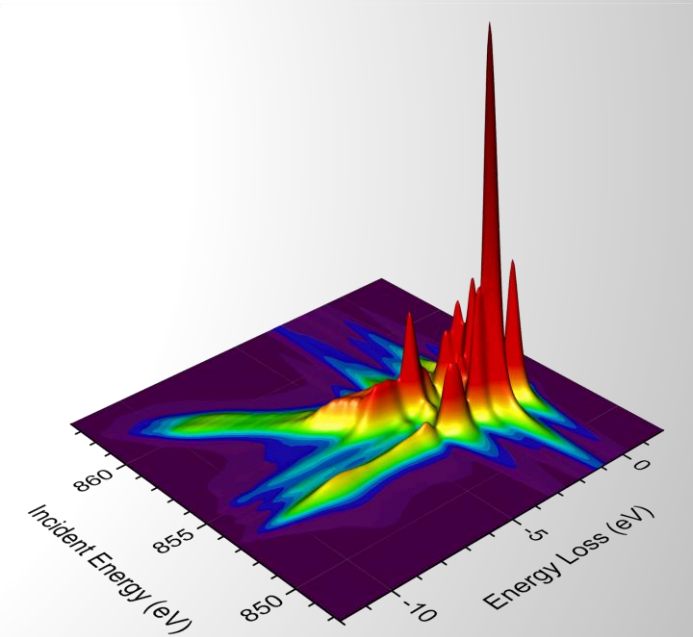# Analysis of soft XAS and RIXS with multiplet models using Quanty

Part 1: Understanding the Spectra

Part 2: Quanty Computations

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June 20, 2023

Interpretation of Data

XAS and RIXS data can contain a lot of valuable information, but it is often not easy to interpret

There are three main approaches toward extracting information from the data:

1. Comparison to reference data

2. Sum rules

3. Model the data with some relevant theory

L$_3$ RIXS of Mn Oxides

Eur. Phys. J. Special Topics **169**, 199 (2009)

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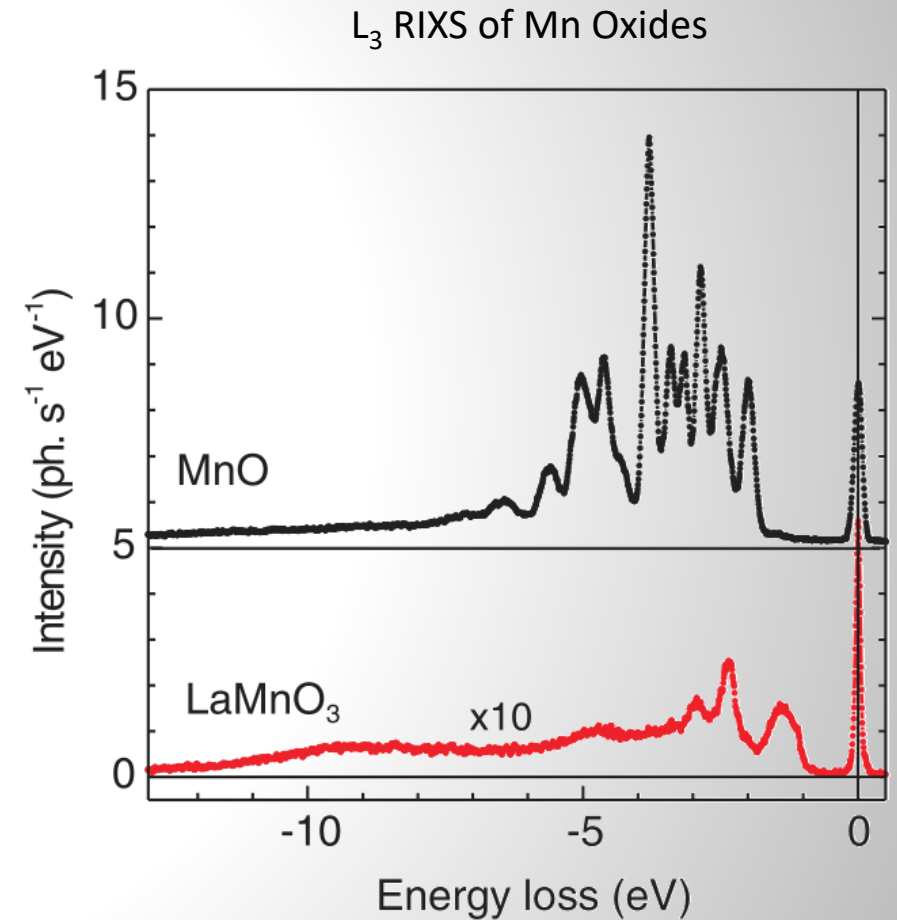
1. Comparison to Reference Data

Example: Studying Ti coordination on reconstructed $SrTiO_3$ (110) surface

XAS with Auger electron yield (AEY) is more surface sensitive than total/secondary electron yield (TEY)

Comparison to reference spectra reveals Ti tetrahedra on the surface of this compound which has only octahedra in bulk
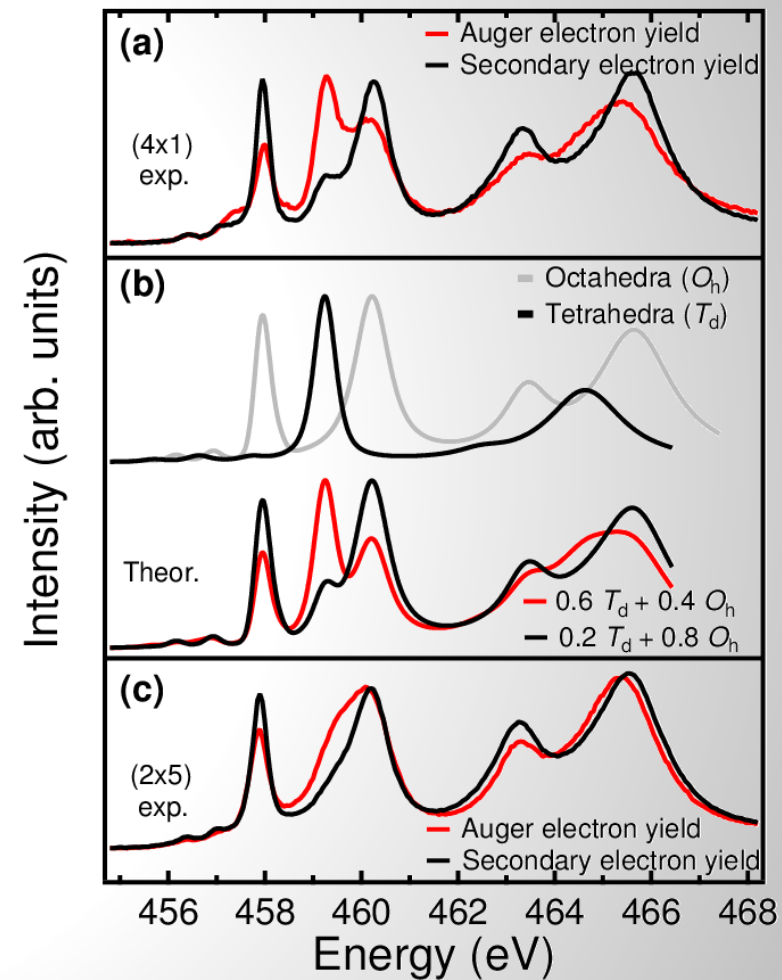
2. Sum Rules

Sum rules provide a way to **get information directly** from the experimental data

Different combinations of **polarized spectra** can provide ground state **expectation values**

Consequence of the dipole operator acting on shells with specific azimuthal quantum numbers

In general, for XAS we have **dipole matrix elements** of the form

$$\langle f | \boldsymbol{\varepsilon} \cdot \boldsymbol{r} | i \rangle = \left\langle f \left| \varepsilon^1 r C_1^{(1)} + \varepsilon^0 r C_0^{(1)} + \varepsilon^{-1} r C_{-1}^{(1)} \right| i \right\rangle$$

Considering the angular parts of the wavefunctions in conjunction with the normalized spherical harmonics $C_q^{(1)}$ leads to the **sum rules** for various polarized spectra.

Linear Polarization and Orbital Occupation Sum Rules

For linear polarized light, on can derive sum rules which relate to orbital occupations

For example, with $s \rightarrow p$ XAS one can determine the number of holes $\underline{n}$ in $p_x/p_y/p_z$ orbitals:

$$\frac{I_{E||\alpha}}{I_{E||x} + I_{E||y} + I_{E||z}} = \frac{\underline{n}_\alpha}{\underline{n}} \qquad \alpha \in \{x, y, z\}$$

Example: linear dichroism in XAS of nickelate heterostructures determines relative occupation of $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals

$$X = \frac{\underline{n}_{3z^2-r^2}}{\underline{n}_{x^2-y^2}} = \frac{3I_{E||z}}{4I_{E||x} - I_{E||z}}$$
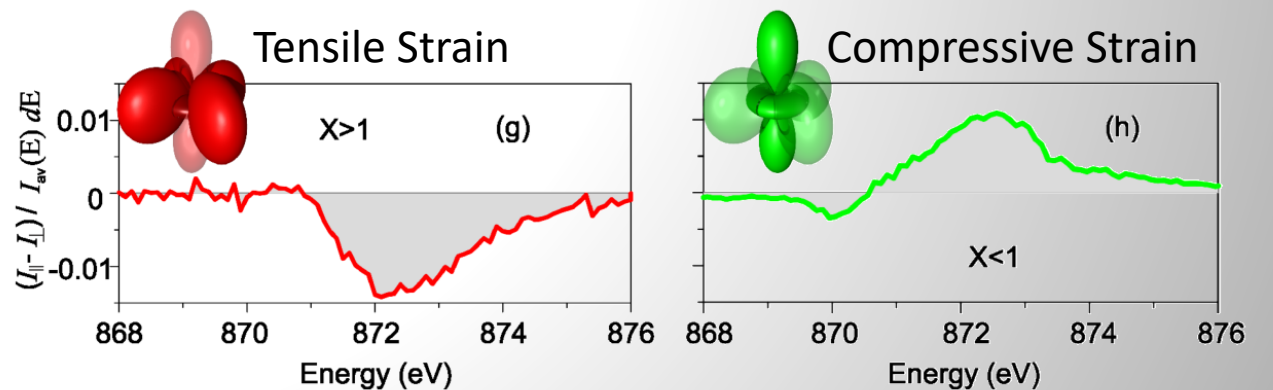
With circular polarized light, we can determine the orbital and spin moments in ferromagnetic materials

$$m_{\text{orb}} = -\frac{4 \int_{L_3+L_2} (\mu_+ - \mu_-)\, d\omega}{3 \int_{L_3+L_2} (\mu_+ + \mu_-)\, d\omega} (10 - n_{3d})$$

$$m_{\text{spin}} = -\frac{6 \int_{L_3} (\mu_+ - \mu_-)\, d\omega - 4 \int_{L_3+L_2} (\mu_+ - \mu_-)\, d\omega}{\int_{L_3+L_2} (\mu_+ + \mu_-)\, d\omega} \times (10 - n_{3d})$$

