Resonant Inelastic X-ray Scattering

OCEAN NSLS-II & CFN User Meeting 2019

Outline

- Overview
- Flavors of RIXS
- OCEAN Approach
- Missing from OCEAN

Resonant Inelastic X-ray Scattering

- Kotani & Shin, Rev. Mod. Phys. **73**, 203 (2001)
- Ament, *et al.*, Rev. Mod. Phys. **83**, 705 (2011)

- Resonant: Incident photon is tuned to an edge
- Inelastic: Energy loss
- Scattering: Photon in – photon out

Electron-photon interactions

$$H_{e\gamma} = \frac{e}{mc}\mathbf{p} \cdot \mathbf{A} + \frac{e^2}{2mc^2}\mathbf{A} \cdot \mathbf{A}$$

- **p** is the electron momentum
- **A** is the photon vector potential
- e & m are the electrons charge and mass

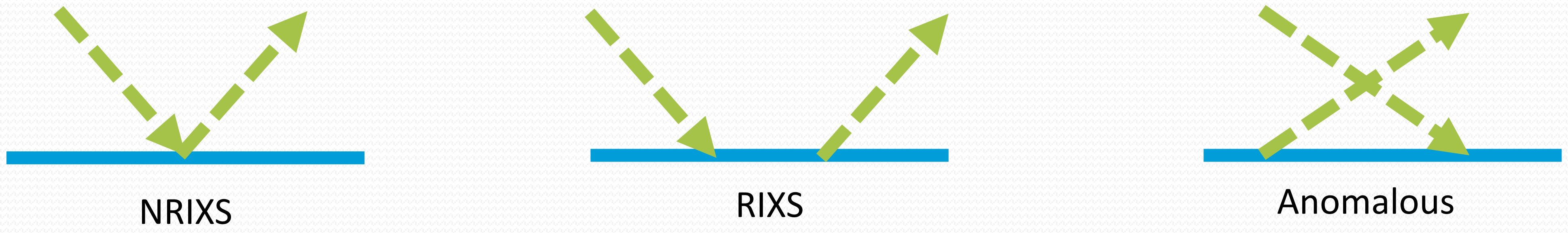
Electron-photon interactions

$$H_{e\gamma} = \frac{e}{mc}\mathbf{p}\cdot\mathbf{A} + \frac{e^2}{2mc^2}\mathbf{A}\cdot\mathbf{A}$$
$$= H_1 \qquad\qquad + H_2$$

- H_1 absorption or emission
- H_2 NRIXS (or Thompson scattering)
- $H_2/H_1 \simeq \alpha/2$

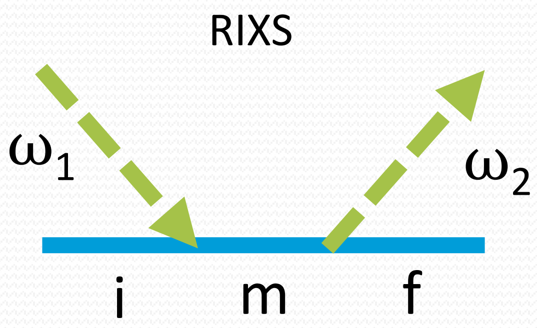
Scattering

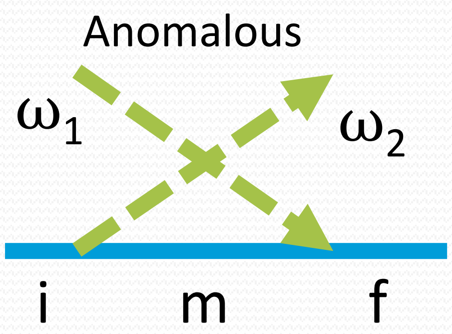
- Photon-in – photon out
  - **A**^{2} or successive **p·A** terms (same order)
  - Kramers-Heisenberg expansion



