Simulating Spectra

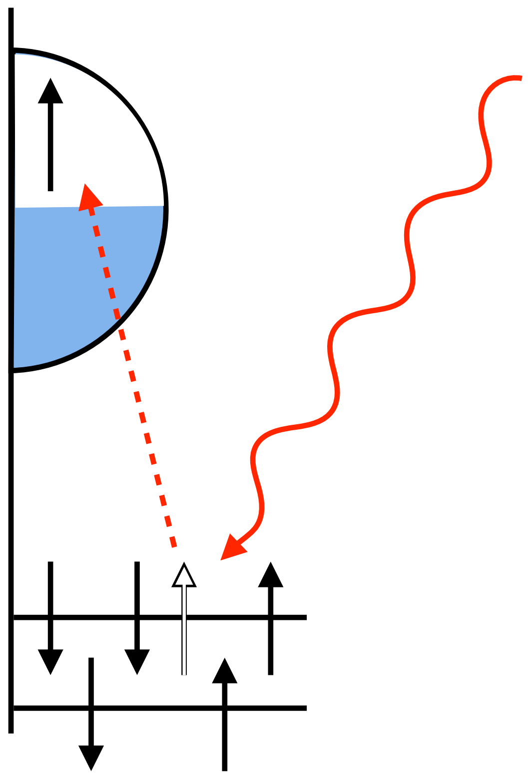
Travis Jones
19 Jan 2018

Introduction

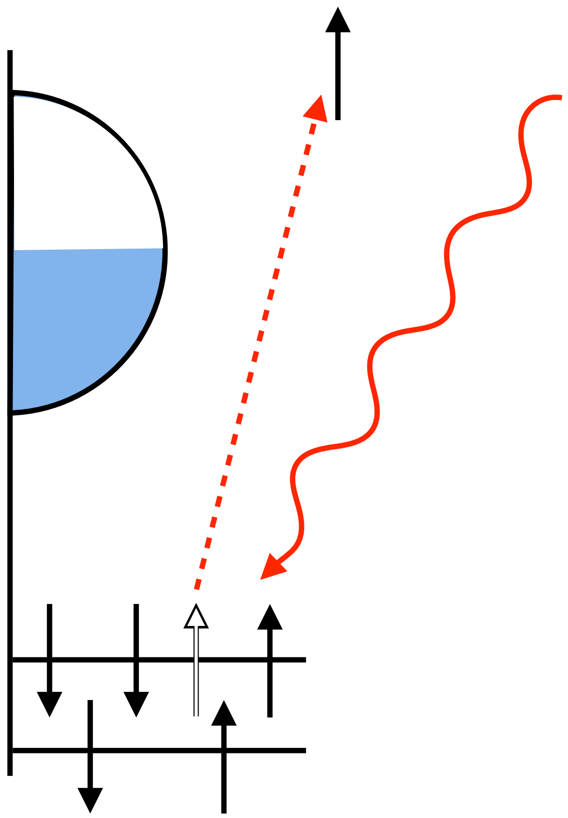
- Why should you care about calculating spectra?
- What kinds of spectra can you compute?
- What types of approaches are there?
- What are the pitfalls?

A few types of X-ray spectroscopy

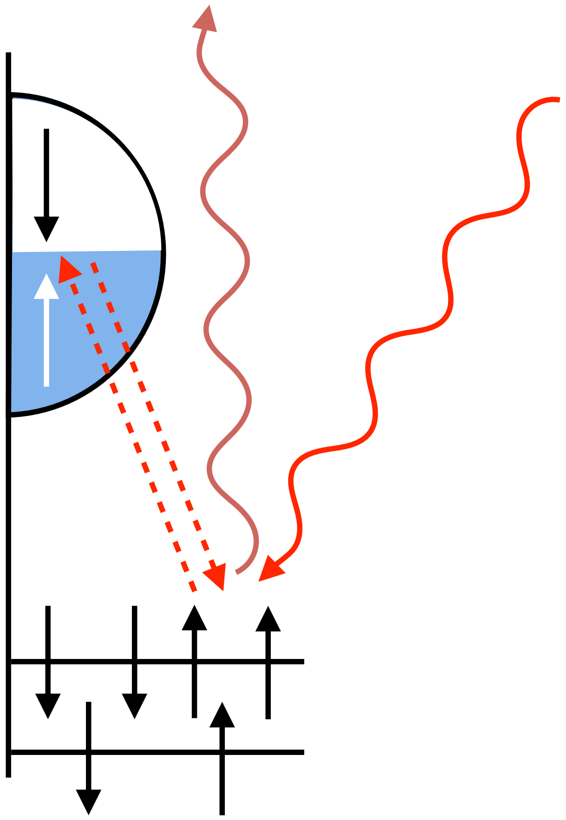
Absorption



Photoemission

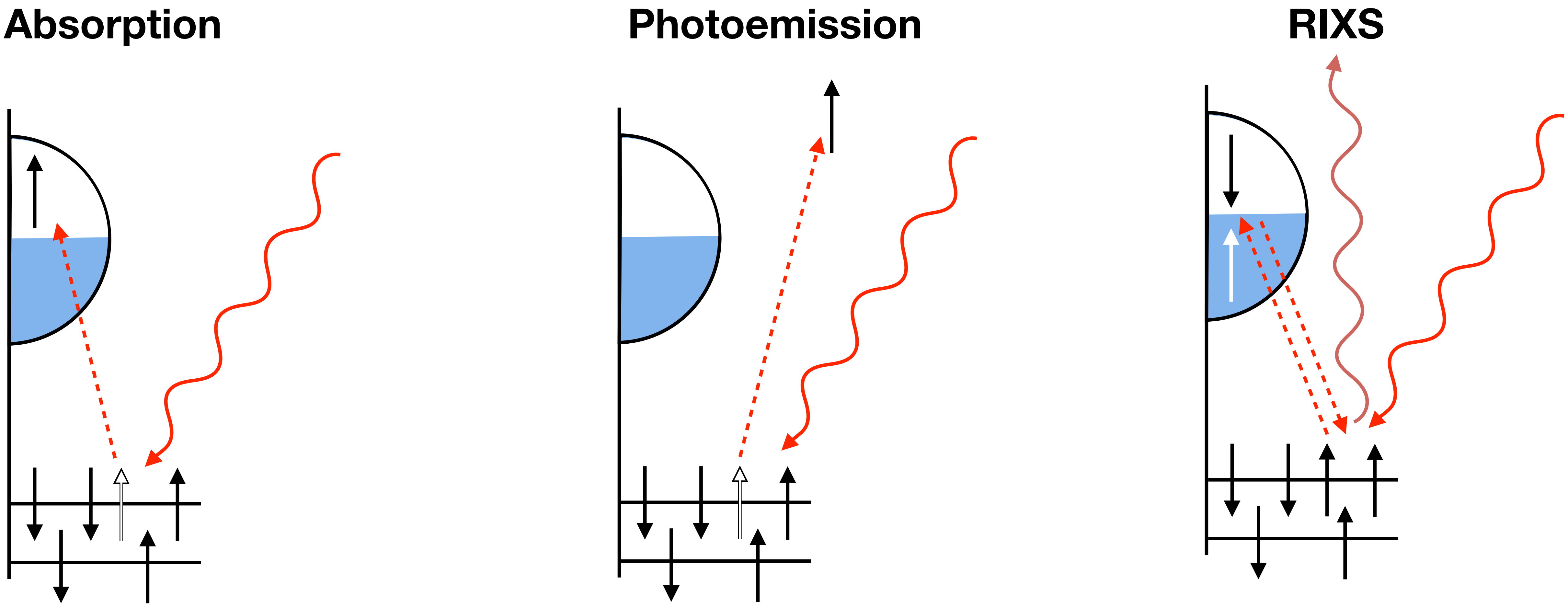


RIXS



A few types of X-ray spectroscopy

- Give different but complementary information



Absorption

Photoemission

RIXS

A few types of X-ray spectroscopy

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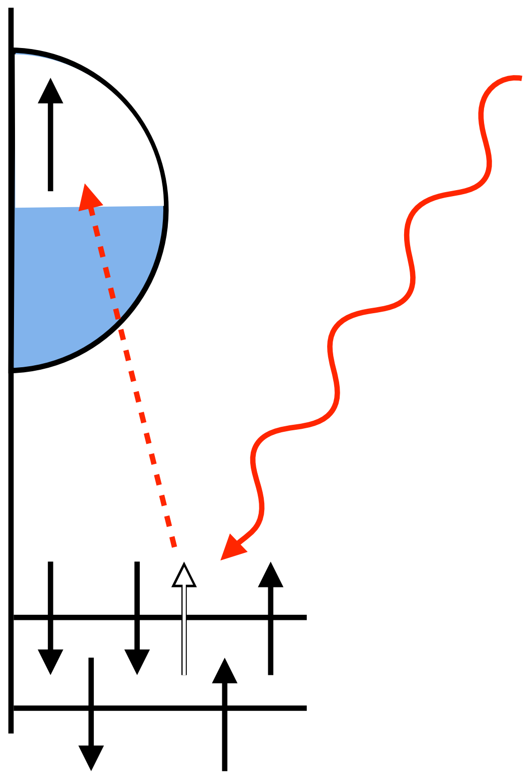
Absorption



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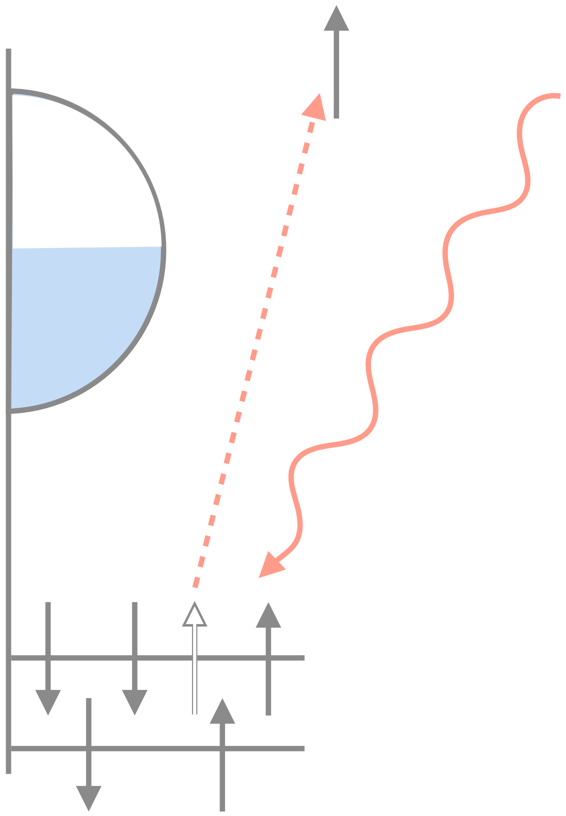

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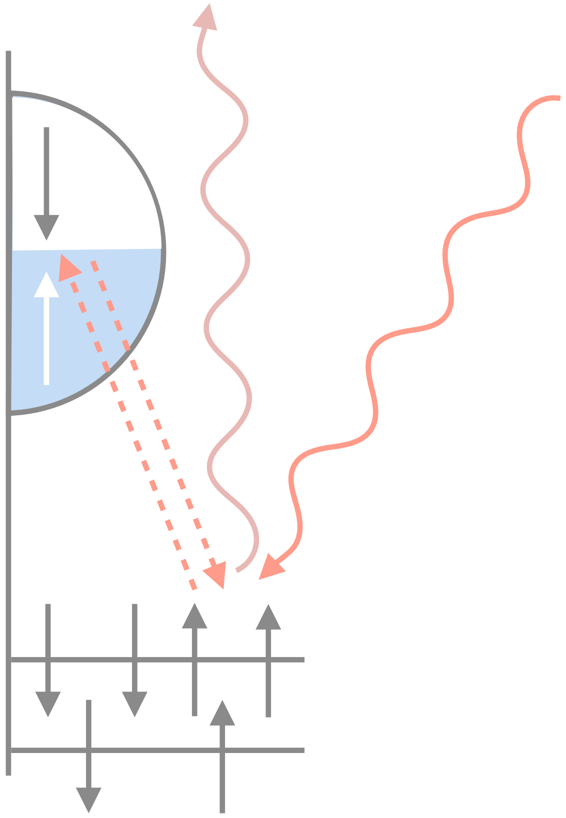
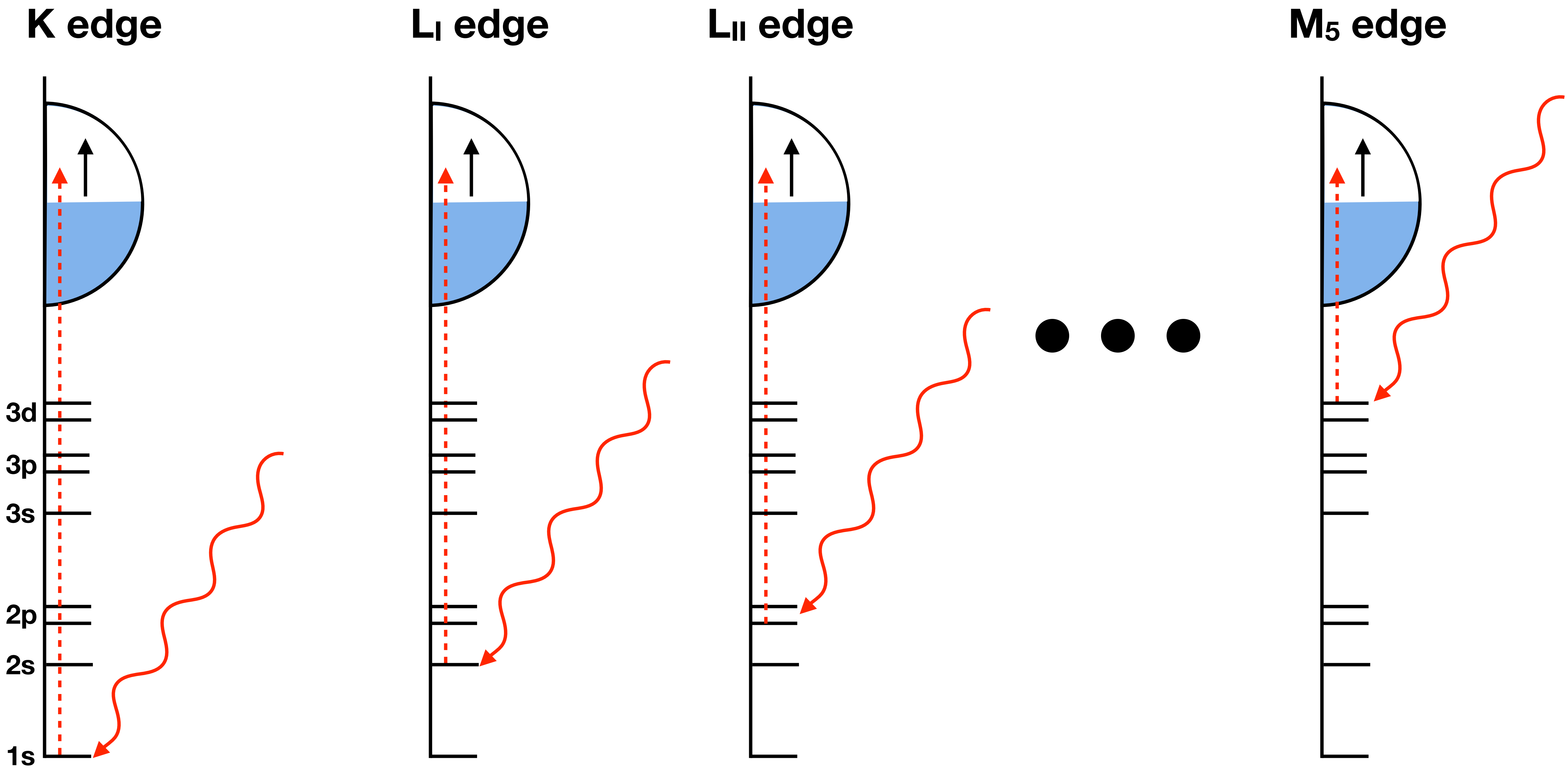


Vocabulary

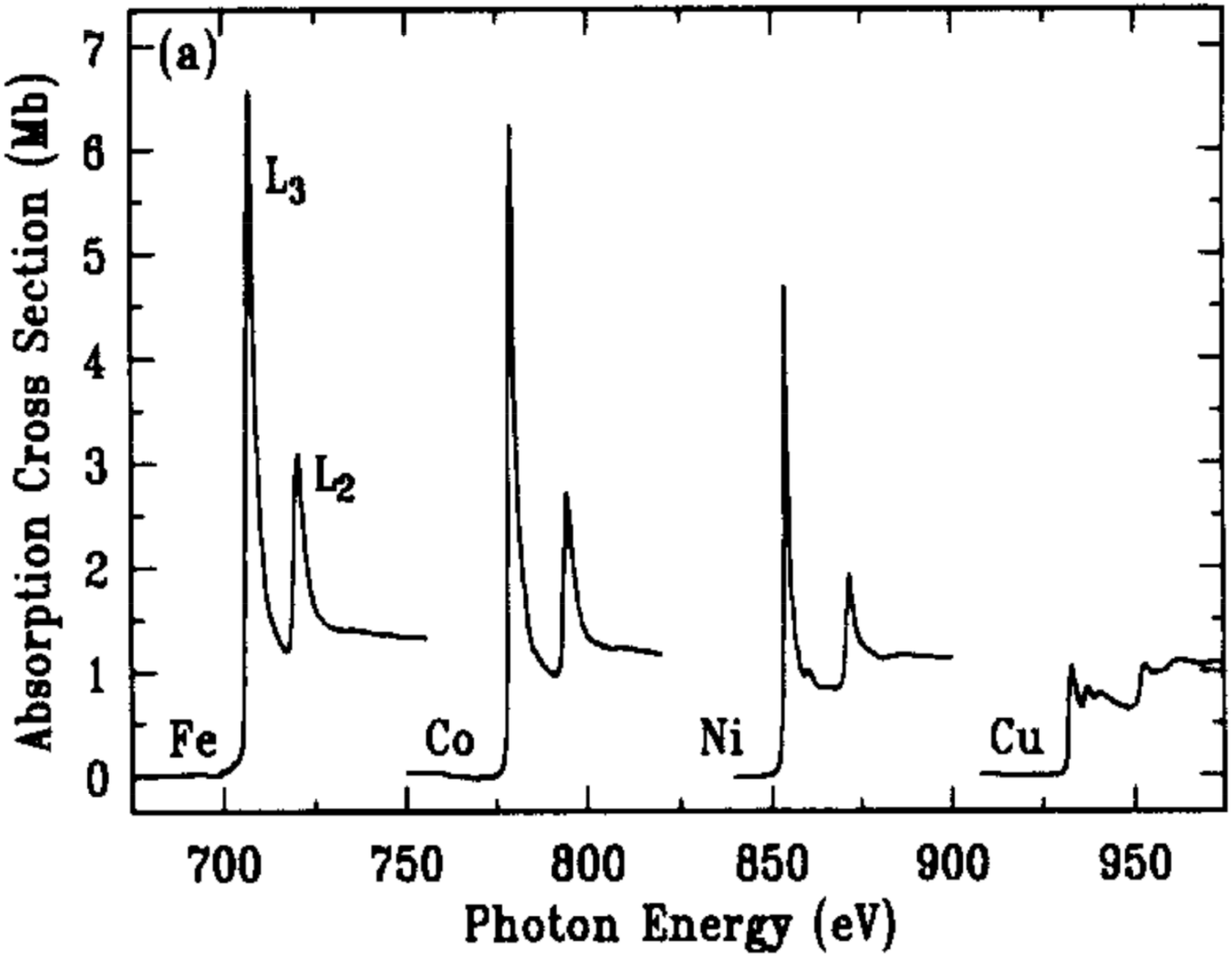
- Name identifies (*n*,*l*) quantum number of core electron involved
    - Letter give *n* starting with K
    - Number gives *l* starting with I



What do we need to understand to describe XAS using theory?

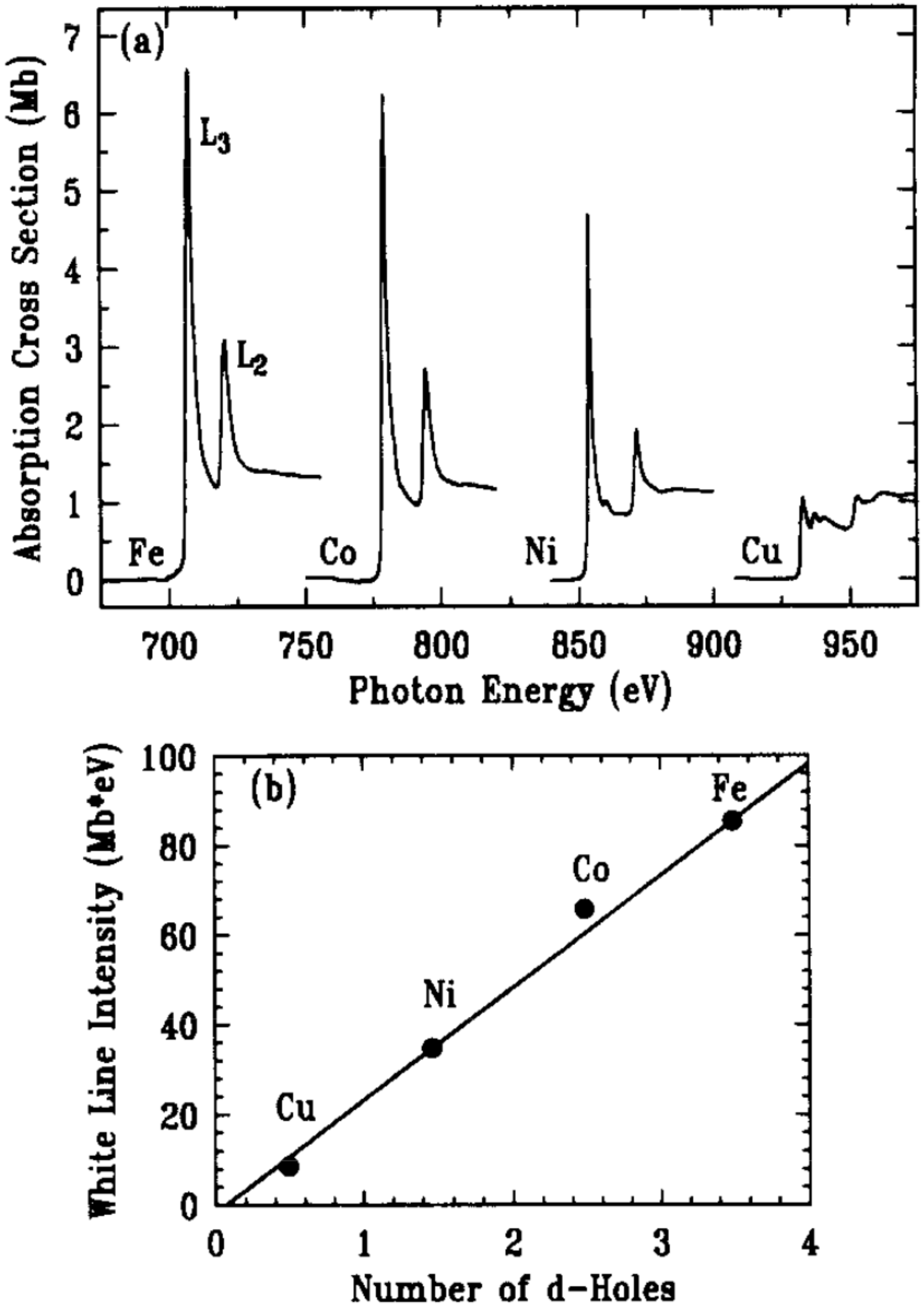
XAS $L_{III,II}$

- Edge onset and hydrogen like atoms



J. Stöhr, J. Elec. Spec. Rel. Phenom. **75**, 253 (1995).

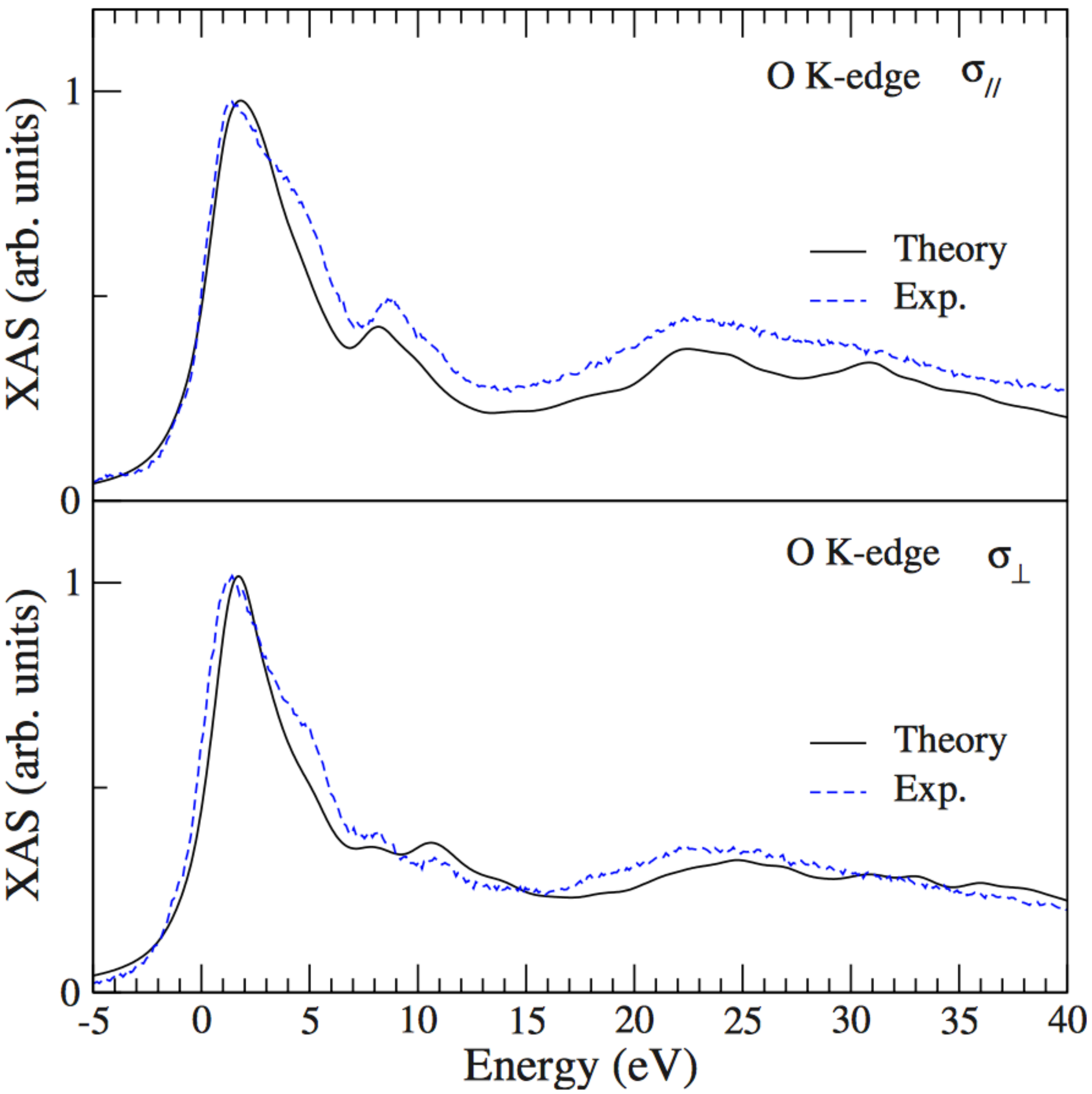
Useful sum-rules



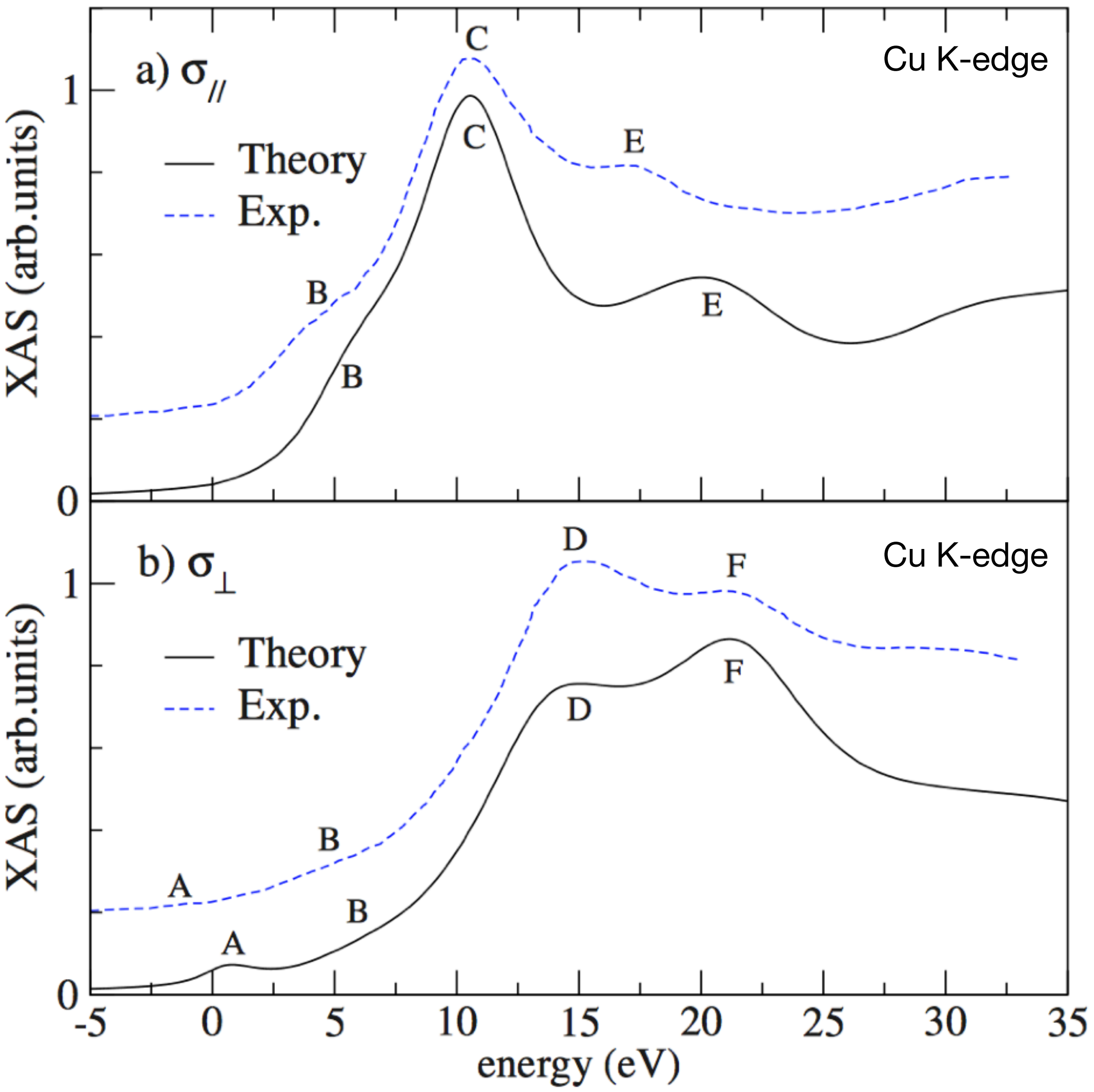
XAS K-edge

- K-edge looks like the empty density of states on absorber

α-quartz SiO_2



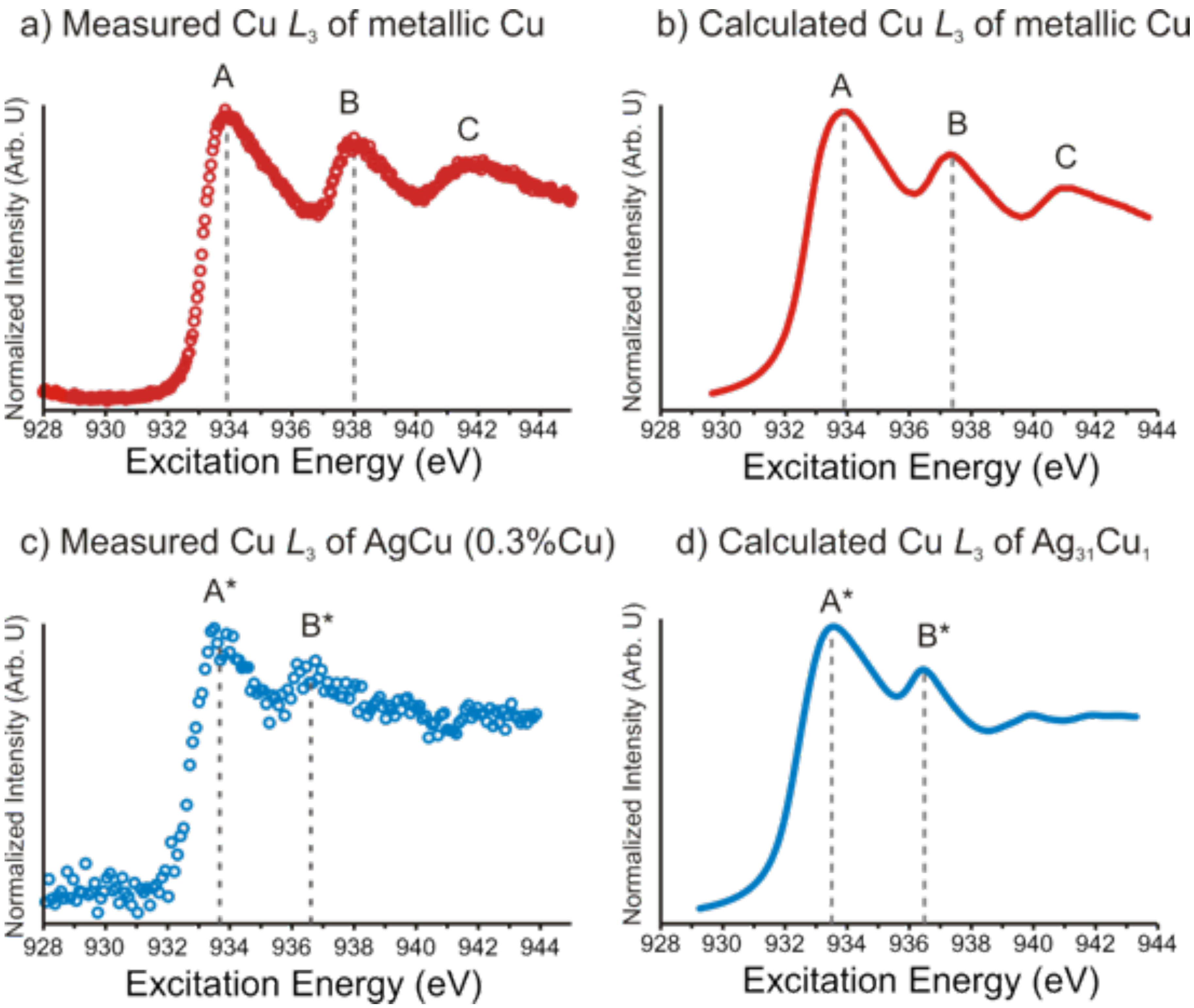
La_2CuO_4



Christos Gougoussis et al. PRB 80, 075102 (2009)