*Caution: m_{spin} expression is simplified, and is not always applicable
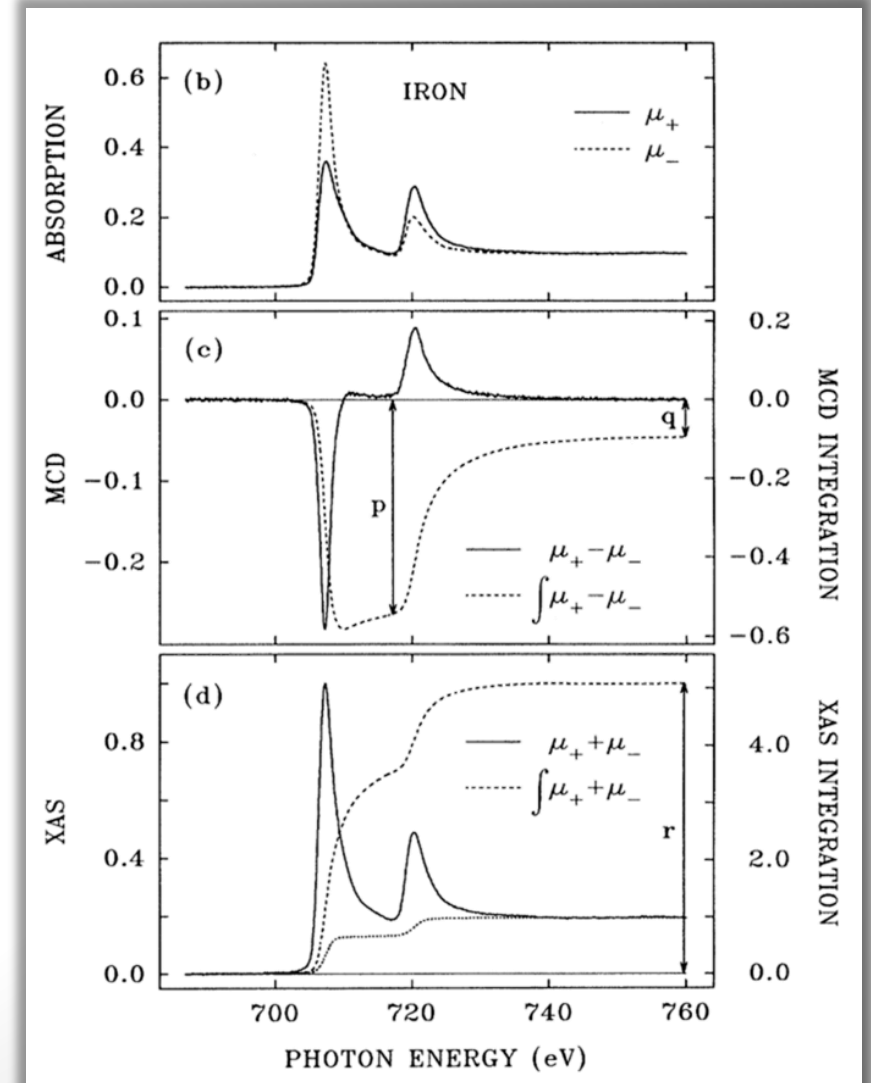
3. Modelling Data using Theory

Simulate/fit spectra using a theoretical model

Model is constructed to capture the physics which govern the particular spectral response

Usually a combination of three different goals:

- Understand what controls different spectral features

- Determine model parameters from fits to experiment

- Test the accuracy of your theory

Modelling Data using Theory

Use quantum mechanics to model spectra

For a given model Hamiltonian:

- Find ground state $|\Psi_0\rangle$

$$H\Psi = E\Psi$$

- Calculate spectrum

$$S(\omega, \epsilon) = \sum_f \left|\langle \Psi_f | \epsilon \cdot \boldsymbol{r} | \Psi_0 \rangle\right|^2 \times \frac{\Gamma_f/\pi}{(E_0 + \omega - E_F)^2 + \Gamma_f^2}$$

- Apply experimental broadening (instrumental resolution)

$$I(\omega, \epsilon) = \int_{-\infty}^{+\infty} S(\omega', \epsilon) G(\omega - \omega') \, d\omega'$$

Local Models for XAS and RIXS
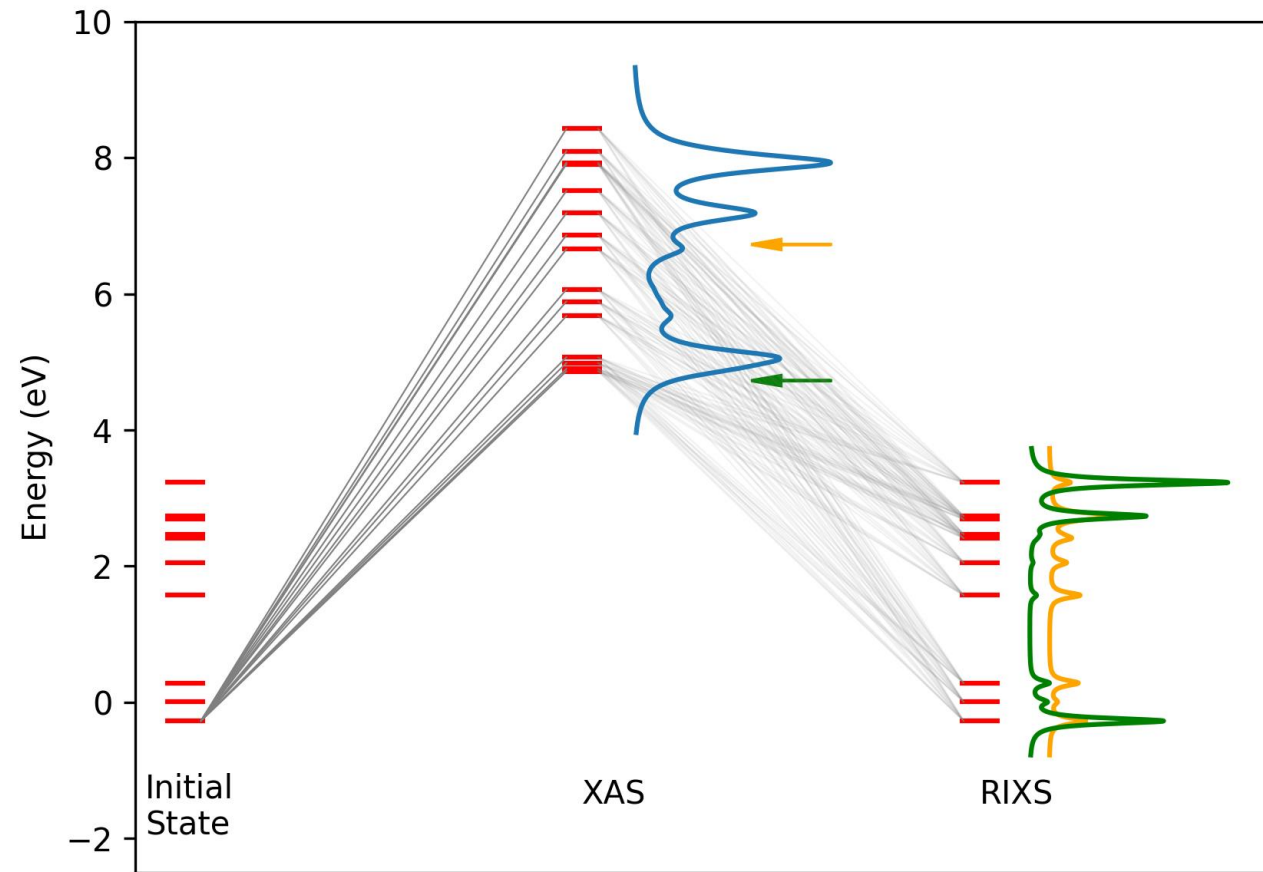
Modelling Data using Theory

Generally with core level spectroscopy, our model needs to capture local many-electron physics

Some models, from more local to more extended:

Multi-electron isolated atom

Crystal field theory

Ligand field theory

Anderson impurity model

Non-interacting methods (DFT)

The best model to use will depend on what the material is, what the technique is, and what resonance we are looking at

We'll mainly focus on the resonances of correlated atoms, so we'll look at the local many-body models in more detail

L_3 RIXS of Mn Oxides
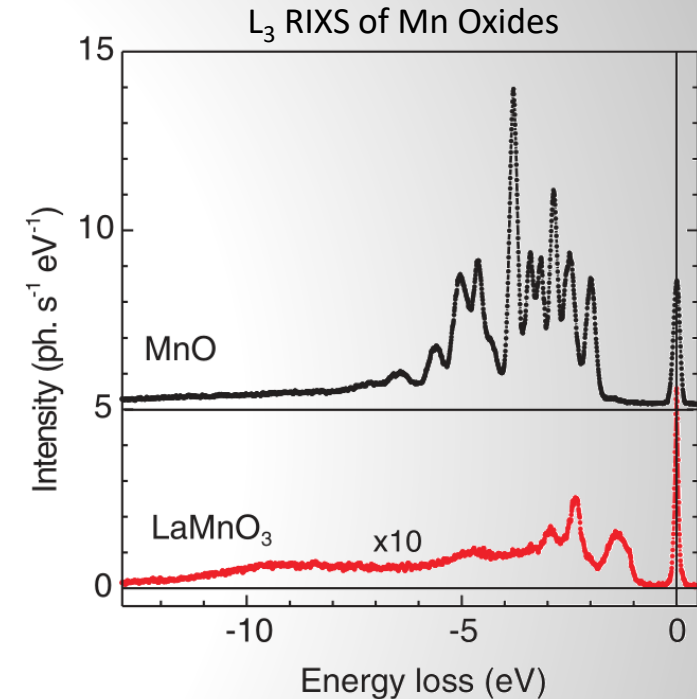
Isolated Atom

We are using QM, so need to solve the Schrödinger Equation: $\quad H\Psi = E\Psi$

Hamiltonian for an isolated atom:

$$H = -\frac{\hbar^2}{2m}\sum_j \nabla_j^2 - \sum_j \frac{Z_j e^2}{r_j} + \sum_{j>k} \frac{e^2}{r_{jk}} + \sum_j \xi(r_j)\boldsymbol{l}_j \cdot \boldsymbol{s}_j$$
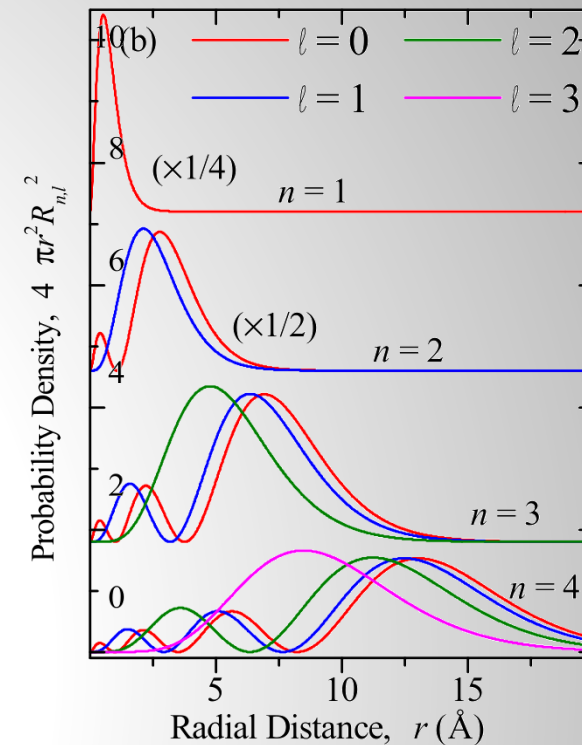
For a single electron atom (hydrogen), we have the usual radial and angular wavefunctions:

$$\psi_{nlm_l}(r,\theta,\phi) = R_{nl}(r)Y_{lm_l}(\theta,\phi)$$
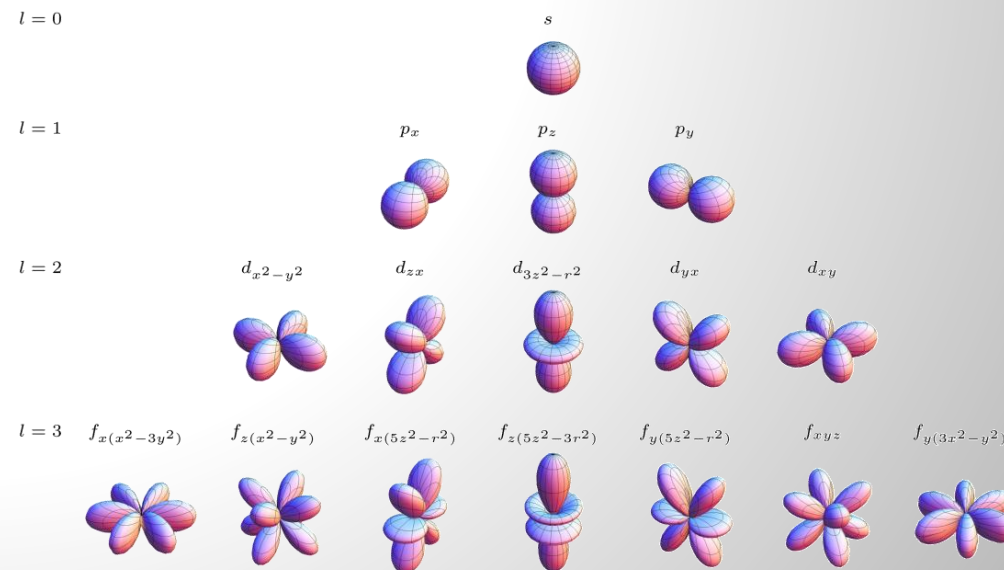
Isolated Atom