Scattering

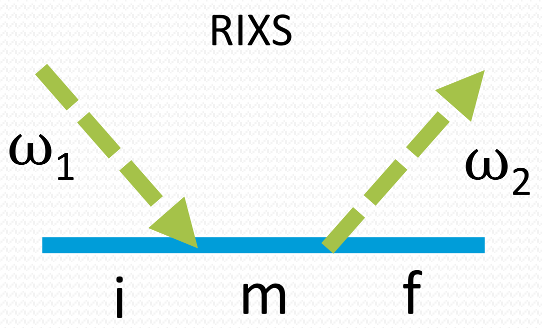
- Dropping the A^2 term

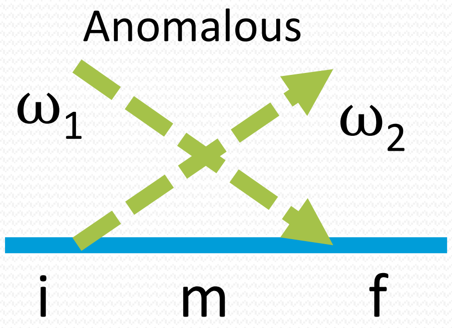




Scattering

- Dropping the A^2 term





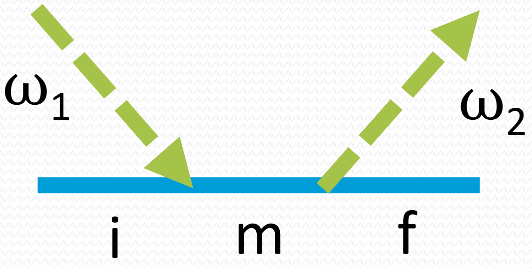
- RIXS:

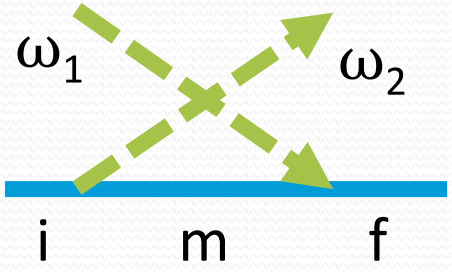
$$\sum_f \left| \sum_m \left[\frac{\langle f|\hat{d}_2|m\rangle\langle m|\hat{d}_1|i\rangle}{E_m - E_i - \omega_1} \right] \right|^2 \delta(E_f - E_i + \omega_2 - \omega_1)$$

  - Resonant energy denominator

Scattering

- Dropping the A^2 term





- RIXS: $$\sum_f \left| \sum_m \left[\frac{\langle f|\hat{d}_2|m\rangle\langle m|\hat{d}_1|i\rangle}{E_m - E_i - \omega_1} \right] \right|^2 \delta(E_f - E_i + \omega_2 - \omega_1)$$

- Anomalous: $$\sum_f \left| \sum_m \left[\frac{\langle f|\hat{d}_2|m\rangle\langle m|\hat{d}_1|i\rangle}{E_m - E_i + \omega_2} \right] \right|^2 \delta(E_f - E_i + \omega_2 - \omega_1)$$

Outline

- Overview
- Flavors of RIXS
  - Core-to-core
  - Direct
  - Indirect
  - Core-hole clock emission
- OCEAN Approach