XAS $L_{II,III}$-edge

- $L_{II,III}$-edge looks like the empty density of states on absorber



a) Measured Cu L_3 of metallic Cu

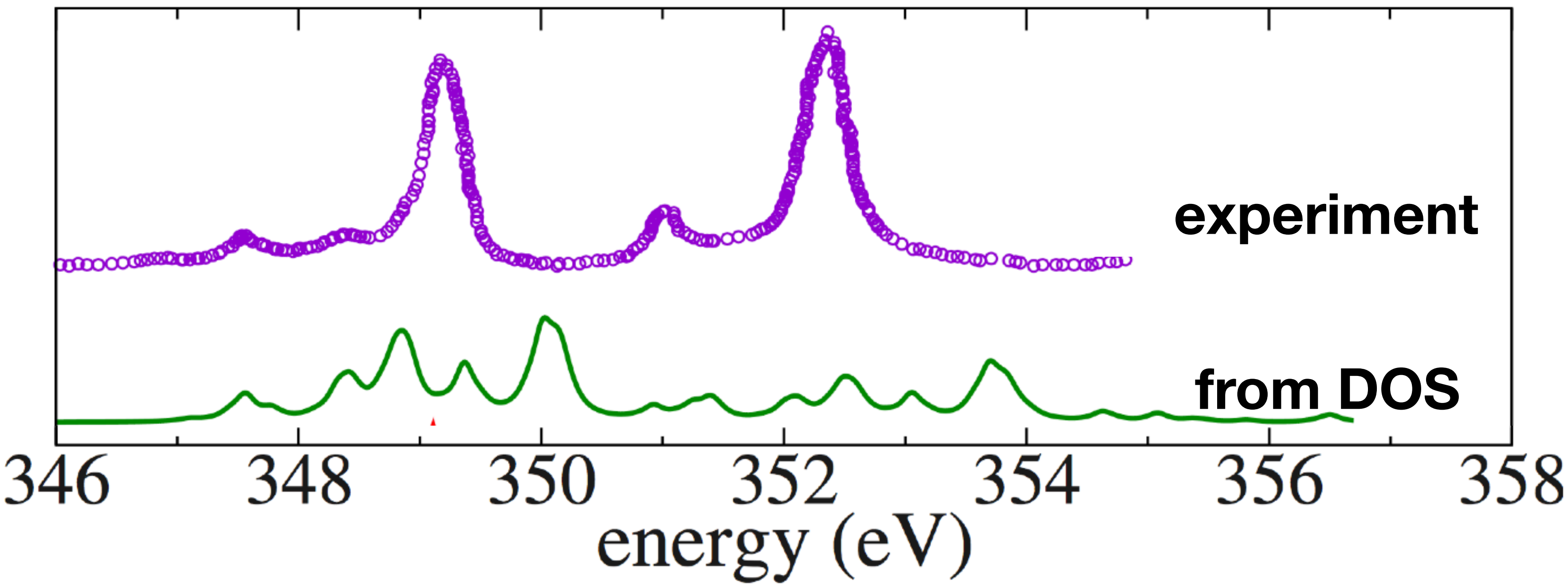
b) Calculated Cu L_3 of metallic Cu

c) Measured Cu L_3 of AgCu (0.3%Cu)

d) Calculated Cu L_3 of $Ag_{31}Cu_1$

XAS $L_{II,III}$-edge

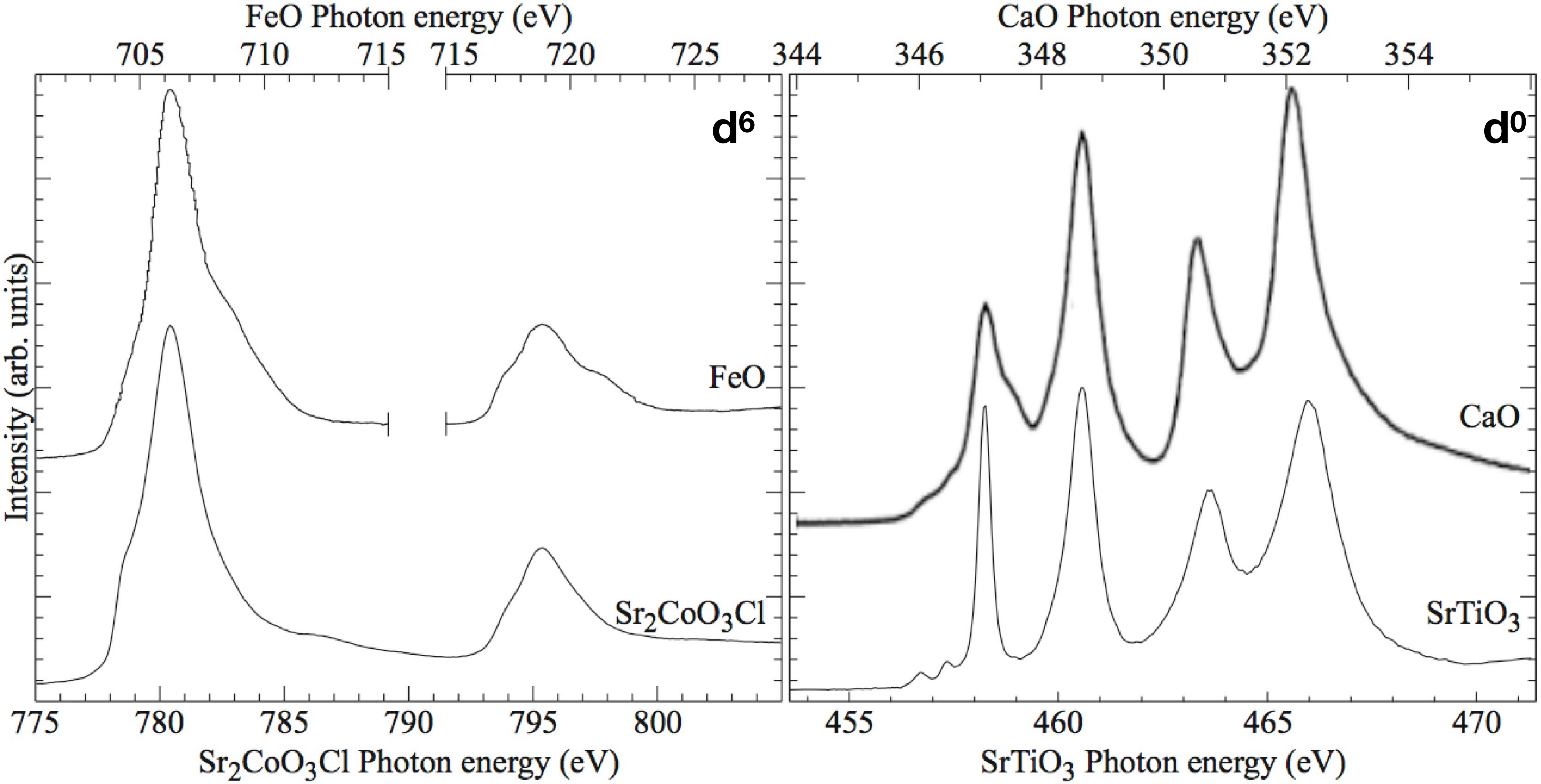
- ~~$L_{II,III}$-edge looks like the empty density of states on absorber~~
- Apparently depends on the material



PHYSICAL REVIEW B **82**, 205104 (2010)

XAS $L_{II,III}$

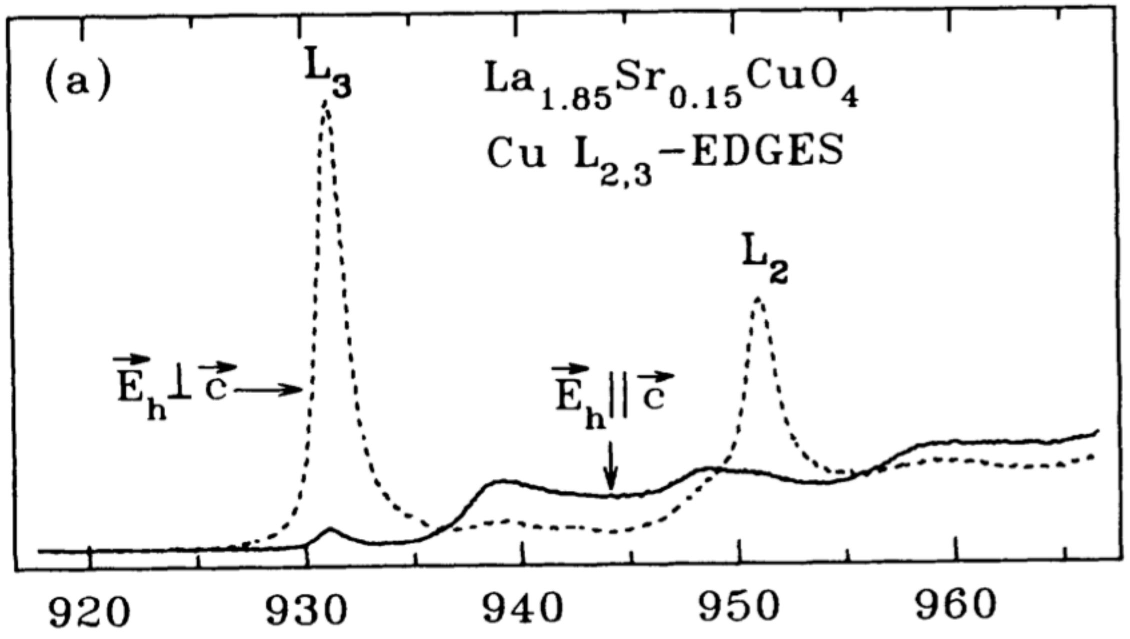
- In some cases spectrum seems to reflect d electron count



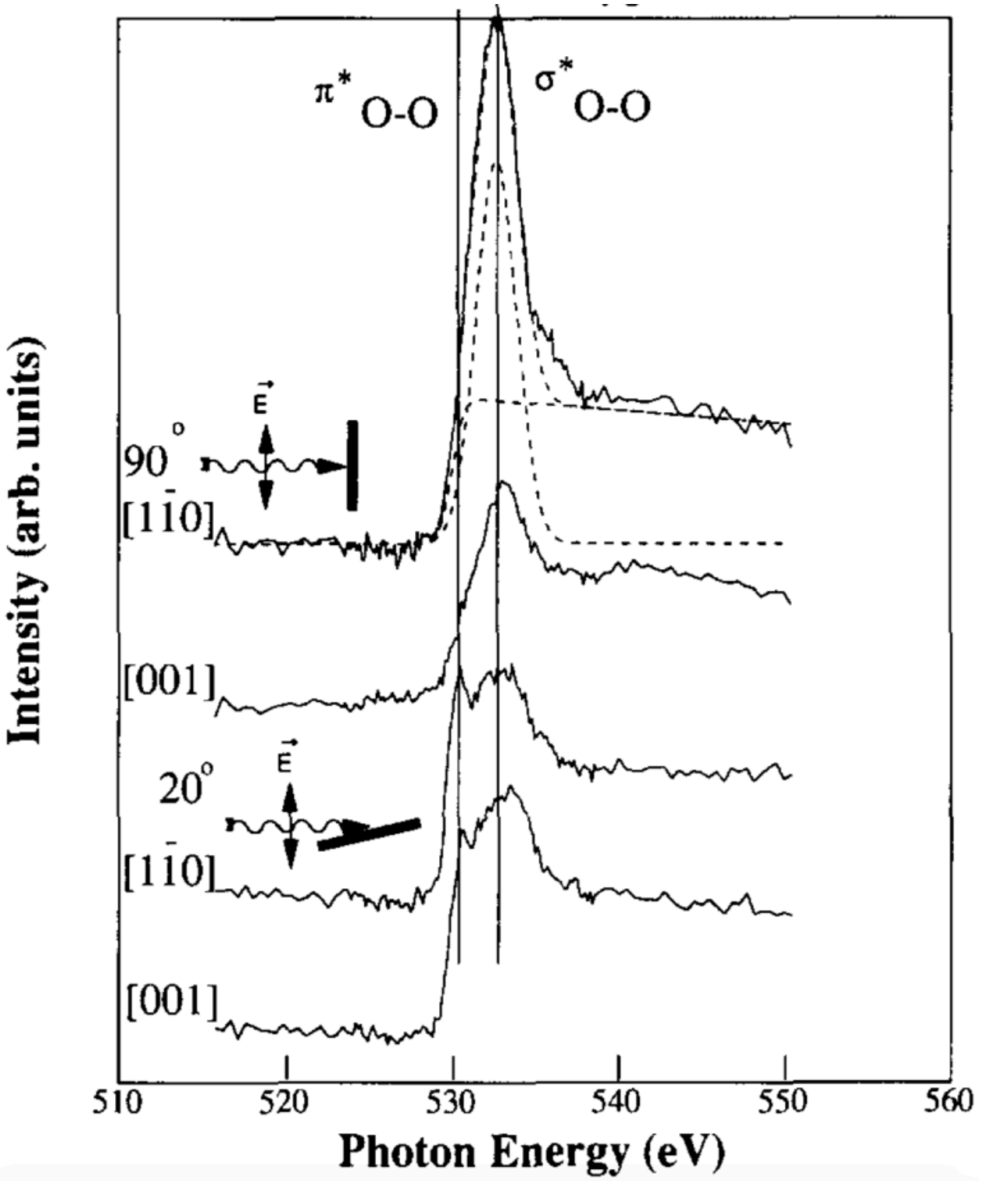
L. H. Tjeng et al

Polarization dependence

- Changing E vector gives different spectra for single crystals



C. T. Chen et al PRL 68, 2543 (1992)



J. Pawel-Crew et al Surf. Sci. 339, 25 (1995)

How can we understand these spectra?

One electron Selection Rules

- Transition described by Fermi’s golden rule

final state

initial state

$$\sigma\left(\omega\right)=\sum_{f}\left|\langle f\right|T\left|i\rangle\right|^{2}\frac{\mathrm{i}/\pi}{\omega-E_{f}+\mathrm{i}\Gamma/2}$$

Transition operator

Energy Conservation

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Transition operator for light-matter interaction

Energy Conservation

$$T=\vec{p}\cdot\hat{\epsilon}\,e^{\mathrm{i}\,\vec{k}\cdot\vec{r}}$$

Multipolar approximation

- We can simplify the transition operator

$$T = \vec{p} \cdot \hat{\epsilon}\, e^{\mathrm{i}\,\vec{k} \cdot \vec{r}}$$

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$$T = \vec{p} \cdot \hat{\epsilon}\, e^{\mathrm{i}\,\vec{k}\cdot\vec{r}}$$

- By expanding the plane wave as

$$e^{\mathrm{i}\,\vec{k}\cdot\vec{r}} = 1 + \mathrm{i}\left(\vec{k}\cdot\vec{r}\right) + \frac{1}{2!}\,\mathrm{i}\left(\vec{k}\cdot\vec{r}\right)^2 \ldots$$

Multipolar approximation

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- How do we know which terms to keep?

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  - Option 1: Dimensional analysis

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- How do we know which terms to keep?
  - Option 1: Dimensional analysis
  - Option 2: Look at $\left(\vec{k} \cdot \vec{r}\right)$

Multipolar approximation

- Edge energy approximately energy of electron in *n* shell

$$E = \hbar\omega \approx \frac{Z}{n} \approx \frac{Z\alpha\hbar c}{R_n}$$

Multipolar approximation

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- Wavenumber is

$$\left|\vec{k}\right| = k = \frac{E}{\hbar c}$$

- Keep 1 term for Z << 137

$$\left|\vec{k} \cdot \vec{r}\right| \approx Z\alpha \approx \frac{Z}{137}$$

One electron Selection Rules

- Looks like the dipole approximation is pretty good

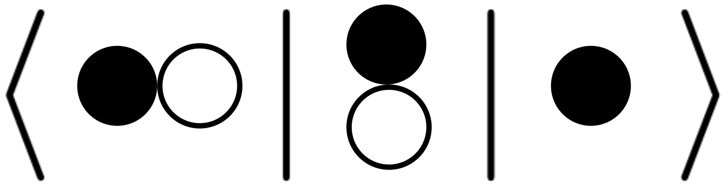
$$T = \vec{p} \cdot \hat{\epsilon}$$

- What does it do in our Golden rule expression?

$$\sigma\left(\omega\right) = \sum_f \left|\langle f|\, \vec{p}\cdot\hat{\epsilon}\, |i\rangle\right|^2 \frac{\mathrm{i}/\pi}{\omega - E_f + \mathrm{i}\,\Gamma/2}$$

Dipole transitions

$$\sigma\left(\omega\right)=\sum_{f}\left|\left\langle f\right|T\left|i\right\rangle\right|^{2}\frac{\mathrm{i}/\pi}{\omega-E_{f}+\mathrm{i}\Gamma/2}$$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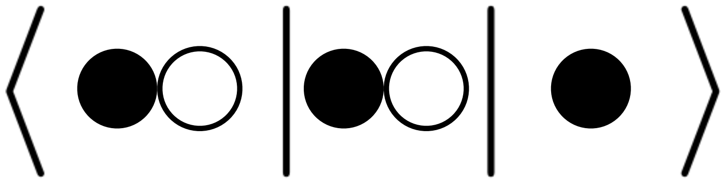
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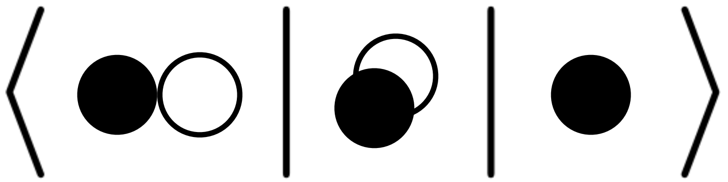
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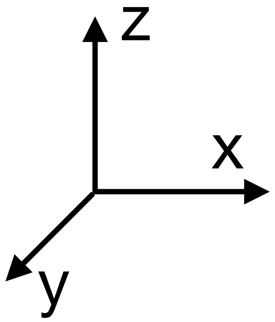

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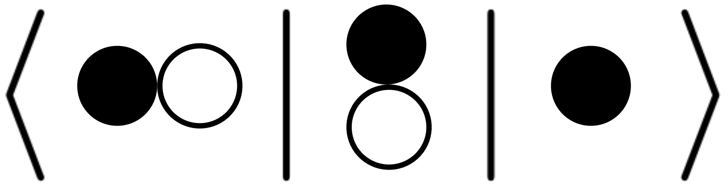

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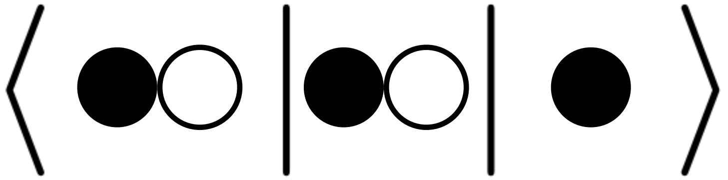

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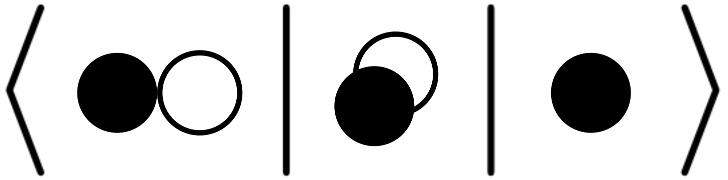

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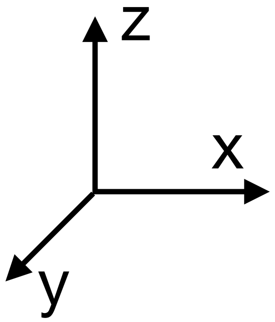

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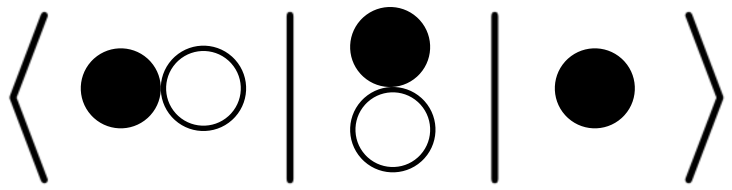

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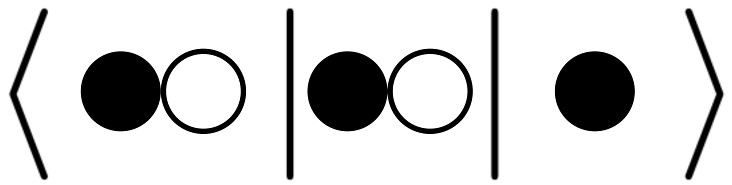

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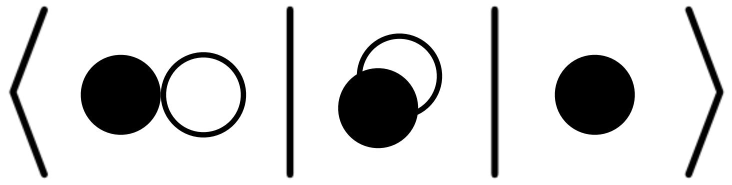

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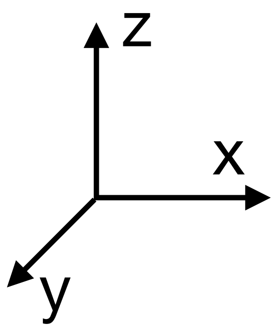

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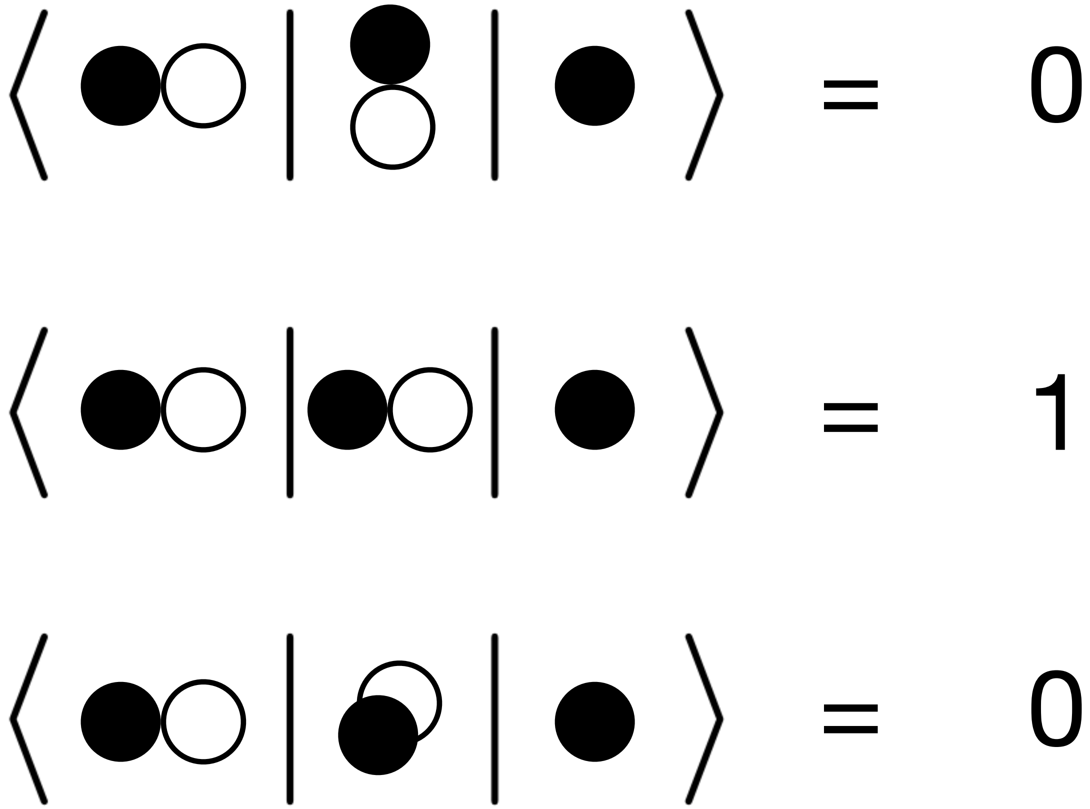

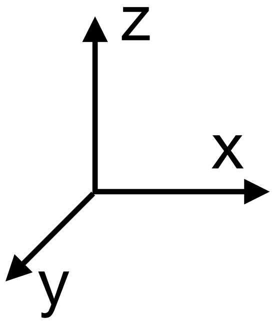

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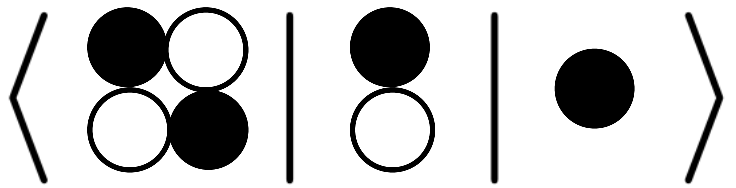

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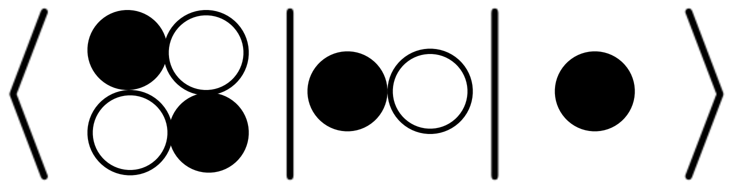

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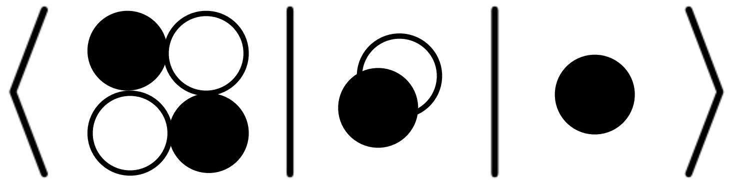

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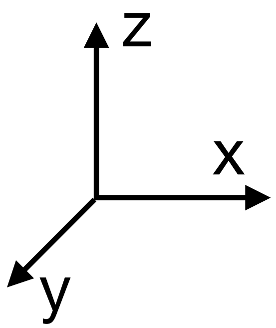

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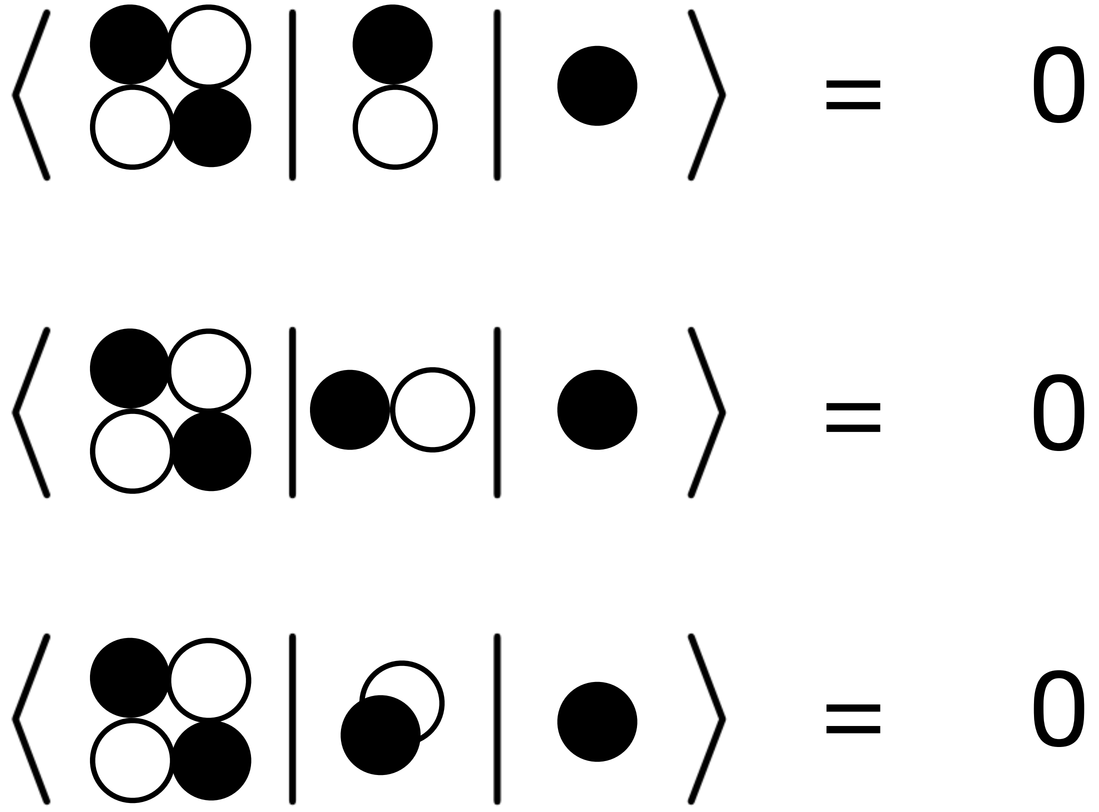

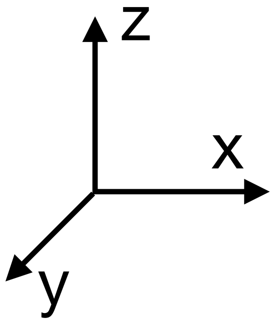

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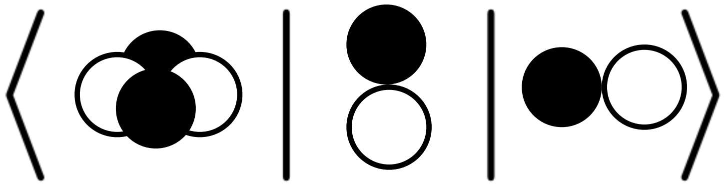

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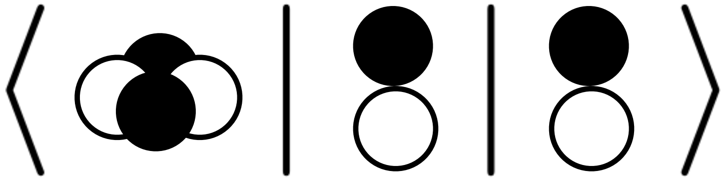

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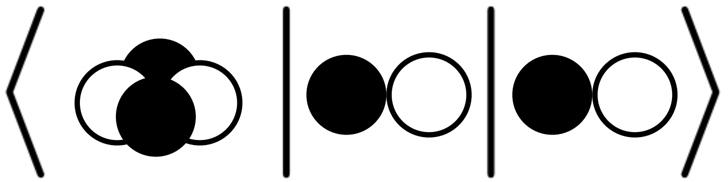

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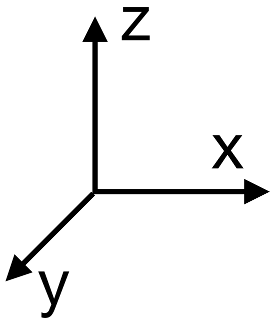


Dipole transitions

$$\sigma\left(\omega\right)=\sum_{f}\left|\langle f|\,T\,|i\rangle\right|^{2}\frac{\mathrm{i}/\pi}{\omega-E_{f}+\mathrm{i}\Gamma/2}$$

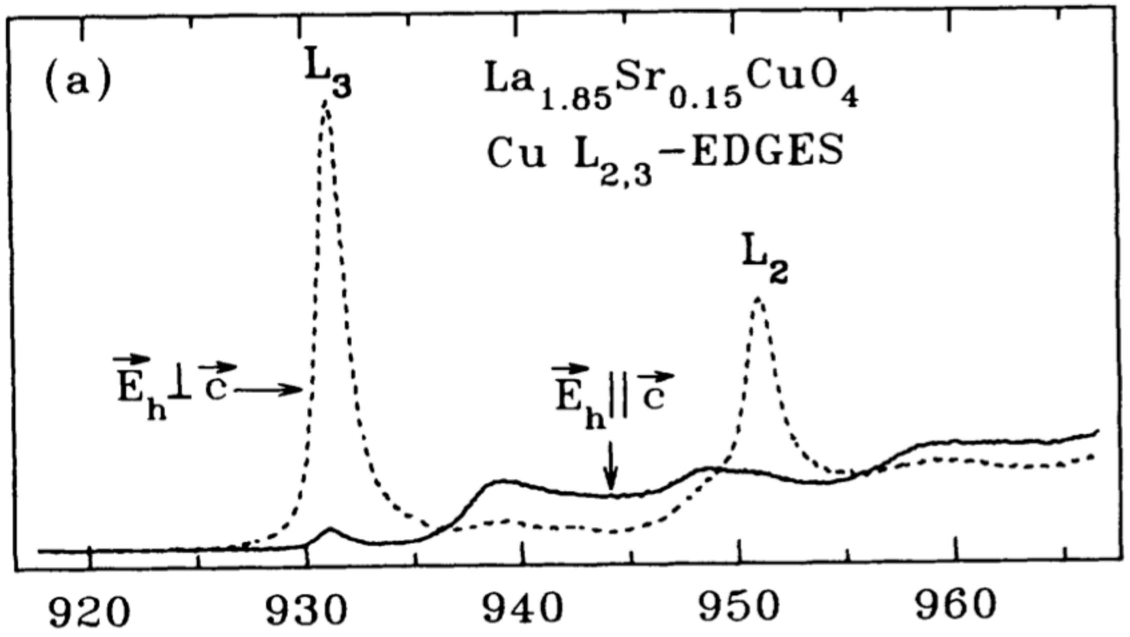
- Dipole transitions are between Δ*l* ± 1
- σ is a tensor that obeys the point group symmetry

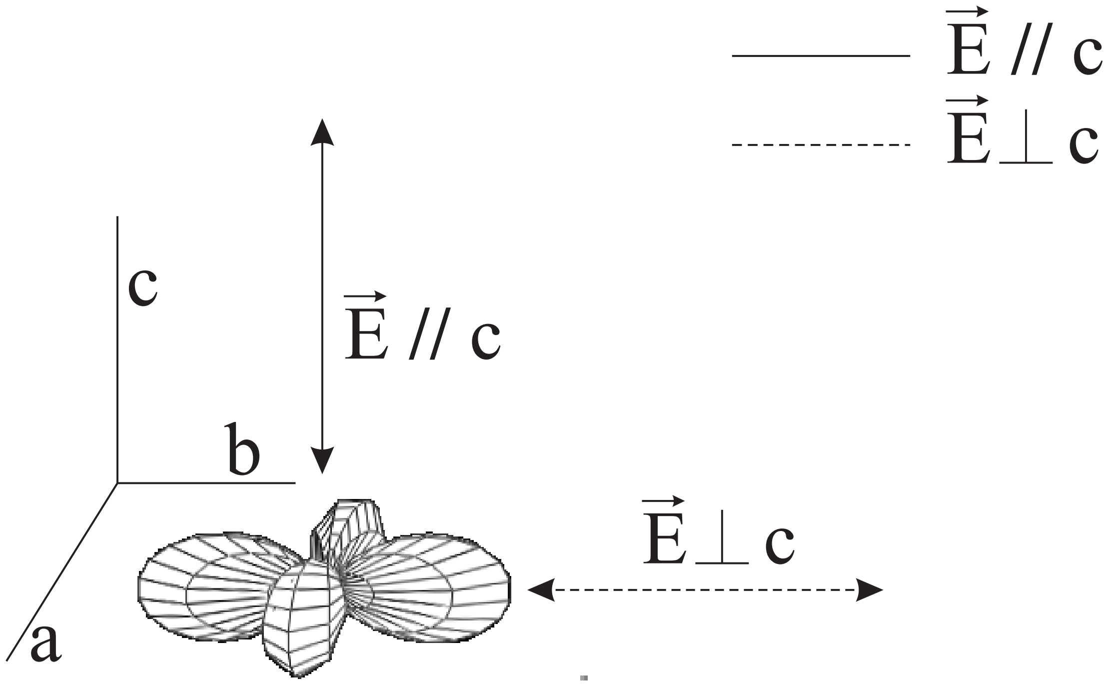
$$\begin{pmatrix}\sigma_{xx} & \sigma_{xy} & \sigma_{xz}\\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz}\\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz}\end{pmatrix}$$

- Powders are isotropic—trace of σ

Now we can understand angular dependence

- Changing E vector probes different elements of σ
- Holes in the d_{x2-y2}





C. T. Chen et al PRL 68, 2543 (1992)

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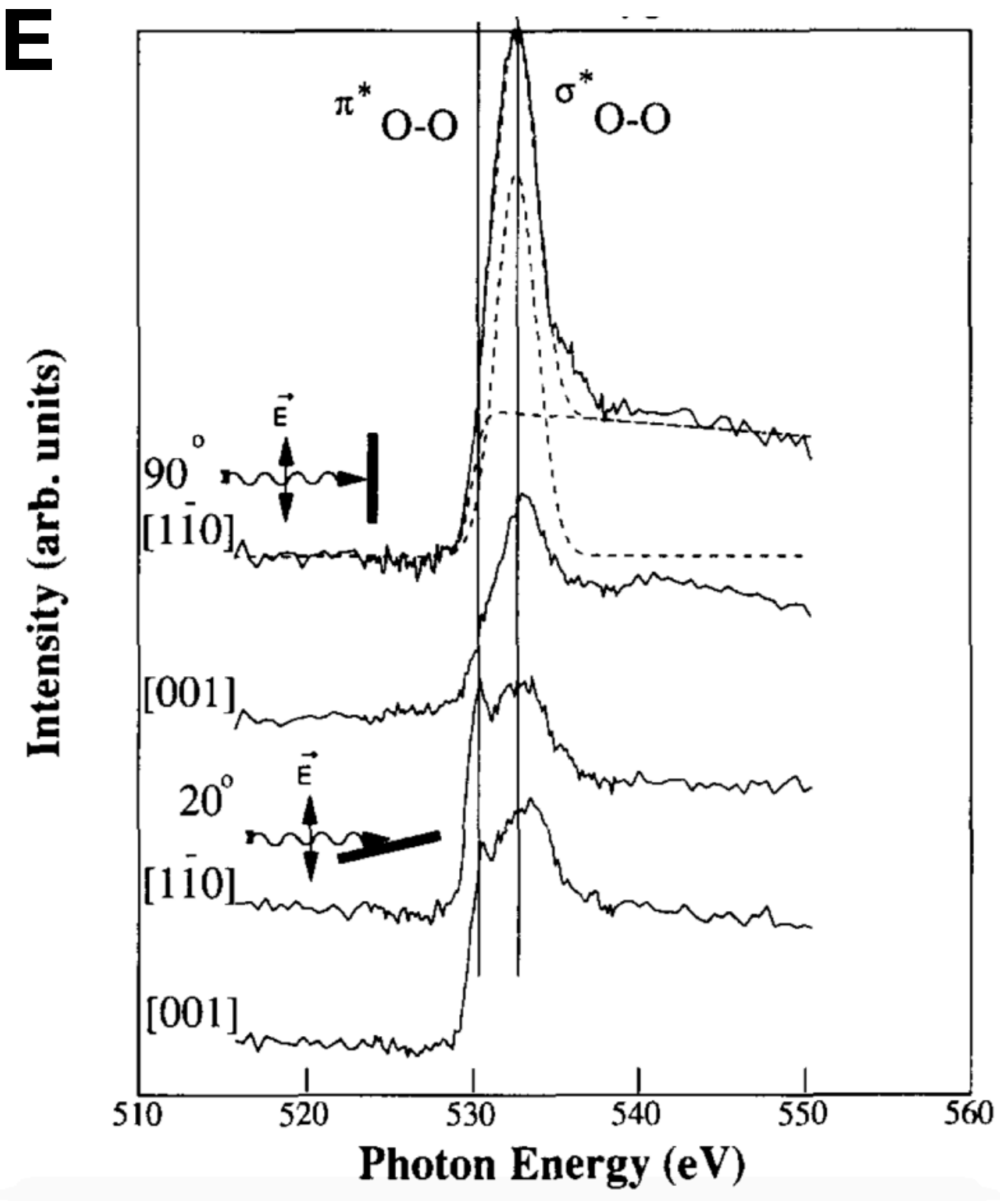
- Changing E vector probes different elements of σ
- Empty π* along [1$\bar{1}$0] with out-of-plane **E**
- Empty σ* along [1$\bar{1}$0] with in plane **E**