For spectroscopy, we do not need a full solution for the whole atom

Just need the many-electron eigenstates of active subshells

The closed subshells just give rigid energy shifts of our eigenstates/spectra

So we define an effective H which gives the eigenstates of the open shells

$$H = -\frac{\hbar^2}{2m}\sum_j \nabla_j^2 - \sum_j \frac{Z_j e^2}{r_j} + \sum_{j>k} \frac{e^2}{r_{jk}} + \sum_j \xi(r_j)\boldsymbol{l}_j \cdot \boldsymbol{s}_j$$

Isolated Atom

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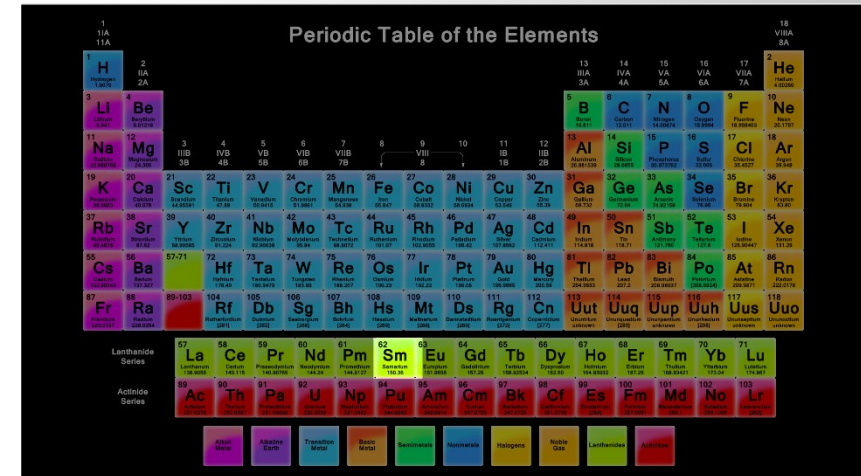
So we define an effective H which gives the eigenstates of the open shells

$$H = \sum_{j>k} \frac{e^2}{r_{jk}} + \sum_{j} \xi(r_j) \boldsymbol{l}_j \cdot \boldsymbol{s}_j$$

Now we switch to second quantization and solve the Schrödinger equation

Valence Shell Eigenstates for an Isolated Atom

Consider a Sm^{3+} ion:

$$1s^2 \ 2s^2 \ 2p^6 \ ... \ 4f^5$$

Since we only consider the 4f shell, we have a basis containing 14 spin-orbitals

The five 4f electrons can occupy any of the fourteen 4f spin orbitals, so we have

$$\binom{14}{5} = 2002 \text{ eigenstates in our basis}$$

Which corresponds to occupation determinants of the form:

$$|11111000000000\rangle, |11110100000000\rangle, |11110010000000\rangle, \text{ etc.}$$

Because of Coulomb and spin-orbit interactions, the states corresponding to the various arrangements of the two electrons will not in general be degenerate and will be linear combinations of the occupations

Valence Shell Eigenstates for an Isolated Atom

$$H = H_U^{ff} + H_{l \cdot s}^f$$

$$H_U^{ff} = \sum_{i,j} \frac{1}{2} \frac{e^2}{|r_i - r_j|} = \sum_{\tau_1,\tau_2,\tau_3,\tau_4} U_{\tau_1,\tau_2,\tau_3,\tau_4} \boldsymbol{f}_{\tau_1}^\dagger \boldsymbol{f}_{\tau_2}^\dagger \boldsymbol{f}_{\tau_3} \boldsymbol{f}_{\tau_4}$$

Coulomb interaction between pairs of electrons

Includes the usual monopole (Mott-Hubbard) part as well as multipole (multiplet) part

Valence Shell Eigenstates for an Isolated Atom
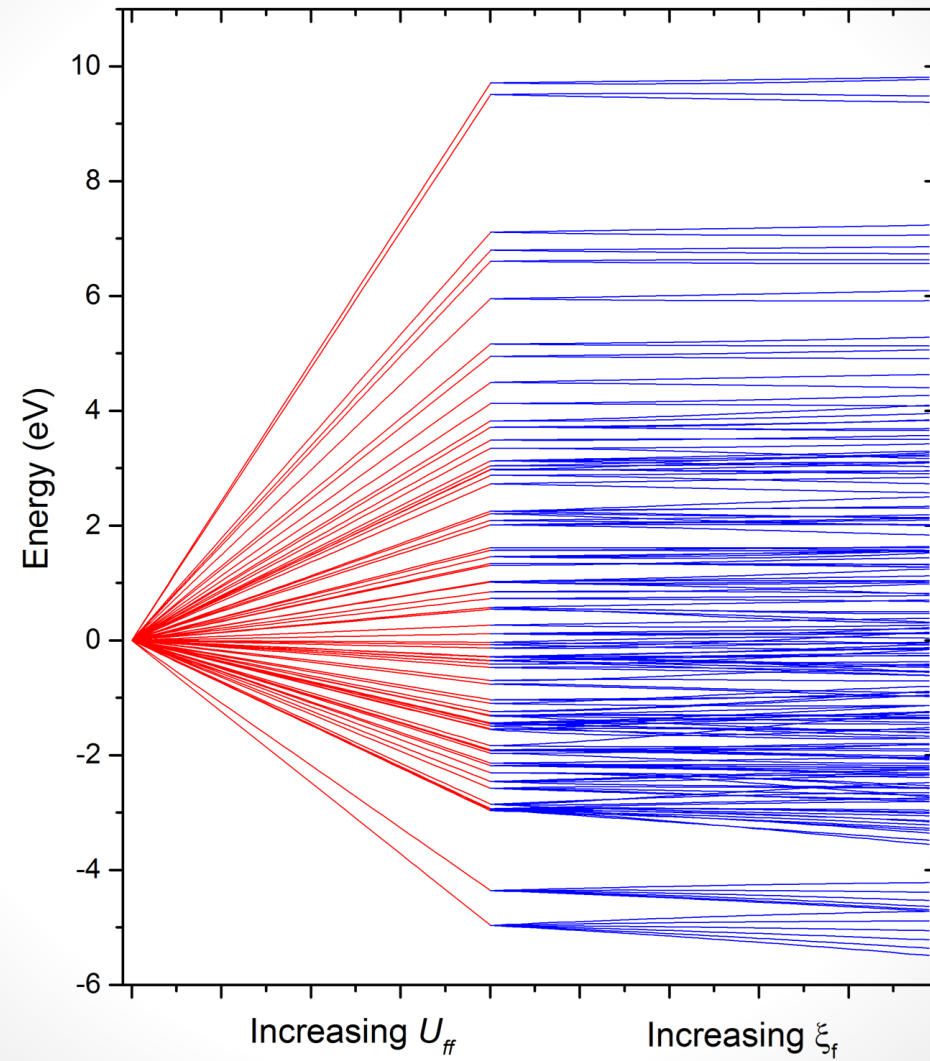
Spectroscopy (XAS) for an Isolated Atom

Now we start from the ground state we found, and calculate the spectrum as described earlier

Note that in the XAS final state, we have another open subshell (in this case the 3d shell because 3d – 4f XAS)

$$H = H_U^{ff} + H_U^{df} + H_{l \cdot s}^{f} + H_{l \cdot s}^{d}$$

If we diagonalize this with $3d^9$ and $4f^{5+1}$ occupations, we get the XAS final states.

Again they will be spread in energy due to Coulomb and spin orbit interactions.

Spectroscopy (XAS) for an Isolated Atom

To the right is Sm^{3+} XAS as we gradually add all terms of the final state atomic Hamiltonian.

The H_0 term is just the onsite energies.

We then add spin orbit interaction and then Coulomb interaction

Also shown is Sm^{2+}, which demonstrates the strong valence sensitivity
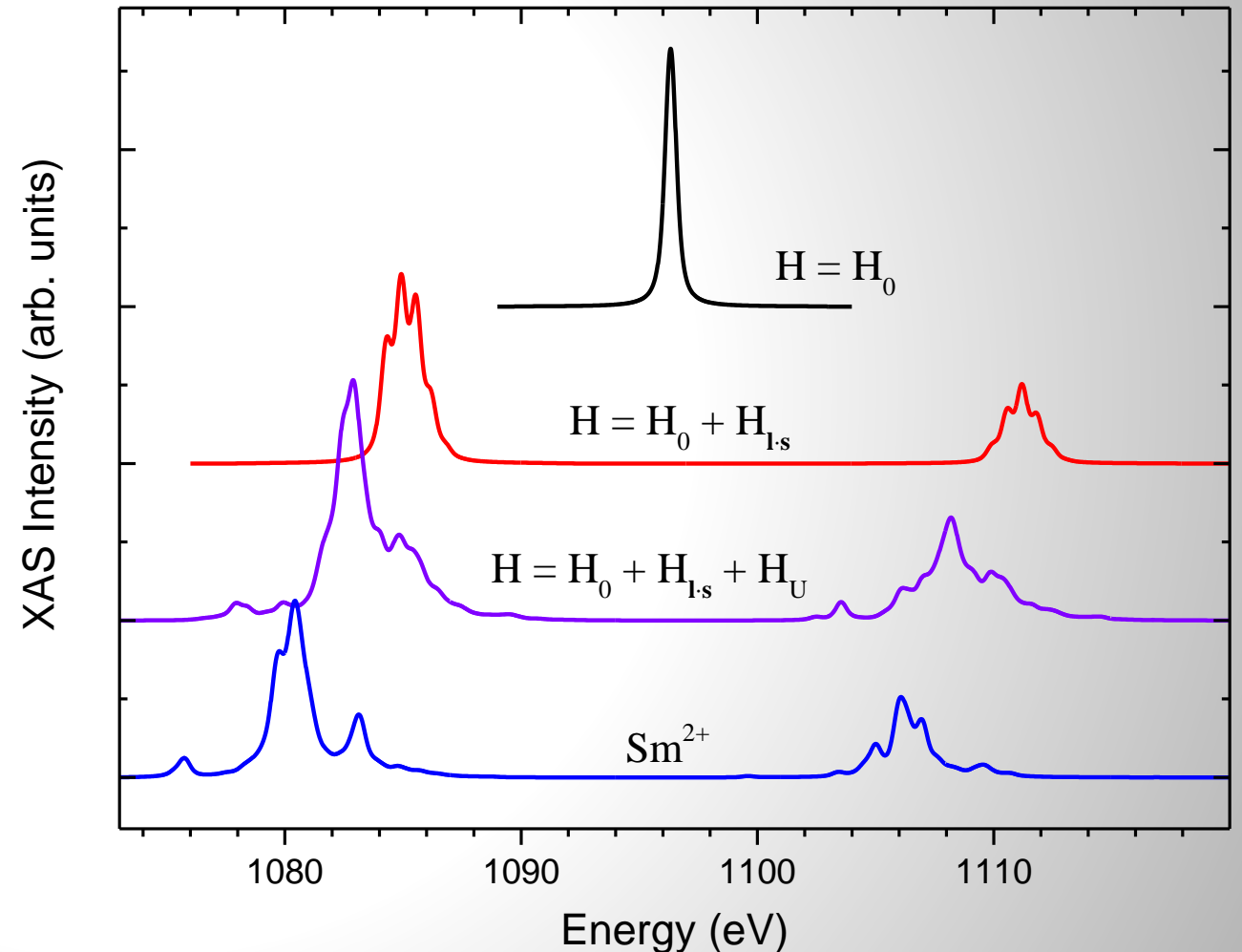
Comparison to Experiment

