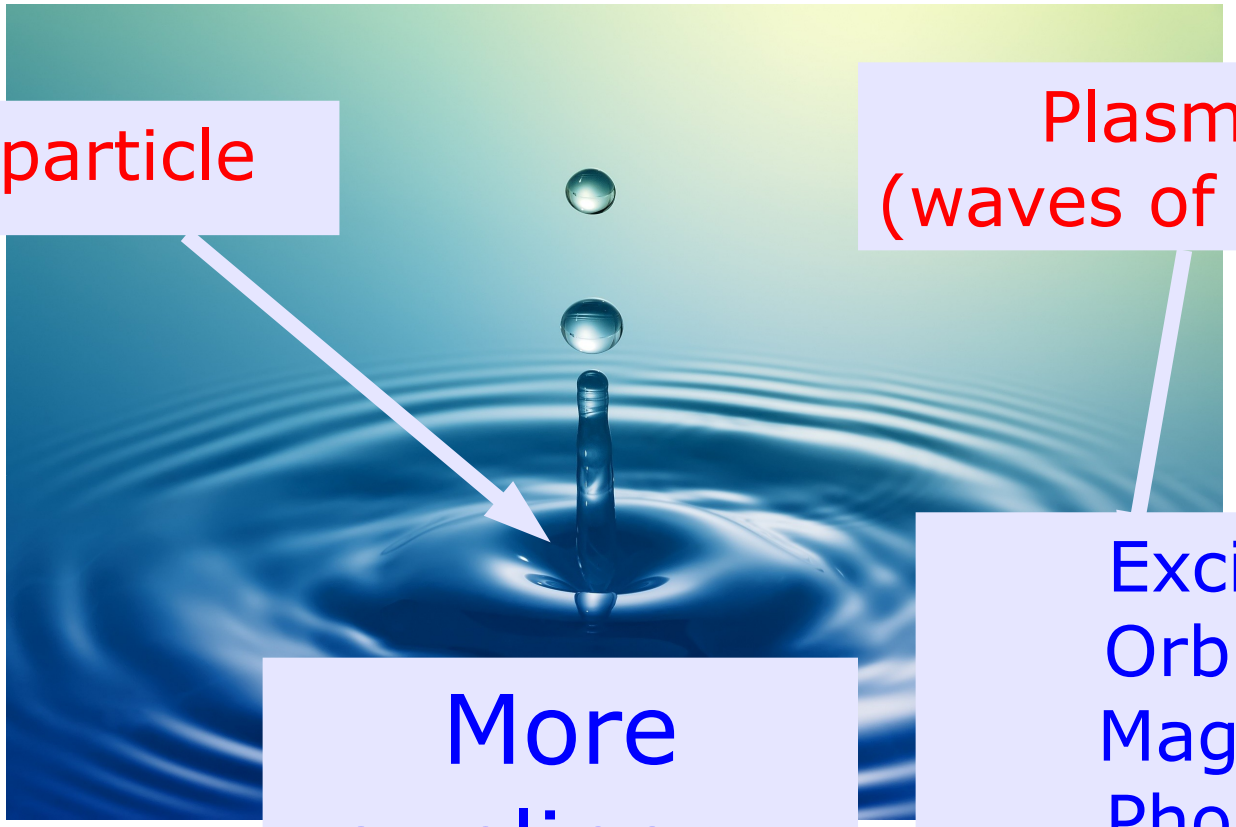


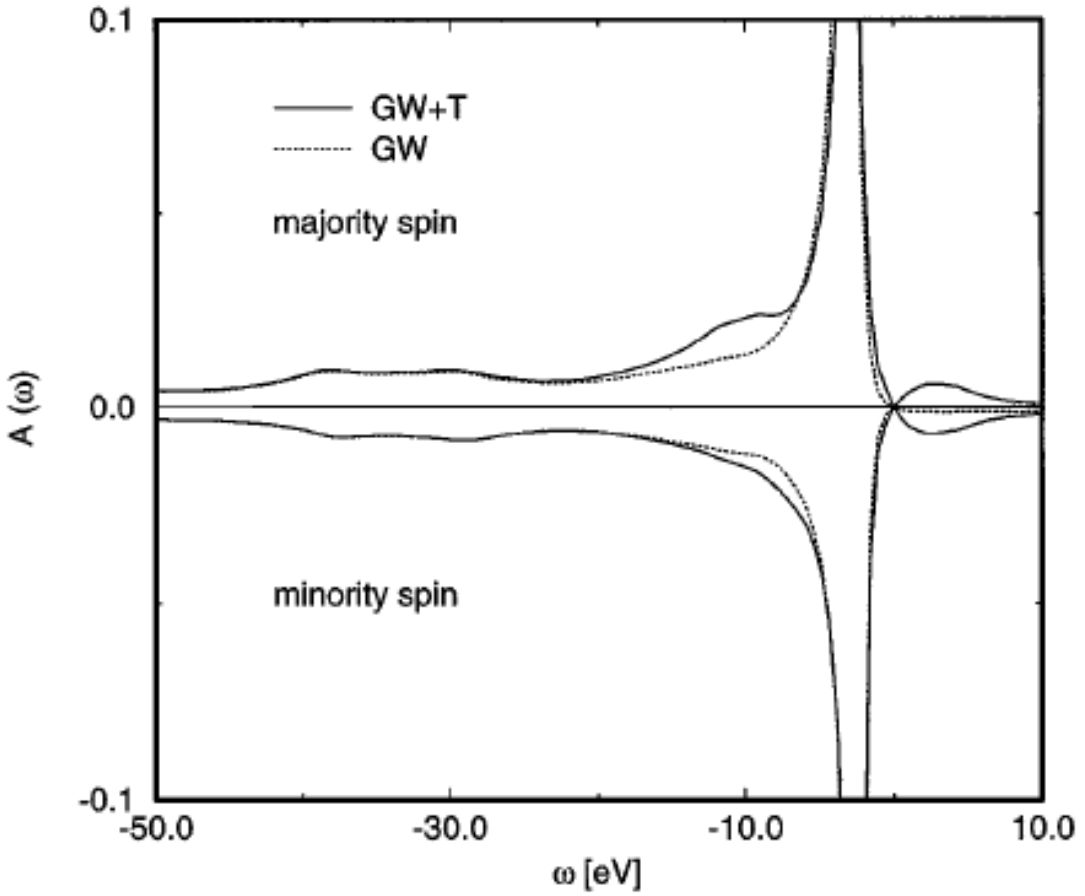
Quasiparticle

Plasmons (waves of charge)

More couplings...

Excitons
Orbitons
Magnons
Phonons
...