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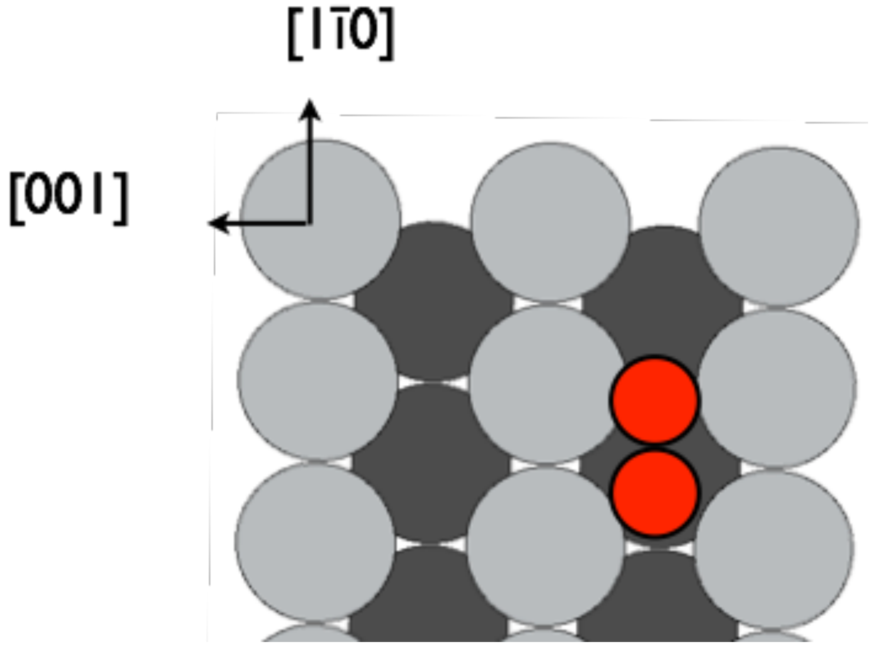

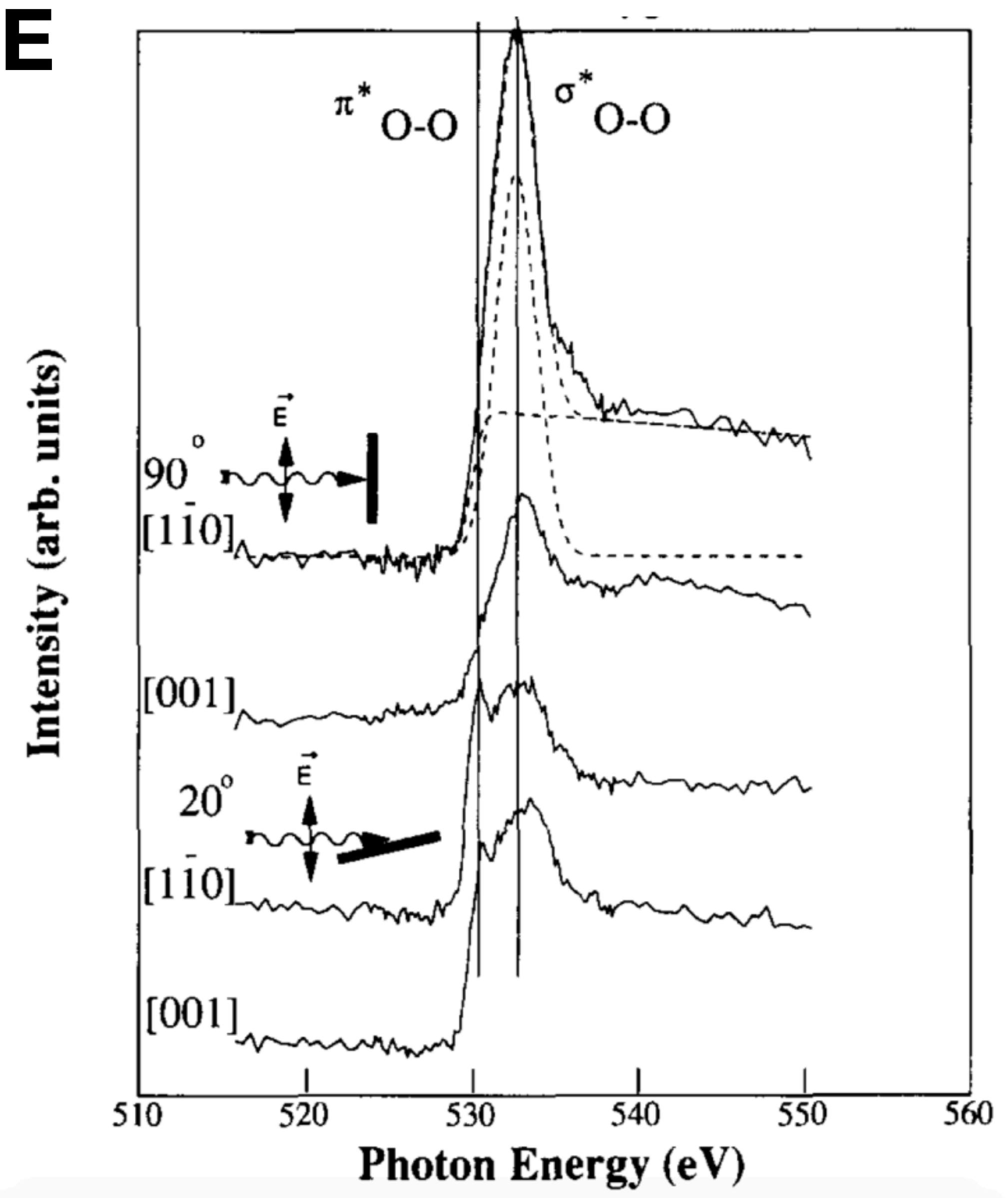

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How to compute

- Can we describe all behavior with one framework?
- In practice pick methodology depending on the type of material and the measurement
- Let’s start with deep K edges for materials that are not strongly correlated because DFT is sufficient for them

Quick DFT

- Most electronic structure calculations done with Kohn-Sham DFT
- Works amazingly well but has serious limits
- Basic idea is to solve KS equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{ext}\left(\vec{r}\right) + v_H\left(\vec{r}\right) + v_{xc}\left(\vec{r}\right)\right)\phi\left(\vec{r}\right) \;=\; \epsilon_i\phi_i\left(\vec{r}\right)$$

- Formally scales as $O(N^3)$
- Not totally correct because we don't know v_{xc}
- To solve we need some basis functions that we can pick

Choices to make

- We have already settled on DFT
- Now we need to think about the type of system
    - Solid?
    - Molecule?
    - Metal?
    - Insulator?
- The answers to these questions will impact the approach
- Say we have solid
    - For metals and insulators we could then use periodic boundary conditions
    - Planewaves are a good basis set for periodic boundary conditions

Planewave DFT

- Expand wave functions in a plane wave basis set
- Advantages
    - FFTs reduce scaling from $O(N^3)$ to $O(N^2)$
    - Systematically improvable with a convergence parameter
- And drawbacks
    - Vacuum costs the same as atoms
    - Cannot handle rapid oscillations of wave functions—need pseudo potentials

PAW approach

- $|i\rangle$ and $|f\rangle$ are *all electron* states
- We want to use pseudo states

linear mapping between pseudo and all electron wave functions

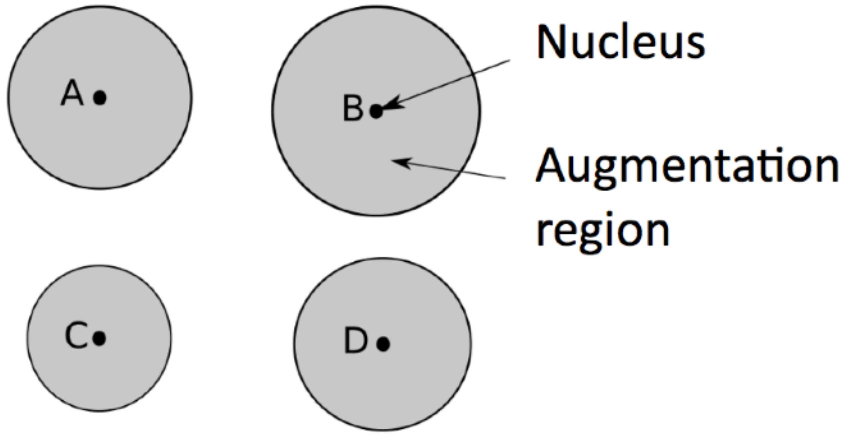
$$|\Psi\rangle = T\left|\widetilde{\Psi}\right\rangle$$

$$T = \hat{1} + \sum_{\vec{R},m}\left(\left|\phi_{\vec{R},n}\right\rangle - \left|\widetilde{\phi}_{\vec{R},n}\right\rangle\right)\left\langle p_{\vec{R},n}\right| \longrightarrow$$

projectors
(non-zero in augmentation region)

AE partial waves

pseudo partial waves



P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994)

Dipole and PAW

- Because the core hole is localized only terms on the absorbing atom survive

$$\sigma(\omega) = \sum_f \left| \left\langle \widetilde{\Psi}_f \middle| \widetilde{\Phi}_{\vec{R}_0} \right\rangle \right|^2 \frac{\mathrm{i}/\pi}{\omega - E_f + \mathrm{i}\,\Gamma/2}$$

Sum over projectors

$$\widetilde{\Phi}_{\vec{R}_0} = \sum_n \left| p_{\vec{R}_0,n} \right\rangle \left\langle \widetilde{\phi}_{\vec{R}_0,n} \middle| D \middle| \psi_i \right\rangle$$

- To compute the spectrum you need
    - Core wave function on absorber ψ_i
    - AE partial waves centered on absorber
    - PAW projectors

PHYSICAL REVIEW B **80**, 075102 (2009)

What does it all mean?

XAS is (in this case) measuring a lifetime broadened projected density of states in the presence of a core.

$$\sigma\left(\omega\right)=\sum_{f}\left|\left\langle\widetilde{\Psi}_{f}\left|\widetilde{\Phi}_{\vec{R}_{0}}\right.\right\rangle\right|^{2}\frac{\mathrm{i}/\pi}{\omega-E_{f}+\mathrm{i}\,\Gamma/2}$$

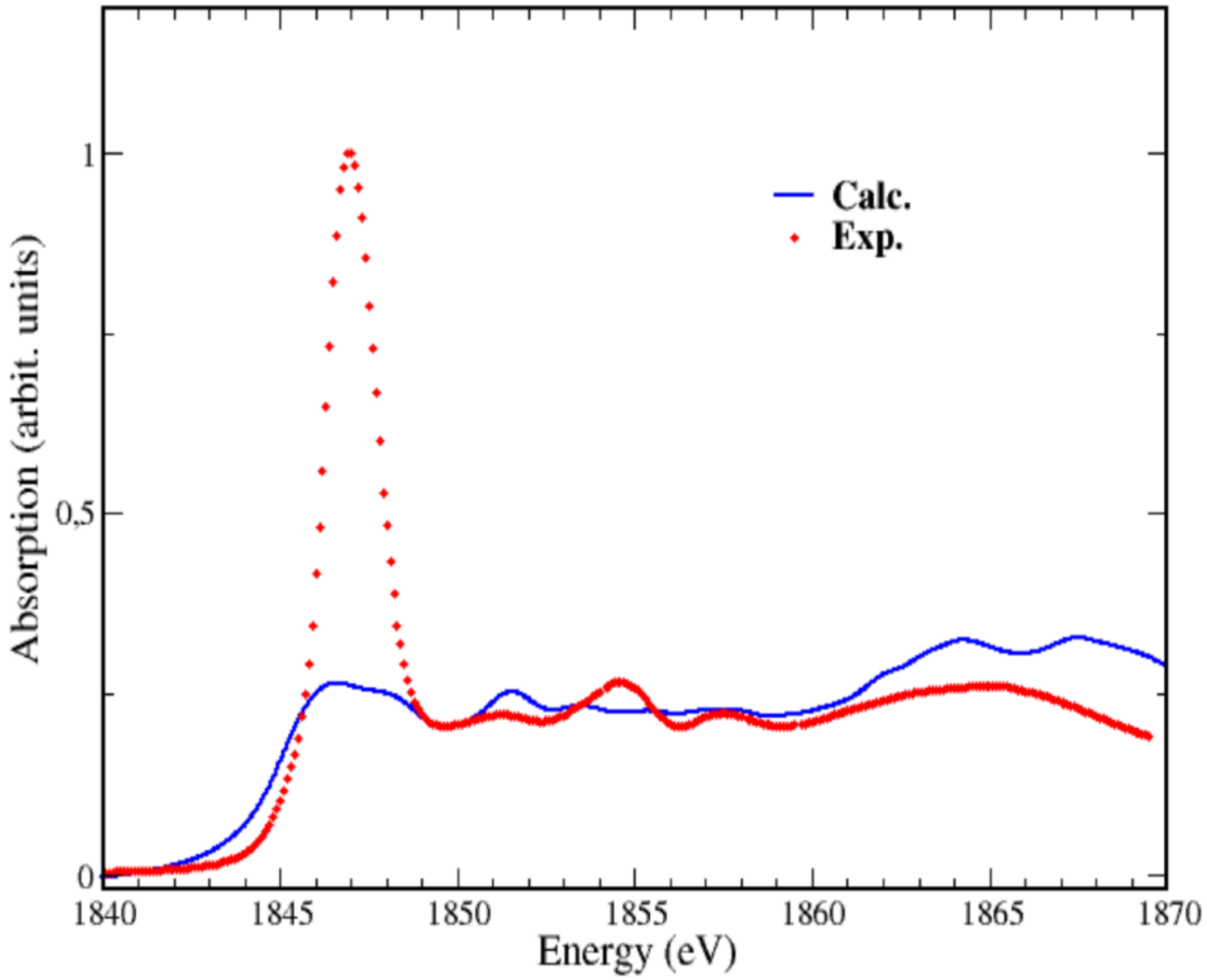
$$\widetilde{\Phi}_{\vec{R}_{0}}=\sum_{n}\left|p_{\vec{R}_{0},n}\right\rangle\left\langle\widetilde{\phi}_{\vec{R}_{0},n}\right|D\left|\psi_{i}\right\rangle$$

Oh the core hole

- There is a core hole in the final state
- But we are using an independent particle approach
- Turns out you don’t always need a core-hole
- Some common approaches are
    - Full core hole
    - Half core hole aka Slater’s transition potential approximation
    - No core hole

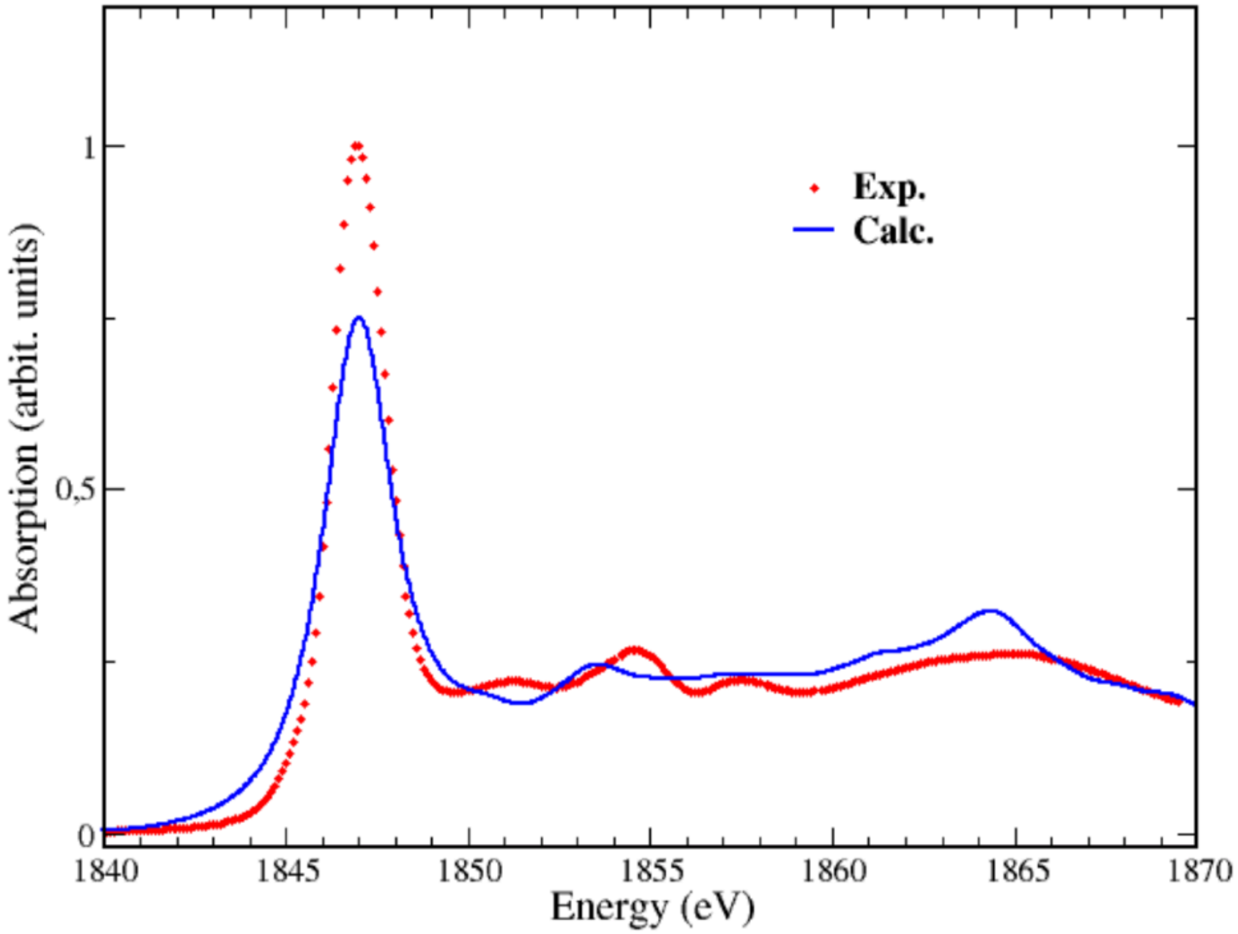
Example α-quartz

- Ignoring the core hole is not a good idea



Example α-quartz

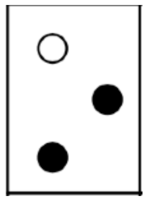
- Adding a core hole does better but there are still problems



Example α-quartz

- Can we do better?

(1×1) cell



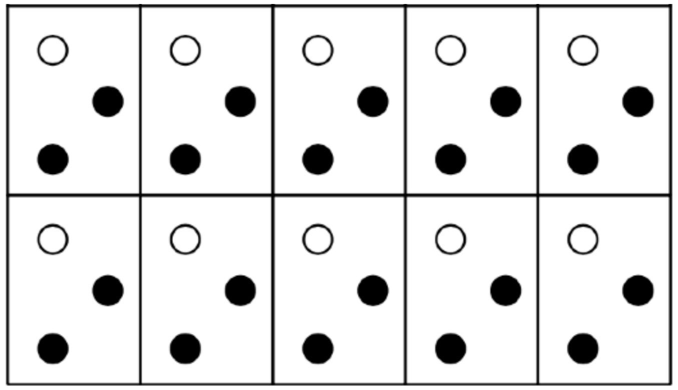
○ **core hole**

● **no core hole**

Example α-quartz

- The core hole sees is periodic image

(1×1) cell with PBC

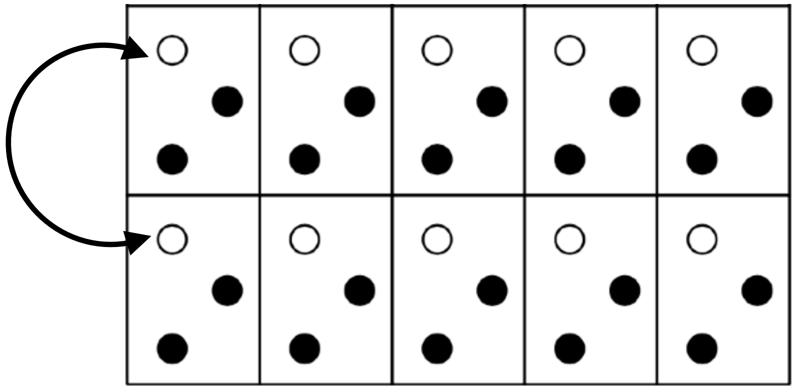


○ **core hole**

● **no core hole**

Example α-quartz

- The core hole sees is periodic image



(1×1) cell with PBC

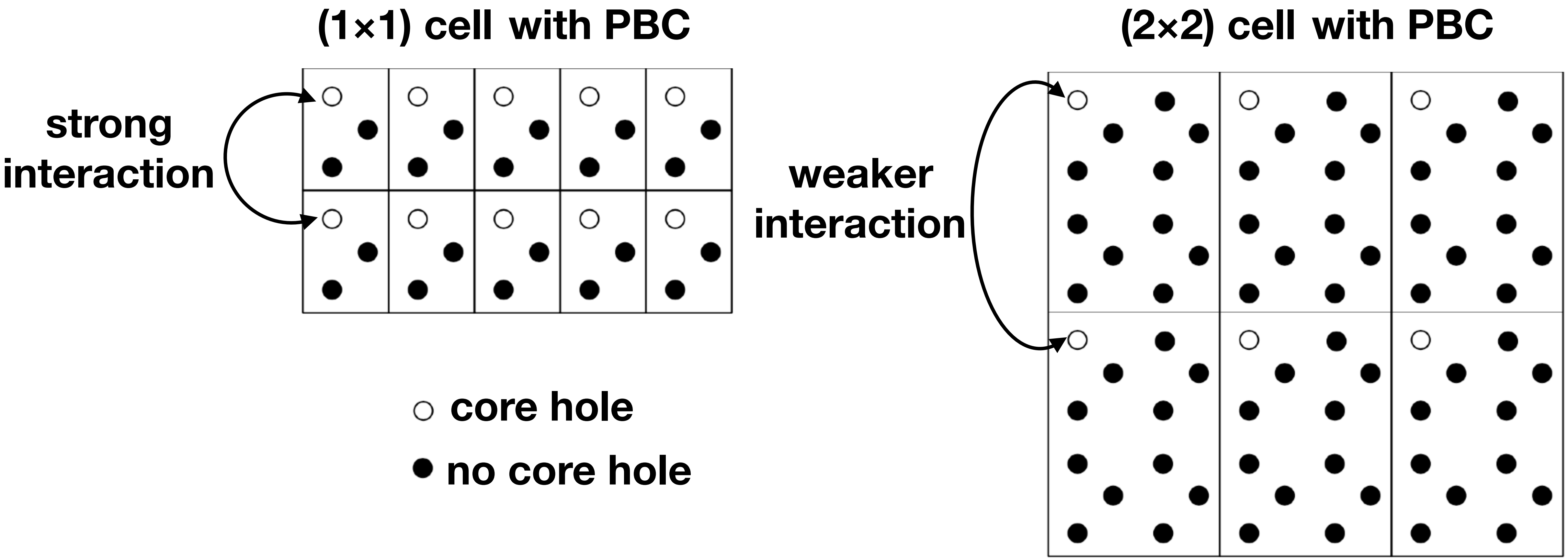
strong interaction

○ **core hole**

● **no core hole**

Example α-quartz

- The core hole sees is periodic image
- Double unit cell size to reduces spurious interaction

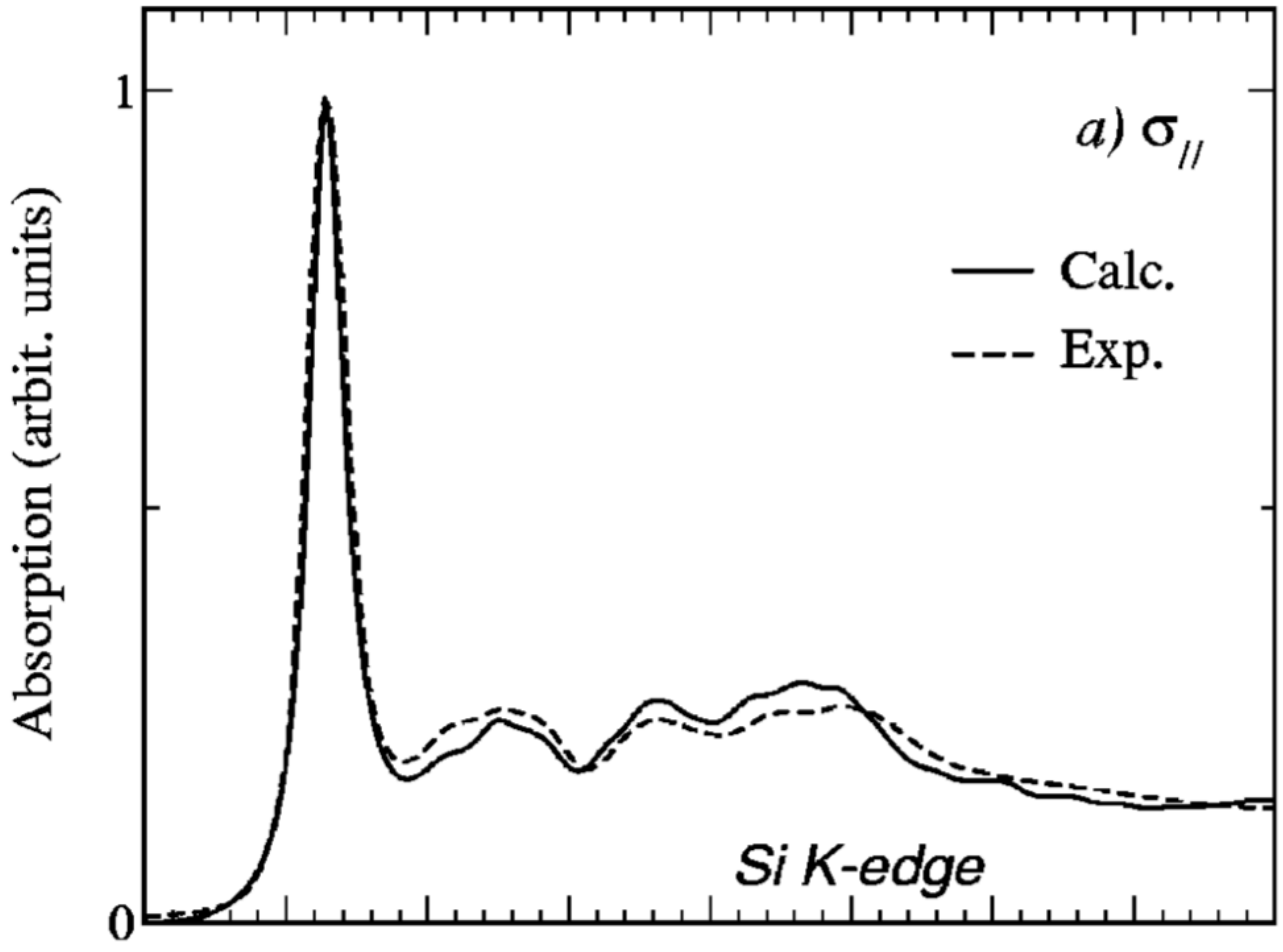


○ core hole

● no core hole

Example α-quartz

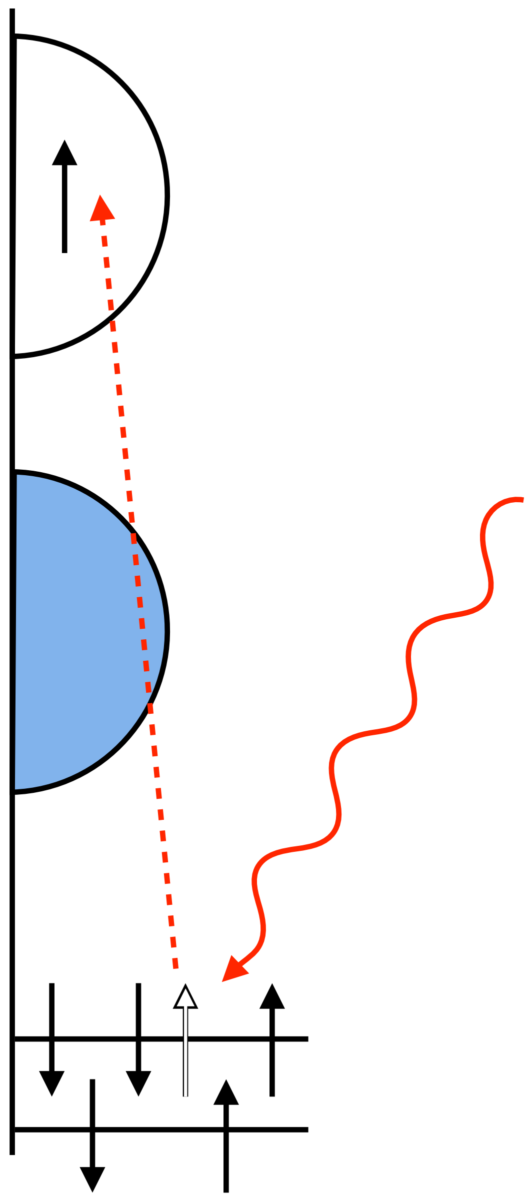
- With a (2x2x2) cell the calculation is converged



M. Taillefumier et al., *Phys. Rev. B* **66**, 195107 (2002)

What happened?

- Core-valence interaction pulls states down



What happened?

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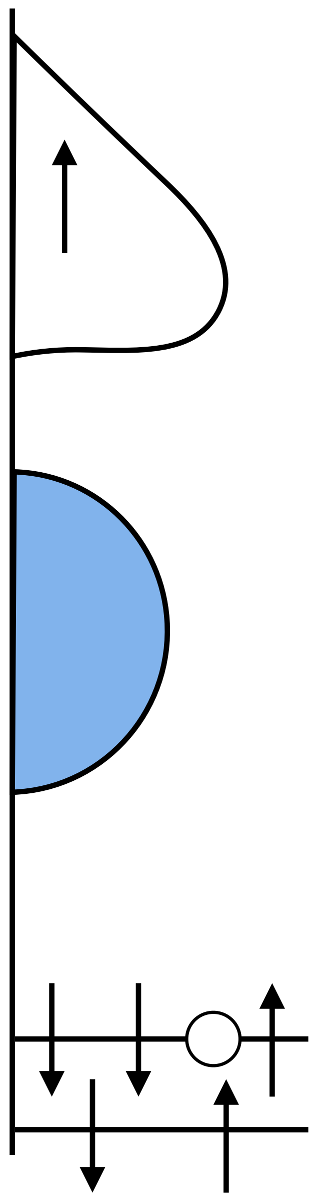
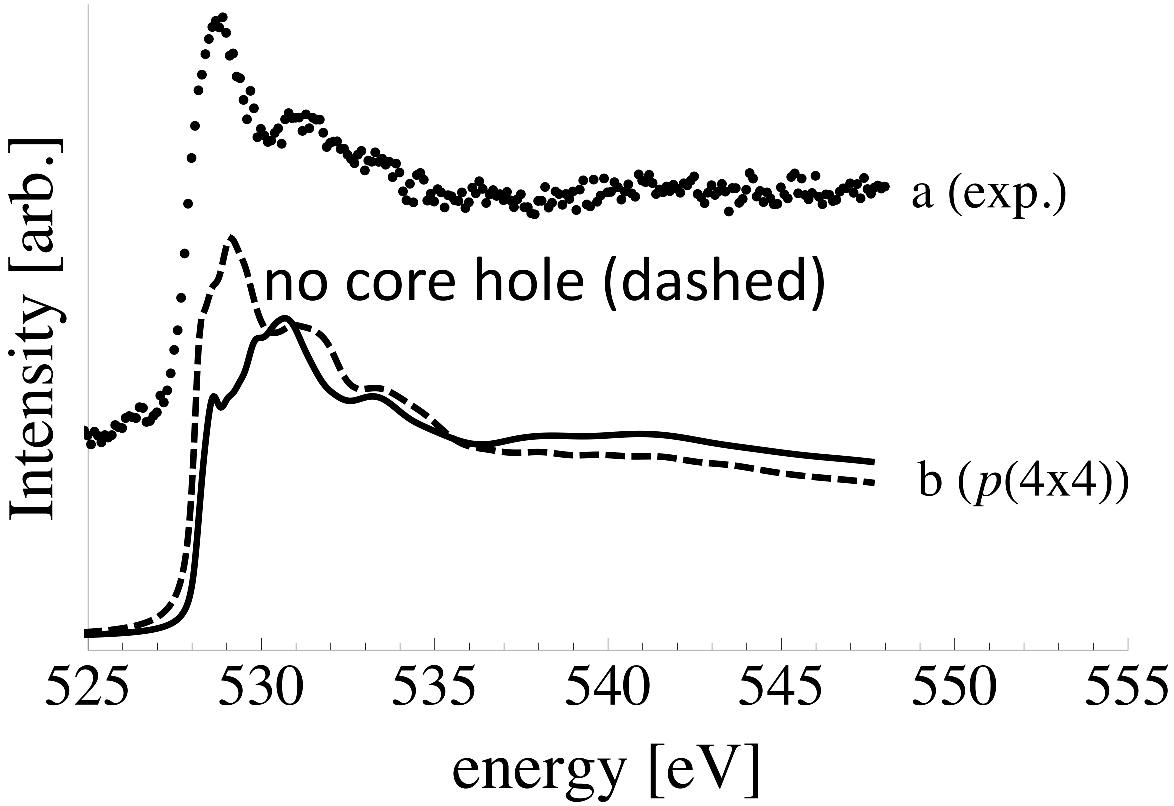