For 4f systems, this purely atomic model can give very good agreement with experiment

But this also means we aren't really sensitive to material-dependent properties.
- 3d → 4f XAS is primarily a probe of valence (with some exceptions)
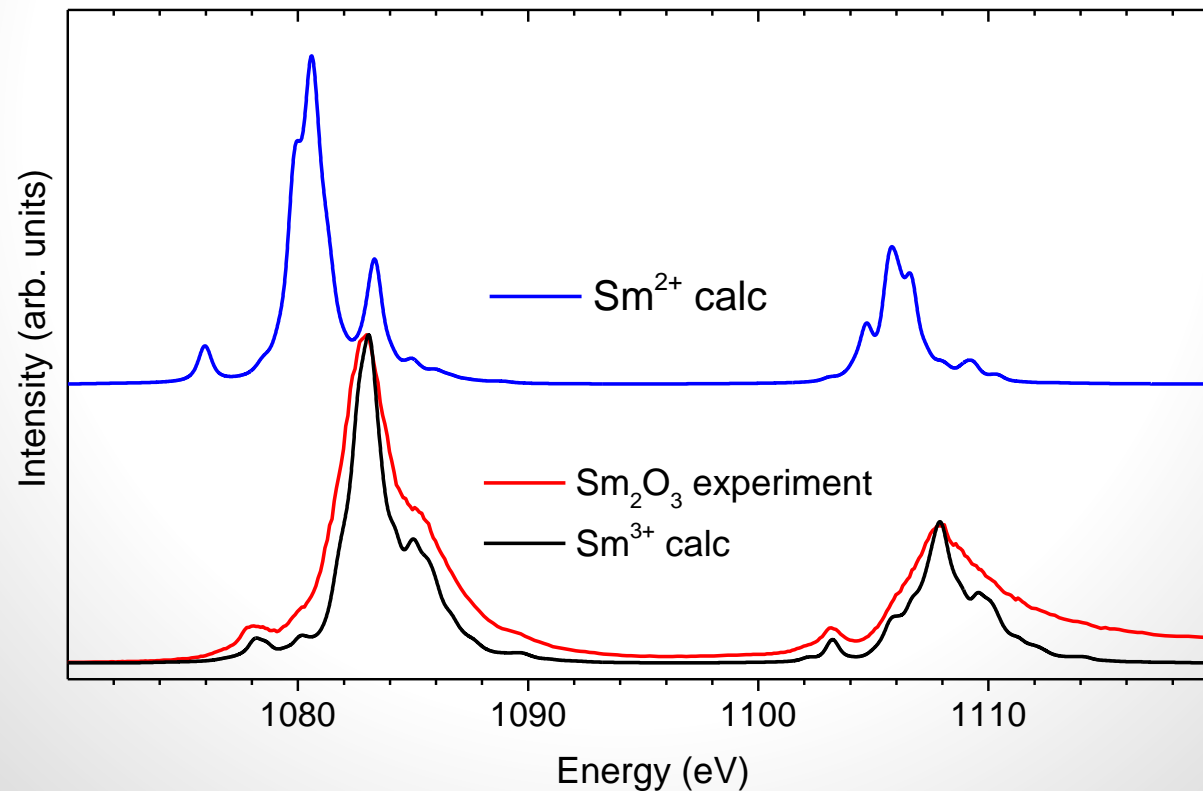
Now try to account for local environment

The valence electrons of our atom of interest are perturbed by the nearest neighbors

Crystal field theory accounts for this by adding a specific potential to the valence electrons

Now we add a new operator to our Hamiltonian, accounting for the specific point group defined by nearest neighbours, which shifts the energies of the orbitals

$$H = H_U^{dd} + H_{l \cdot s}^d + H_{CF}$$

$$H_{CF} = \sum_{\tau} \varepsilon_{d,\tau} \boldsymbol{d}_{\tau}^{\dagger} \boldsymbol{d}_{\tau}$$

For O_h point group symmetry:

$$H_{CF} = \sum_{\tau \in e_g} 6Dq \cdot \boldsymbol{d}_{\tau}^{\dagger} \boldsymbol{d}_{\tau} - \sum_{\tau \in t_{2g}} 4Dq \cdot \boldsymbol{d}_{\tau}^{\dagger} \boldsymbol{d}_{\tau}$$
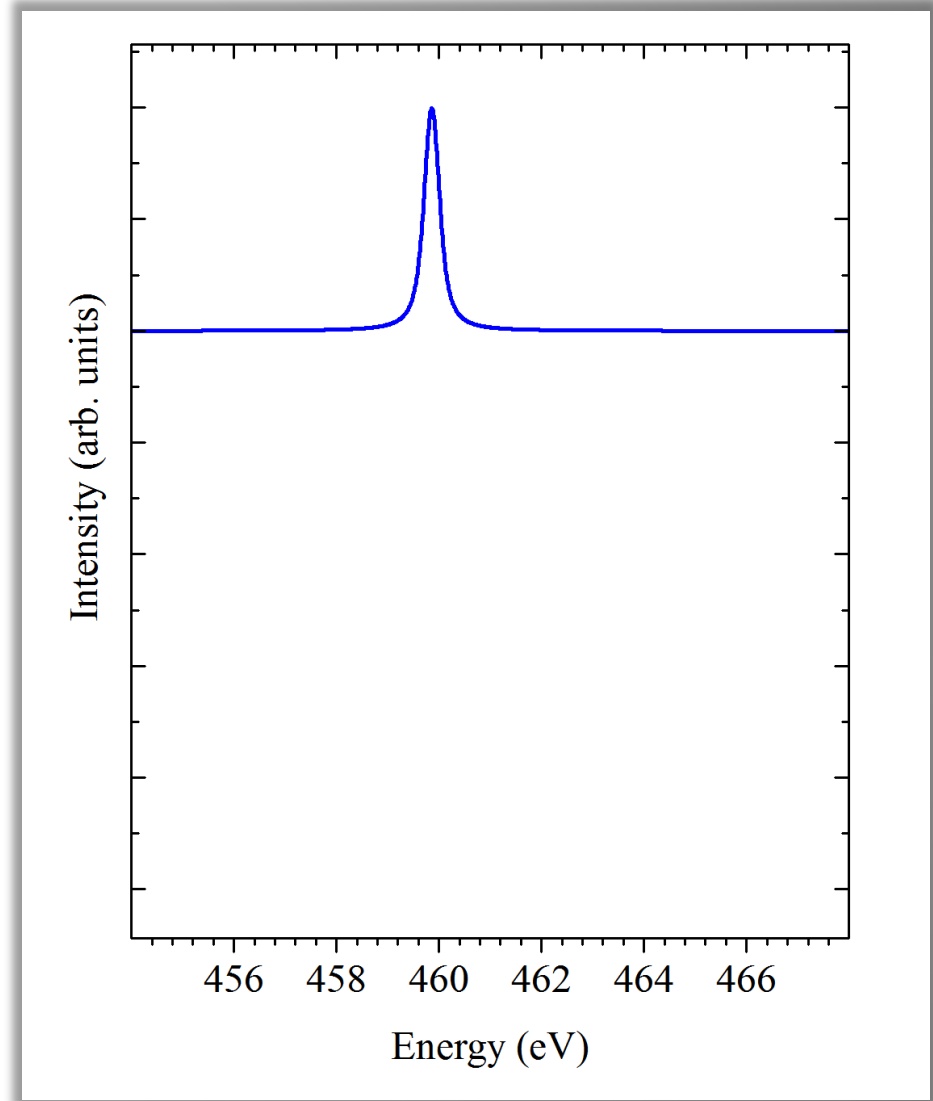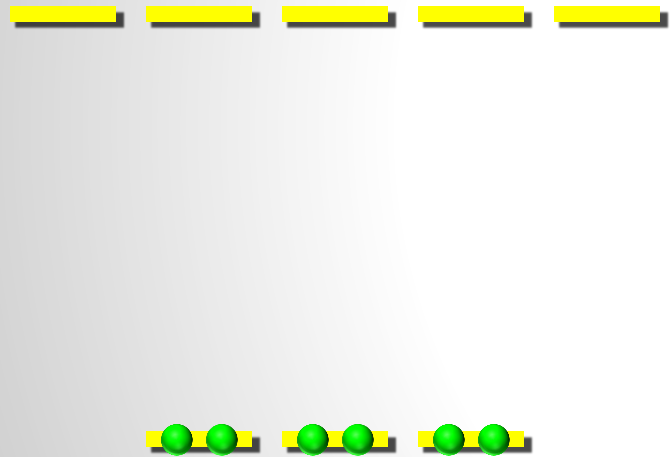
CFT Example: Ti^{4+} XAS

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$+U^{dd} + U^{pd}$

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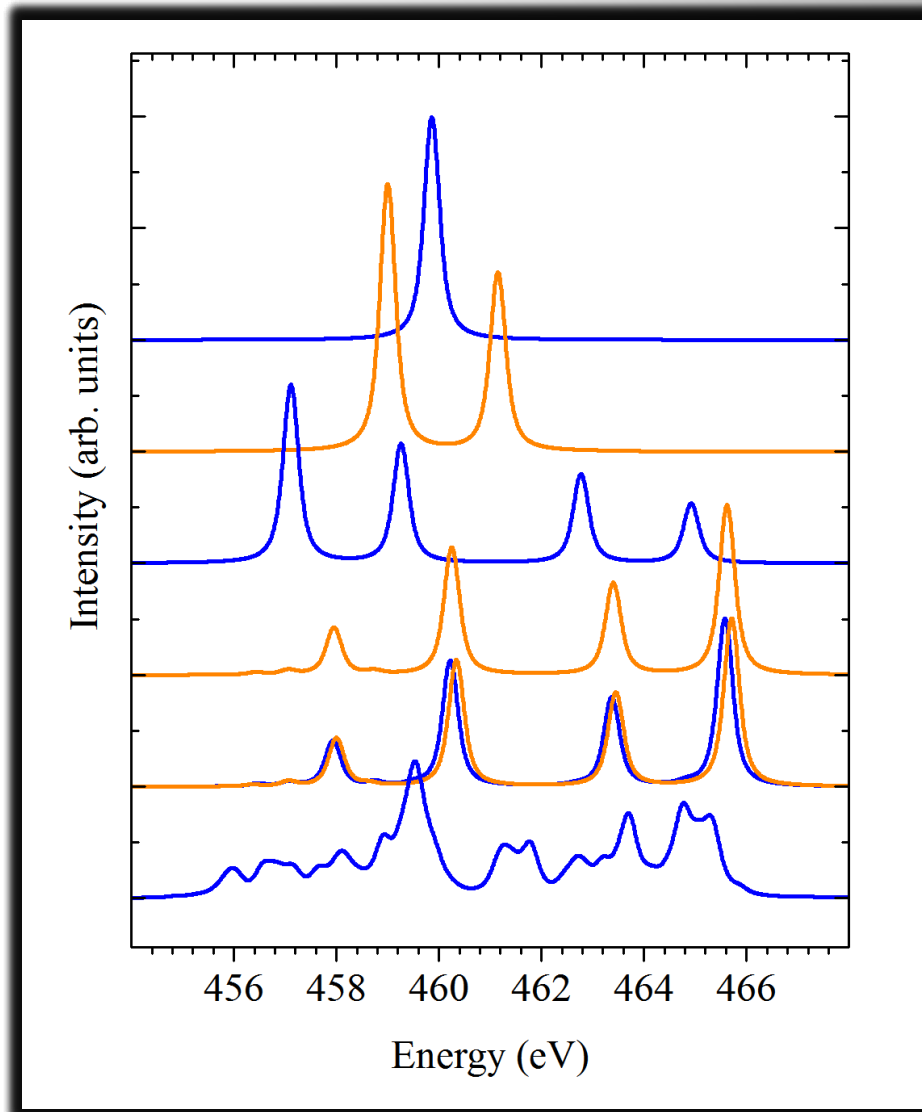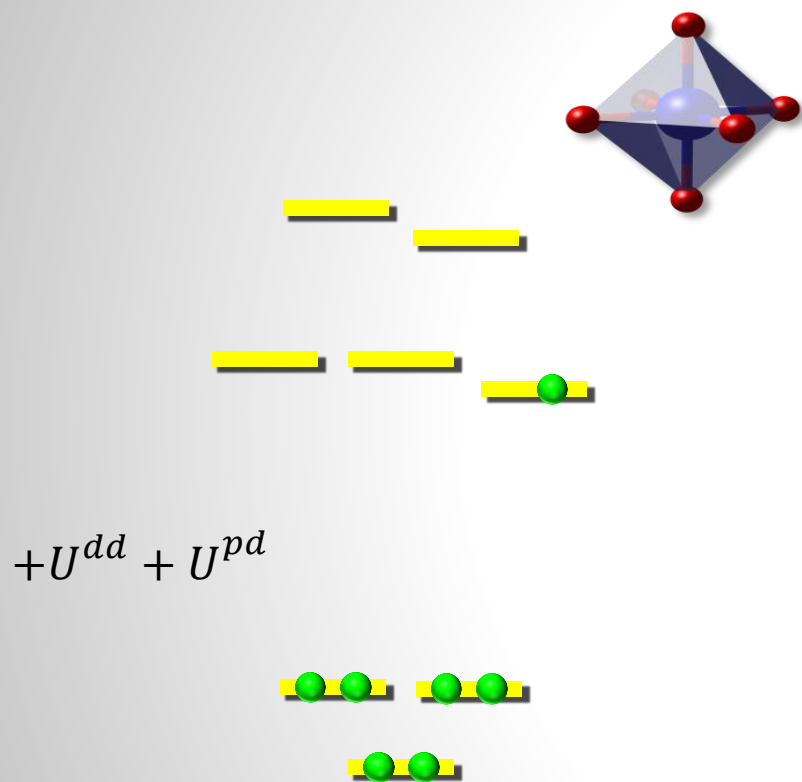
We use specific crystal field operators depending on local point group symmetry