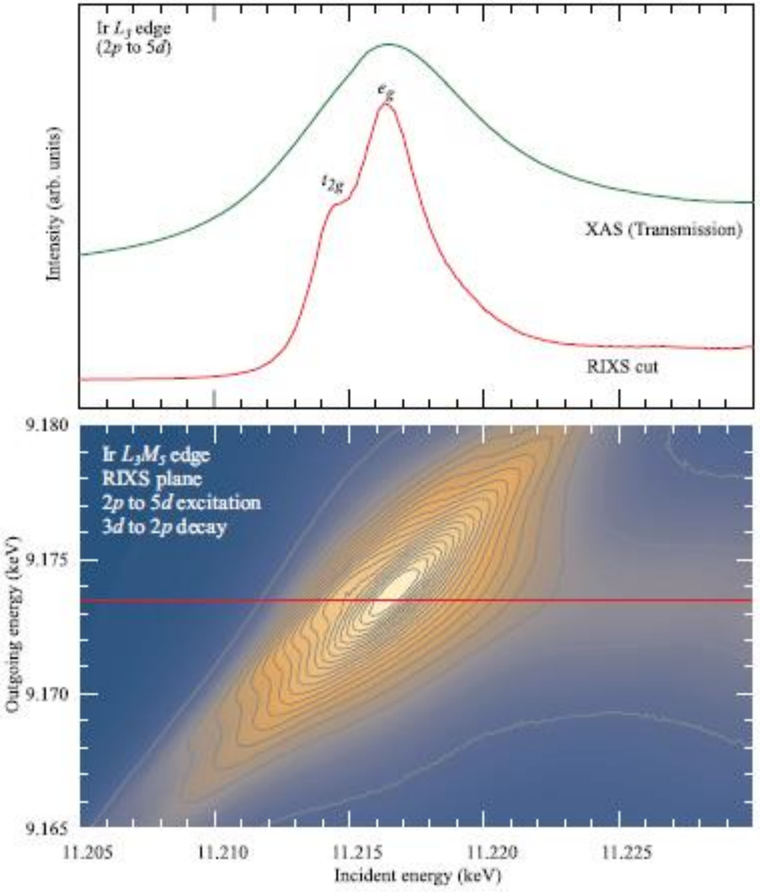
Core-to-core RIXS

- Core-to-core
  - 1s2p, 1s3p, etc.
  - Large energy transfer
- Primarily used as x-ray absorption stand-in
  - K. Hämäläinen *et al.*, Phys. Rev. Lett. **67**, 2850 (1991)
  - Constant loss mimics XAS
  - Lower intrinsic core-hole broadening

Core-to-core RIXS

- Primarily used as x-ray absorption stand-in
- Modeling
  - Just run absorption
  - Full RIXS

Exp. results for Sr_2IrO_4



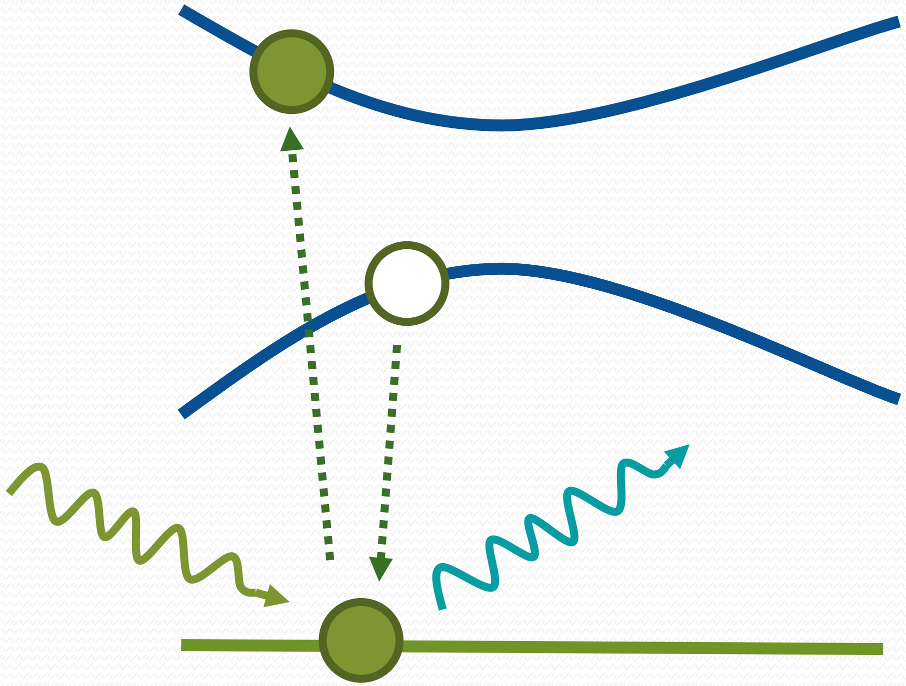
Agrestini *et al.*, Phys. Rev. B **95**, 205123 (2017)

Valence RIXS

- Emitted photon nearly the same energy as absorbed
  - No core-level hole in final state
- Two types
  - Direct
  - Indirect