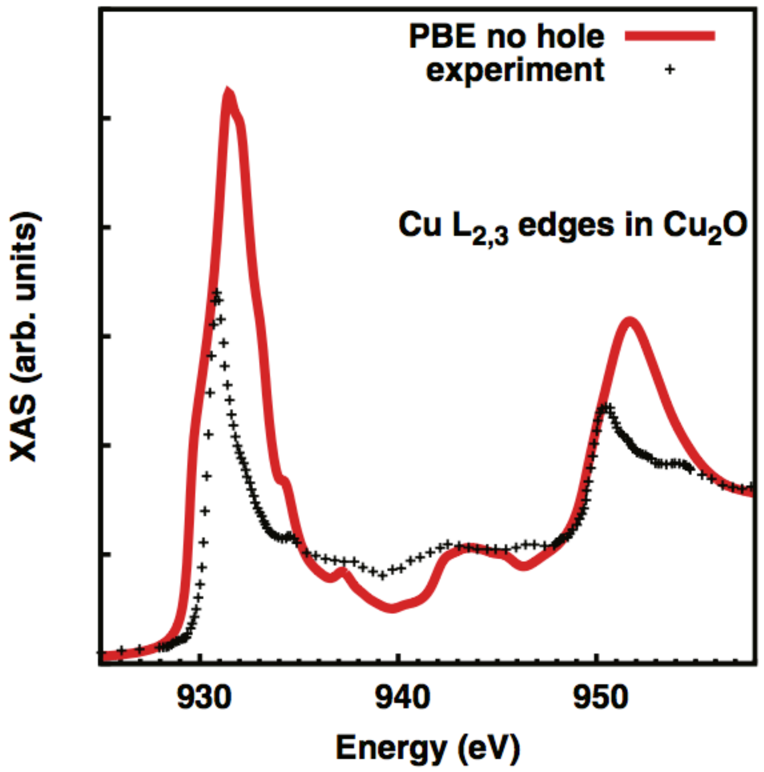
Sometimes no hole

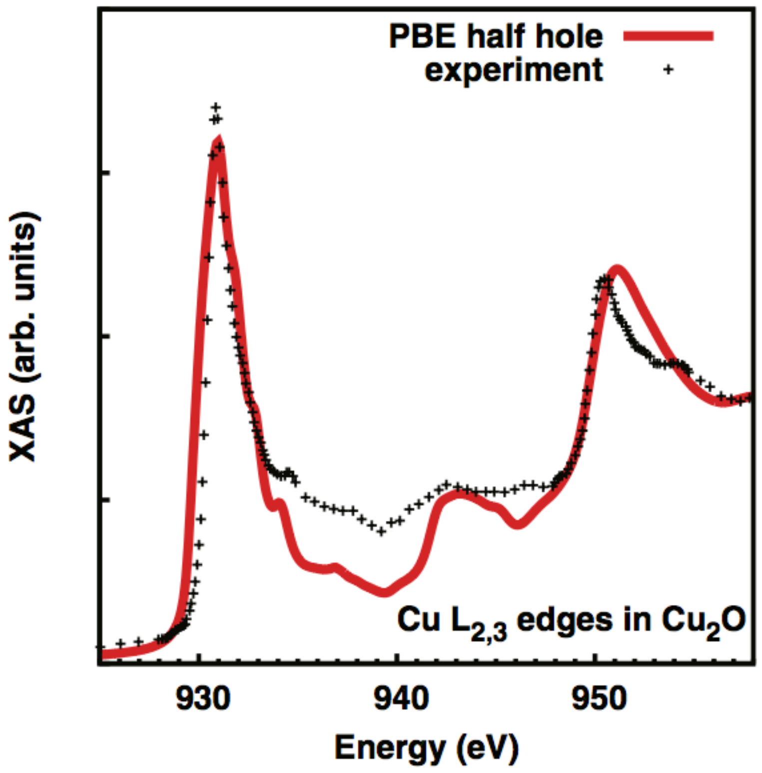
- The core valence interaction can appear to be completely screened



Sometimes half a hole

- The core valence interaction can appear to be partially screened



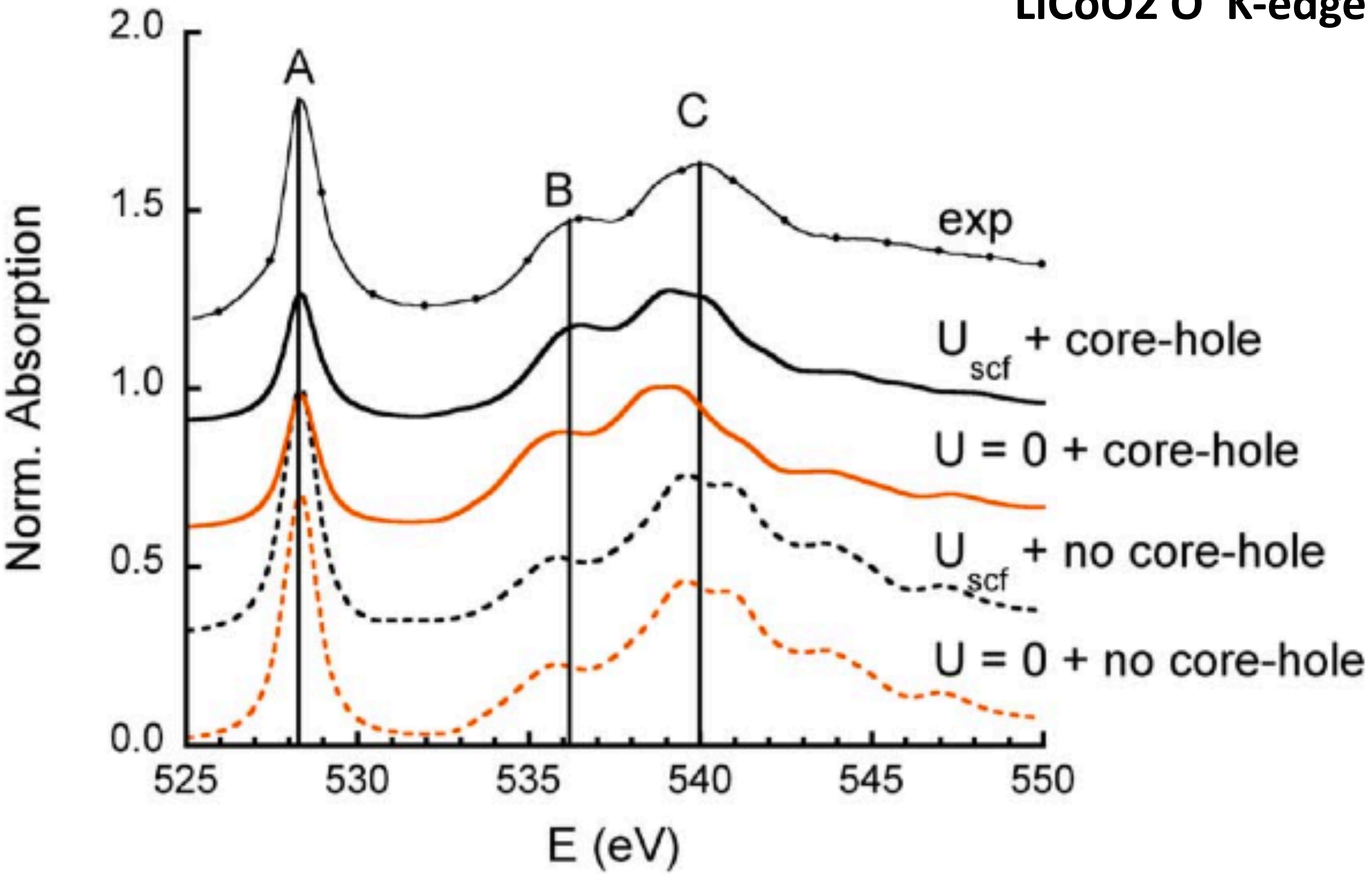


O. Bunău and M. Calandra, *Phys*. *Rev*. *B* **87**, 205105 (2013).

Sometimes it does not matter

- Or the core hole potential may not do much

LiCoO2 O K-edge



Juhin et al. PRB 81, 115115 (2010)

The good and bad about core holes

- The core hole problem comes from describing two particle system with independent particle approximation (IPA)
    - Good news is IPA works well for K edges
    - Bad news is we don’t know how much core hole potential to include *a priori*
- If we want a better answer we need to turn to a two-particle theory
    - Good news is we have one in the Bethe-Salpeter equation (BSE)
    - Bad news is its computationally expensive

BSE

- Hamiltonian similar to before

$$H_{\mathrm{BSE}} = H_e - H_h - V_D + V_X$$

- Single particle electron and hole Hamiltonians

$$H_e - H_h$$

- Screened Coulomb interaction

$$V_D$$

- Non-local exchange

$$V_X$$

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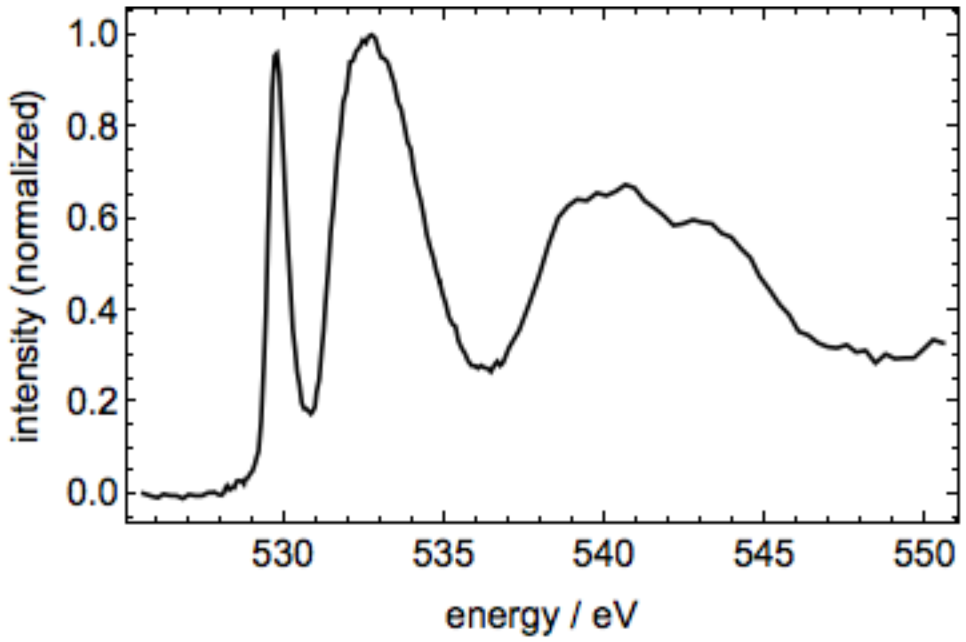
$$V_D$$

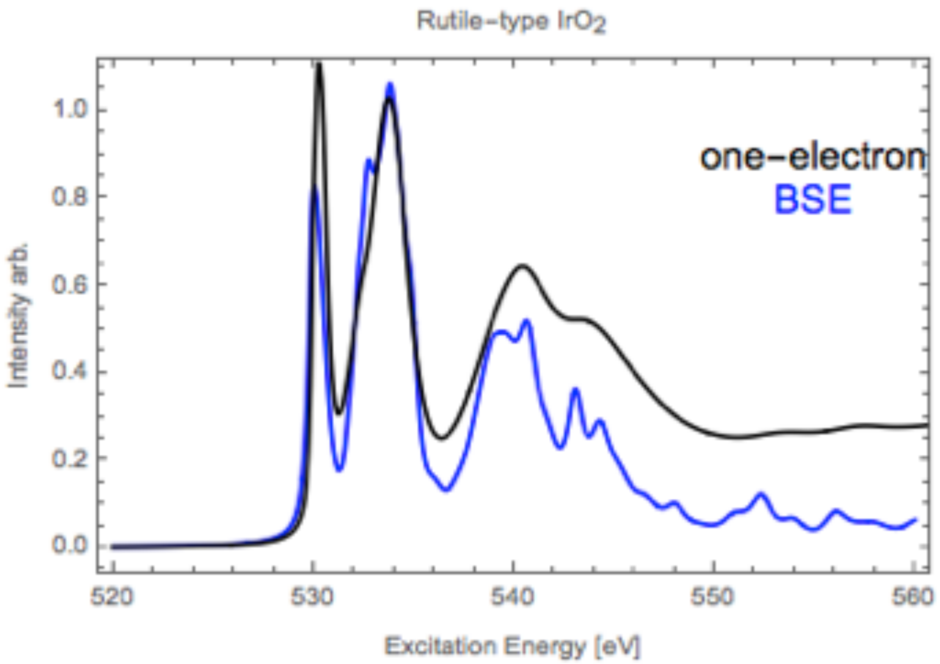
- Non-local exchange

$$V_X$$

BSE

- BSE and IPA are formally similar
- One difference is screened Coulomb interaction

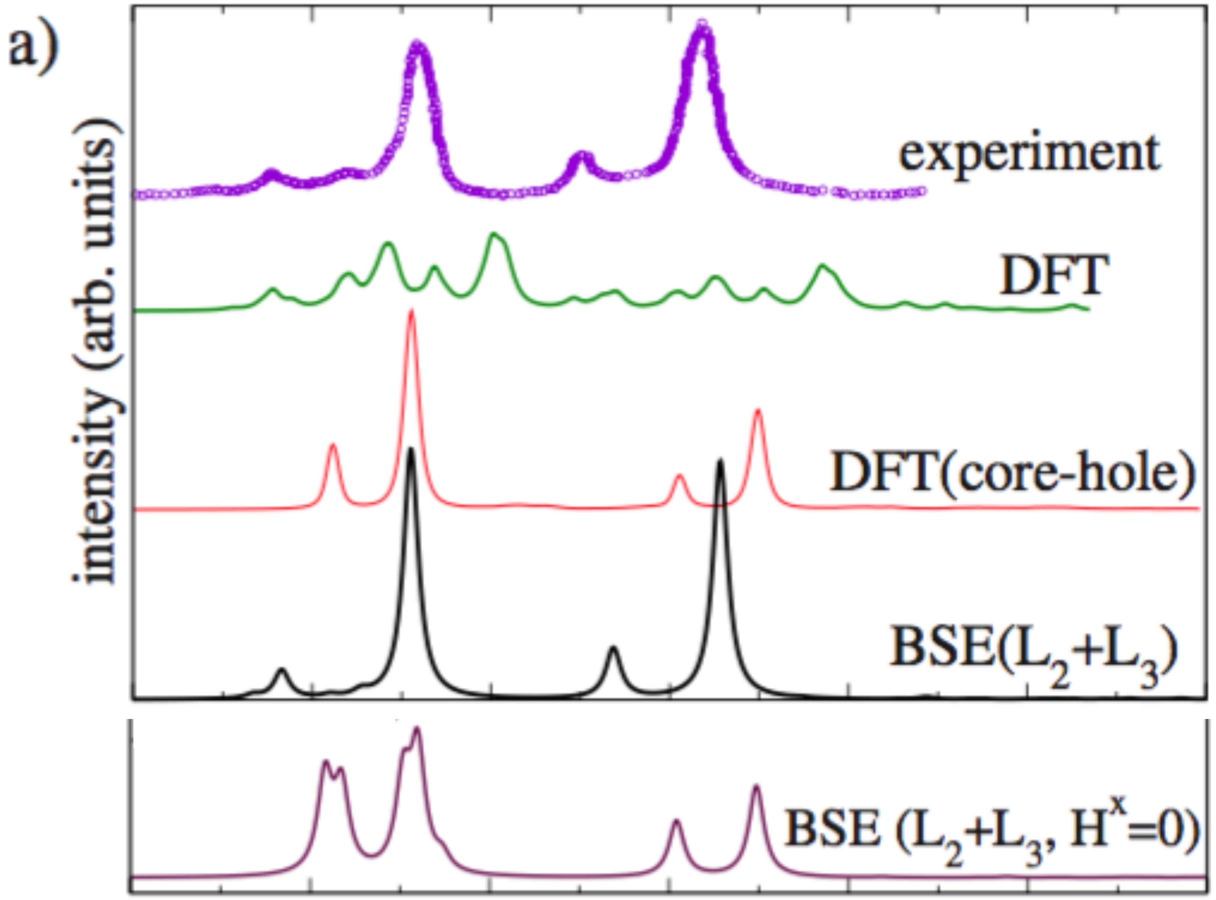




BSE

- A bigger difference is the non-local exchange
- It mixes L_{II} and L_{III} edges

CaF$_2$



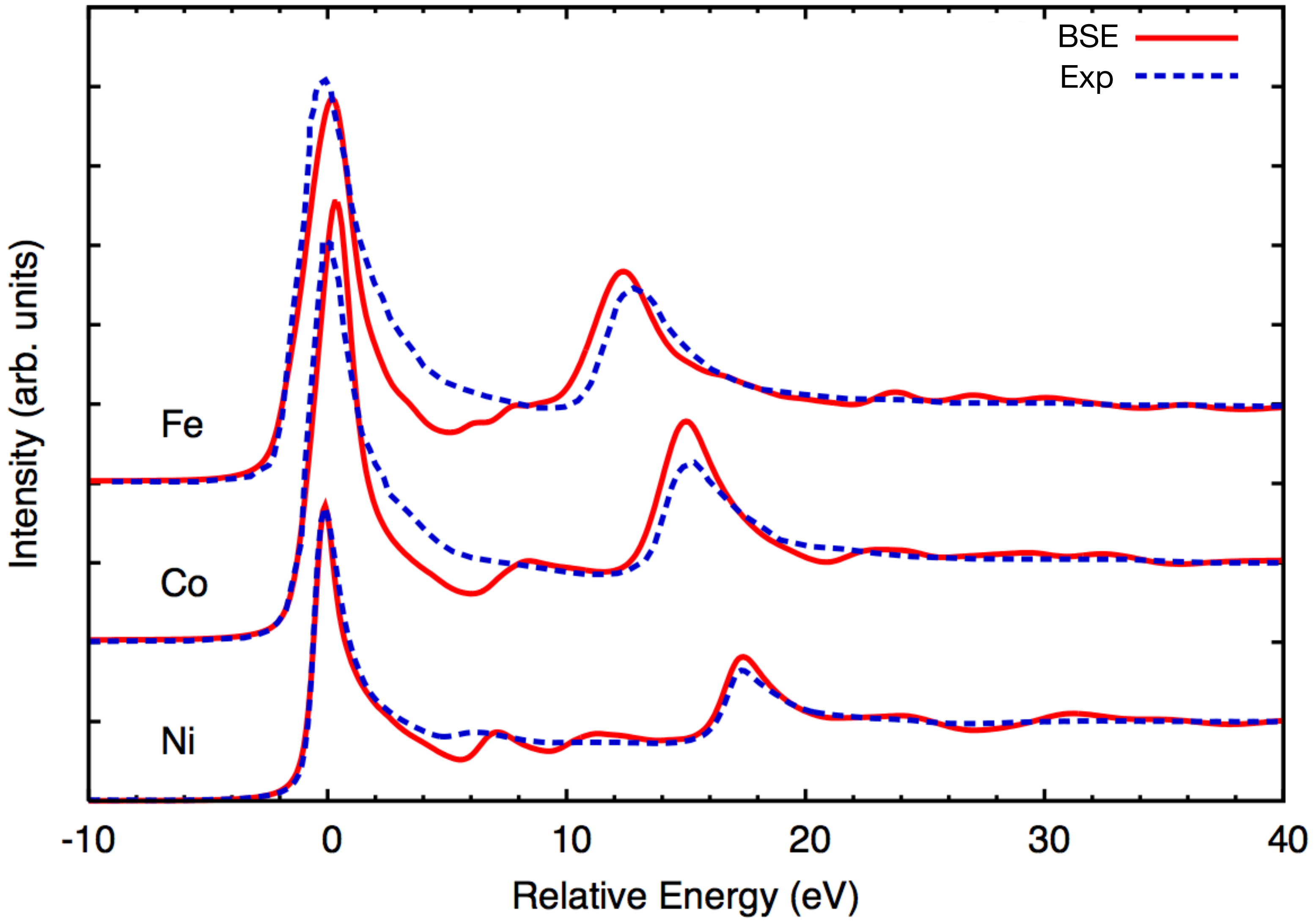
no core hole

no non-local exchange

PHYSICAL REVIEW B **82**, 205104 (2010)

Computing $L_{II,III}$ edges

- BSE can capture non-statistical L_{III}/L_{II} branching



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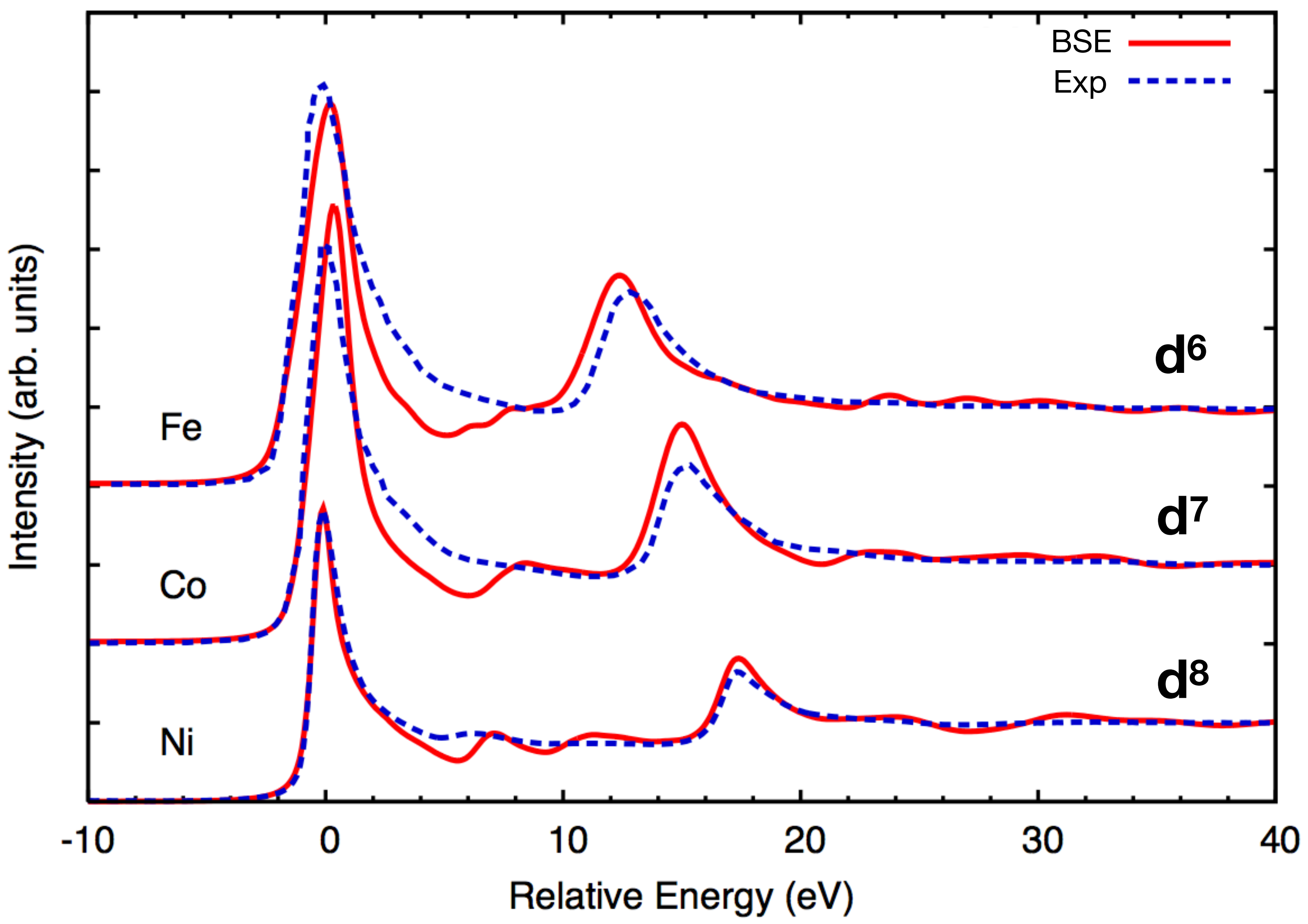
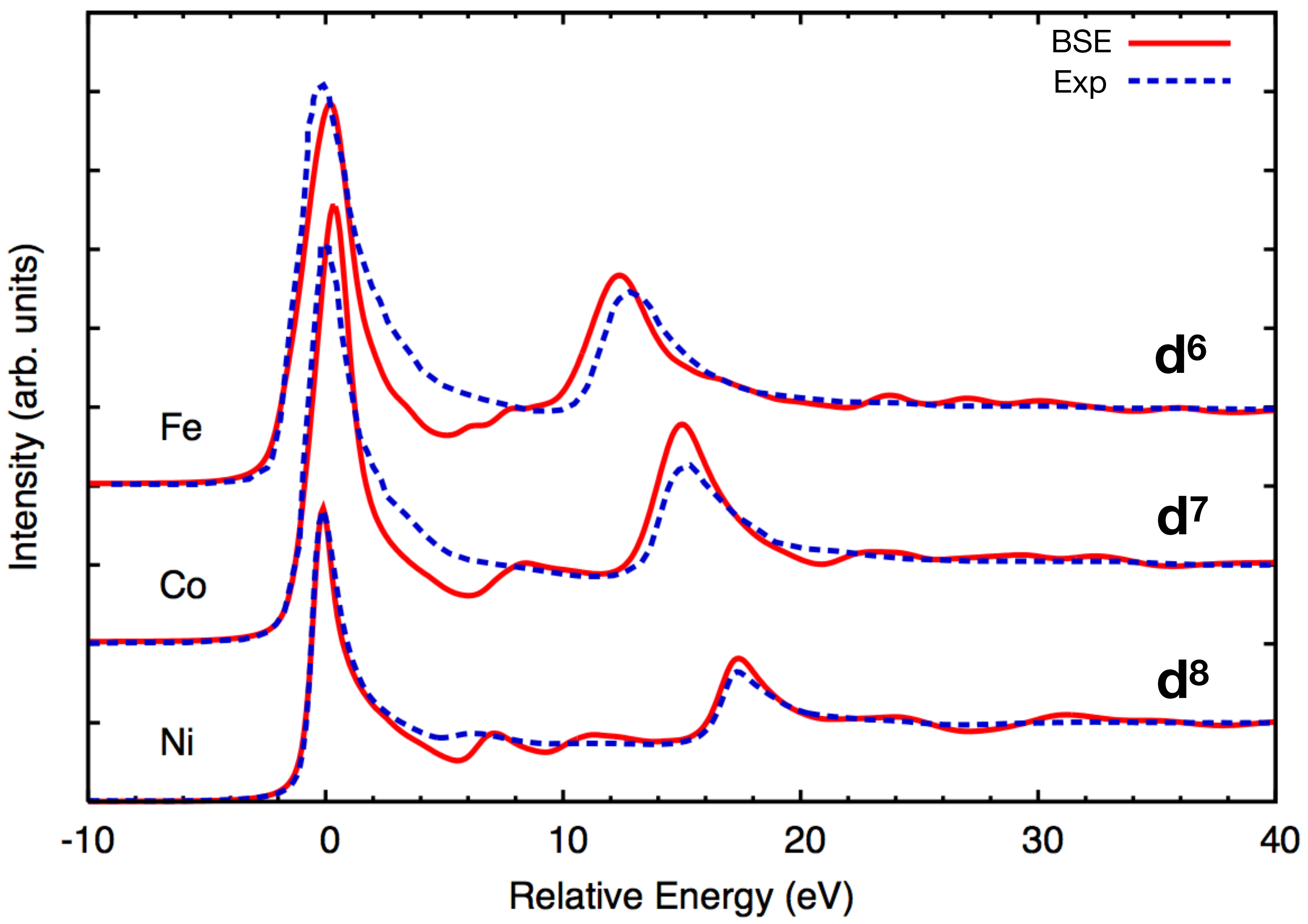


Computing $L_{II,III}$ edges

- Non-local exchange means L_{III} alone does not give d hole count



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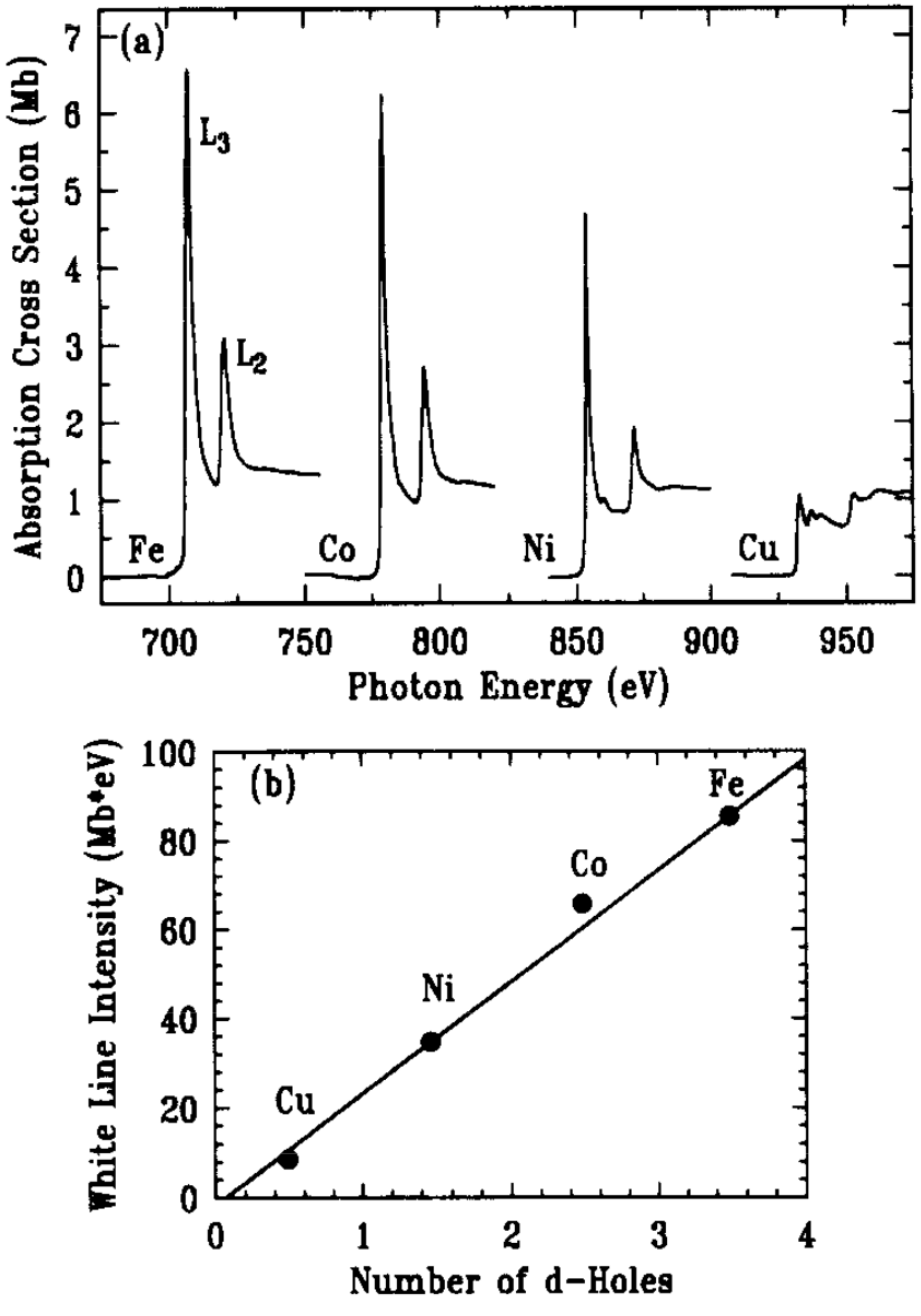
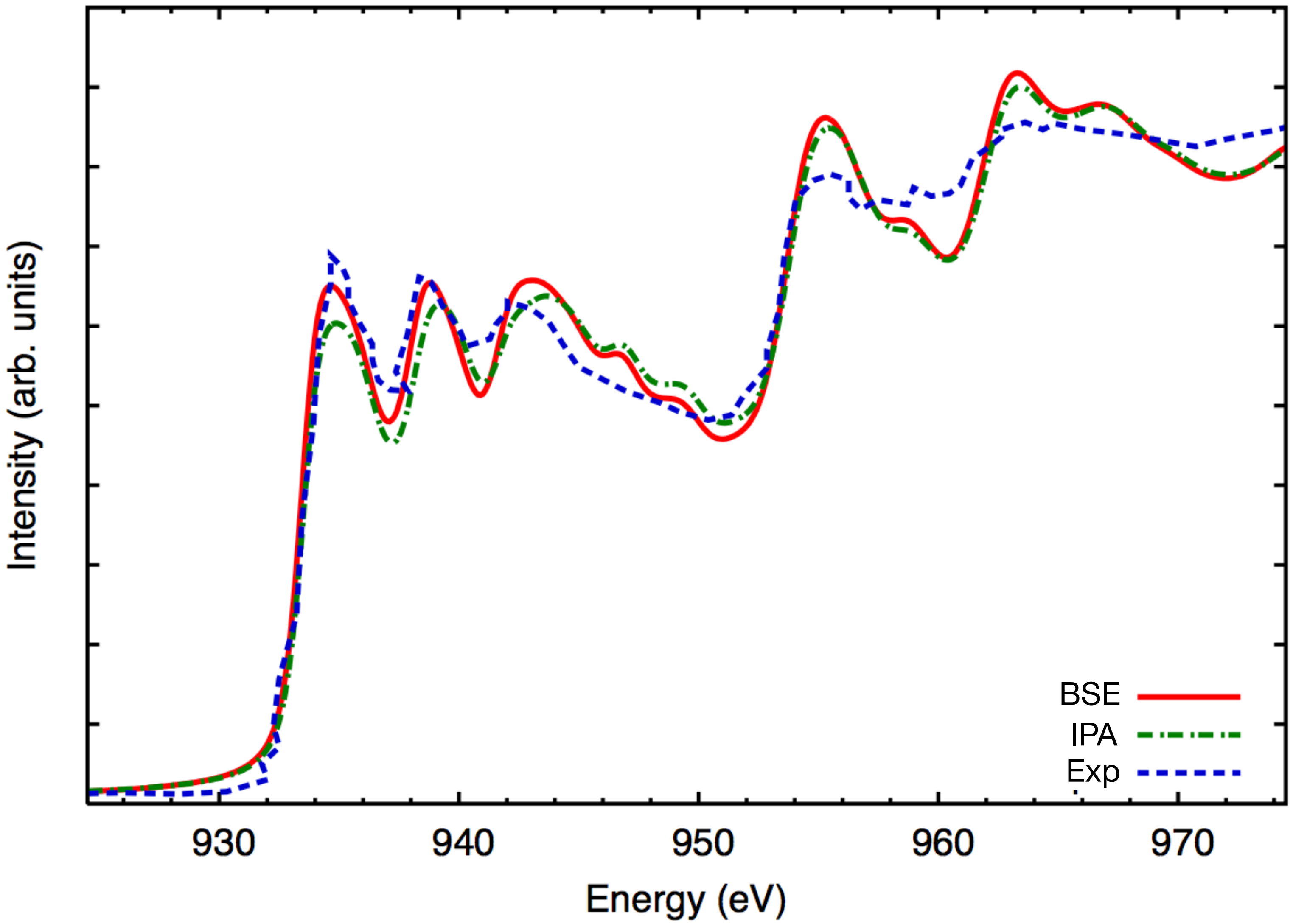


Computing $L_{II,III}$ edges

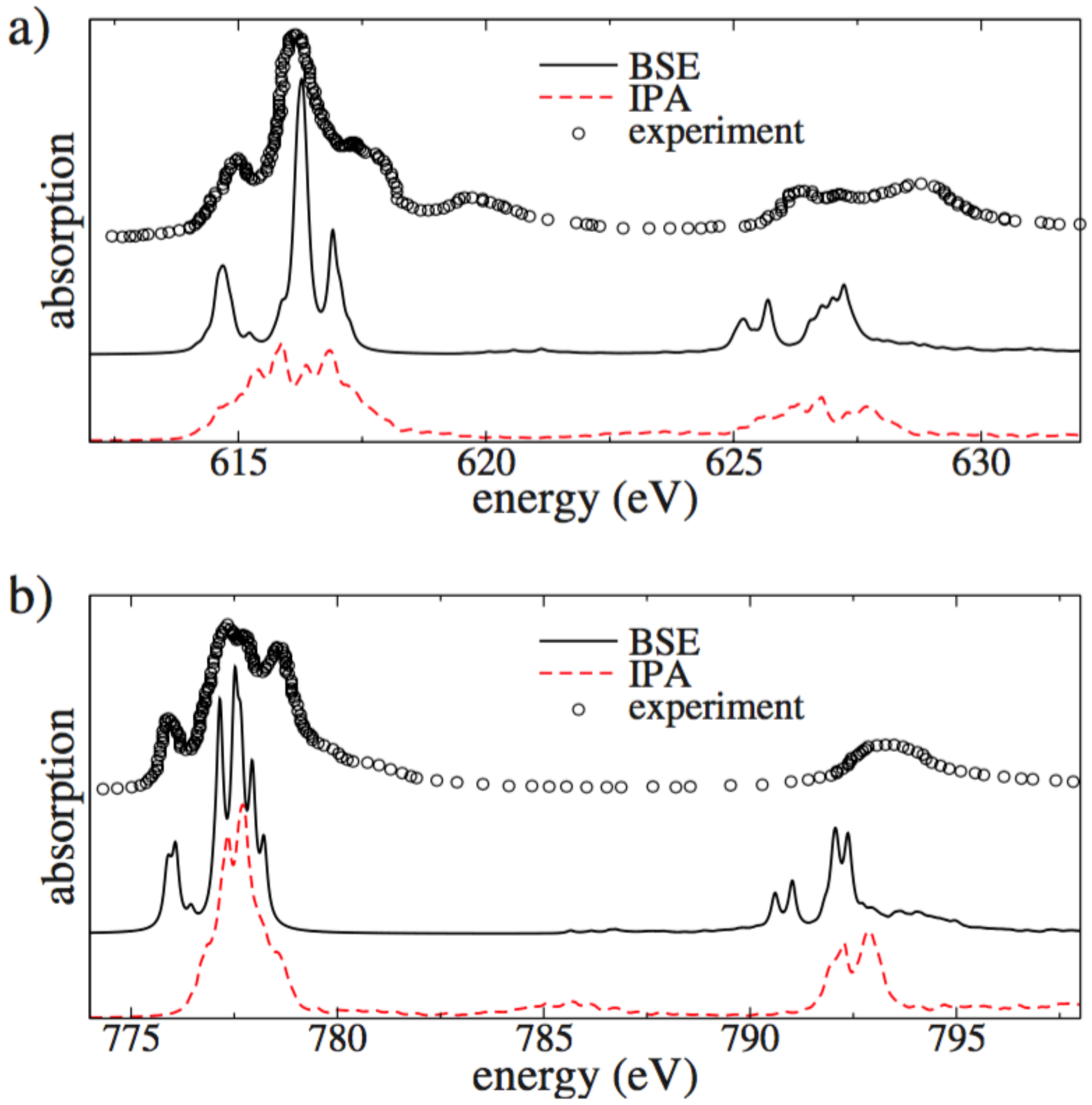
- But when there is no white-line IPA can work

Cu metal is d^{10}



When does BSE fail?