The five 3d orbitals (or seven 4f orbitals) split in energy into different groups (and may mix) depending on the symmetry
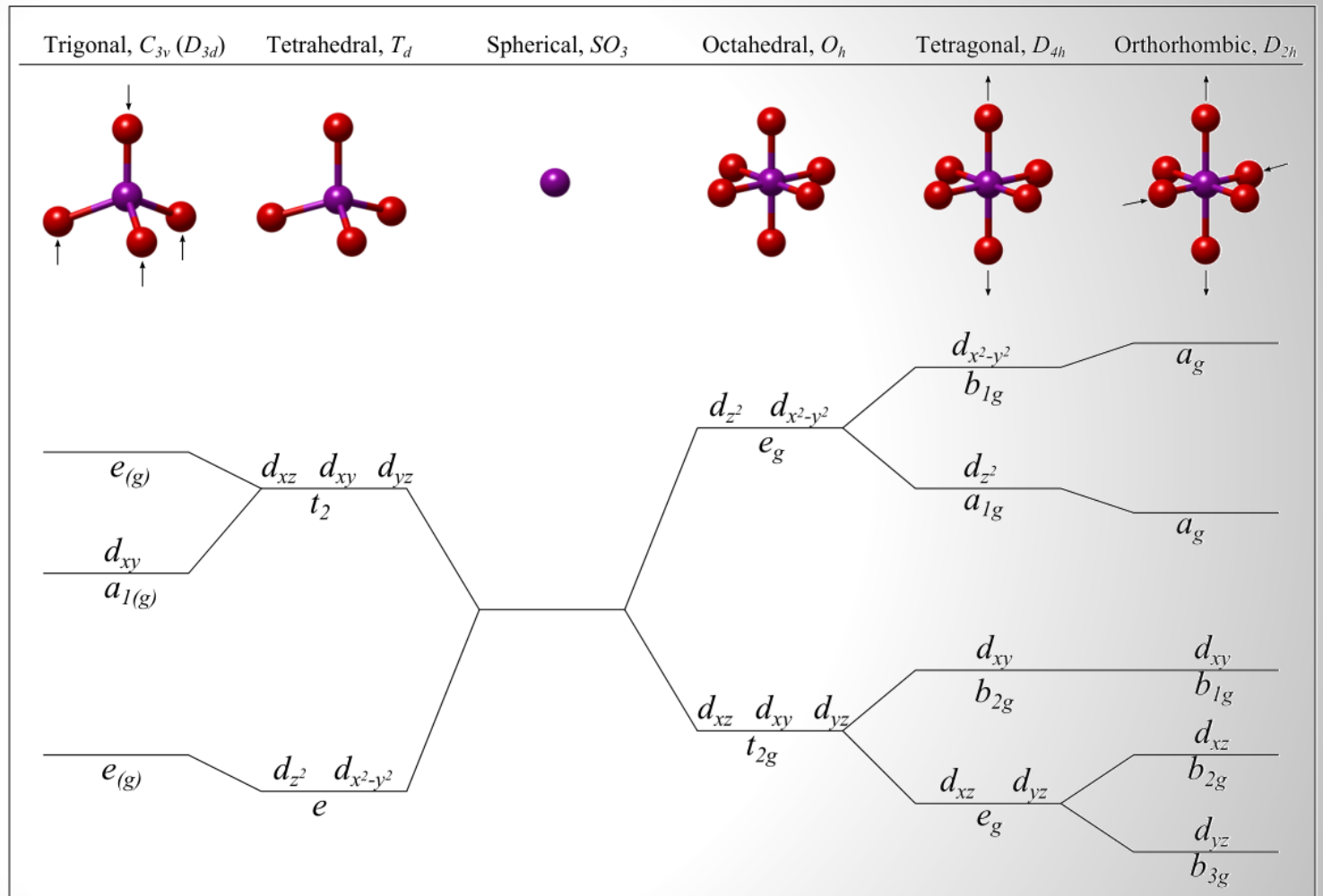
Example: CFT Analysis of RIXS to Locate Impurities

Mn^{2+} RIXS calculated as function of 10Dq shows difference between octahedral (upper dashed) and tetrahedral (lower dashed) coordination.

From this we showed that at low doping (11%), Mn atoms are in tetrahedral (Zn) sites. At high doping, they form clusters with octahedral coordination.
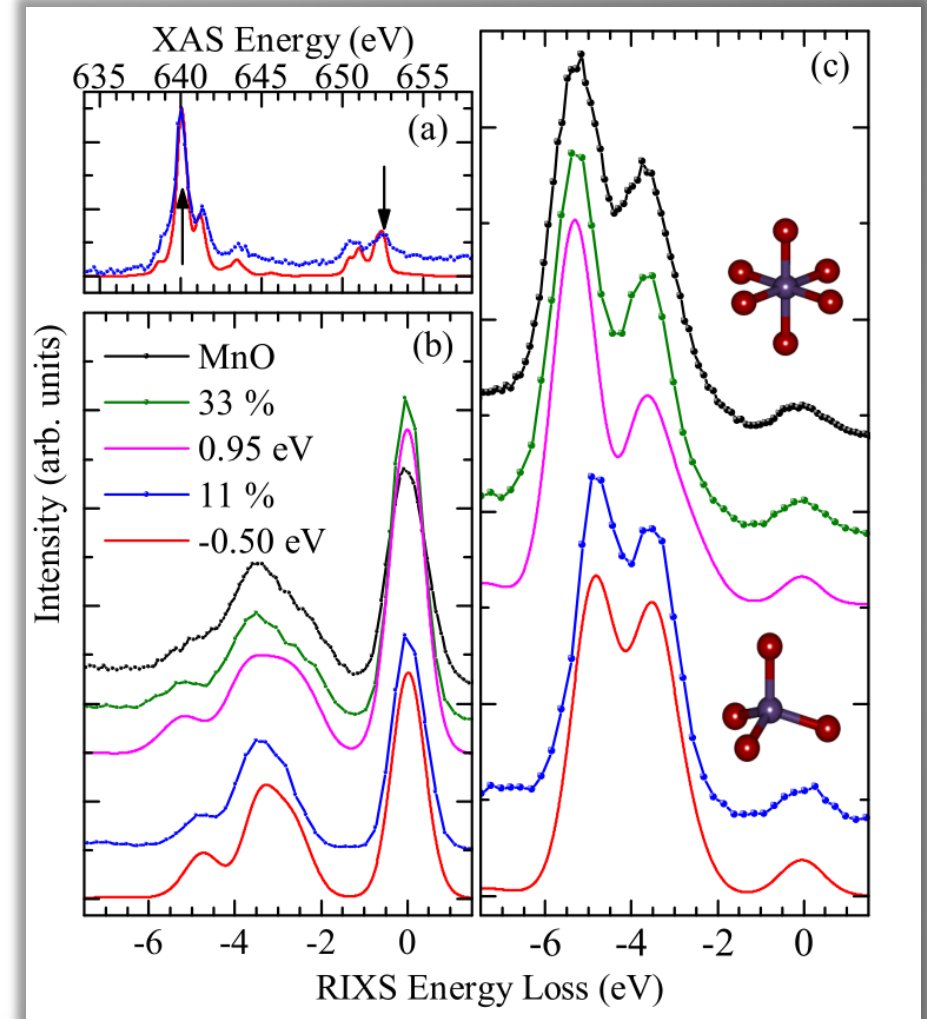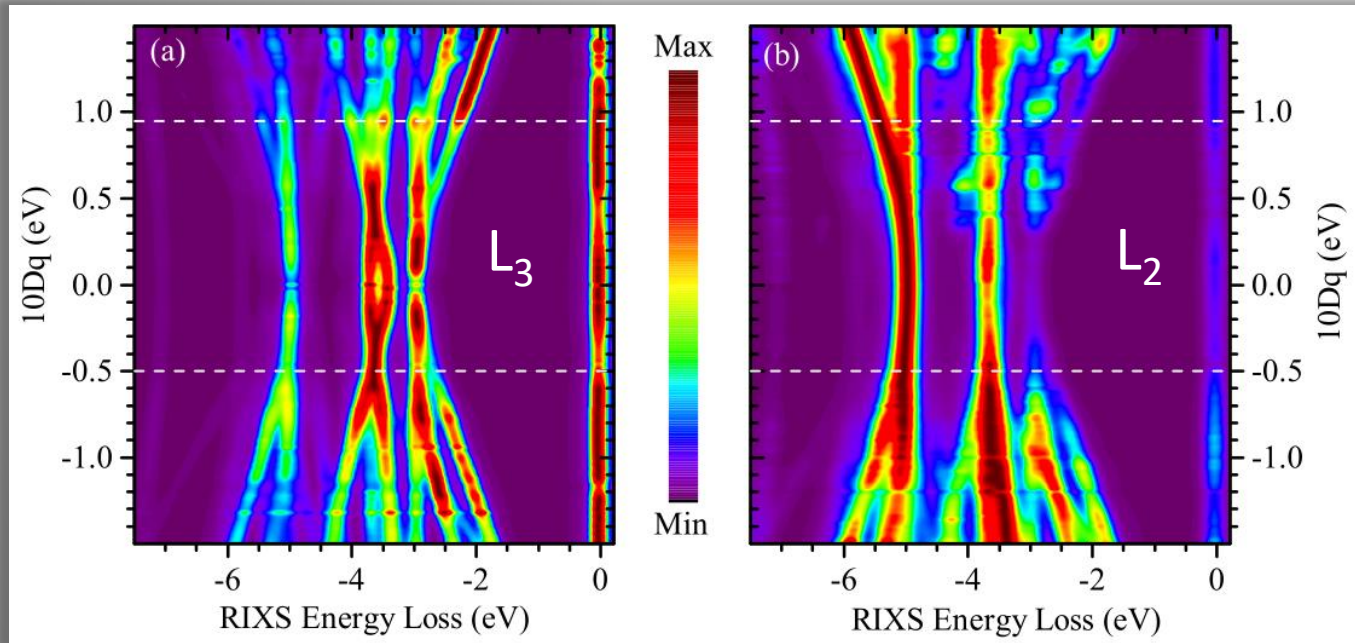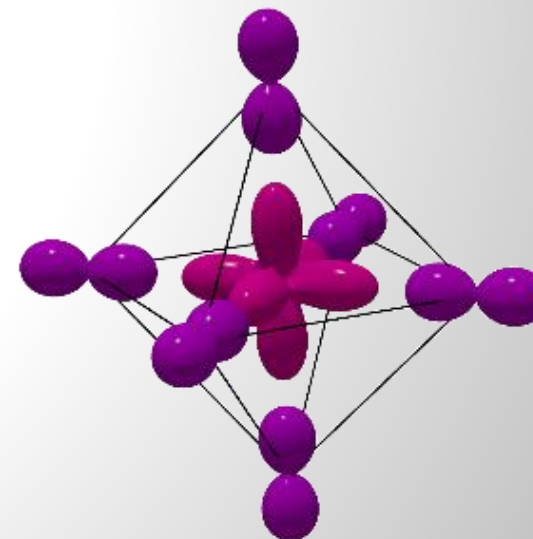
Increasing Complexity – Ligand Field Theory