Outlook: coupling with other excitations

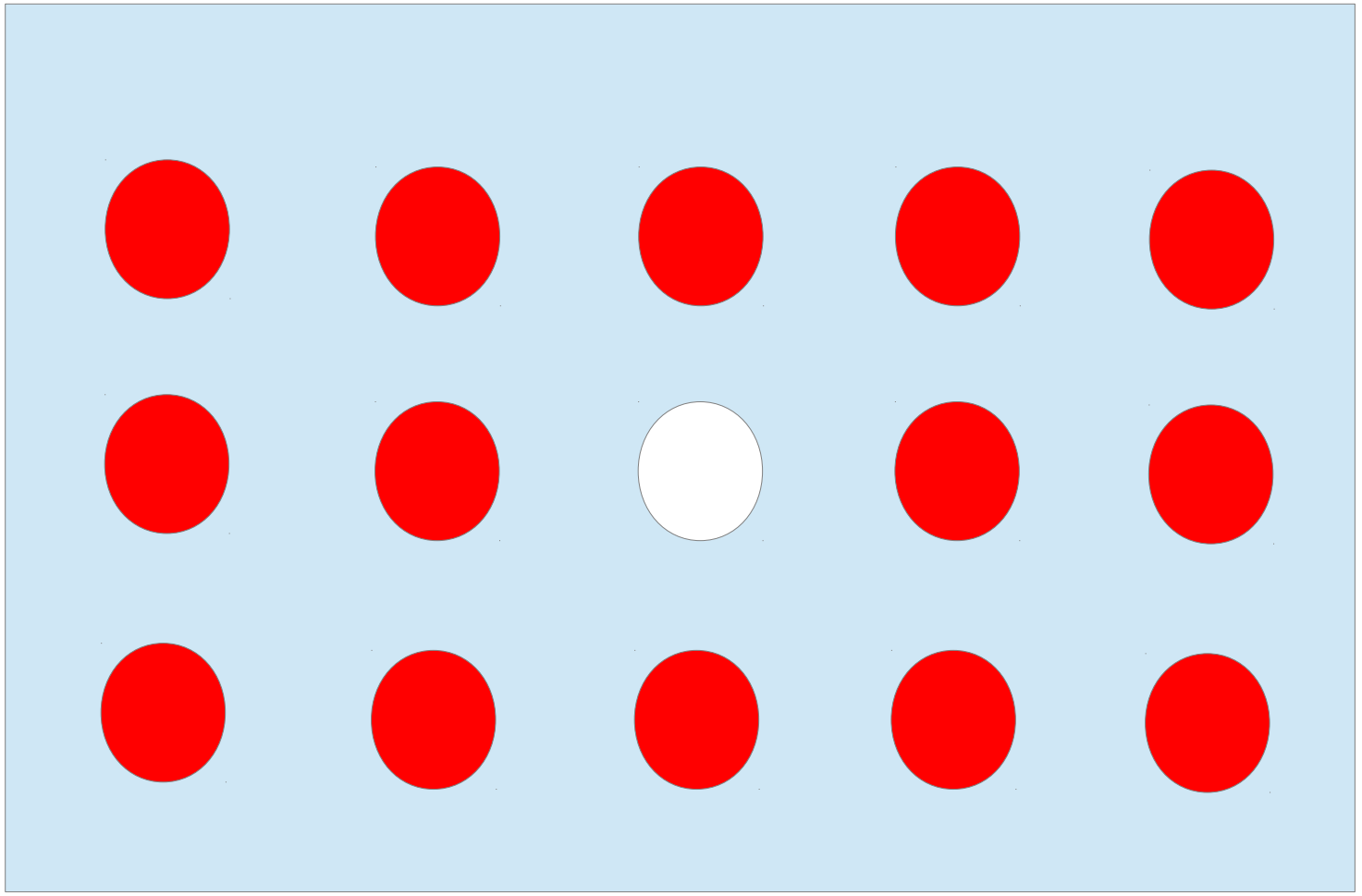


6 eV satellite in Ni: 2-hole bound state