- Formally defined for one-hole and one-electron excitation
- If many particles are present it might not work—especially when correlated

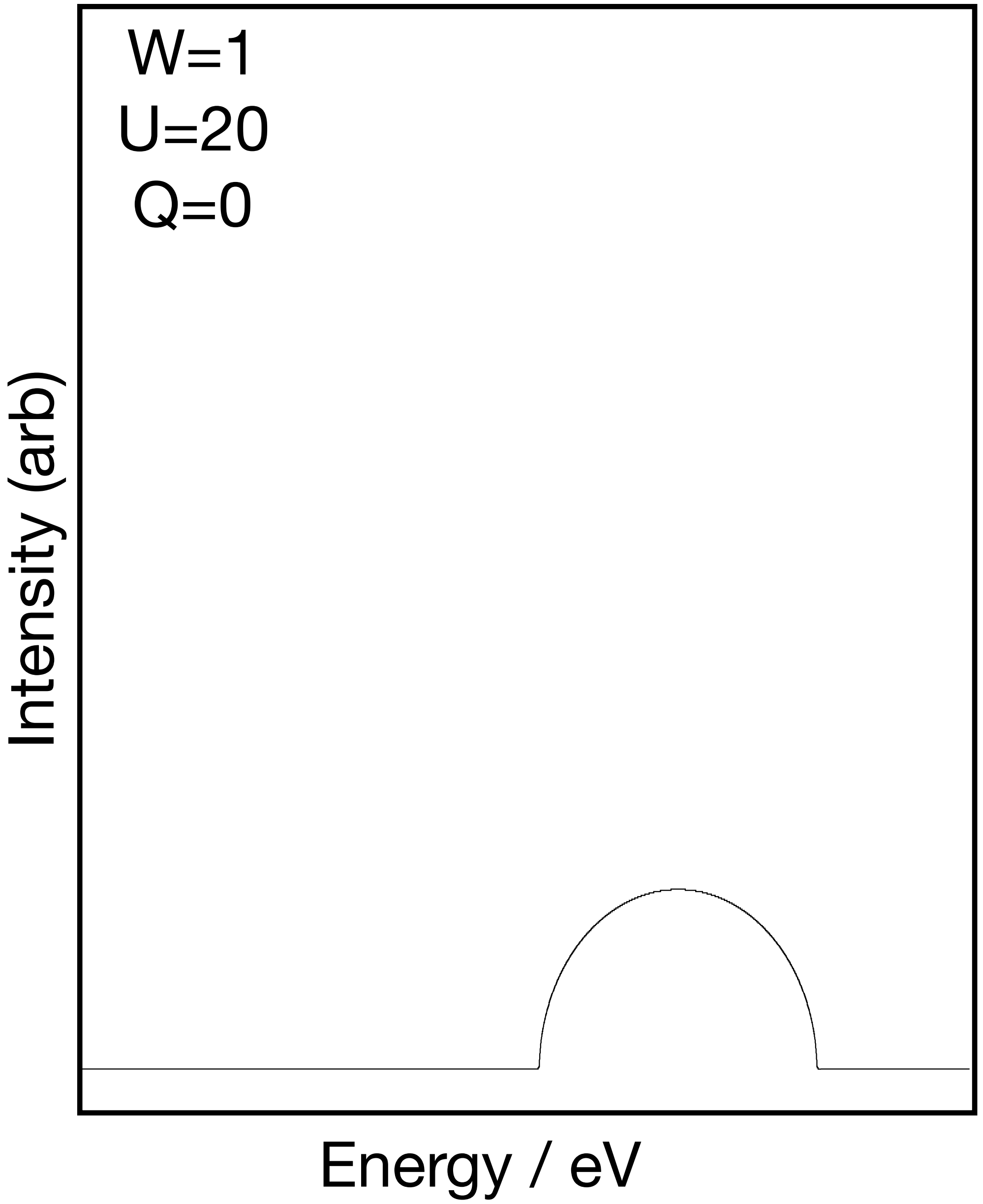


PHYSICAL REVIEW B **82**, 205104 (2010)

Many-body problem

Core-hole potential

- What if we have a strong core hole potential (Q)?



M.W. Haverkort, G. Sangiovanni, P. Hansmann, A. Toschi, Y. Lu, S. Macke EPL, **108** 57004 (2014)

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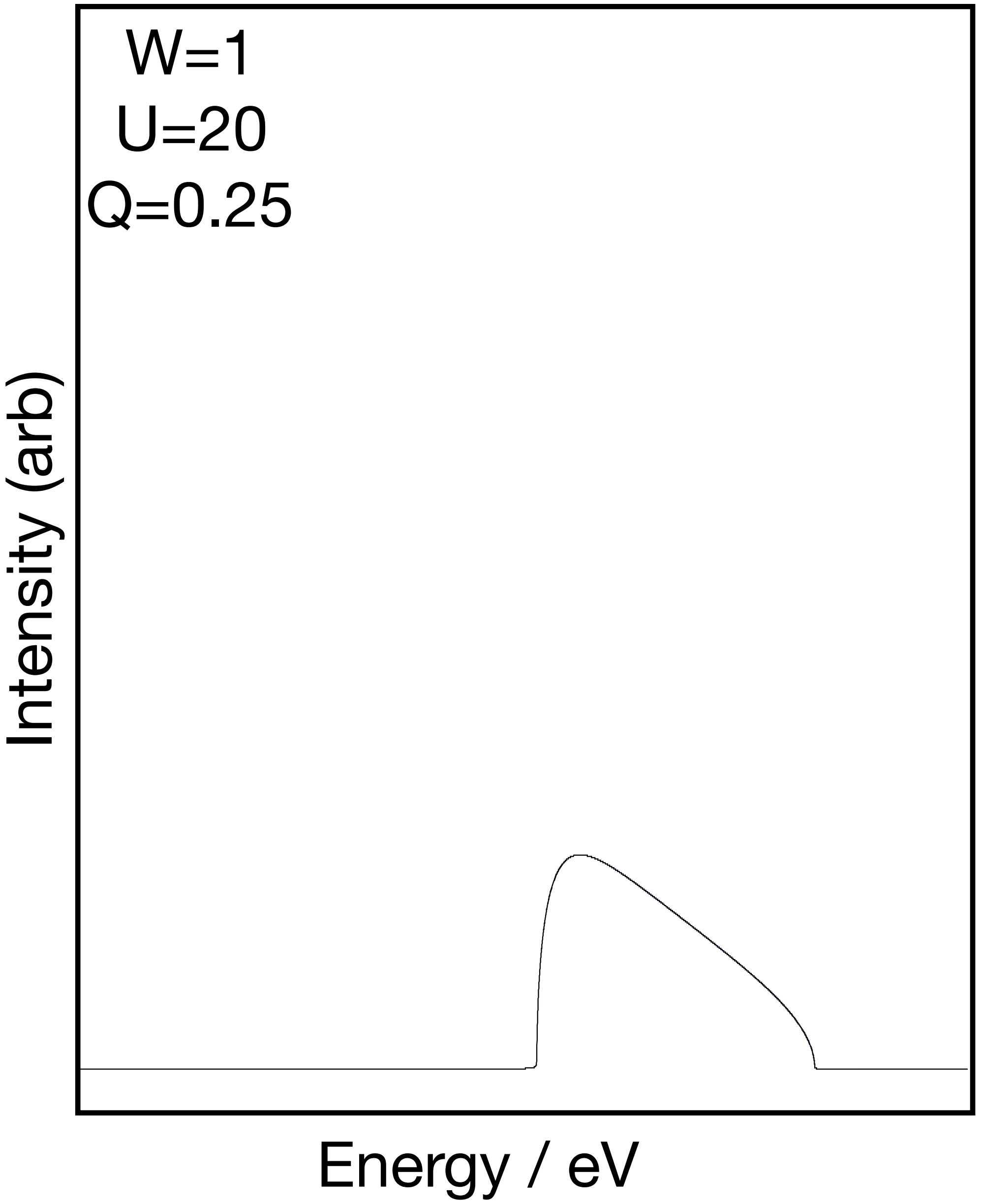

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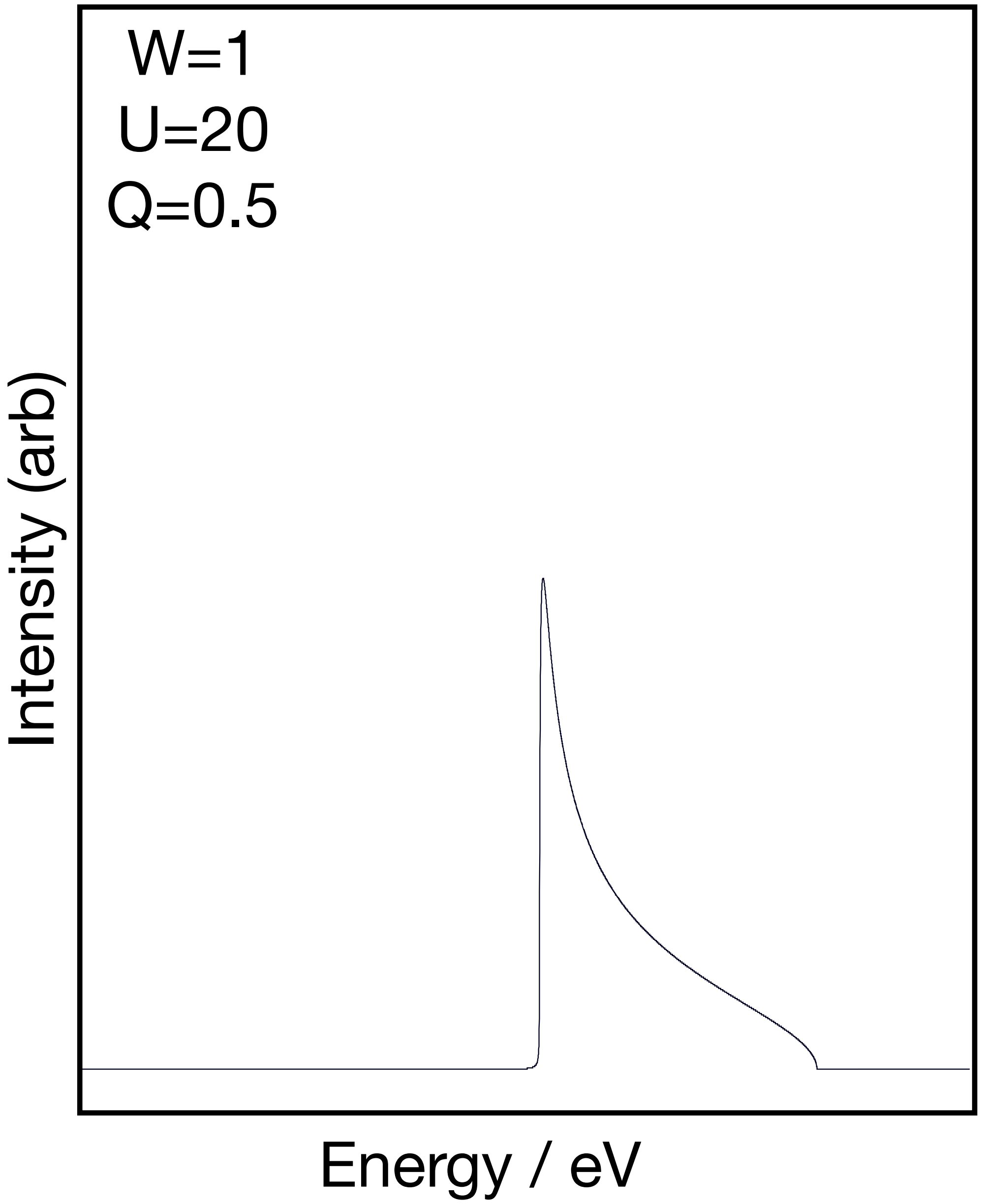

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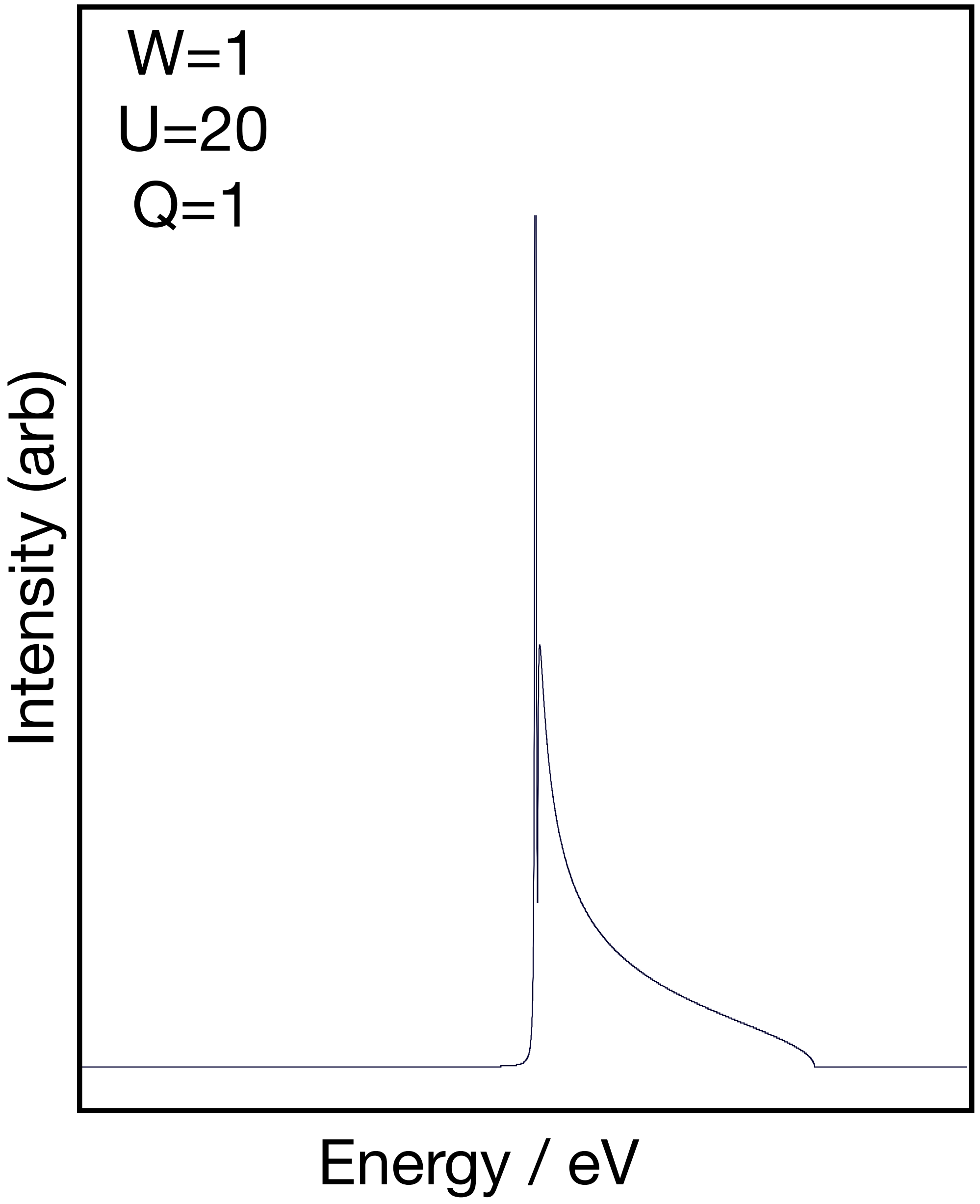

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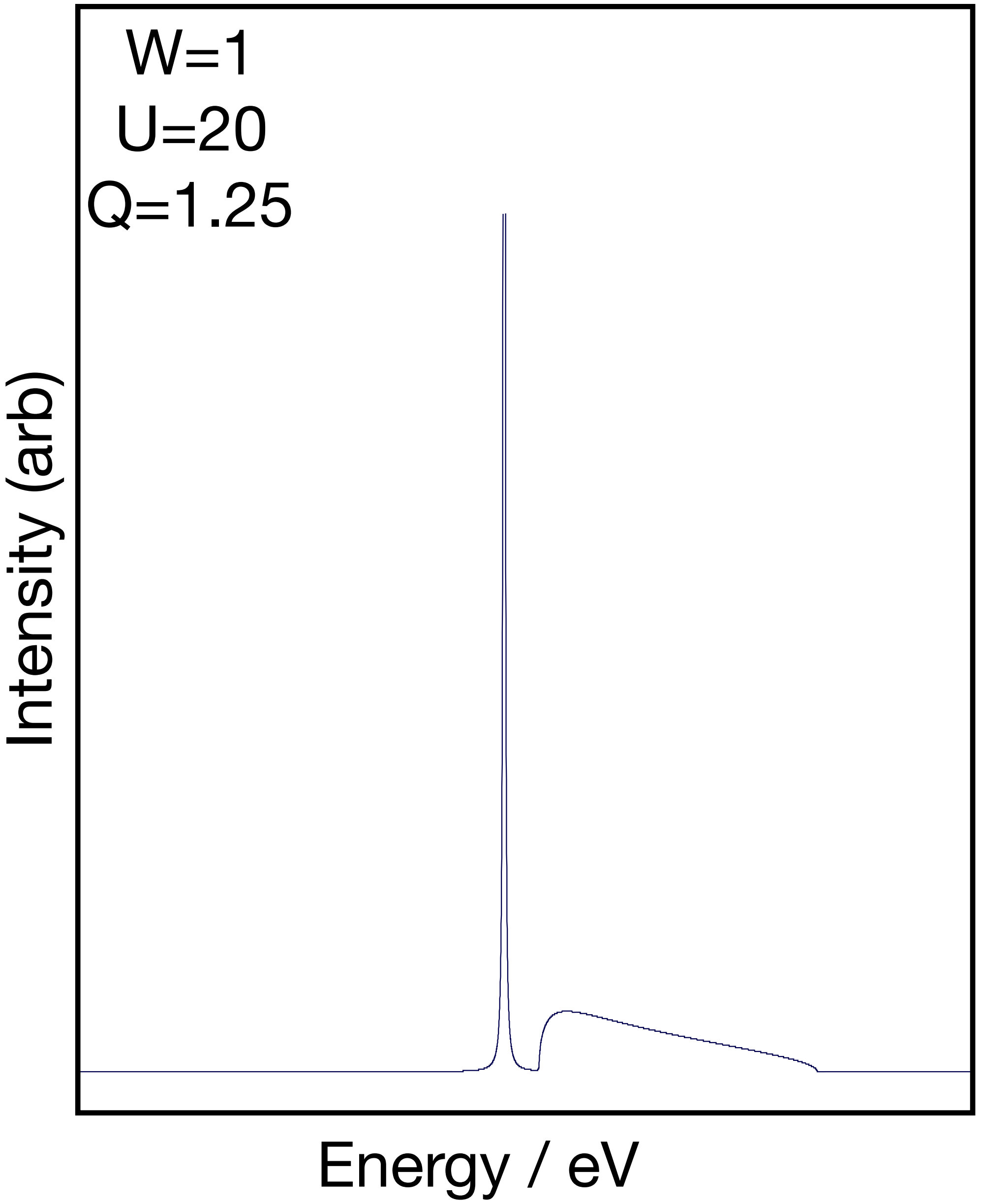

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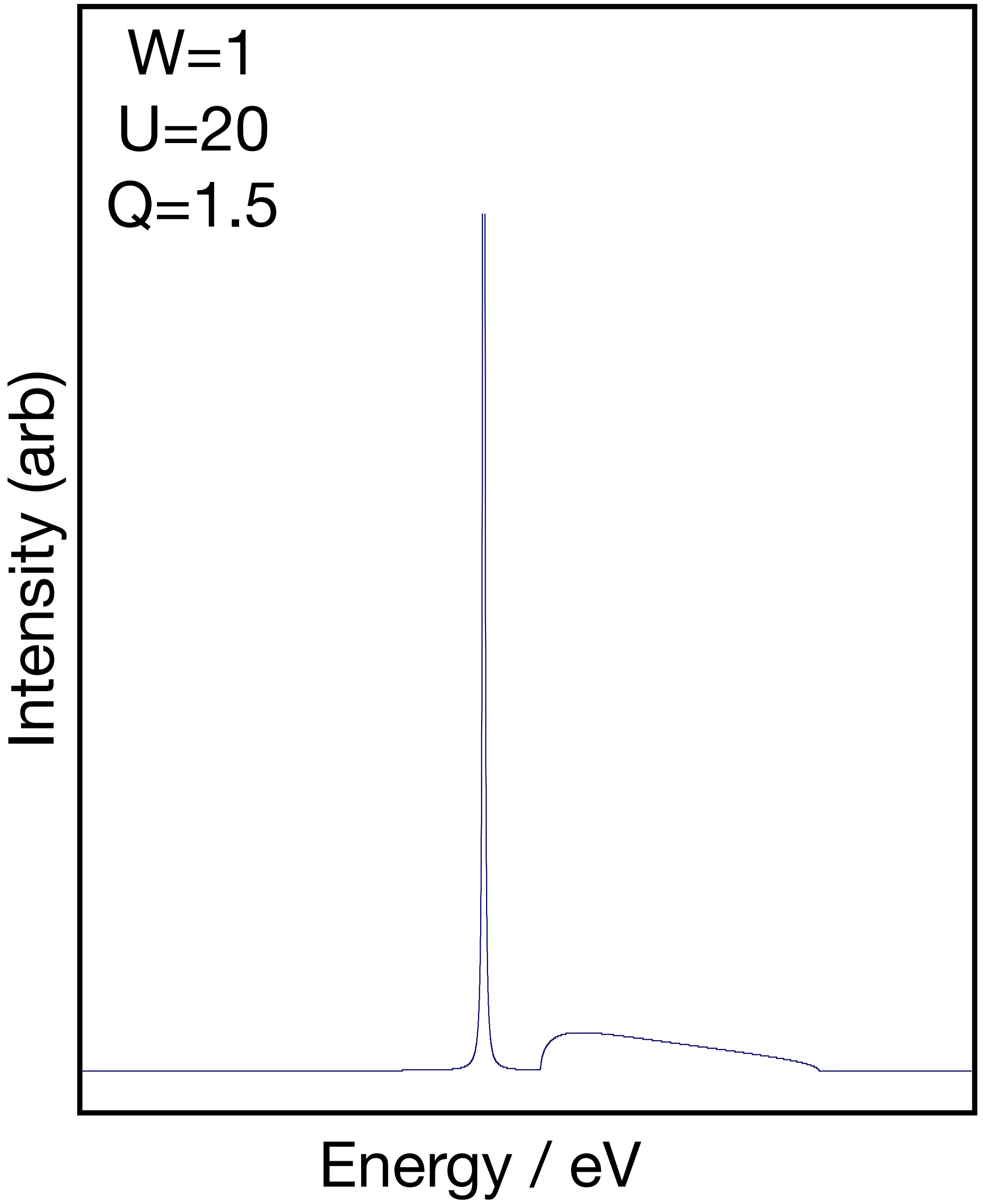

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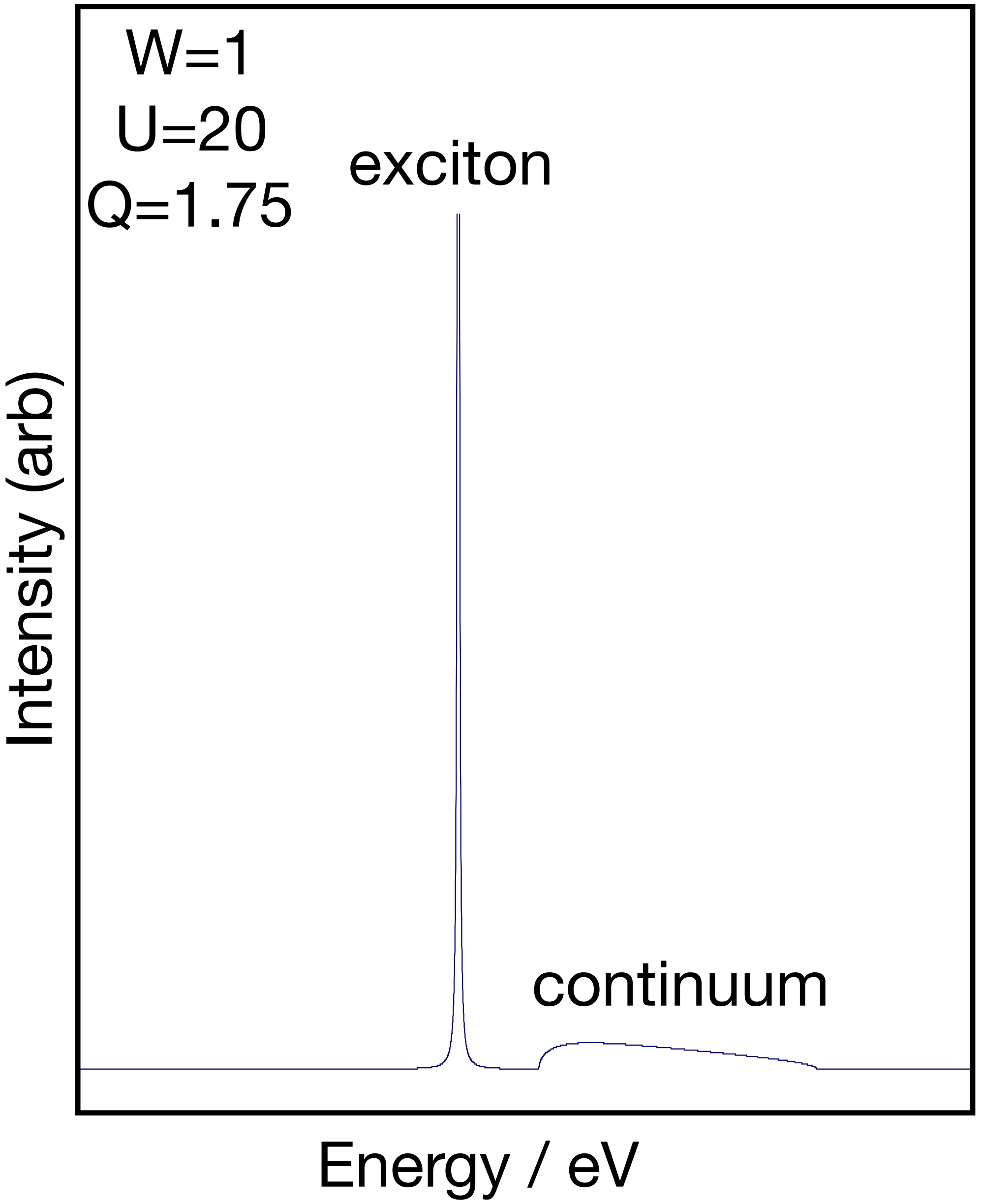
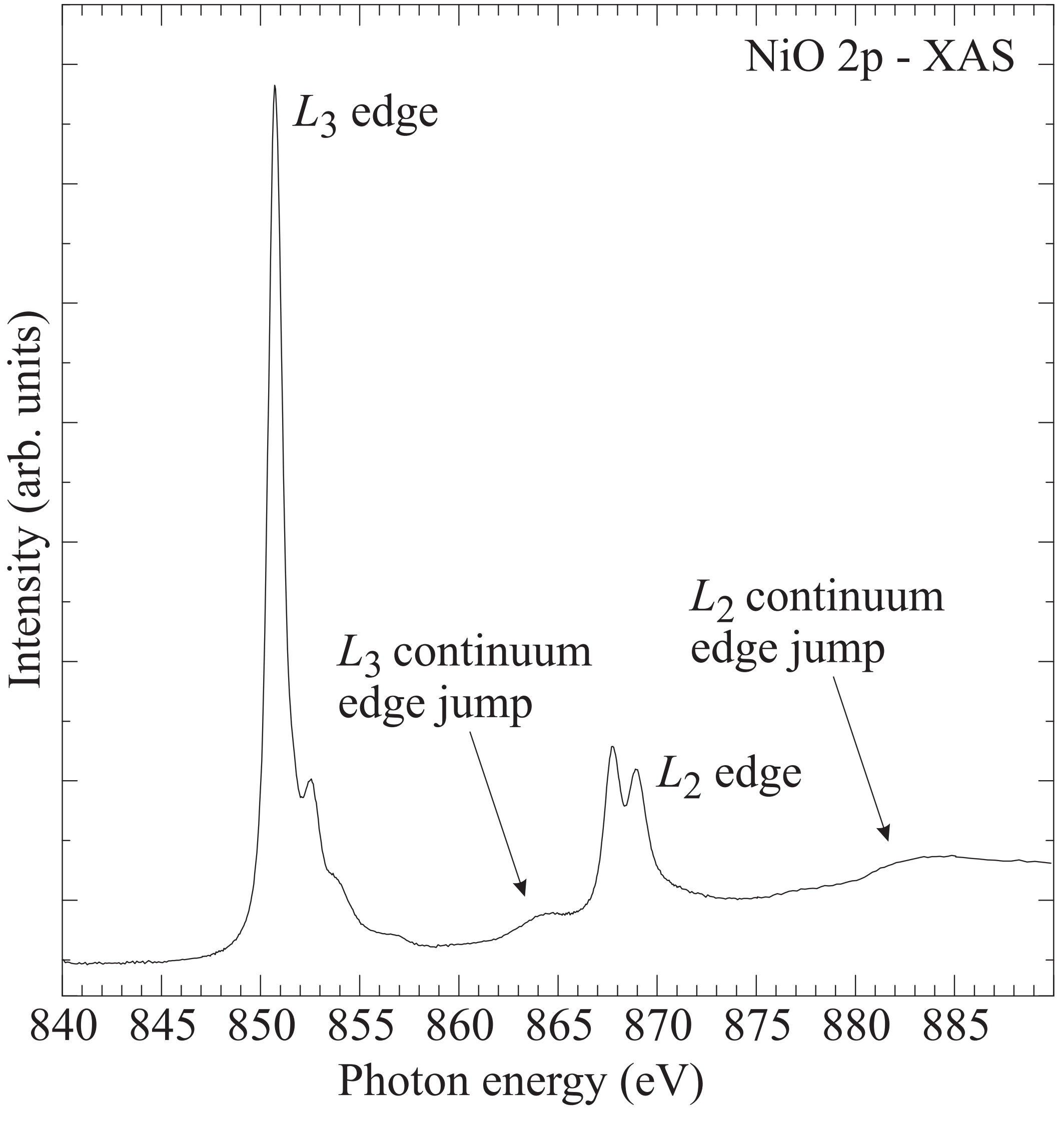


M.W. Haverkort, G. Sangiovanni, P. Hansmann, A. Toschi, Y. Lu, S. Macke EPL, **108** 57004 (2014)

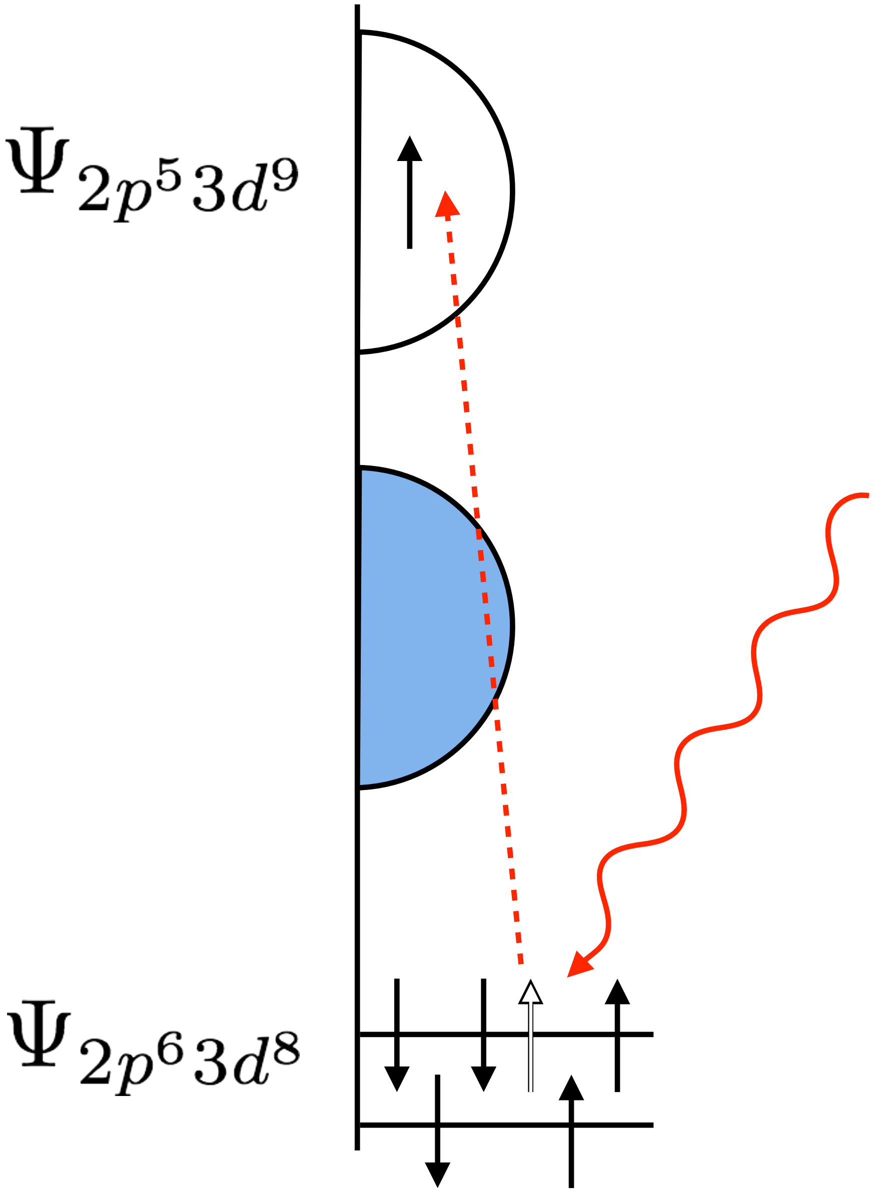
Strong core-valence interaction

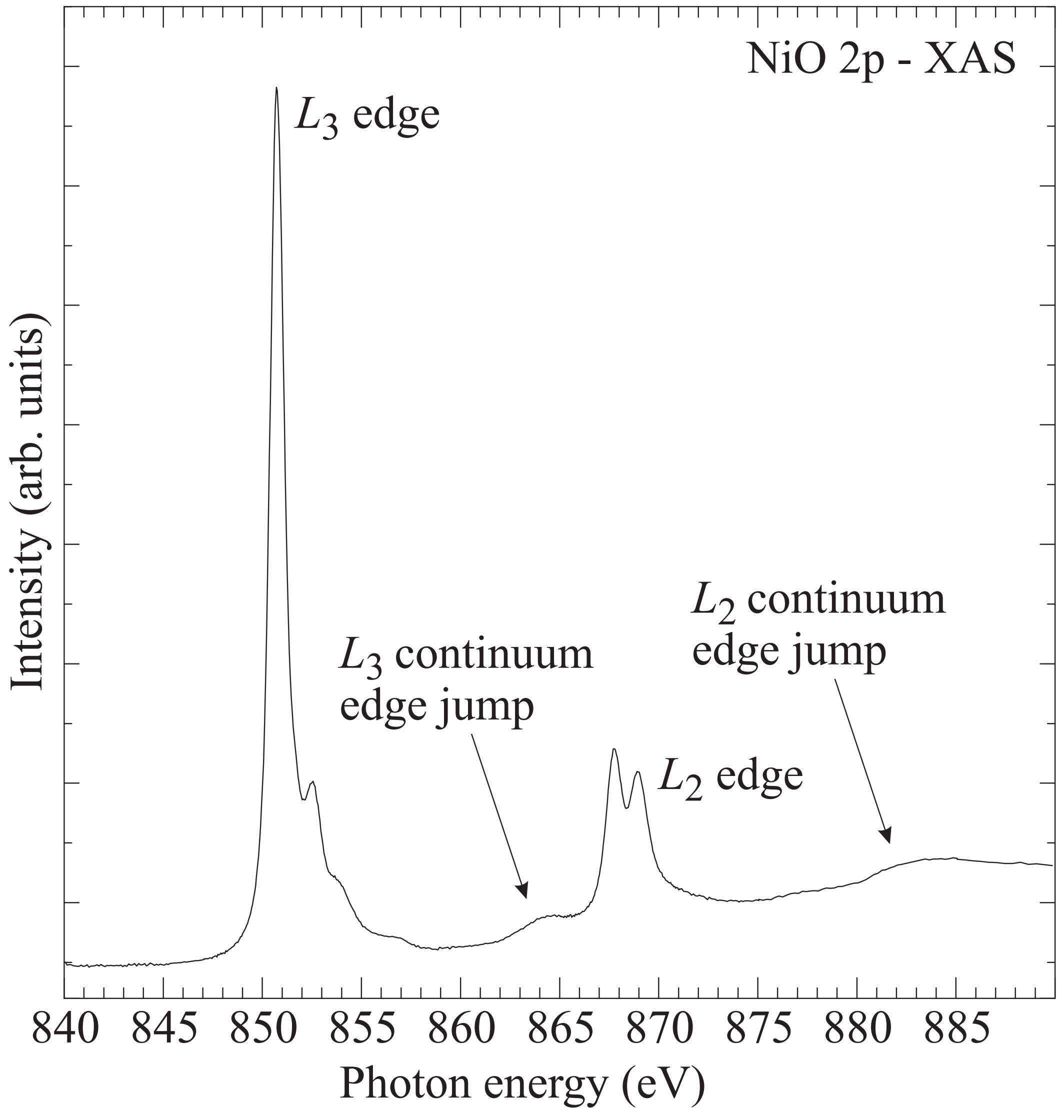
- We no longer see a PDOS—exciton instead
- We can use a different approach to capture the physics