Crystal field model works quite well in a lot of cases – in particular for ionic compounds or rare earth compounds

Covalence effects are approximated in CFT with renormalization of parameters
- Generally larger crystal fields and smaller Coulomb interaction (Slater) parameters in CFT

But often we need to include covalence explicitly: ligand field theory

Instead of approximating neighbors as point charges, we
directly include their orbitals in our basis

We can take advantage of symmetry to reduce the complexity of the problem

The local orbitals mix with linear combinations of neighboring orbitals which have the same rotation properties of the local orbitals in the point group of the model

E.g. for 10 3d orbitals, we define 10 "ligand" orbitals which are linear combinations of the actual 2p anion orbitals

For 3d eigenstates, we now have 20 spin orbitals in our basis. I.e. for Mn2+ ($3d^5$),

$$|1111100000\ 1111111111\rangle$$

Add hybridization operator to Hamiltonian

$$H = H_0^d + H_U^{dd} + H_{l \cdot s}^d + H_{CF} + \textcolor{red}{H_0^L + H_{hyb}}$$

$$H_{hyb} = \sum_\tau V_\tau \left(\boldsymbol{d}_\tau^\dagger \boldsymbol{L}_\tau + \boldsymbol{L}_\tau^\dagger \boldsymbol{d}_\tau \right)$$

Ligand Field Theory

Through hybridization, we now have bonding and antibonding states

Compare with a simple two level model:

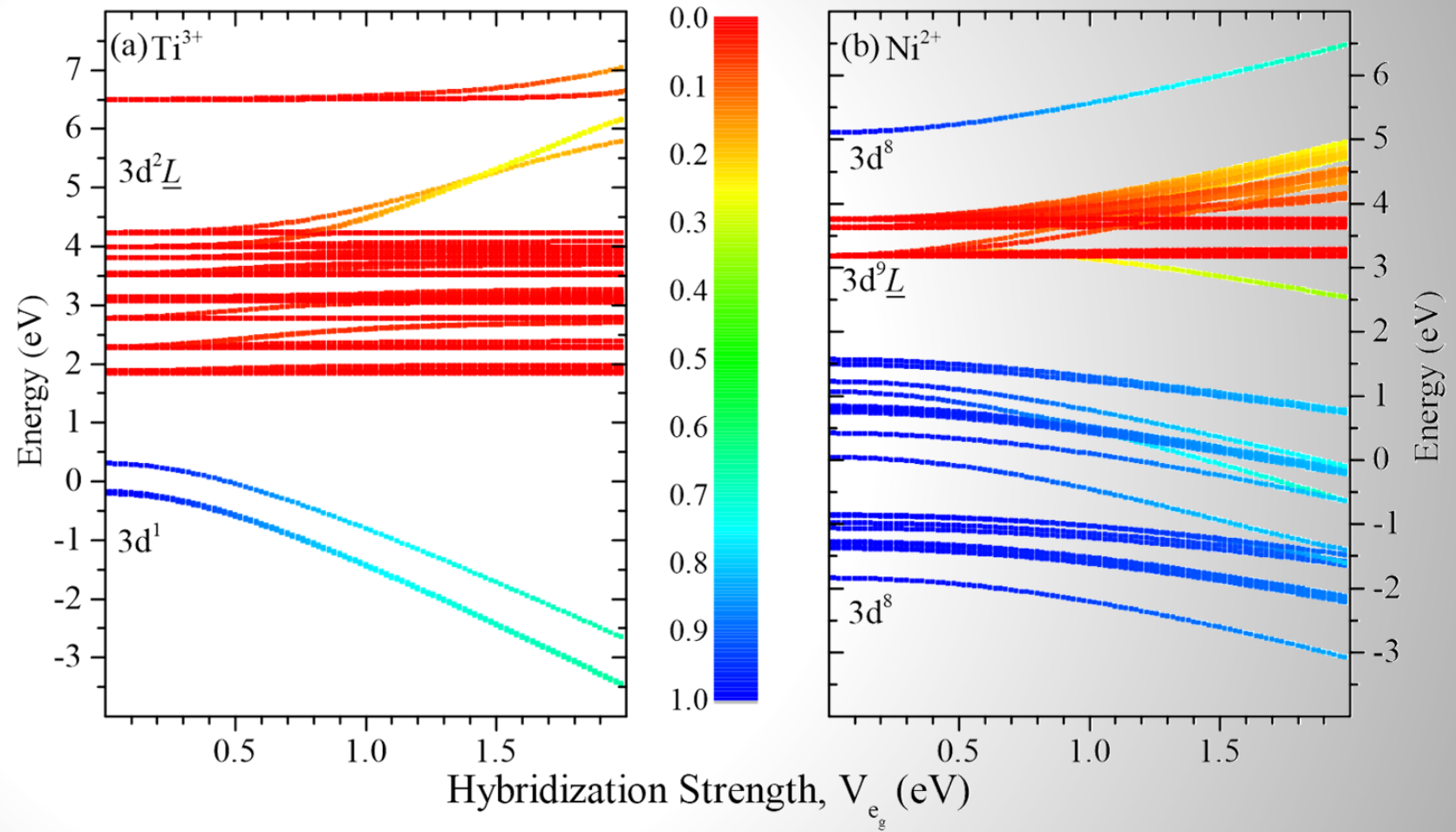$$H = \begin{bmatrix} a & V \\ V & b \end{bmatrix}$$

Set $a = 0$, $b = 0.2$
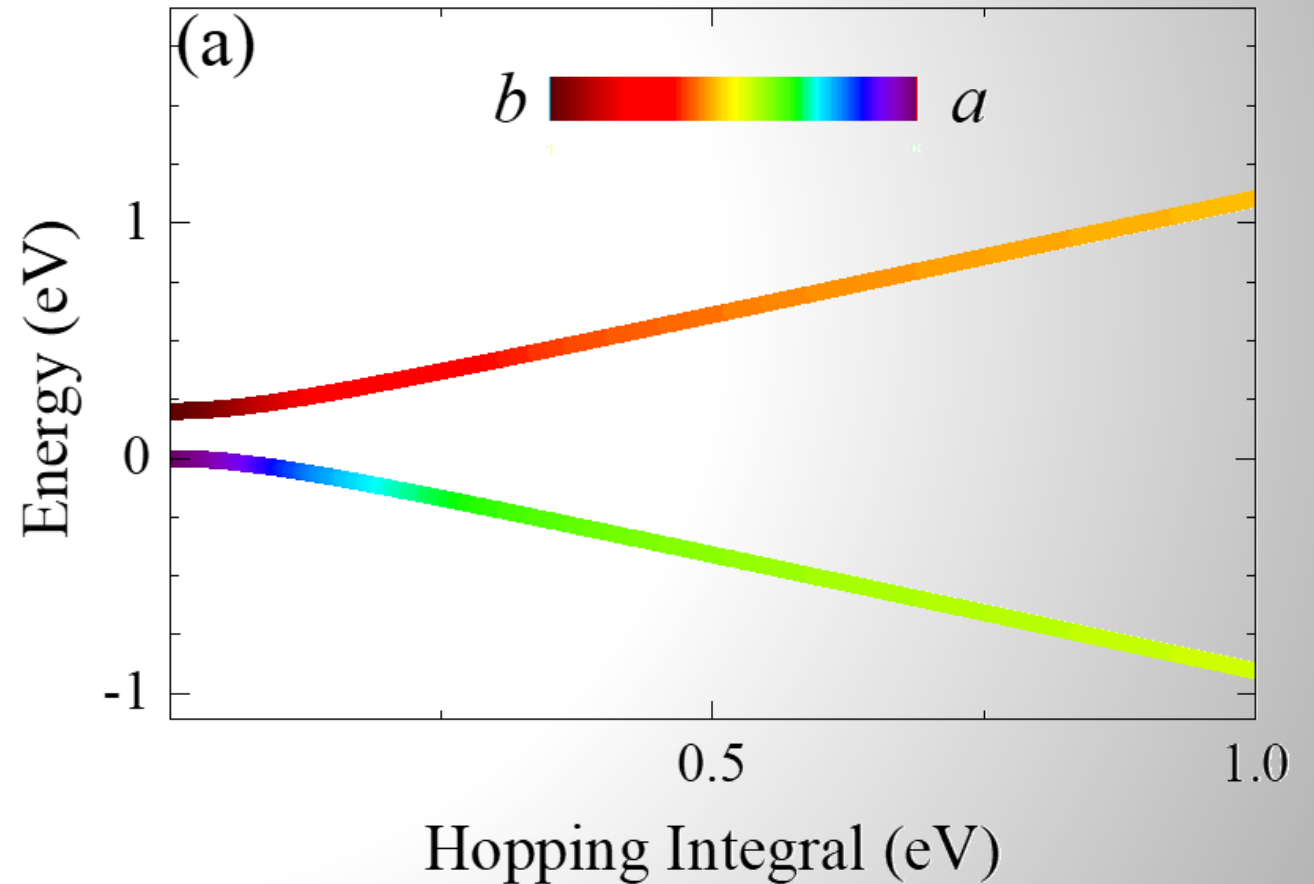
Ligand Field Theory

In LFT, each of our "levels" is an entire configuration (i.e. a matrix).