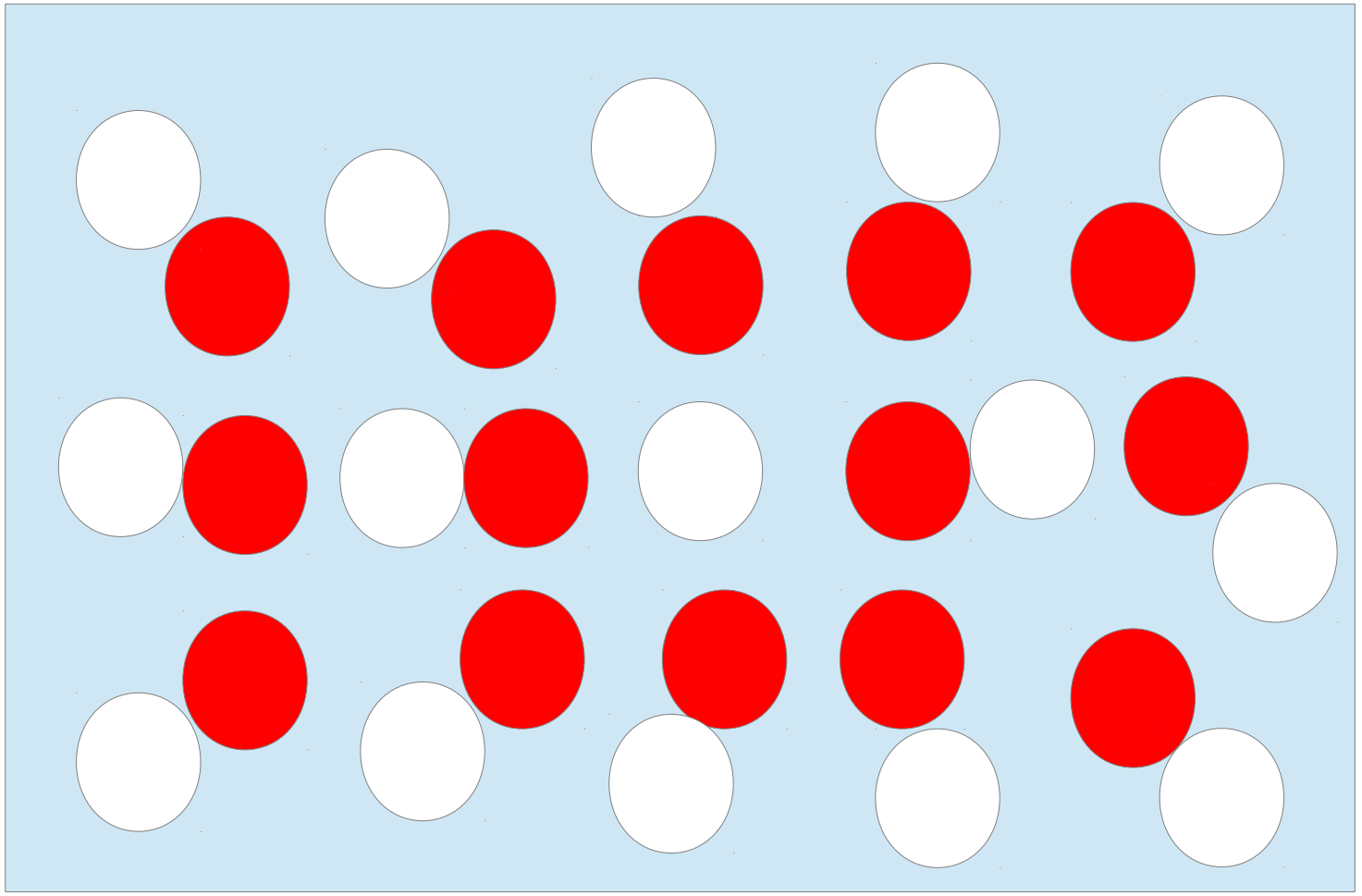
Springer, Aryasetiawan, Karlsson, PRL 80, 2389 (1998)