Configuration interaction

- Now we need to capture correlations





Configuration interaction

- Expand ground state wave function as

$$\psi_0 = \sum_i c_i \left| d^{n+i} \underline{L}^i \right\rangle$$

- Define energies for charge fluctuations

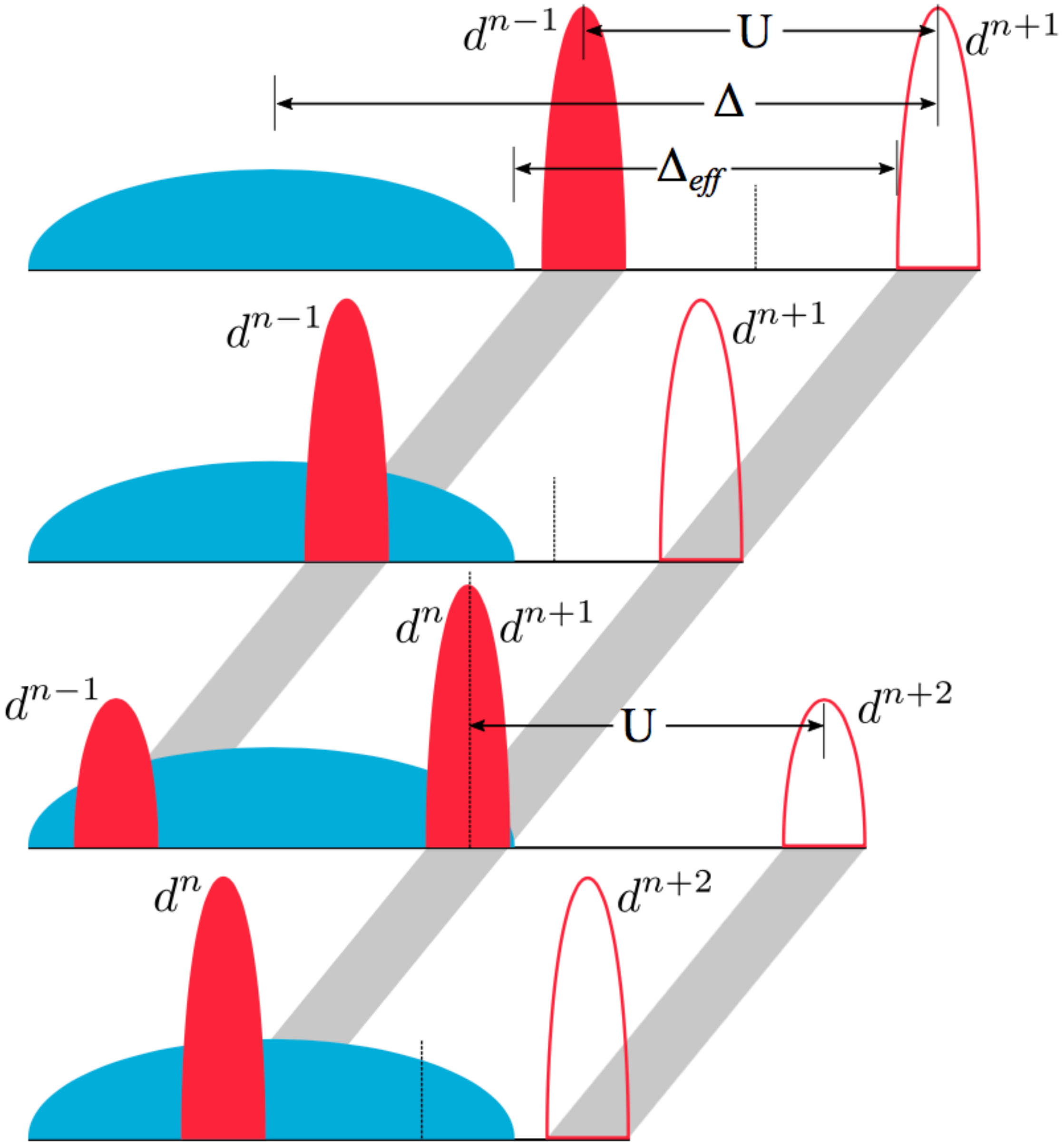
$$U \equiv \left[E\left(d^{n+1}\right) + E\left(d^{n-1}\right) \right] - 2E\left(d^n\right)$$

$$\Delta \equiv E\left(d^{n+1} \underline{L}^1\right) - E\left(d^n\right)$$

- Now we need a basis

Parameters

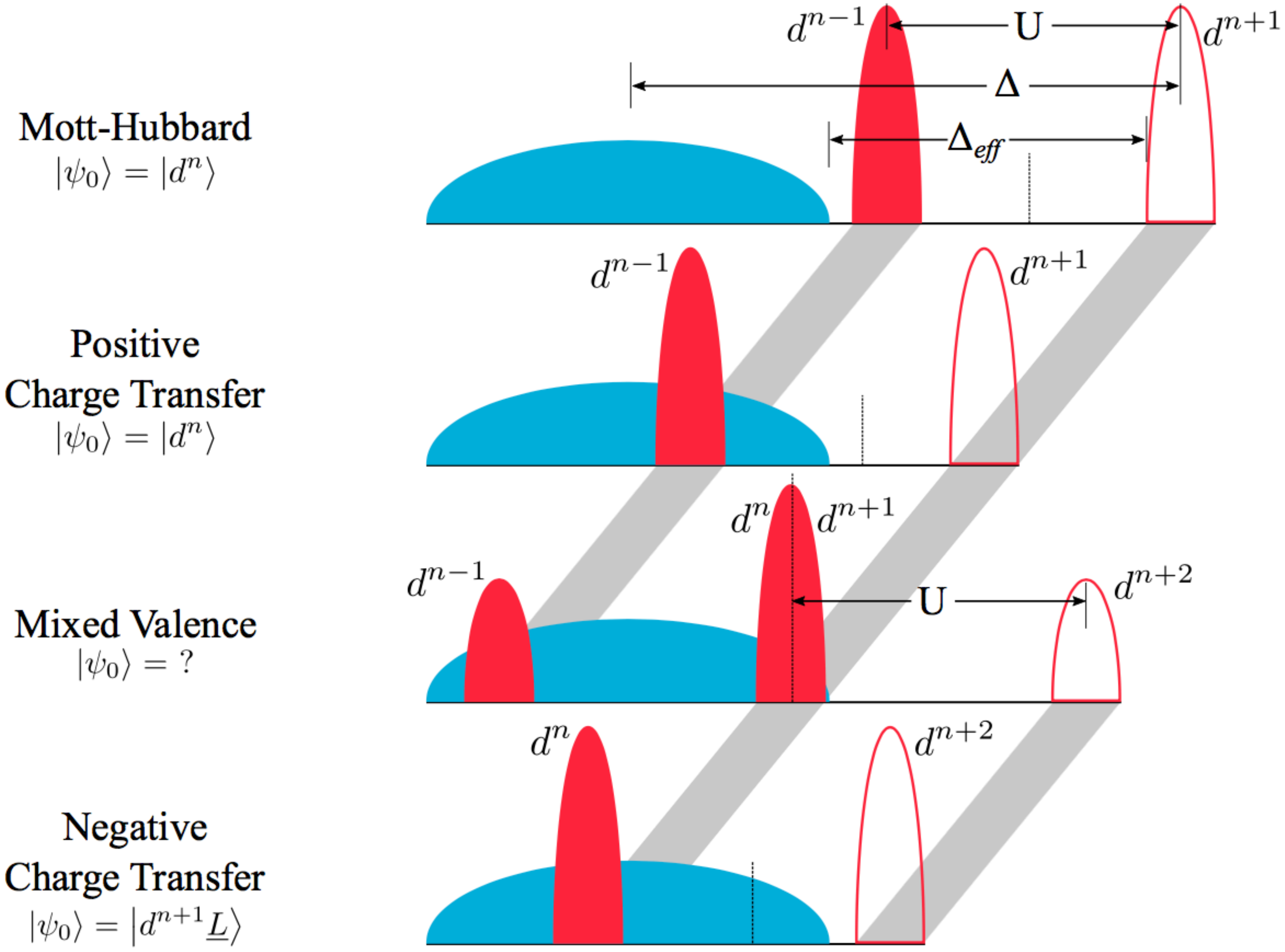
- If view the parameters U and Δ graphically…



"The Explicit Role of Anion States in High-Valence Metal Oxides" in Quantum Materials: Experiments and Theory Modeling and Simulation Vol. 6

Parameters

- If view the parameters U and Δ graphically…
- They tell us something about the electronic structure



"The Explicit Role of Anion States in High-Valence Metal Oxides" in Quantum Materials: Experiments and Theory Modeling and Simulation Vol. 6

Parameter sensitivity

- XAS is not sensitive to U and Δ because excited electron screens

ground state

$d^{n+1}\underline{L}^1$

Δ

d^n

XAS final state

$\underline{c}d^{n+2}\underline{L}^1$

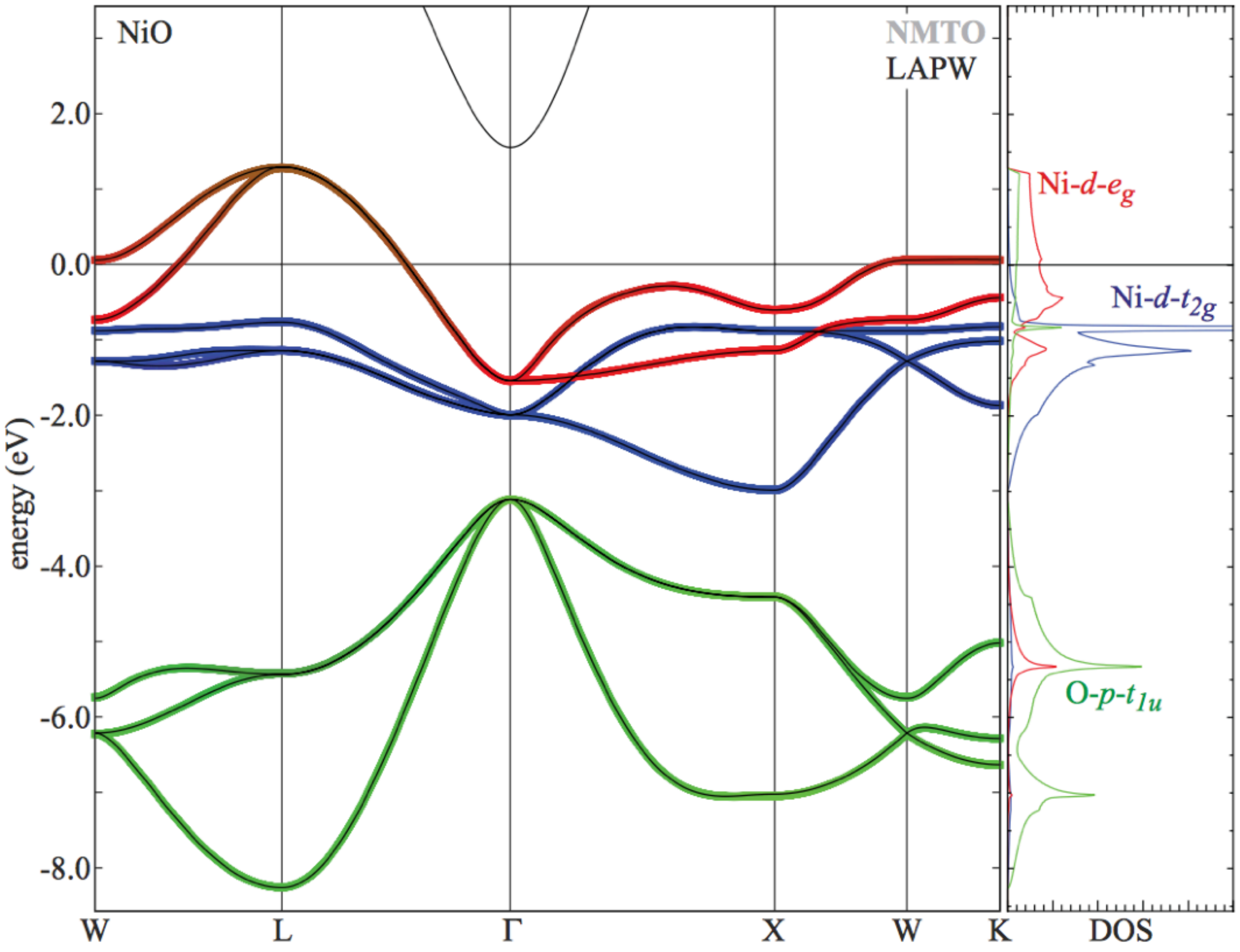
$U + \Delta - Q \sim \Delta$

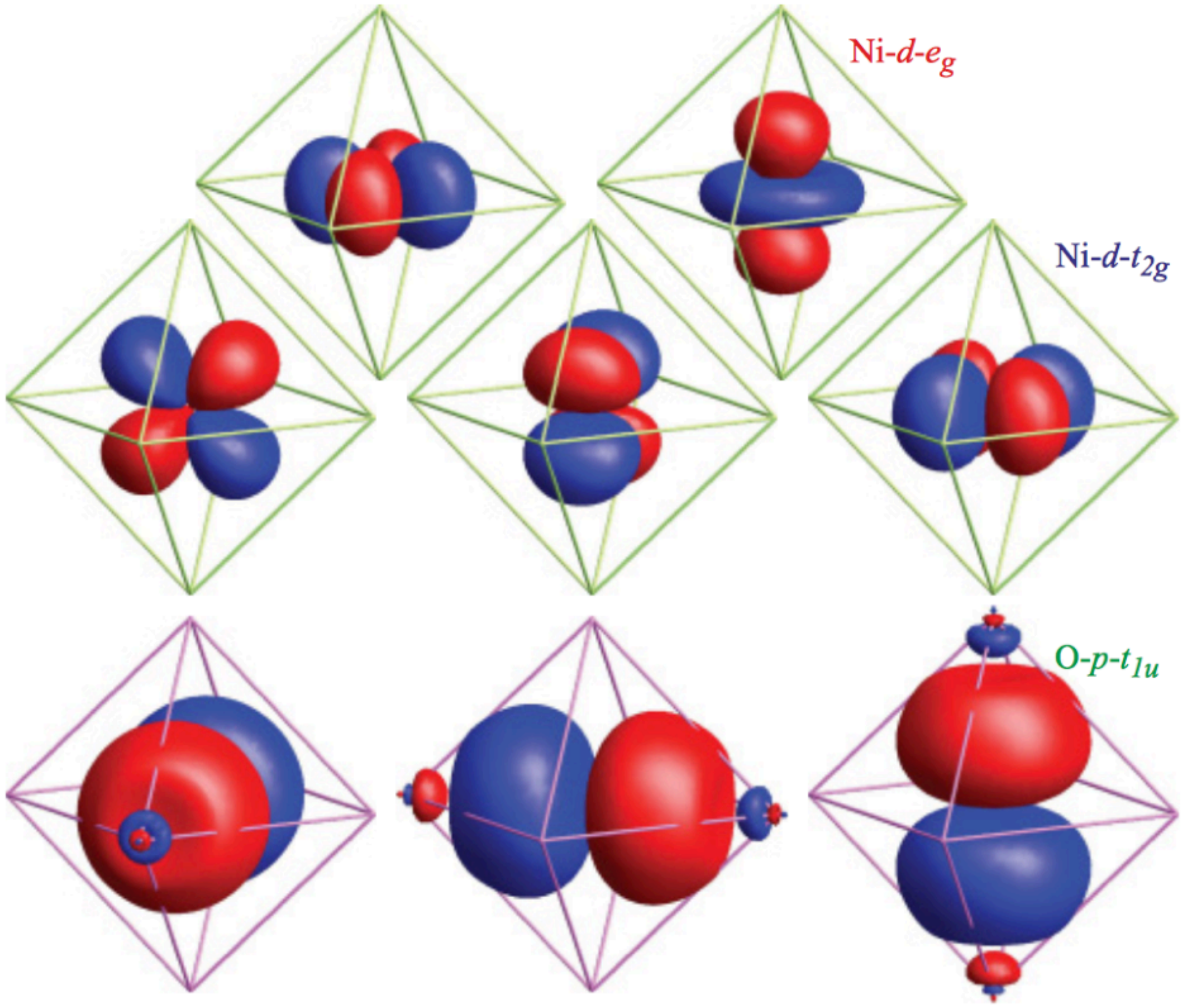
$\underline{c}d^{n+1}$

Q is the core hole potential

Local many-body problem

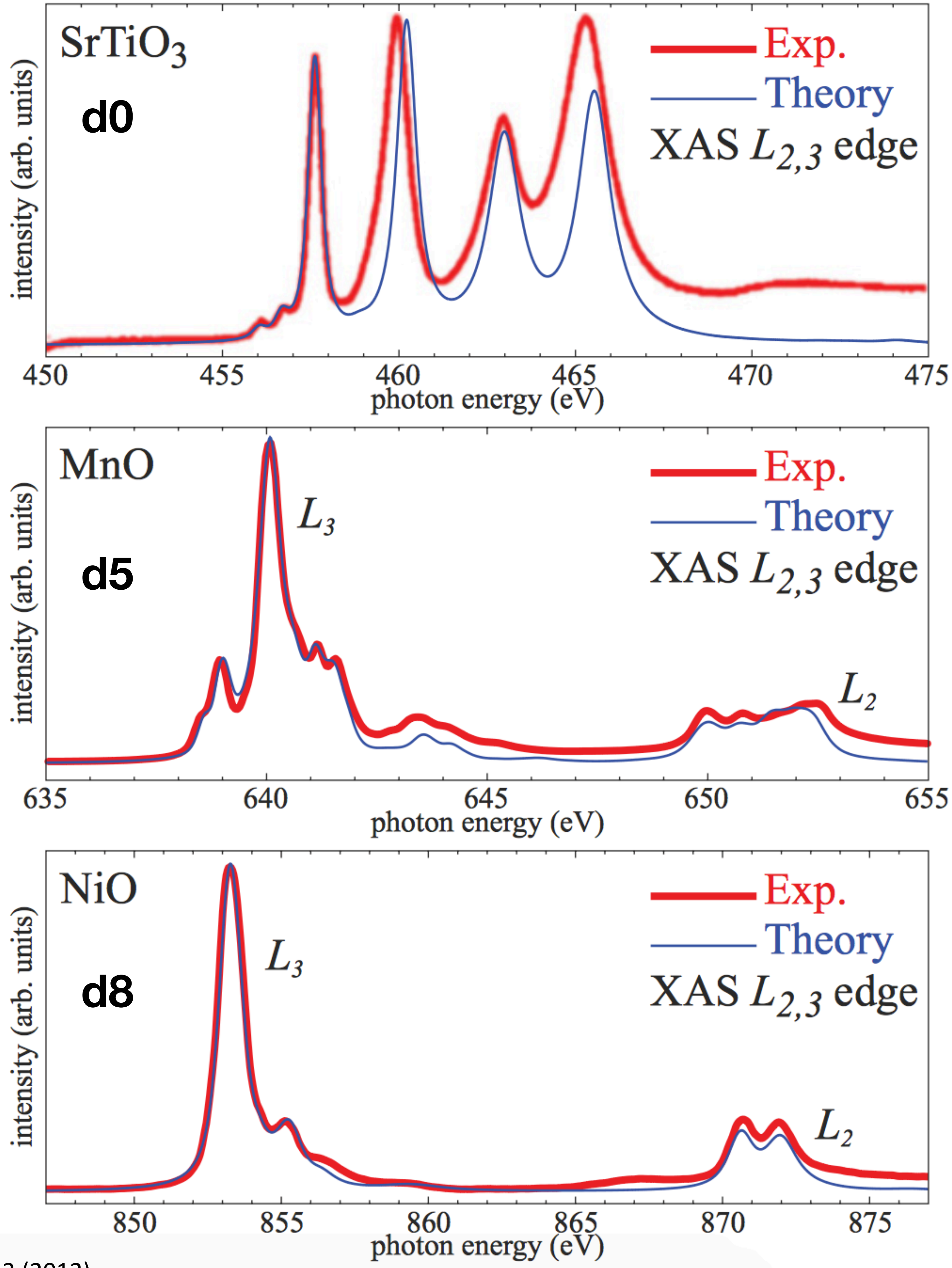
- Start with the LDA (or better) potential
- Create a set of Wannier functions
- Build local Hamiltonian on this basis and potential and include all local many body interactions





M.W. Haverkort, M. Zwierzycki, O.K. Andersen, PRB **85**, 165113 (2012).

Spectra dominated by multiplets



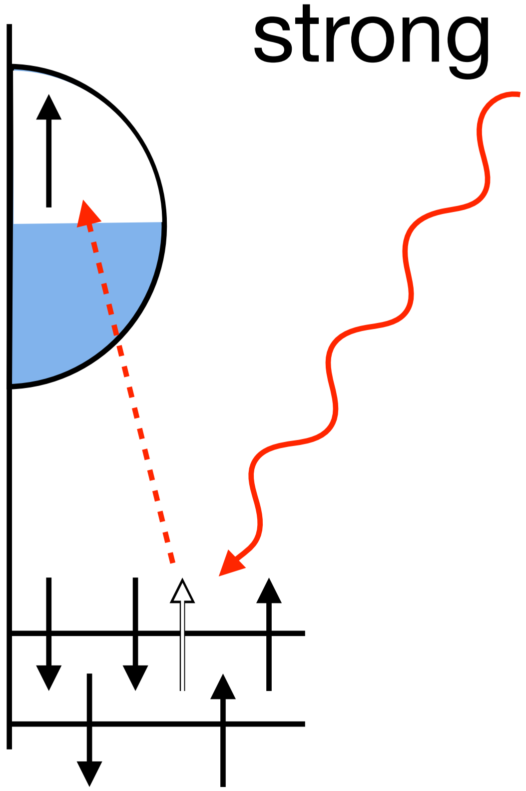
M.W. Haverkort, M. Zwierzycki, O.K. Andersen, PRB **85**, 165113 (2012).

Summary of CI approach

- The bad
    - Based on parameters (U and Δ) that are not easy to compute *a priori*
    - Computationally expensive for large basis
- The good
    - XAS rather insensitive to U and Δ
    - If you can find the values of U and Δ you will know a great deal about the system
    - Small basis often fine for excitons

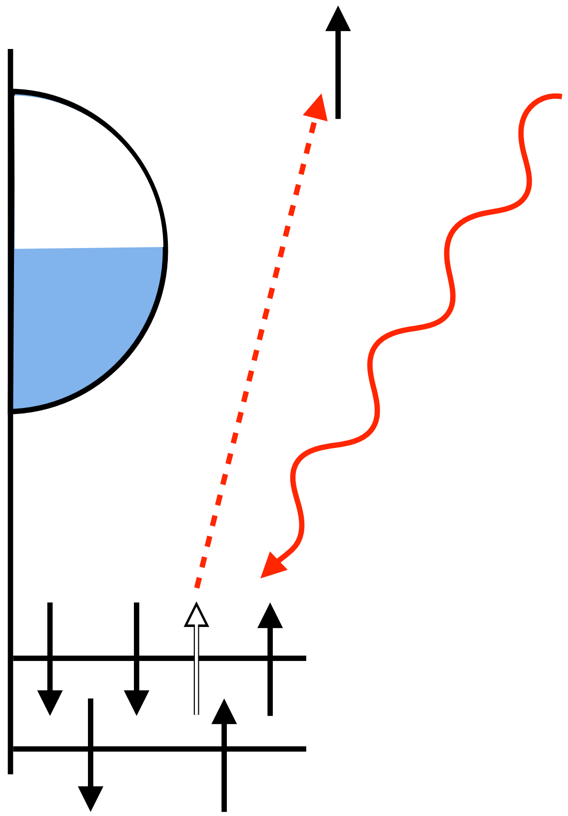
Summary of XAS

- Polarization dependence comes from dipole selection rule
- $L_{II,III}$ needed in sum rule — mixing due to non-local exchange
- Dichotomy of results on different materials/energy scales
  - PDOS when correlations and core hole potential are weak
  - Multiplets when correlations and core hole potential are strong



XPS

- Typically used for chemical shift, stoichiometry, etc…
- To get the zero of XAS you need to know the core level binding energy

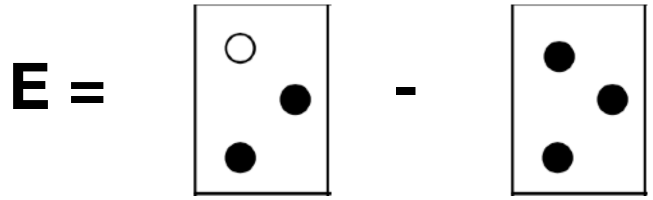


Core level binding energy

- Computing a core level binding energy is straightforward with DFT
- You only get relative binding energy
- You can compute the initial state contribution separately from the final state contributions
    - Initial state shift is just the energy of the KS level relative to some reference
    - Final state shift involves relaxations

Final state shift

- Energy difference between final and initial state



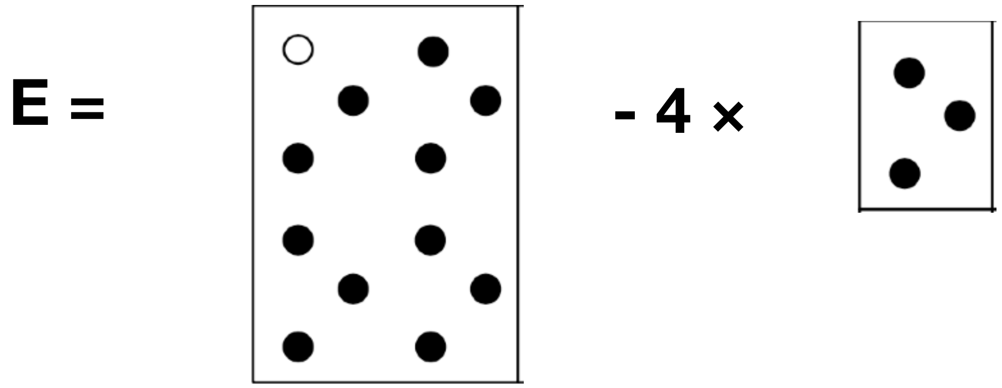
E = -

○ **core hole**

● **no core hole**

- Perform SCF calculation with core hole to get energy of final state

- With PBC will require supercell



E = **- 4 ×**

○ **core hole**

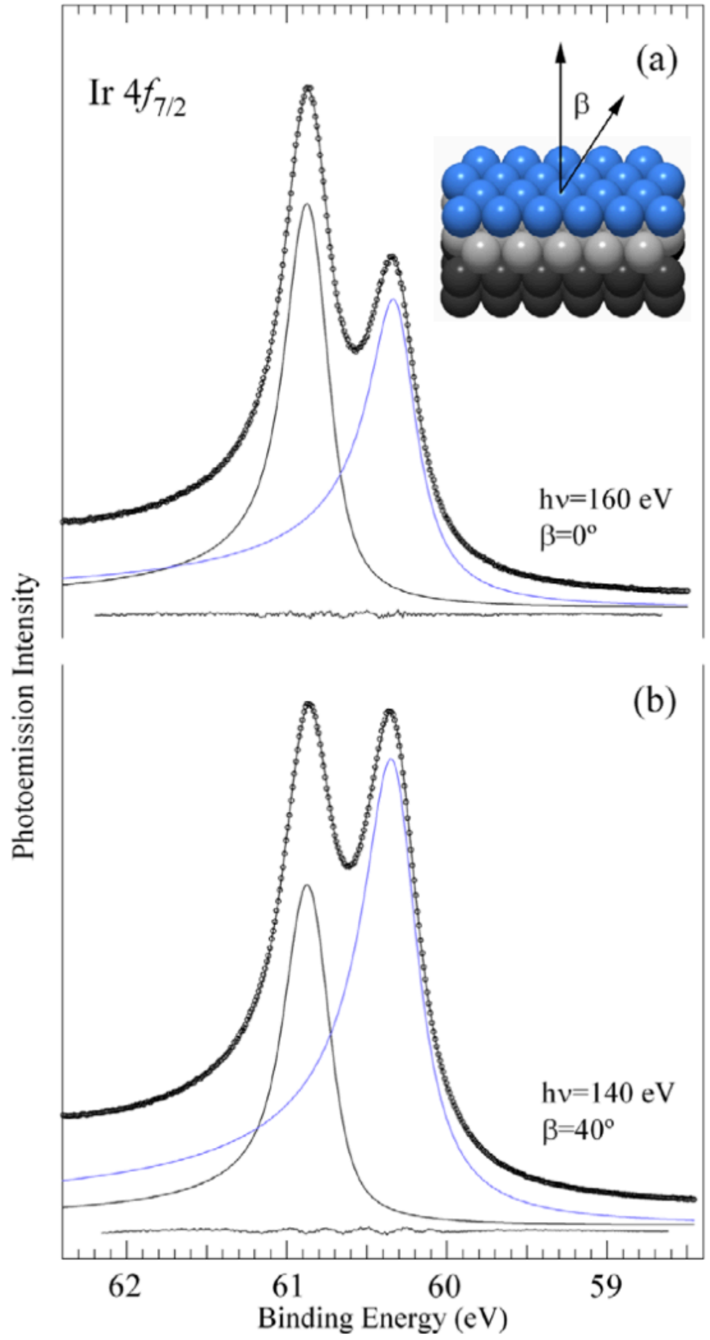
● **no core hole**

- Can also use Slater’s transition state approximation

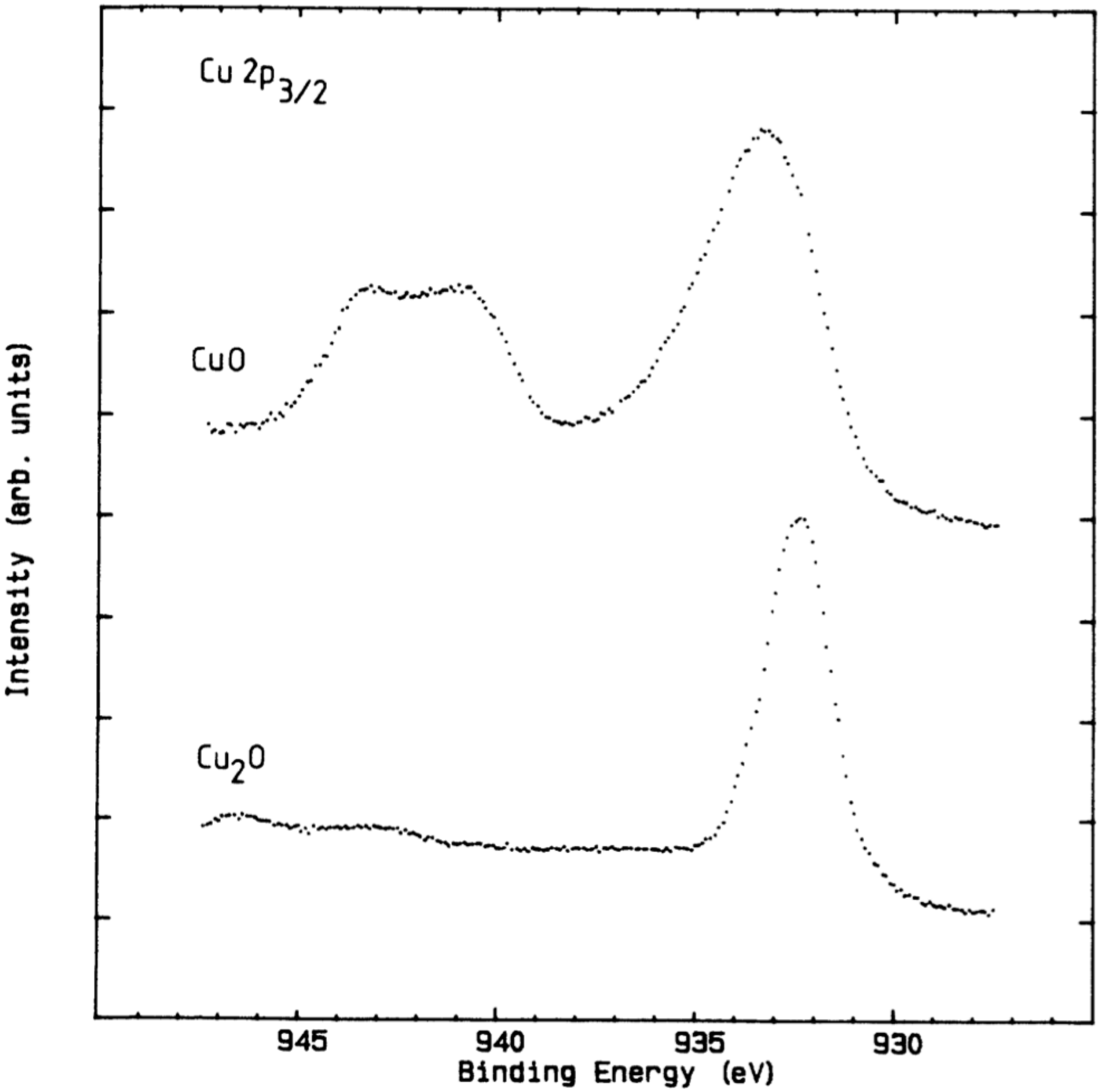
XPS

- But the spectra are not delta functions
- Final states are always screened
- How they are screened matters
- Multiple peaks/shape give insight into contributions to ground state

XPS



M Bianchi et al *New J. Phys.* **11** 063002 (2009)



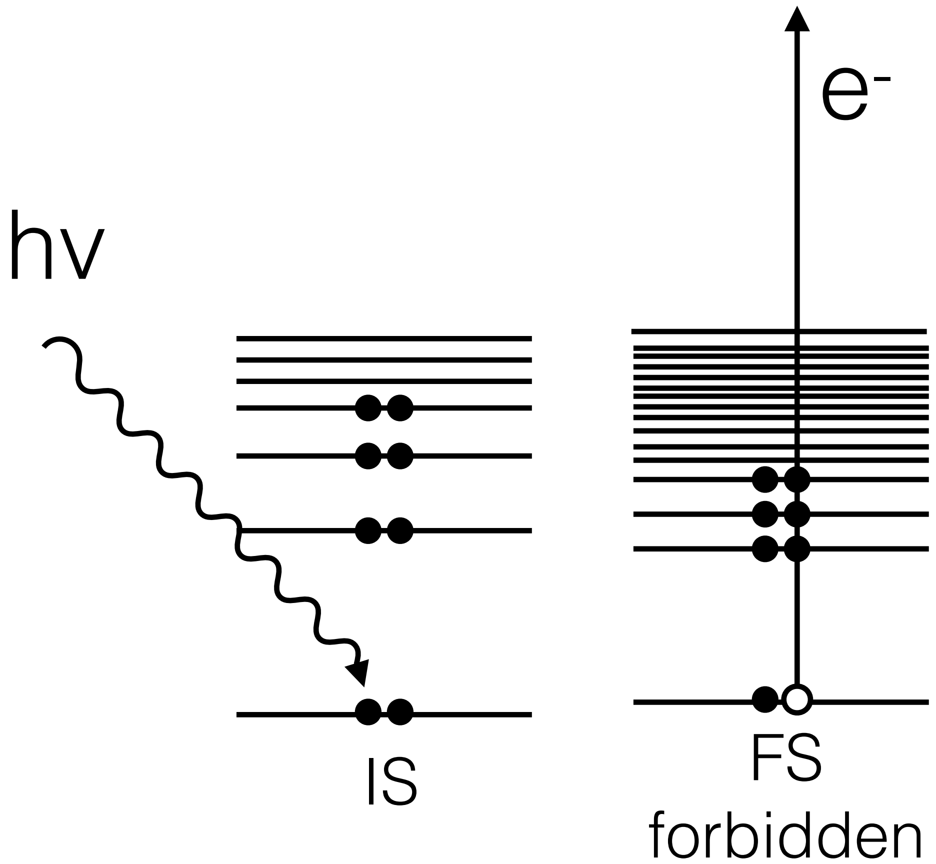
J. Ghijsen, et al. *Phys. Rev. B* **38**, 11322