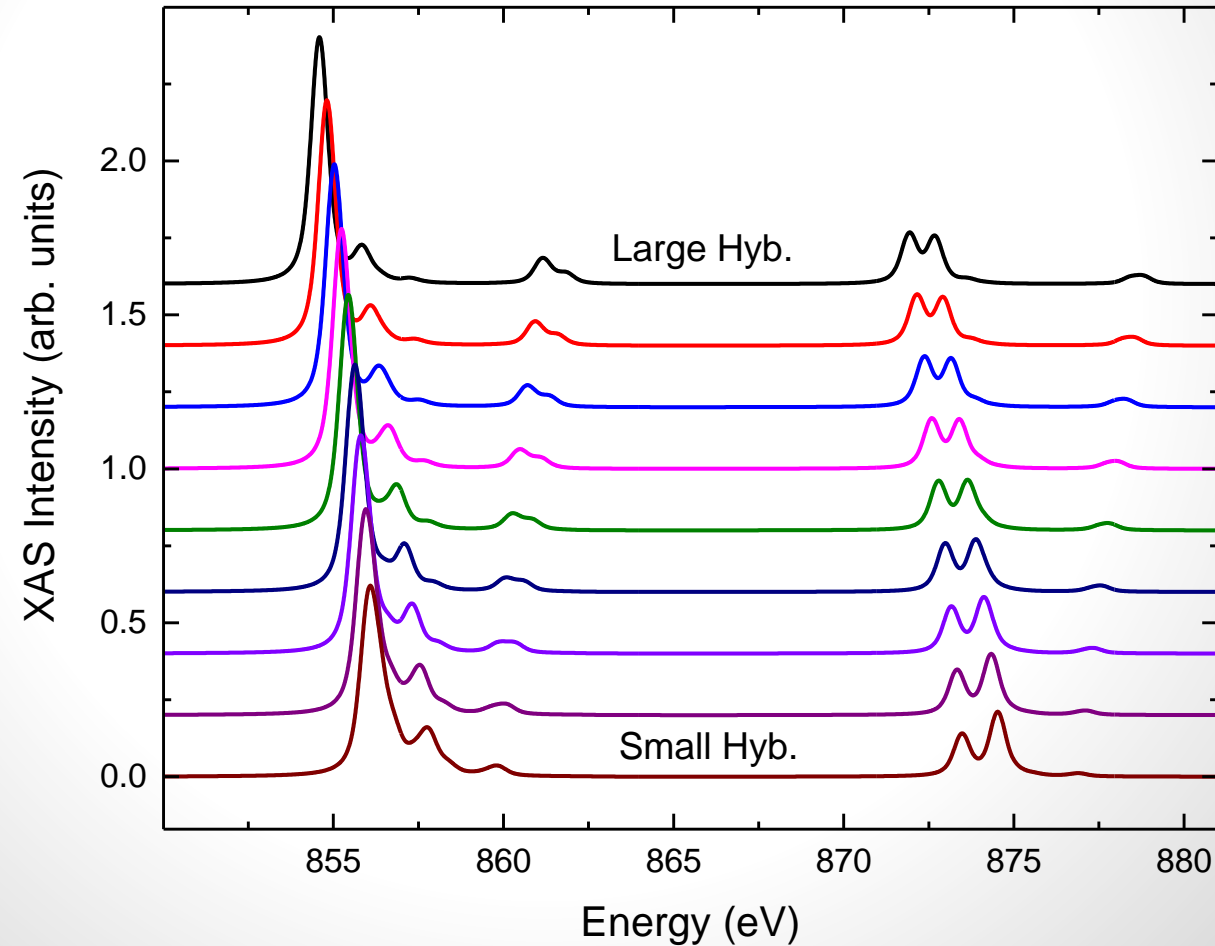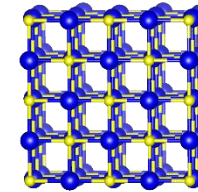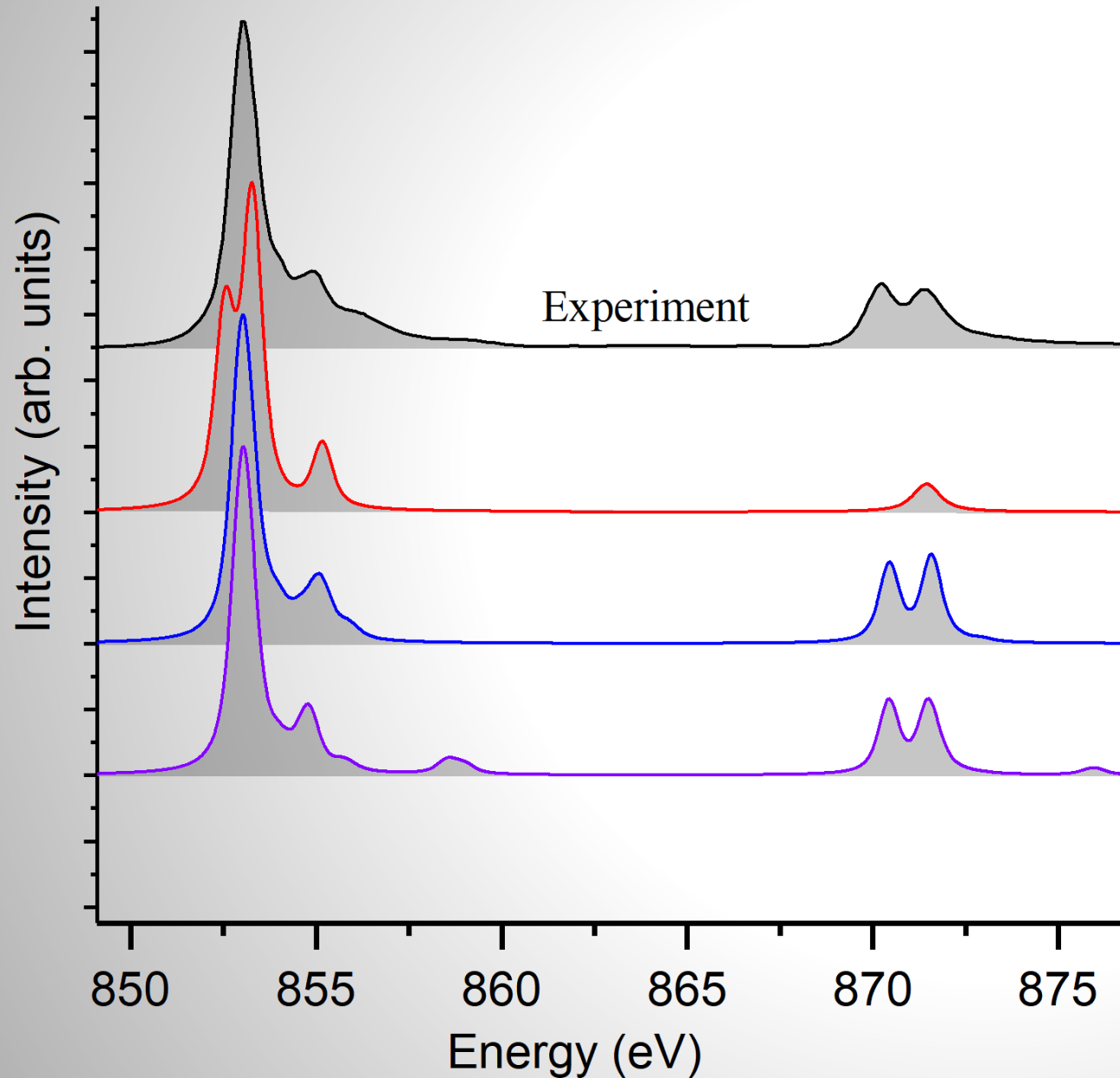$$H = \begin{bmatrix} d^n & V \\ V & d^{n+1}\underline{L} \end{bmatrix}$$

Ligand Field Theory

A mixed ground state wavefunction means we can reach different final states in our spectroscopy

For the final states:

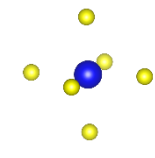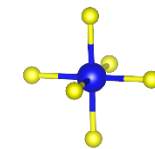Modelling L$_{2,3}$ XAS Spectra from Local Perspective
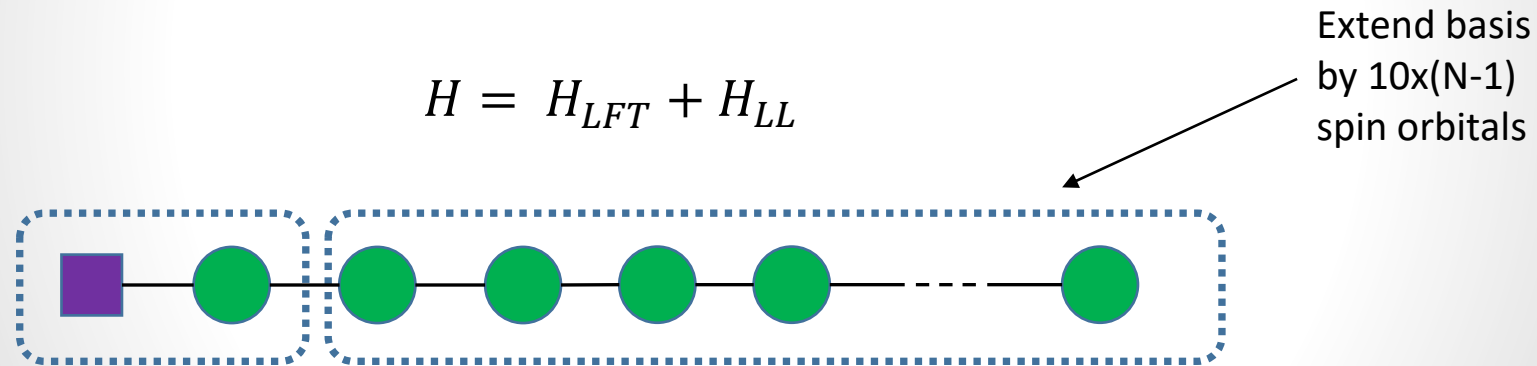
Increasing Complexity – Impurity Model

Ligand field theory works very well to account for covalence in these local spectroscopy techniques

However, in some cases it is important to include more than the nearest neighbor ligands to account for the ligand bandwidth

When we include more ligands we have an Anderson impurity model

$$H = H_{LFT} + H_{LL}$$

Extend basis by 10x(N-1) spin orbitals

$$H_{LL} = \sum_{i=2}^{N}\left[\varepsilon_L L_i^\dagger L_i \; + T_{LL}\left(L_{i-1}^\dagger L_i \; + L_i^\dagger L_{i-1}\right)\right]$$

* τ dependence left out for clarity

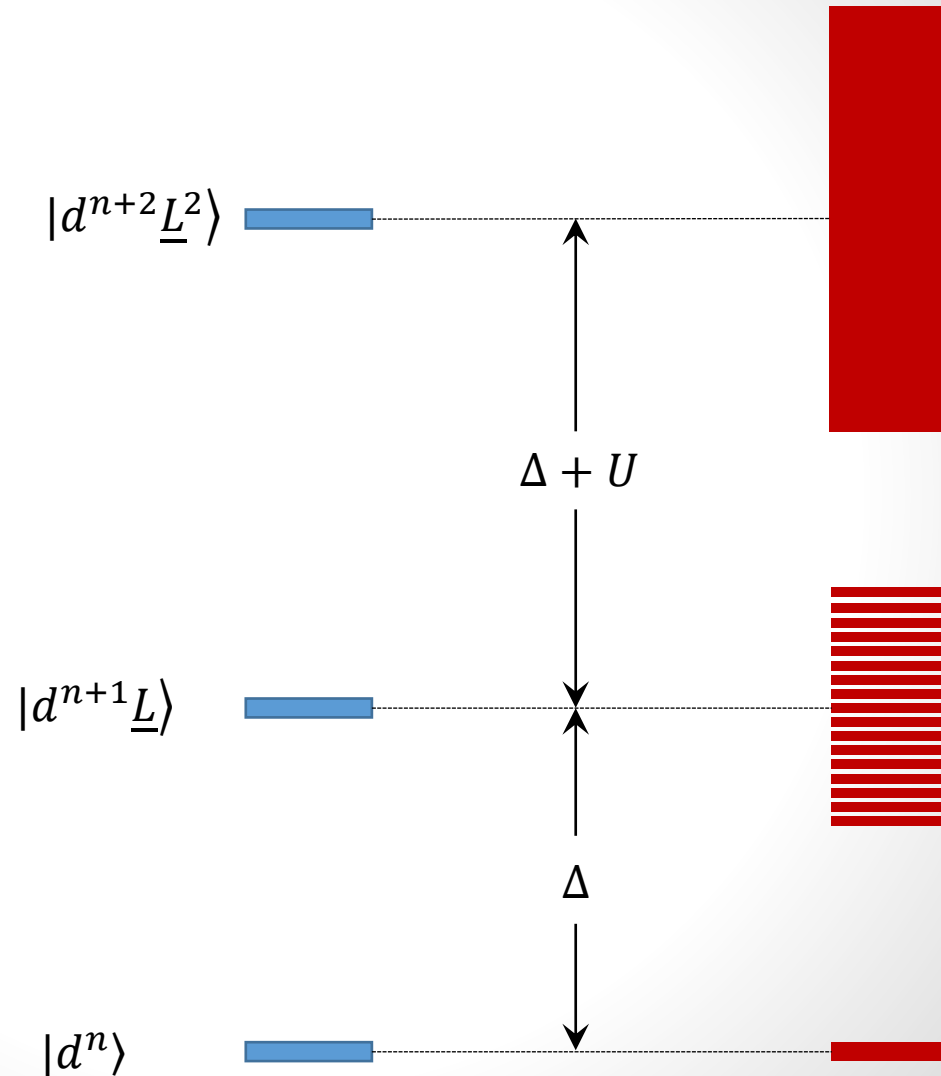# Compare with Two-Level (LFT) Model

Ligand Field:

$$H = \begin{bmatrix} a & V \\ V & b \end{bmatrix}$$

Impurity:

$$H = \begin{bmatrix} a & V_{ab} & - & - & - \\ V_{ab} & b_1 & V_{bb} & - & - \\ - & V_{bb} & b_2 & V_{bb} & - \\ - & - & V_{bb} & ... & V_{bb} \\ - & - & - & V_{bb} & b_n \end{bmatrix}$$
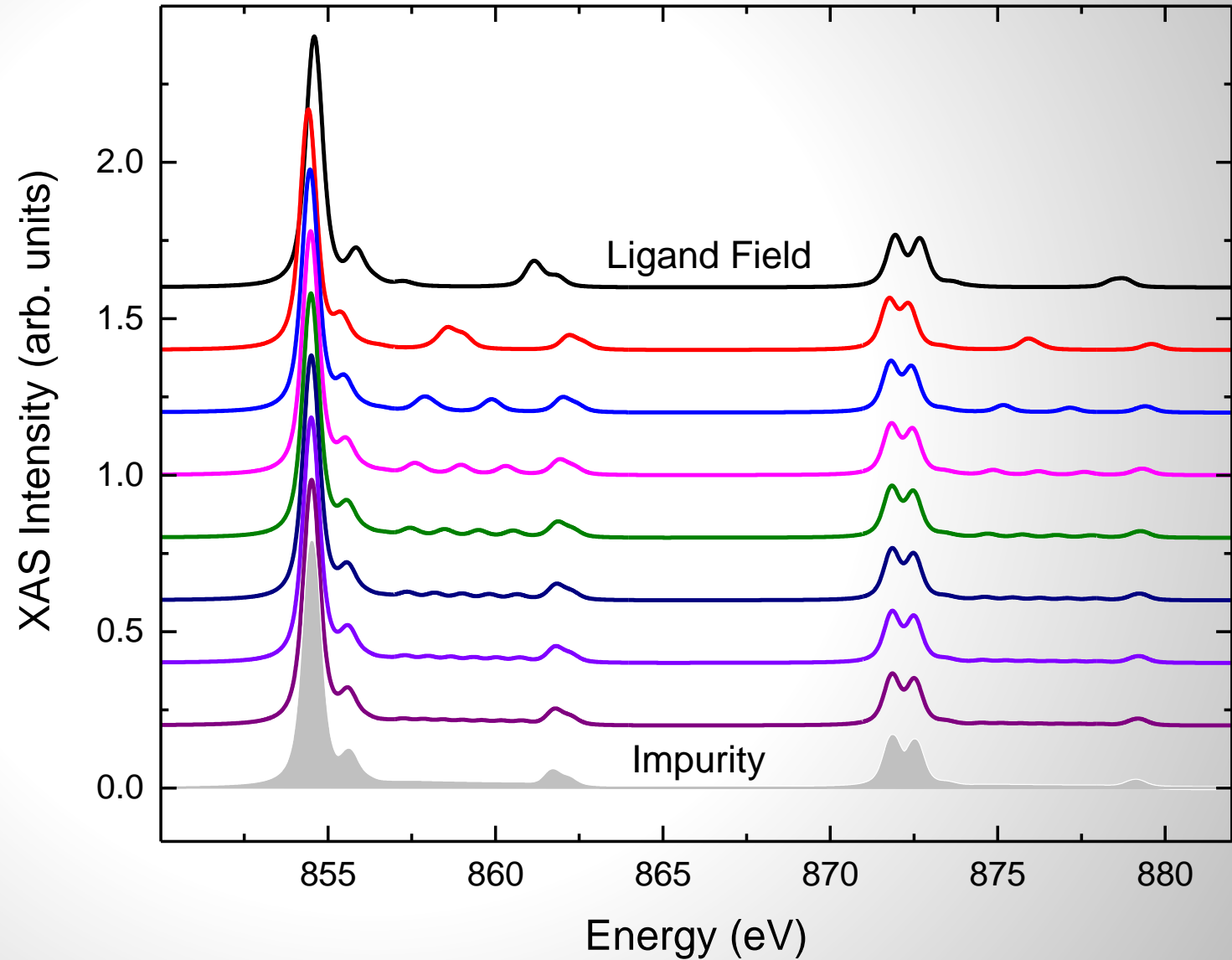
Energetics of Ligand Field and Impurity Models

$|d^{n+2}\underline{L}^2\rangle$

$\Delta + U$

We now have many copies of
configurations which leads to
continua of states

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

Δ

$|d^n\rangle$
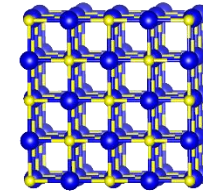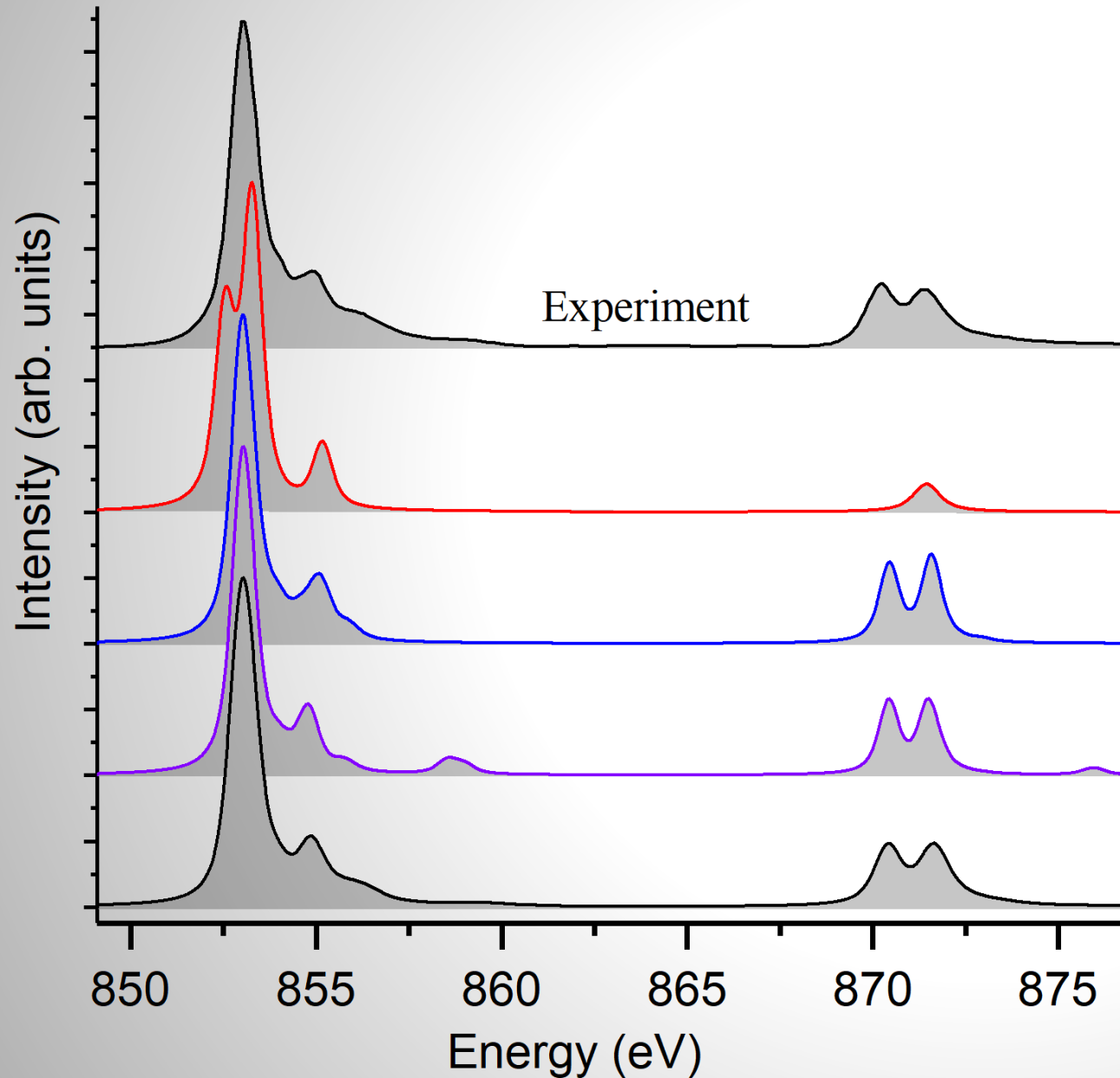
The larger the number of ligand band discretizations, the closer we get to true continuum features in our spectra

Modelling L$_{2,3}$ XAS Spectra from Local Perspective
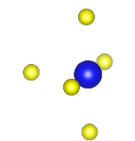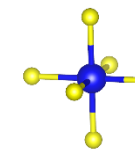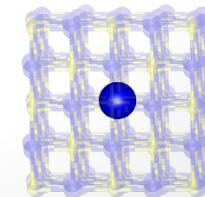
Modelling L$_{2,3}$ RIXS Spectra from Local Perspective

Using more advanced models also helps to capture all RIXS features
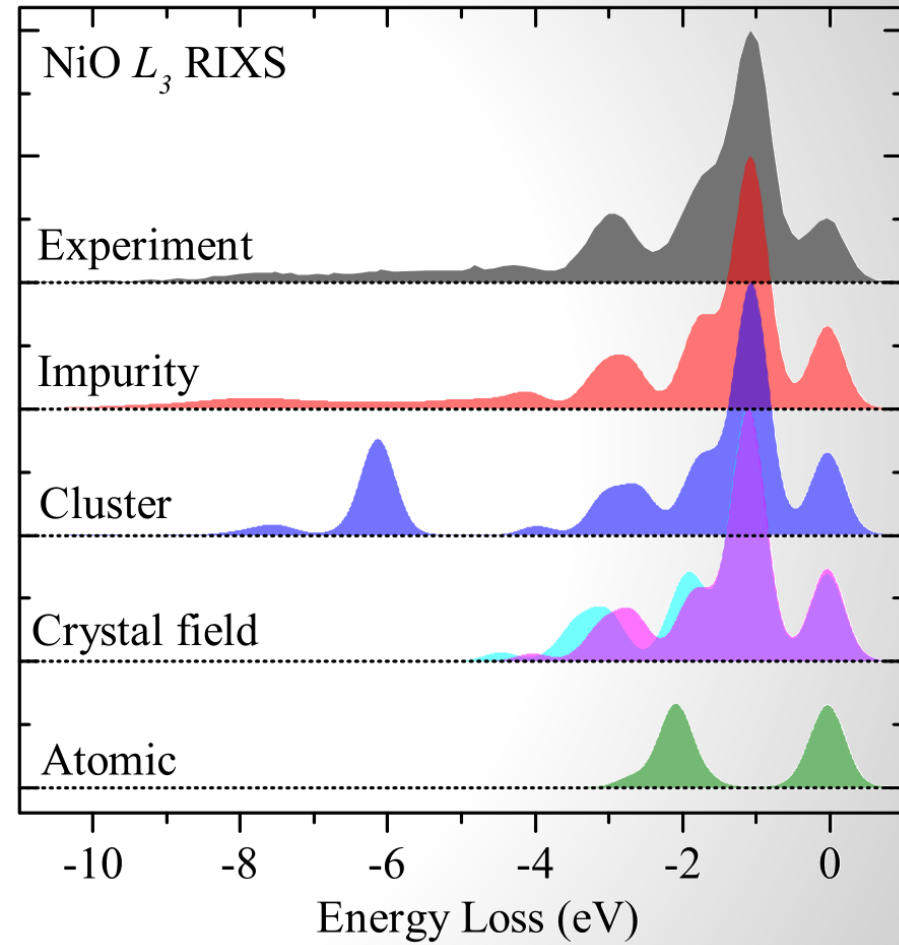
Summary (Part 1)

In systems where electrons are relatively localized, we can simulate XAS and RIXS with local models

Going from extreme ionic to extreme covalent limits, we can increase our model complexity:
- isolated atom
- crystal field
- ligand field
- impurity
- other (multi-site models, metallic impurity model, etc)

In Part 2, we'll look at how to implement these models in Quanty