Back up slides

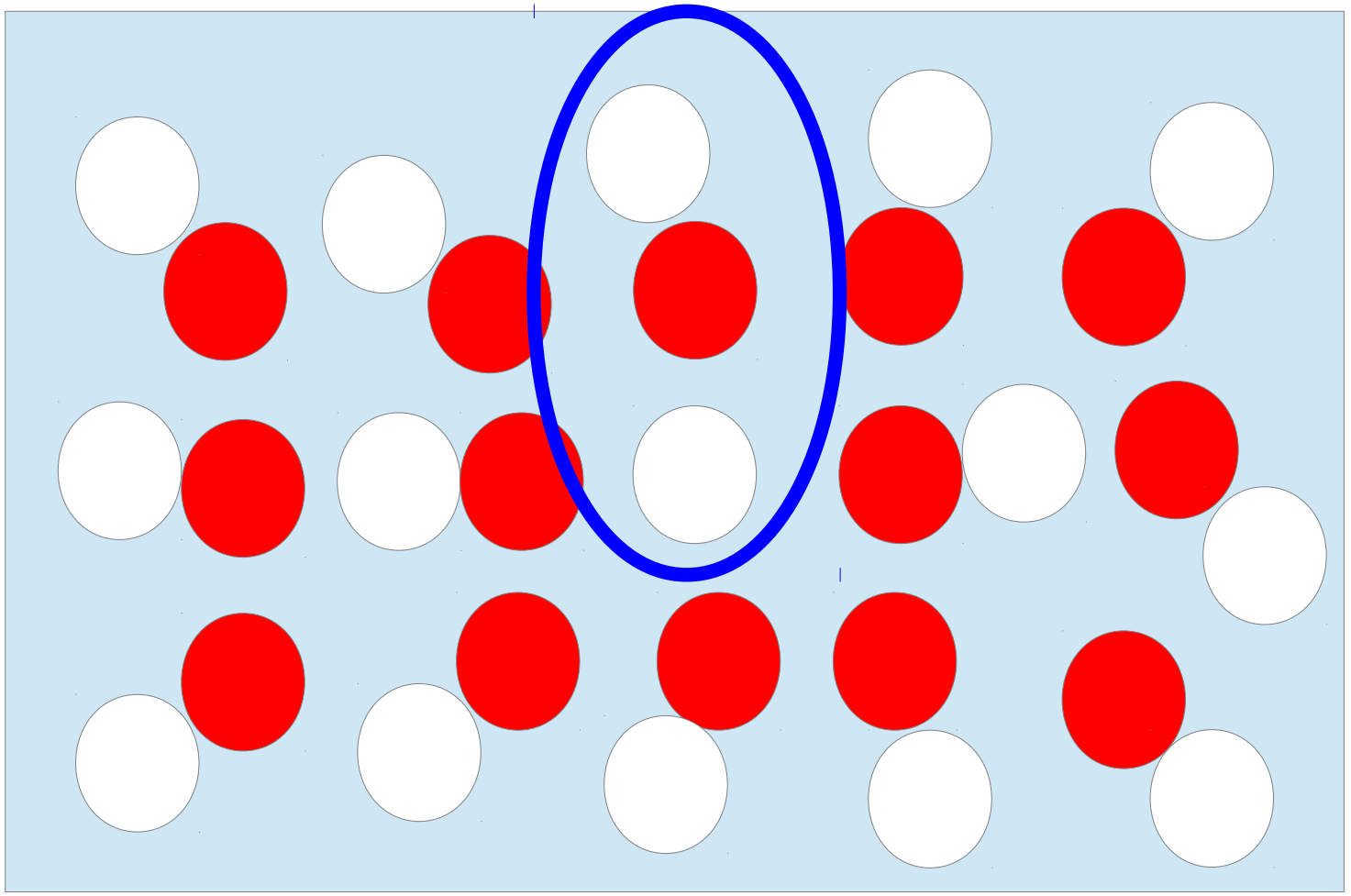
Interacting particles

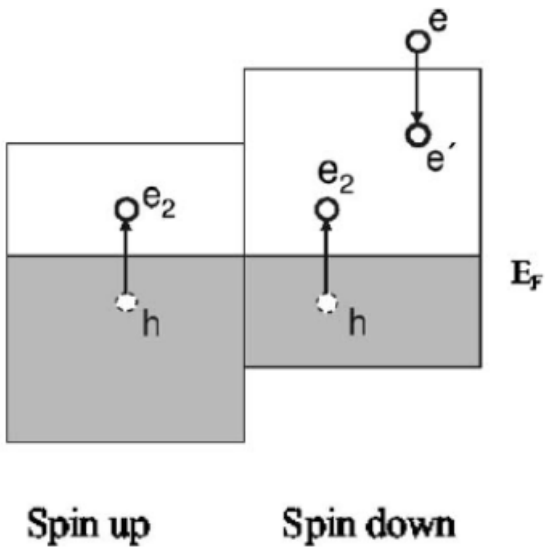


Interacting particles



Interacting particles



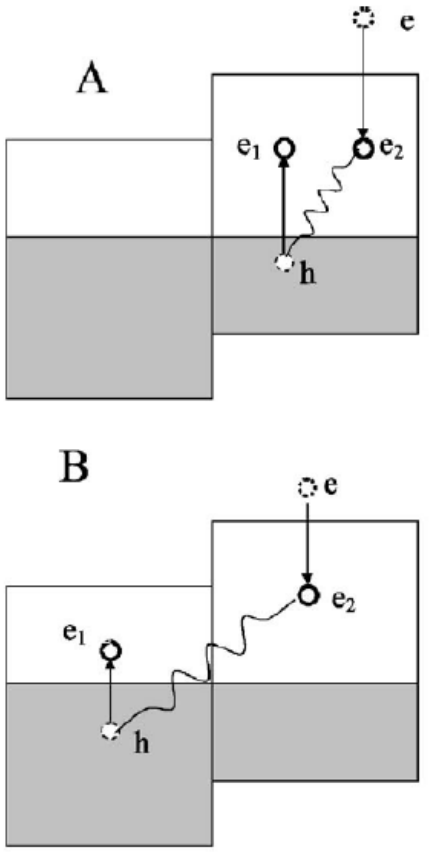


GW

- Add one primary electron e, spin $\downarrow$
- Disexcitation $(e, \downarrow) \rightarrow (e', \downarrow)$
- Creation of electron-hole pairs e_2-h in both spin channels.

Note

- primary electron: final spin = initial spin (no spin flips)
- no interaction between primary electron and secondary particles
- analogously for additional hole



T matrix

- Add one primary electron e, spin $\downarrow$
- Disexcitation $(e, \downarrow) \rightarrow (e_2, \downarrow)$
- Creation of electron-hole pairs e_1-h in both spin channels
- Interaction between primary electron and hole of electron-hole pair (A,B)
- Interaction between primary electron and electron of electron-hole pair (C)