Line shapes for metals

- X-ray edge of a metal is complicated because 10^{23} conduction electrons respond to creation core hole
- Original work on absorption
  - Exciton theory predicts adsorption edges have power law divergence near threshold (Mahan 1967)
  - Orthogonality catastrophe requires electron-hole excitations for non-zero absorption (Anderson 1967)
  - Asymptotically exact solution available near threshold (Nozieres and deDomincis 1969)
- Same many body physics present in XPS (Doniach and Sunjic 1970)

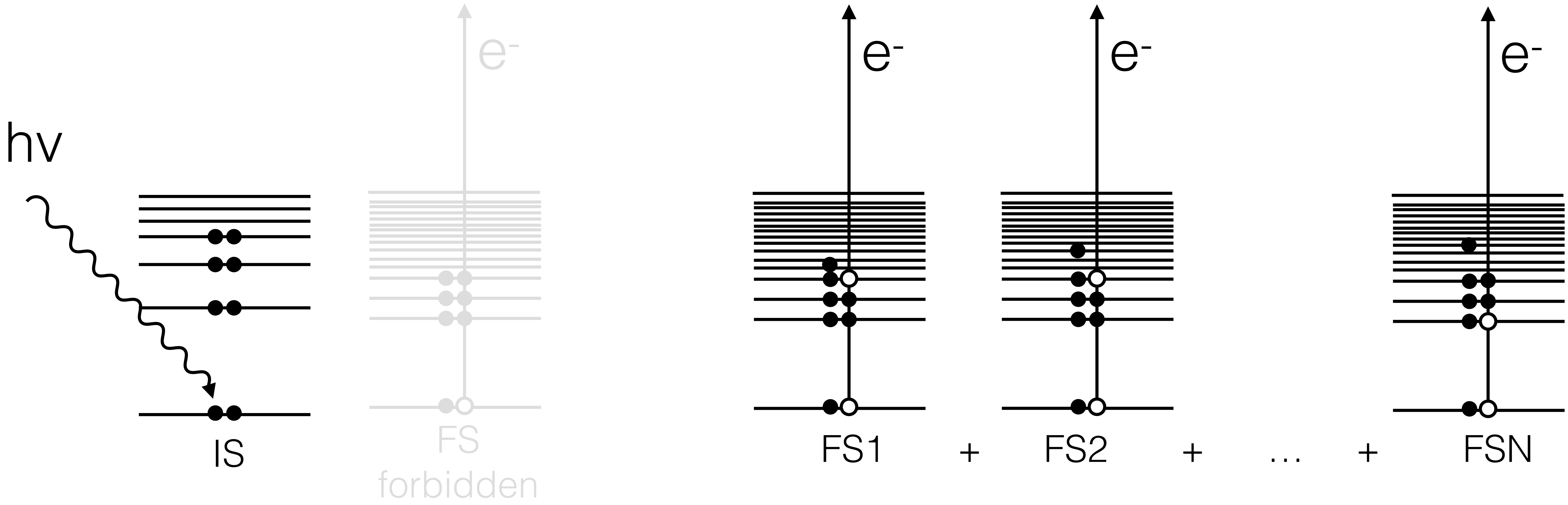
DS

- Orthogonality catastrophe makes main line asymmetric



DS

- Orthogonality catastrophe makes main line asymmetric



DS

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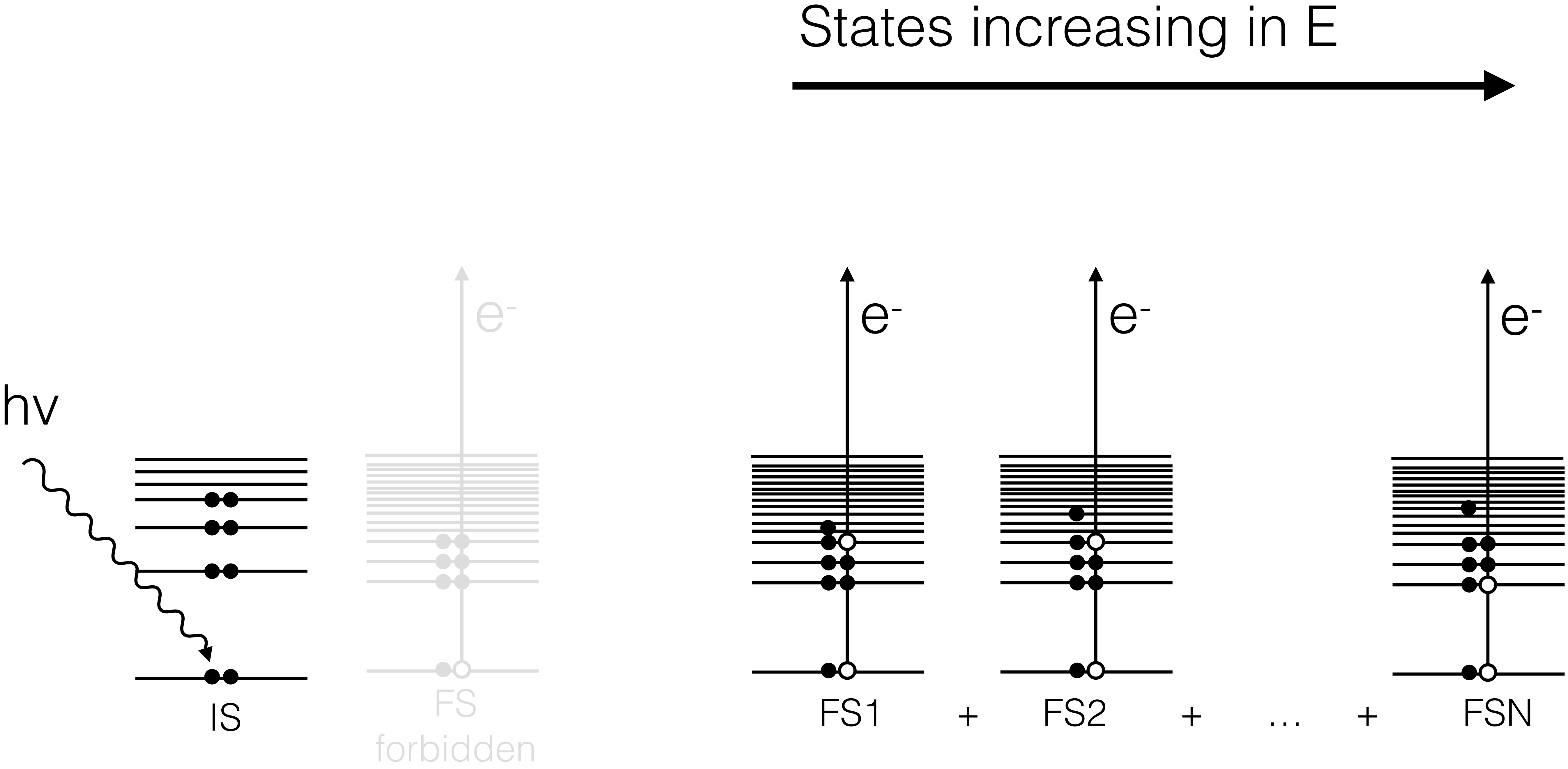


States increasing in E

hν

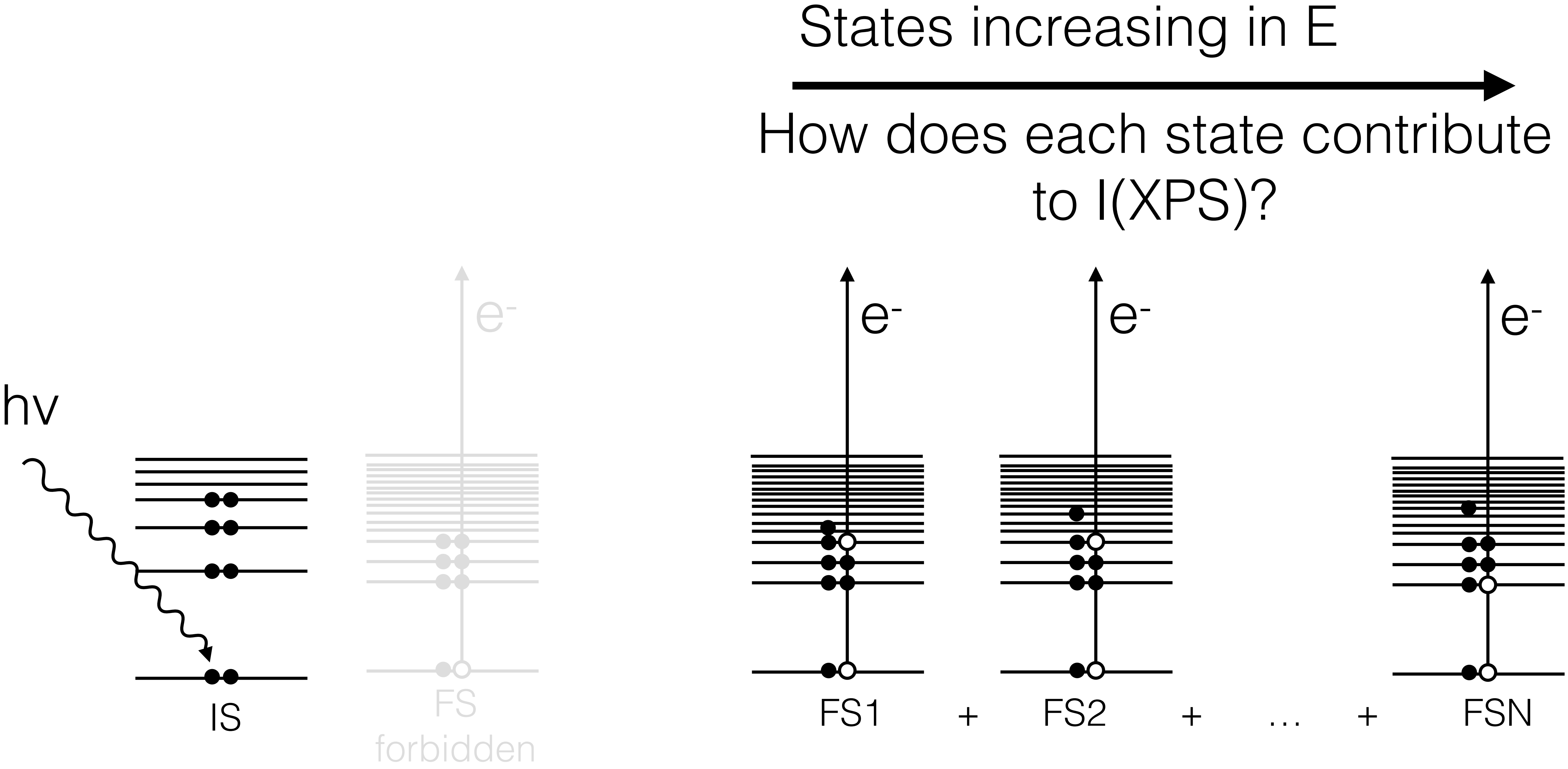
IS

FS
forbidden

FS1 + FS2 + … + FSN

DS

- Orthogonality catastrophe makes main line asymmetric

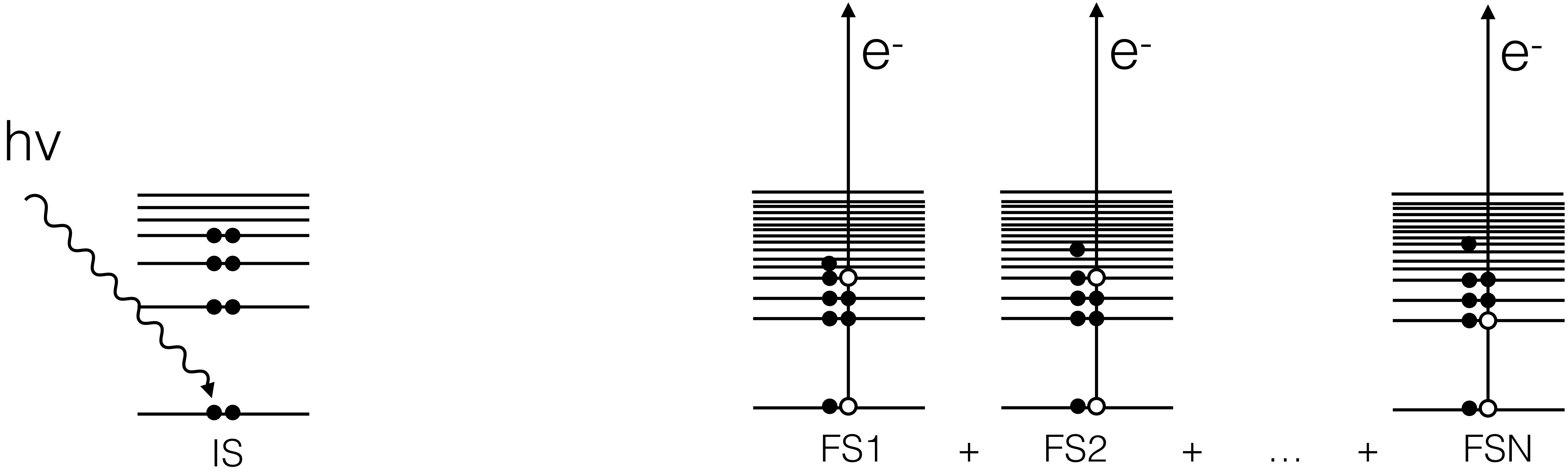


States increasing in E

How does each state contribute to I(XPS)?

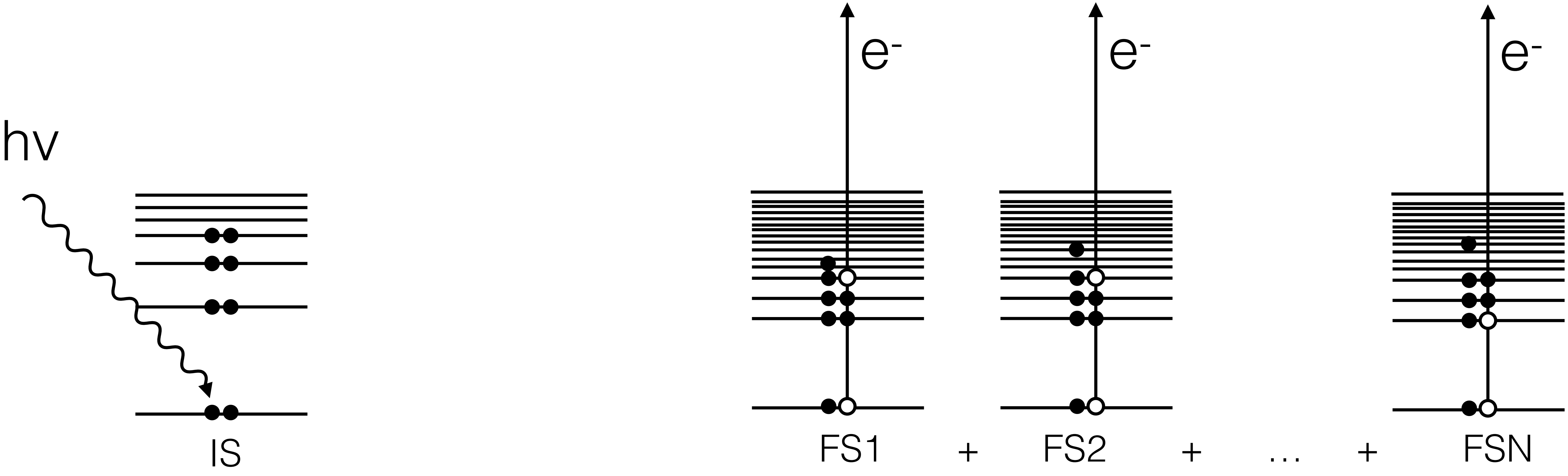
DS

- Orthogonality catastrophe makes main line asymmetric
- Probability for an excitation from i to j is M^2/ε_{ij}^2



DS

- Orthogonality catastrophe makes main line asymmetric
- Probability for an excitation from i to j is M^2/ε_{ij}^2
- Total probability density function is $P(E) \propto \int_{-\infty}^{\infty} \exp(-i\,E\,t)\,\exp\left(\sum_{ij} \frac{M^2 \exp(i\,\epsilon_{ij}\,t) - 1}{\epsilon_{ij}^2}\right) dt$



DS

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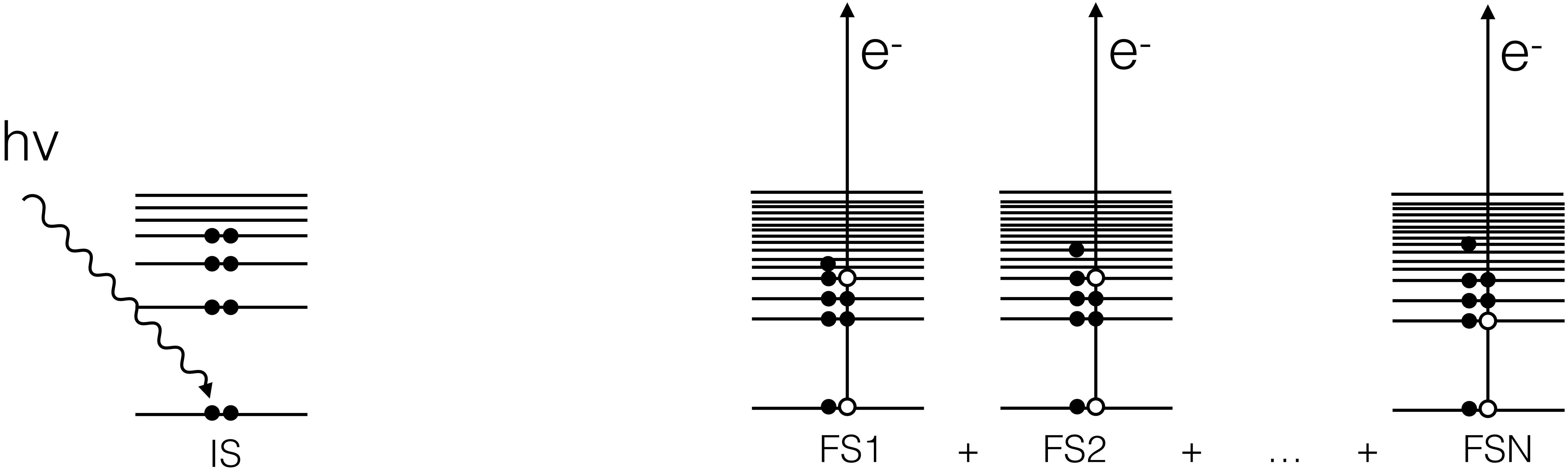
- Convolve with Lorentzian and Gaussian to get line shape



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- Total probability density function is $P(E) \propto \int_{-\infty}^{\infty} \exp(-i E t) \exp\left(\boxed{\sum_{ij} \frac{M^2 \exp(i \epsilon_{ij} t) - 1}{\epsilon_{ij}^2}}\right) dt$
- Convolve with Lorentzian and Gaussian to get line shape
- Make it solvable by assuming
    - matrix elements small and equal
    - DOS continuous ⇒ replace sum with integral over joint DOS
    - DOS constant ⇒ JDOS is linear

DS

- Assumptions restrict validity to neighborhood near Ef!

Requirement of constant DOS problematic

- I(E) integrals do not coverage because JDOS is linear

$$\mathtt{I}\,(\mathtt{E}) \sim \int_{-\infty}^{\infty} e^{-i E t}\, e^{-\lambda\, |t|}\, e^{-\frac{\sigma^2 t^2}{2}}$$

$$\exp\left(\int_0^{\infty} \mathrm{JDOS}\,(E)\, \frac{e^{i E' t-1}}{(E')^2}\, dE'\right) dt$$

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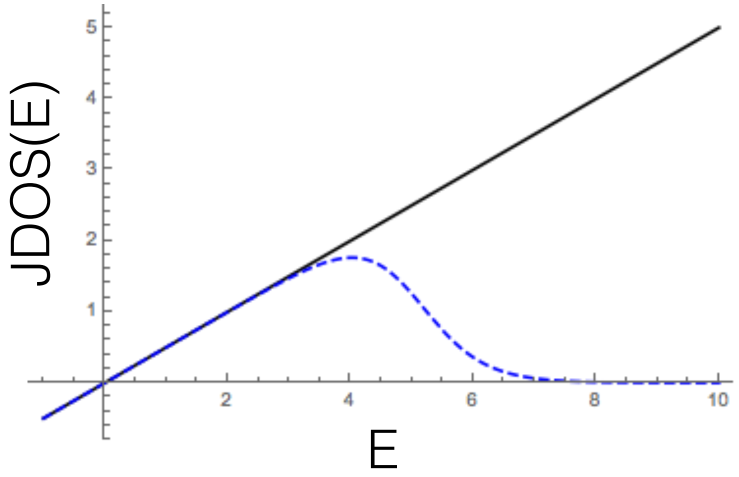
- JDOS must tend to zero as E goes to infinity



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- I(E) integrals do not coverage because JDOS is linear

$$I\,(E) \sim \int_{-\infty}^{\infty} e^{-i\,E\,t}\, e^{-\lambda\,|t|}\, e^{-\frac{\sigma^2\,t^2}{2}}\, \exp\left(\int_0^{\infty} \text{JDOS}\,(E)\, \frac{e^{i\,E'\,t-1}}{(E')^2}\, dE'\right) dt$$

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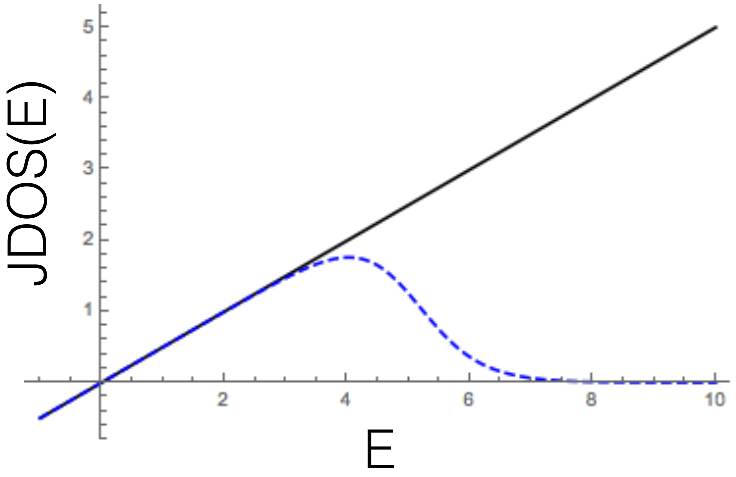

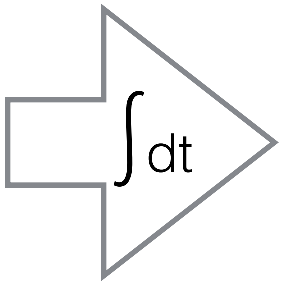

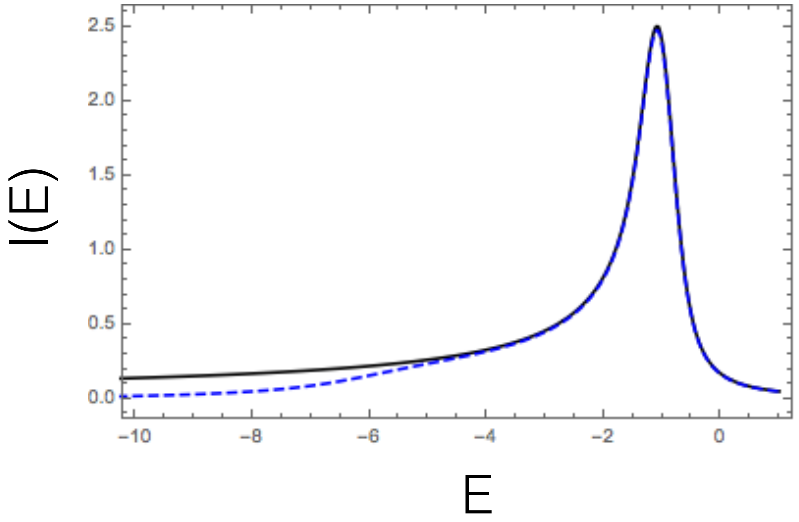

Requirement of constant DOS problematic

- I(E) integrals do not coverage because JDOS is linear

$$I\,(E) \sim \int_{-\infty}^{\infty} e^{-i E t}\, e^{-\lambda\,|t|}\, e^{-\frac{\sigma^2 t^2}{2}} \exp\left(\int_0^{\infty} \text{JDOS}\,(E)\, \frac{e^{i E' t-1}}{(E')^2}\, dE'\right) dt$$

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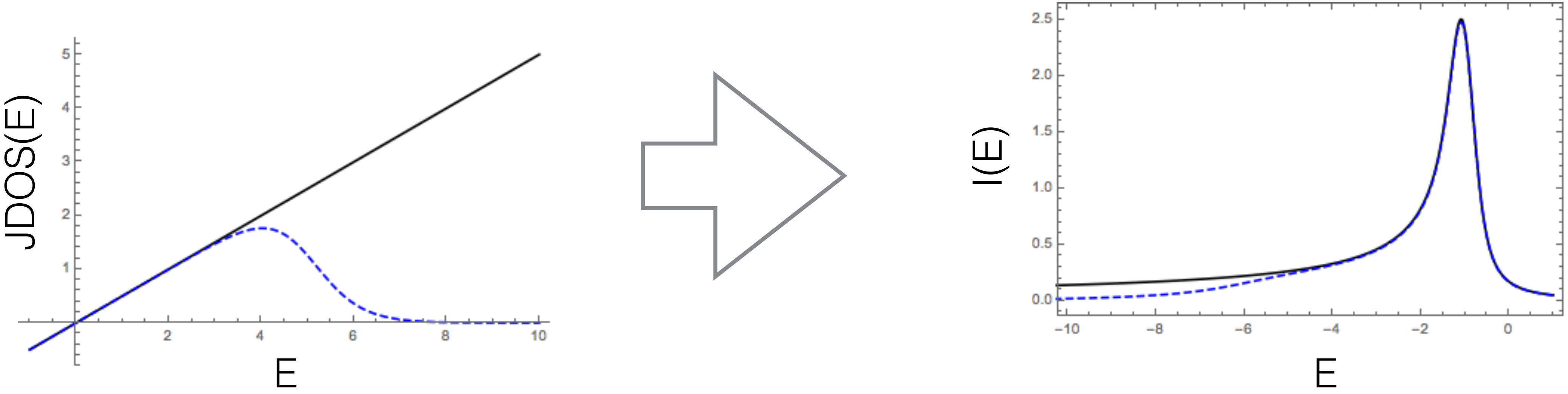
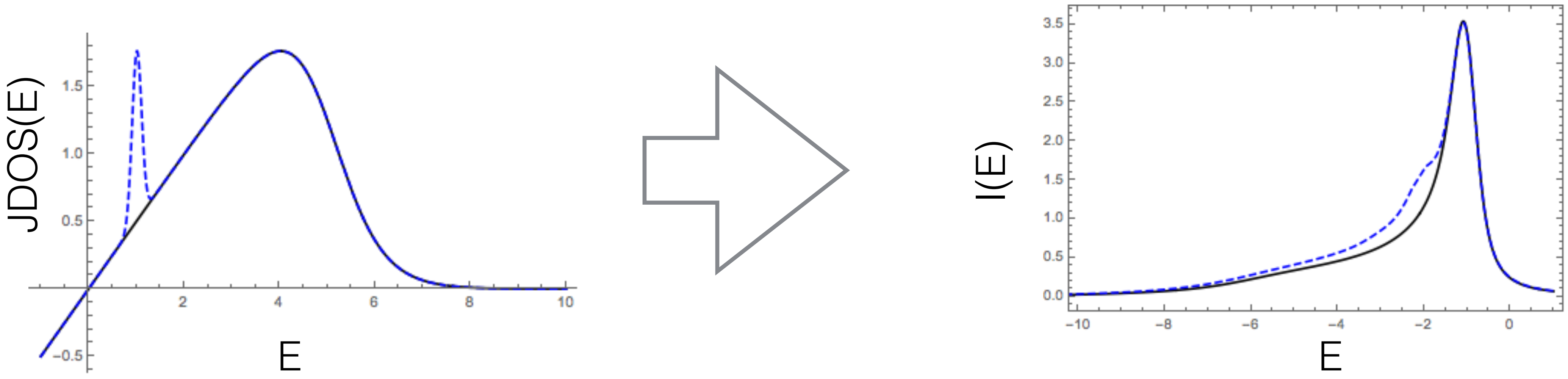
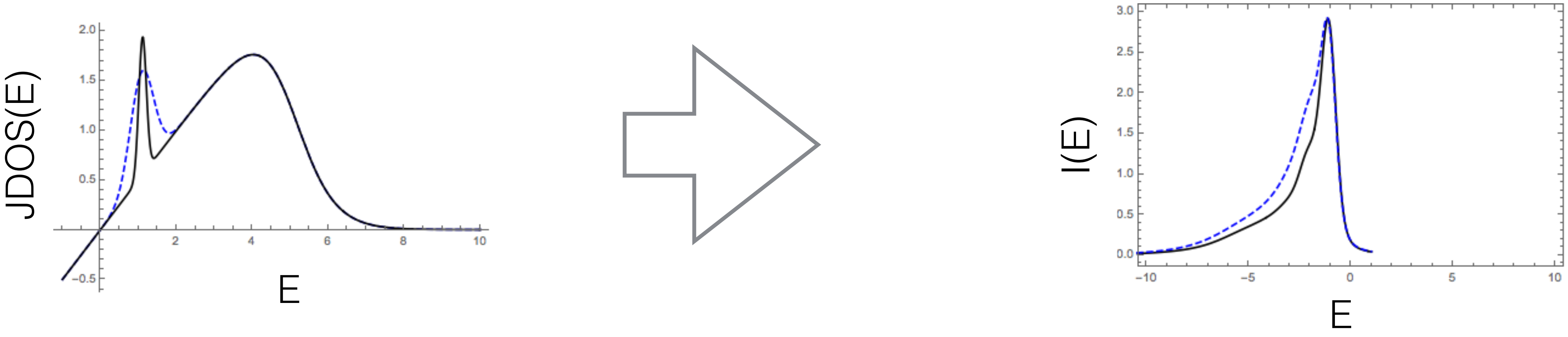


- Features in DOS near Ef will appear in spectra

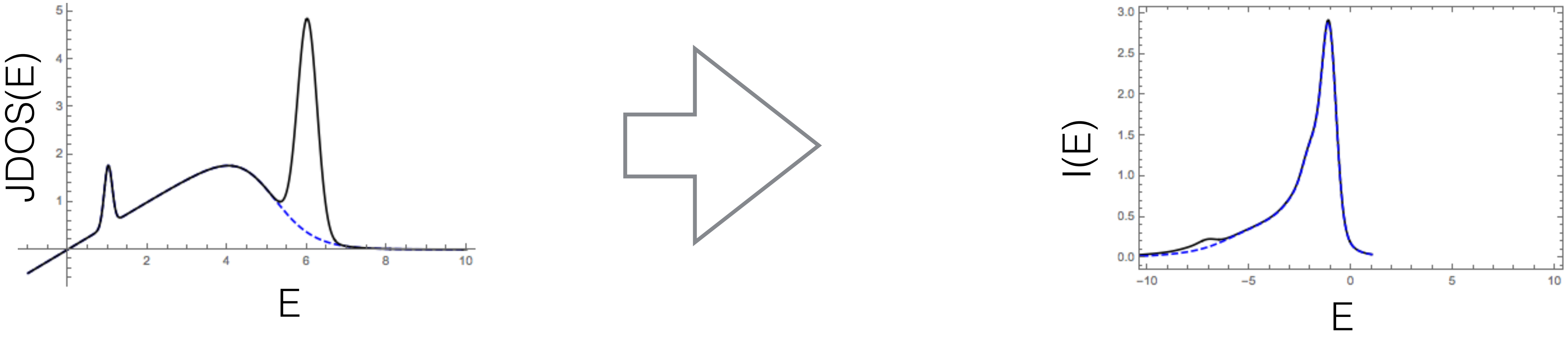


JDOS Features

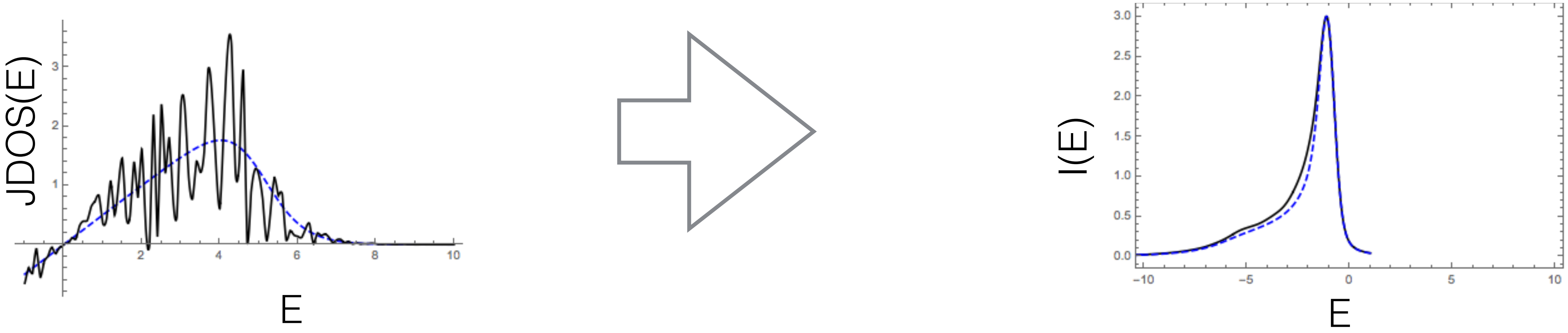
- Size and shape of of JDOS features influence peak shape



- High energy features have weaker influence

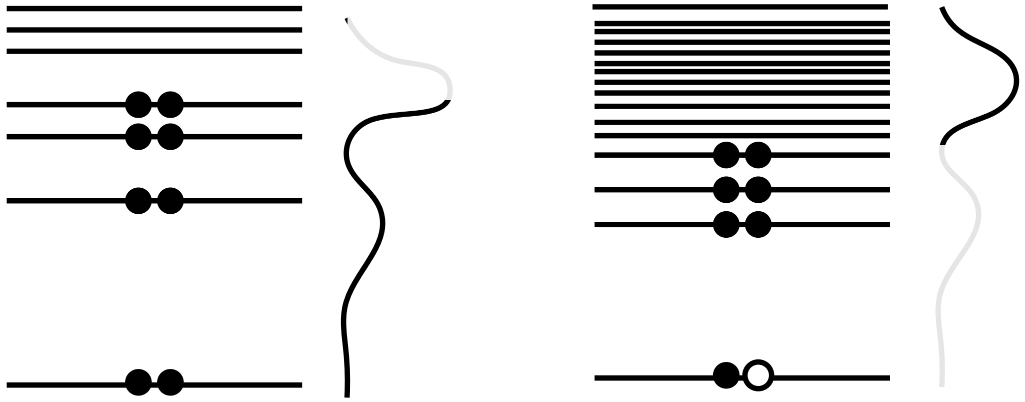


- JDOS features can appear averaged

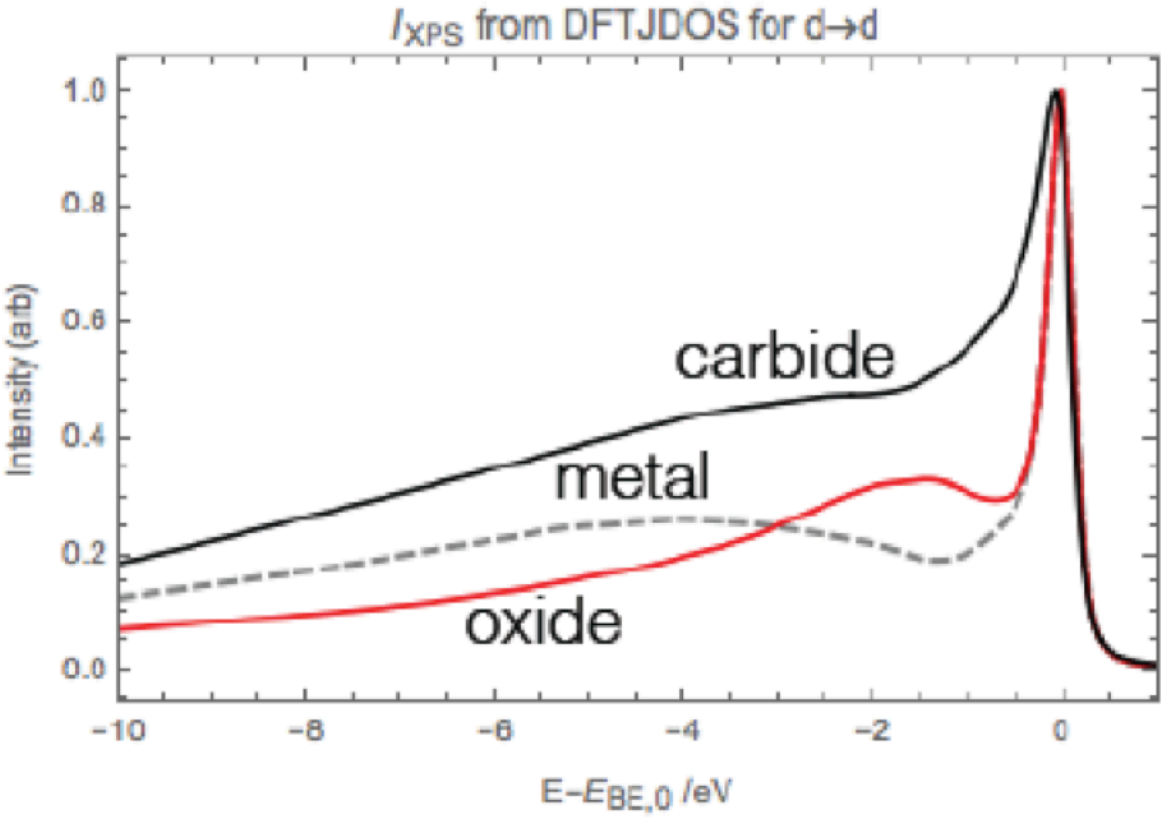


JDOS from DFT

- Can just use JDOS from DFT calculations (still ignoring matrix elements)
- Use occupied IS DOS and unoccupied FS DOS to generate JDOS



∫dE’ IS DOS(E’) × FS DOS(E’+E) = JDOS



Non-metallic?