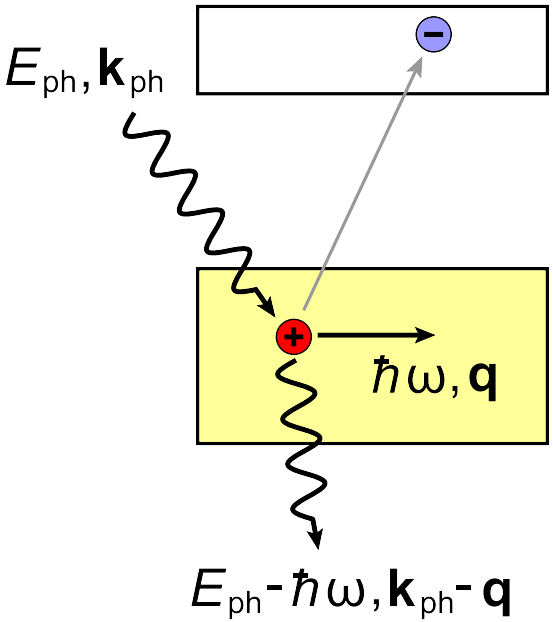
Note

- (B) spin flips: coupling with spin-waves, magnons, paramagnons
- analogously for additional hole

$$\mathcal{B}_f(\omega) = \int_{\omega}^{\mu} d\omega' f(\omega')$$

- Assumption: the bare signal produces a constant flux of secondary electrons at all energies
- The background is added to the theoretical spectrum (overall factor fitted to experiment)

Probing Neutral Electronic Excitations



Inelastic scattering of

Electrons

- electron-energy loss spectroscopy (EELS)
- low $\mathbf{q}$

X-rays

- non-resonant inelastic x-ray scattering (IXS)
- large $\mathbf{q}$

➡ charge density fluctuations (interband transitions, excitons, plasmons)

charge-density response function $\chi(\mathbf{r}_1\mathbf{r}_2, t_1 - t_2)$

$$\chi(\mathbf{r}_1\mathbf{r}_2, t_1 - t_2) = \frac{1}{i\hbar} \langle N | \mathcal{T}\, \Delta n(\mathbf{r}_1, t_1)\, \Delta n(\mathbf{r}_2, t_2) | N \rangle$$

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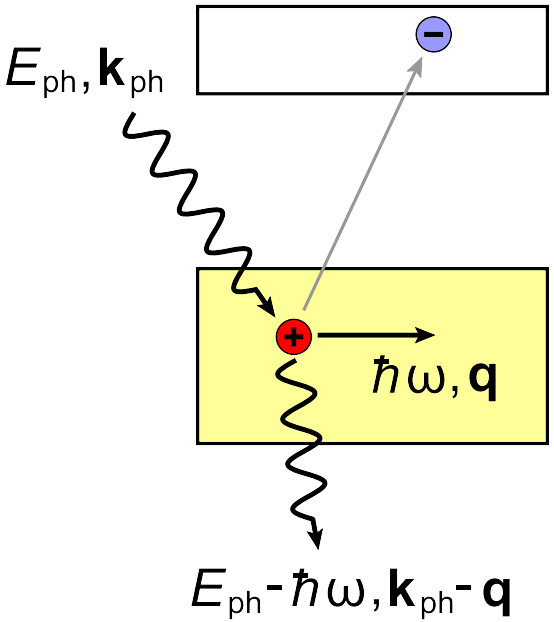

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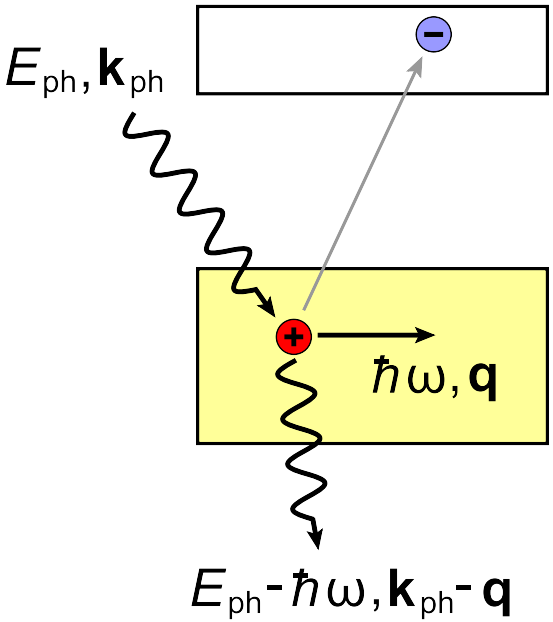
$$\varepsilon^{-1}(\mathbf{q}, \omega) = 1 + v(\mathbf{q})\chi(\mathbf{q}\mathbf{q}, \omega)$$

Probing Neutral Electronic Excitations



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dynamic structure factor $S(\mathbf{q}, \omega)$

$$S(\mathbf{q}, \omega) \sim \chi(\mathbf{q}\mathbf{q}, \omega)$$