- Primary screening is charge transfer from ligands
- Return to CI picture

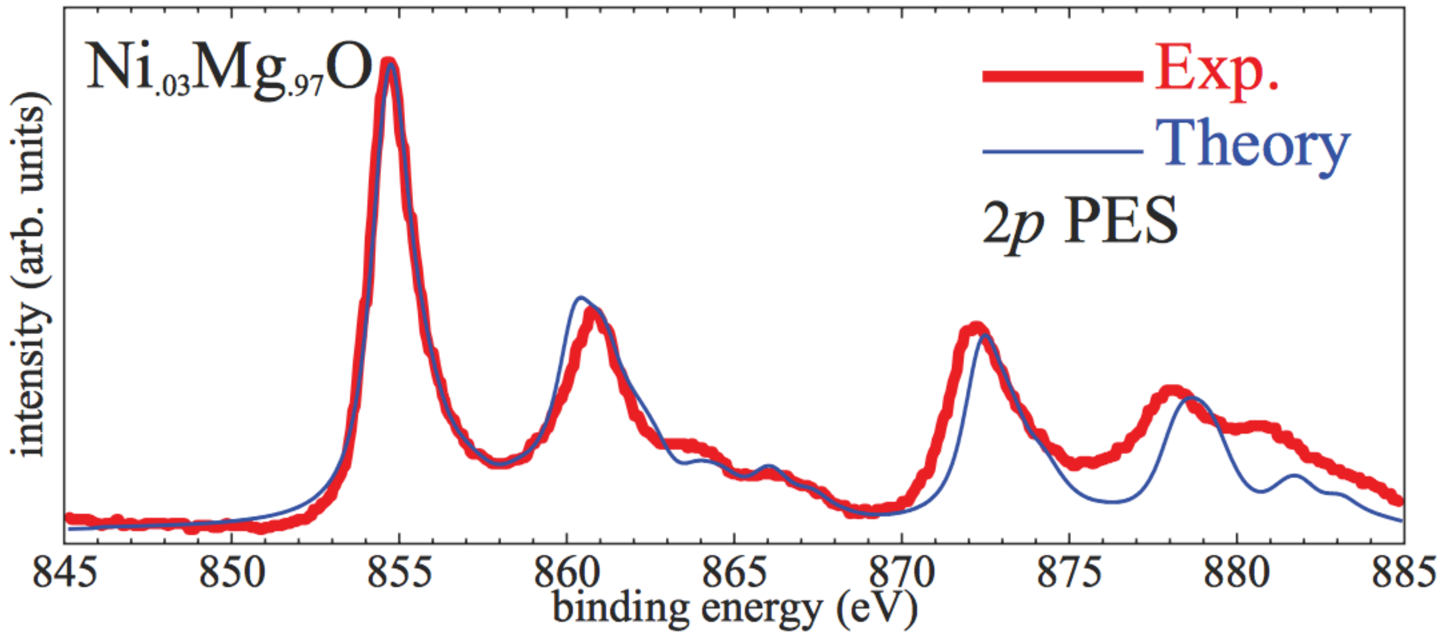
$$\psi_0 = \sum_i c_i \left| d^{n+i} \underline{L}^i \right\rangle$$

$$U \equiv \left[E\left(d^{n+1}\right) + E\left(d^{n-1}\right) \right] - 2E\left(d^n\right)$$

$$\Delta \equiv E\left(d^{n+1} \underline{L}^1\right) - E\left(d^n\right)$$

Local many-body problem

- Use Wannier functions from LDA to build local Hamiltonian and potential
- Include all local many body interactions

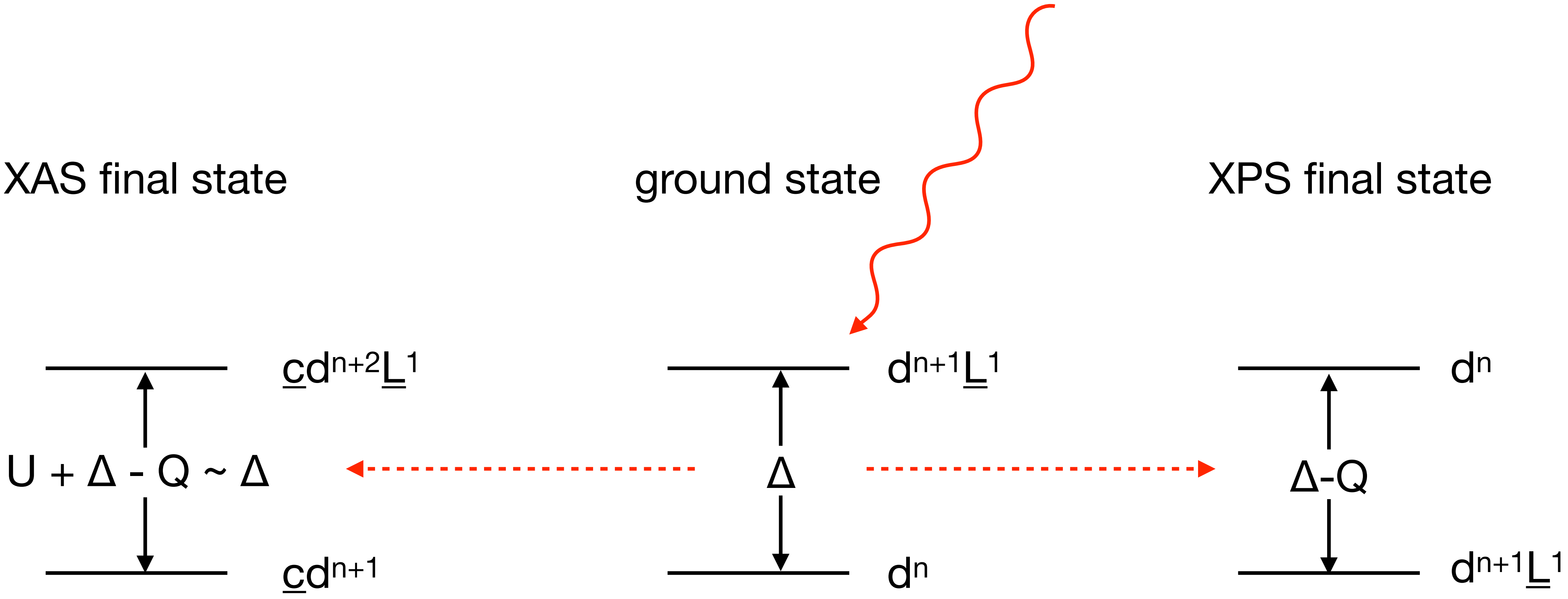


M.W. Haverkort, M. Zwierzycki, O.K. Andersen, PRB **85**, 165113 (2012).

- Nice results … but sensitive to U and Δ

U and Δ

- XAS is not sensitive to U and Δ because it is charge neutral
- XPS is very sensitive to U and Δ because valence electrons screen



XAS final state

$\underline{c}d^{n+2}\underline{L}^1$

$U + \Delta - Q \sim \Delta$

$\underline{c}d^{n+1}$

ground state

$d^{n+1}\underline{L}^1$

Δ

d^n

XPS final state

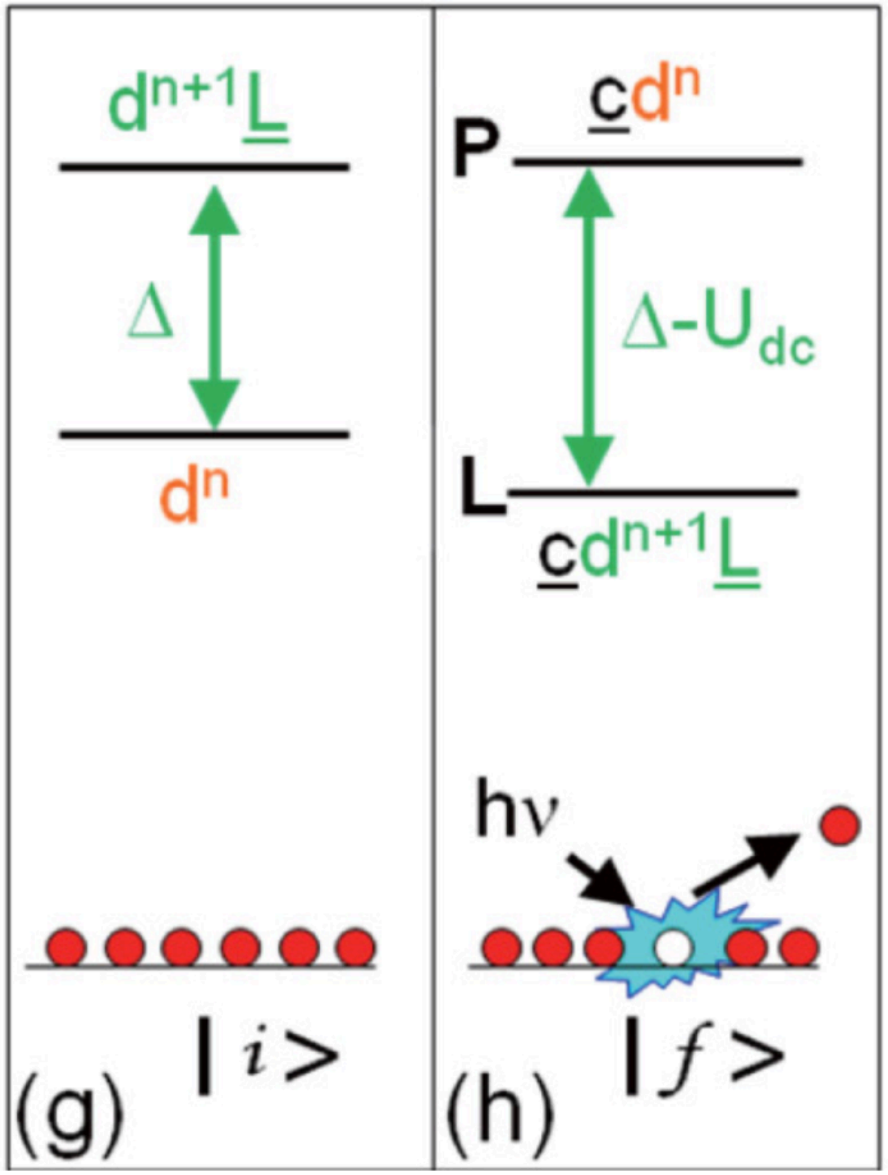
d^n

Δ-Q

$d^{n+1}\underline{L}^1$

And non-local screening

- Can even add non-local screening to channel to handle metallic and insulating systems within same framework



PHYSICAL REVIEW B **87**, 045108 (2013)

And non-local screening

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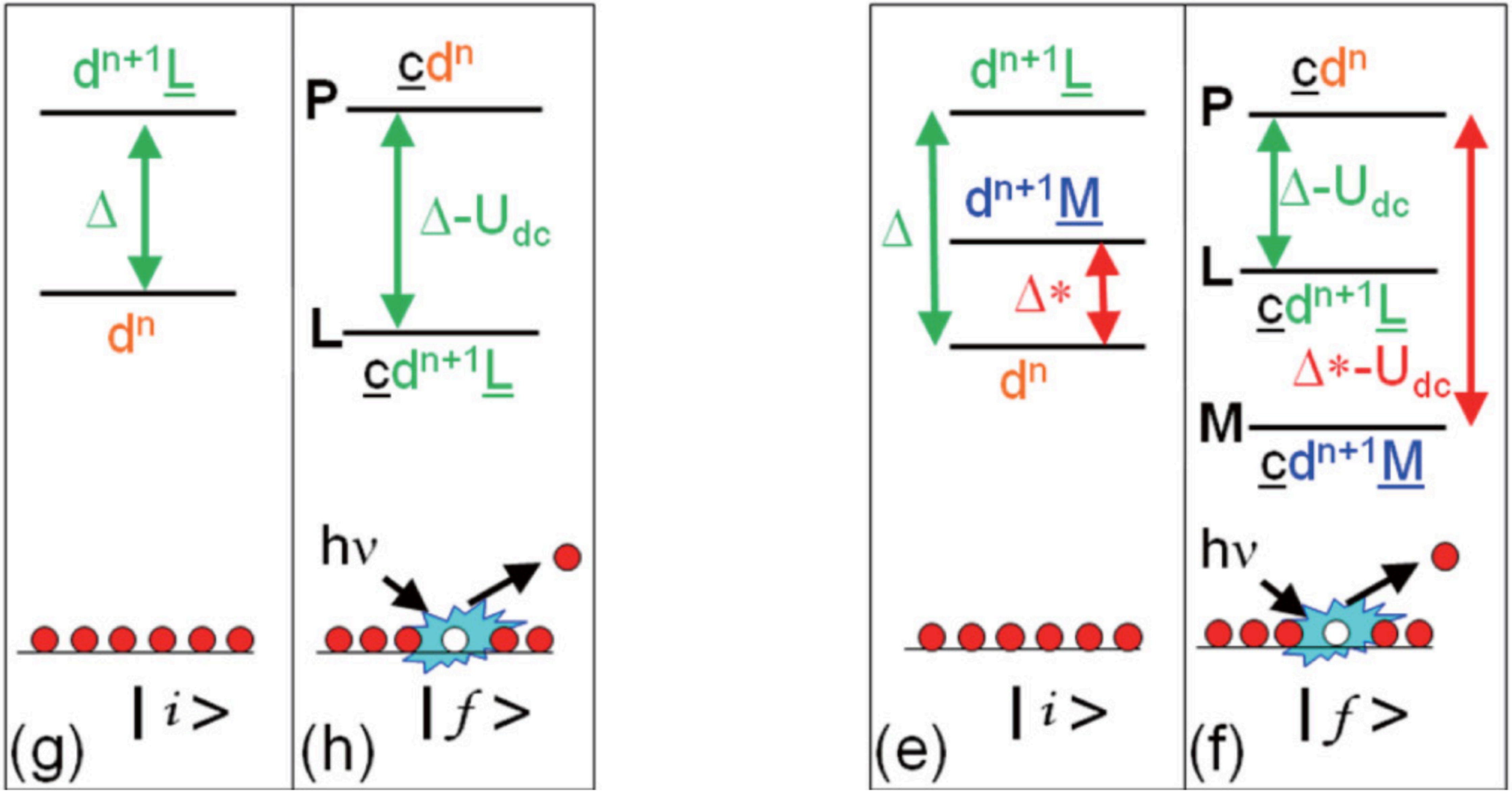

PHYSICAL REVIEW B **87**, 045108 (2013)

And non-local screening

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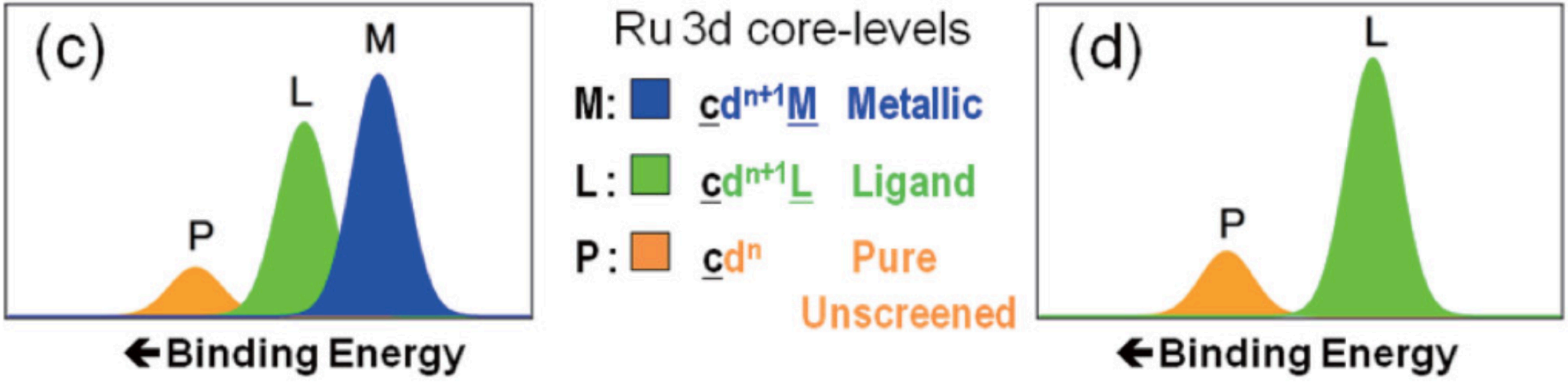
Schematic result for $Hg_2Ru_2O_7$ metal insulator transition



PHYSICAL REVIEW B **87**, 045108 (2013)

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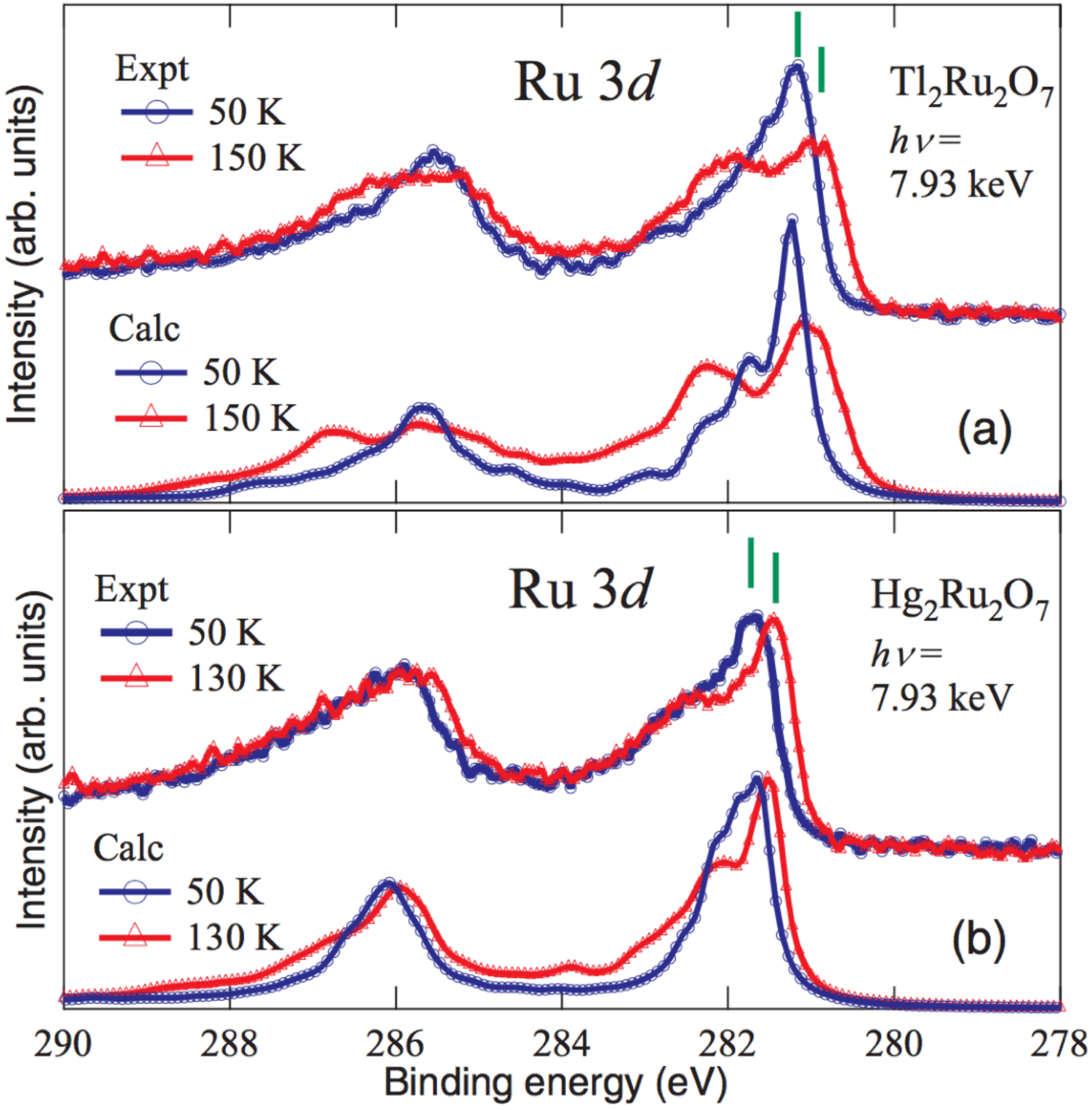
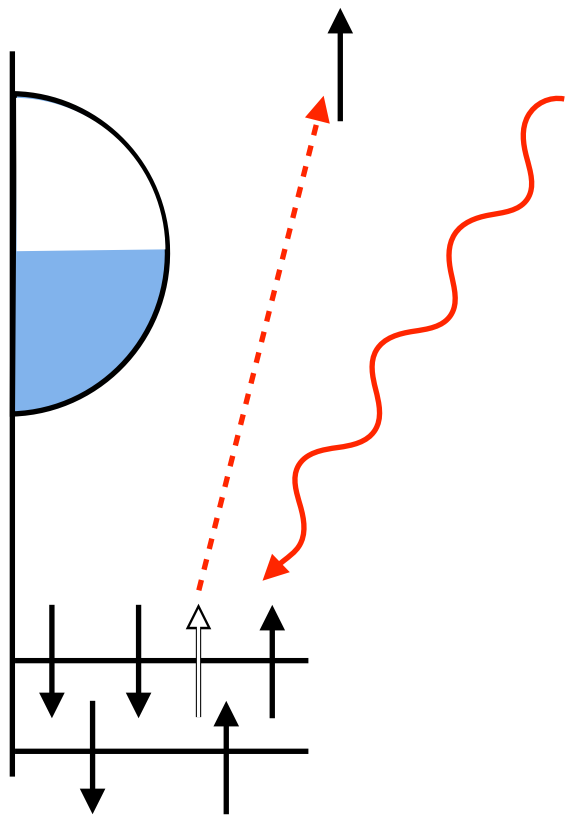


PHYSICAL REVIEW B **87**, 045108 (2013)

XPS summary

- Core level binding energies straight from DFT
- IPA gives a delta function
- Many body physics gives useful line shapes
    - Metallic systems can be tackled with DFT
    - Metallic and non-metallic line shapes can be computed with CI-approach



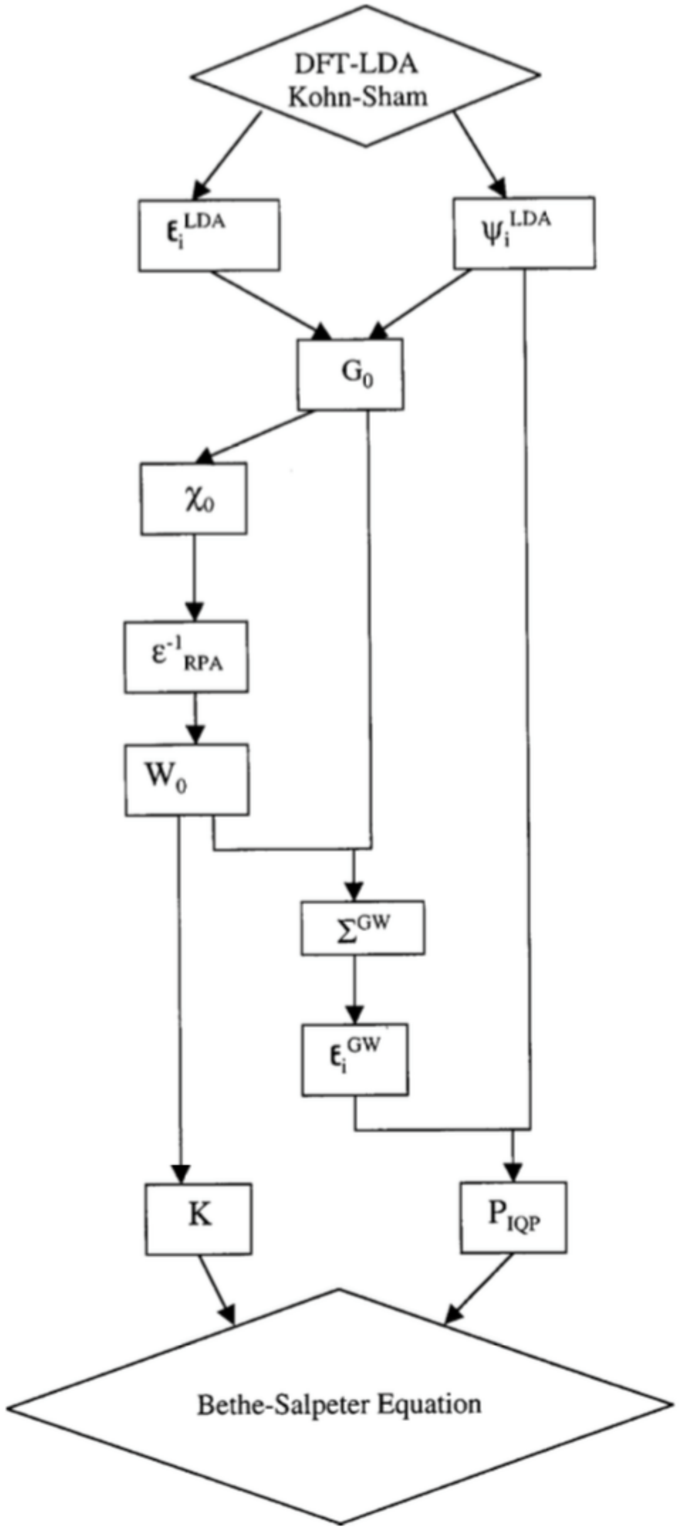
Bringing it all together

- Absorption and emission give complimentary information
    - Screening in XPS due to ligands and/or condition band
    - Screening in XAS from excited electron
    - In insulator XAS edge will not align with XPS BE!
- For non-correlated materials there are lots of options
    - XAS—BSE and IPE (for K edges) … in principle CI and DMFT
    - XPS—JDOS and CI and DMFT
    - Core level shift—Slater transition state, ΔSCF, initial state
- For correlated materials (DFT might even fail you so be careful) the options are limited
    - XAS—BSE for one-electron one-hole excitations otherwise CI and DMFT
    - XPS—CI and DMFT

Questions

BSE NEXAFS

- Treat core-hole correctly
- Get excitonic effects
- L2,3 branching
- Still only with 10% of peak positions and 20% peak strength
- Using NLPP possible errors with non-locality
- Use DFT wave functions -> missing -1/r tail in LDA may be problematic for clusters/surfaces
- Static electron-hole screening -> fine when exciton binding energy not too large otherwise might need Strinati equation
- RPA electron-hole screening -> kernel W evaluated with RPA can overestimate exciton binding energy



Rev. Mod. Phys., Vol. 74, No. 2, April 2002

Why does IPA work?

one-electron approach

$$
\begin{aligned}
h' &= \frac{p^2}{2m} + V'_C + \Sigma' \\
&\equiv h + [V'_C - V_C] + \left[\Sigma' - \Sigma\right].
\end{aligned}
$$

BSE

Why does IPA work?

one-electron approach

$$h' = \frac{p^2}{2m} + V'_C + \Sigma'$$

$$\equiv \boxed{h} + [V'_C - V_C] + \left[\Sigma' - \Sigma\right].$$

non-interacting response

BSE

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$$\equiv \boxed{h} + \boxed{[V'_C - V_C]} + [\Sigma' - \Sigma] .$$

non-interacting response

screened core hole

BSE

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$$\equiv h + [V'_C - V_C] + [\Sigma' - \Sigma] .$$

non-interacting response

screened core hole

dynamically screened exchange

BSE

Why does IPA work?

- Same quasi-particle hamiltonian

one-electron approach

$$h' = \frac{p^2}{2m} + V'_C + \Sigma'$$

$$\equiv h + [V'_C - V_C] + [\Sigma' - \Sigma] .$$

non-interacting response

screened core hole

dynamically screened exchange

BSE

$$h'_{\mathrm{eff}} = h + V_D(i) + V_X(i).$$

non-interacting response

Why does IPA work?

one-electron approach

$$h' = \frac{p^2}{2m} + V'_C + \Sigma'$$

$$\equiv h + [V'_C - V_C] + [\Sigma' - \Sigma].$$

non-interacting response

screened core hole

dynamically screened exchange

BSE

$$h'_{\text{eff}} = h + V_D(i) + V_X(i).$$

non-interacting response

direct screened core hole

Why does IPA work?

one-electron approach

$$h' = \frac{p^2}{2m} + V'_C + \Sigma'$$

$$\equiv h + [V'_C - V_C] + [\Sigma' - \Sigma].$$

$$V'_C(\vec{r}) - V_C(\vec{r}) \equiv V_i(\vec{r}) + \Delta V_{\mathrm{scf}}(\vec{r}).$$

bare potential

induced potential

BSE

$$h'_{\mathrm{eff}} = h + V_D(i) + V_X(i).$$

non-interacting response

direct screened core hole

Why does IPA work?

- Direct screened core hole analogous to BSE

one-electron approach

$$h' = \frac{p^2}{2m} + V'_C + \Sigma'$$

$$\equiv h + [V'_C - V_C] + [\Sigma' - \Sigma].$$

$$V'_C(\vec{r}) - V_C(\vec{r}) \equiv V_i(\vec{r}) + \Delta V_{\mathrm{scf}}(\vec{r}).$$

bare potential

induced potential

BSE

$$h'_{\mathrm{eff}} = h + V_D(i) + V_X(i).$$

$$V_D(\vec{r}) = \int \mathrm{d}^3 r' \, W(\vec{r}, \vec{r}\,'; \omega = 0) \times \frac{1}{N} \sum_{\vec{R}} |\chi^*_{i,\vec{R}}(\vec{r}\,')|^2 \exp[-\mathrm{i}(\vec{k} - \vec{q}) \cdot \vec{R}] \equiv V_i(\vec{r}) + V_{\mathrm{ind}}(\vec{r}),$$

bare potential induced potential

$$\boxed{\Delta V_{\mathrm{scf}}(\vec{r}) \approx V_{\mathrm{ind}}(\vec{r}).}$$

Why does IPA work?

one-electron approach

$$h' = \frac{p^2}{2m} + V_C' + \Sigma'$$

$$\equiv h + [V_C' - V_C] + [\Sigma' - \Sigma].$$

non-interacting response

screened core hole

dynamically screened exchange

BSE

$$h'_{\text{eff}} = h + V_D(i) + V_X(i).$$

non-interacting response

direct screened core hole

unscreened direct exchange

Why does IPA work?

one-electron approach

$$h' = \frac{p^2}{2m} + V'_C + \Sigma'$$

$$\equiv h + [V'_C - V_C] + [\Sigma' - \Sigma].$$

self energy is like dynamically screened exchange

$$\Sigma(\omega) = iG[v + (\epsilon^{-1}(\omega) - 1)v] \boxed{= V_{ex}} + \boxed{\Sigma_C(\omega)}$$

unscreened exchange

dynamic part of self energy

BSE

$$h'_{\text{eff}} = h + V_D(i) + \boxed{V_X(i).}$$

Why does IPA work?

- Exchange differs a bit

one-electron approach

$$h' = \frac{p^2}{2m} + V'_C + \Sigma'$$

$$\equiv h + [V'_C - V_C] + [\Sigma' - \Sigma] .$$

self energy is like dynamically screened exchange

$$\Sigma(\omega) = iG[v + (\epsilon^{-1}(\omega) - 1)v] = V_{ex} + \Sigma_C(\omega)$$

unscreened Fock exchange

dynamic part of self energy

BSE

$$h'_{\text{eff}} = h + V_D(i) + V_X(i).$$

BSE exchange is non-local unscreened for BSE hamiltonian

$$V_X = \hat{a}_c^\dagger(\mathbf{r},\sigma)\hat{a}_b(\mathbf{r}',\sigma')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\hat{a}_c(\mathbf{r}',\sigma)\hat{a}_b^\dagger(\mathbf{r},\sigma')$$

creation annihilation of e/h pairs

$$\boxed{\Sigma' - \Sigma = V_X(i) + \Delta V_{ex} + \Delta\Sigma_C,}$$

change in valence relaxation for exchange

change in dynamic self energy

Why does IPA work?

one-electron approach

$$h' = \frac{p^2}{2m} + V'_C + \Sigma'$$

$$\equiv h + [V'_C - V_C] + \left[\Sigma' - \Sigma\right].$$

BSE

$$h'_{\mathrm{eff}} = h + V_D(i) + V_X(i).$$

$$\boxed{h = h}$$

$$\boxed{\Delta V_{\mathrm{scf}}(\vec{\boldsymbol{r}}) \approx V_{\mathrm{ind}}(\vec{\boldsymbol{r}}).}$$

$$\boxed{\Sigma' - \Sigma = V_X(i) + \Delta V_{ex} + \Delta\Sigma_C,}$$

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BSE

$$h'_{\text{eff}} = h + V_D(i) + V_X(i).$$

$$\boxed{h = h}$$

$$\boxed{\Delta V_{\text{scf}}(\vec{r}) \approx V_{\text{ind}}(\vec{r}).}$$

$$\boxed{\Sigma' - \Sigma = V_X(i) + \Delta V_{ex} + \Delta\Sigma_C,}$$

terms evaluated locally

Why does IPA work?

one-electron approach

$$h' = \frac{p^2}{2m} + V'_C + \Sigma'$$

$$\equiv h + [V'_C - V_C] + \left[\Sigma' - \Sigma\right].$$

BSE

$$h'_{\text{eff}} = h + V_D(i) + V_X(i).$$

$$\boxed{h = h}$$

$$\boxed{\Delta V_{\text{scf}}(\vec{r}) \approx V_{\text{ind}}(\vec{r}).}$$

$$\boxed{\Sigma' - \Sigma = V_X(i) + \Delta V_{ex} + \Delta\Sigma_C,}$$

terms evaluated locally

For (deep) K edge there is no spin orbit and $\langle \boldsymbol{r} | \psi_i \rangle$ is localized so this does not matter

Why does IPA work?

one-electron approach

$$h' \equiv h + [V'_C - V_C] + [\Sigma' - \Sigma].$$

BSE

$$h'_{\text{eff}} = h + V_D(i) + V_X(i).$$

(>100 eV) K edge both are equivalent!

$$\boxed{h = h}$$

$$\boxed{\Delta V_{\text{scf}}(\vec{\boldsymbol{r}}) \approx V_{\text{ind}}(\vec{\boldsymbol{r}}).}$$

$$\boxed{\Sigma' - \Sigma = V_X(i);}$$

L$_{\text{II,III}}$, M$_{\text{II,III}}$, … edges not so lucky

$$\boxed{h = h}$$

$$\boxed{\Delta V_{\text{scf}}(\vec{\boldsymbol{r}}) \approx V_{\text{ind}}(\vec{\boldsymbol{r}}).}$$

$$\boxed{\Sigma' - \Sigma = V_X(i) + \Delta V_{ex} + \Delta\Sigma_C;}$$