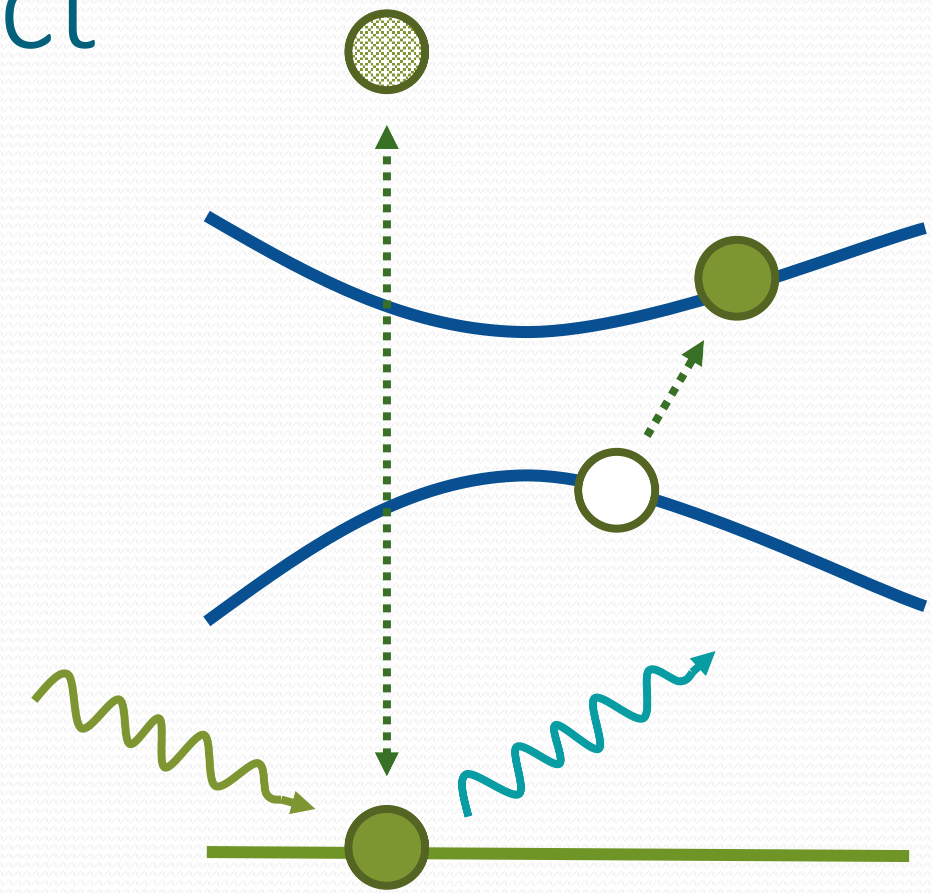
Valence RIXS: Direct

- X-ray in – X-ray out
- Probes low-energy band structure
- Couples to secondary excitations
  - phonons
  - magnons
  - spin-density waves



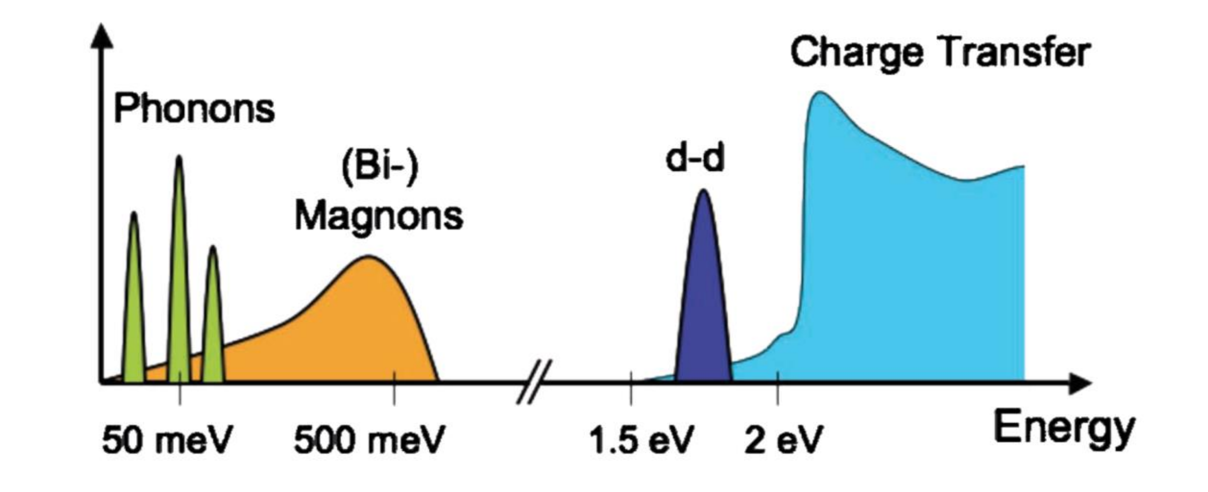
Valence RIXS: Indirect

- X-ray in – X-ray out
- ~~Probes low-energy band structure~~
- Couples to secondary excitations
  - phonons
  - magnons
  - spin-density waves



Valence RIXS

- Two types
  - Direct
  - Indirect
- How do you choose?
  - Experiment segregates by energy
  - Direct RIXS has electron-hole pair
    - Loss $\gtrsim$ band gap



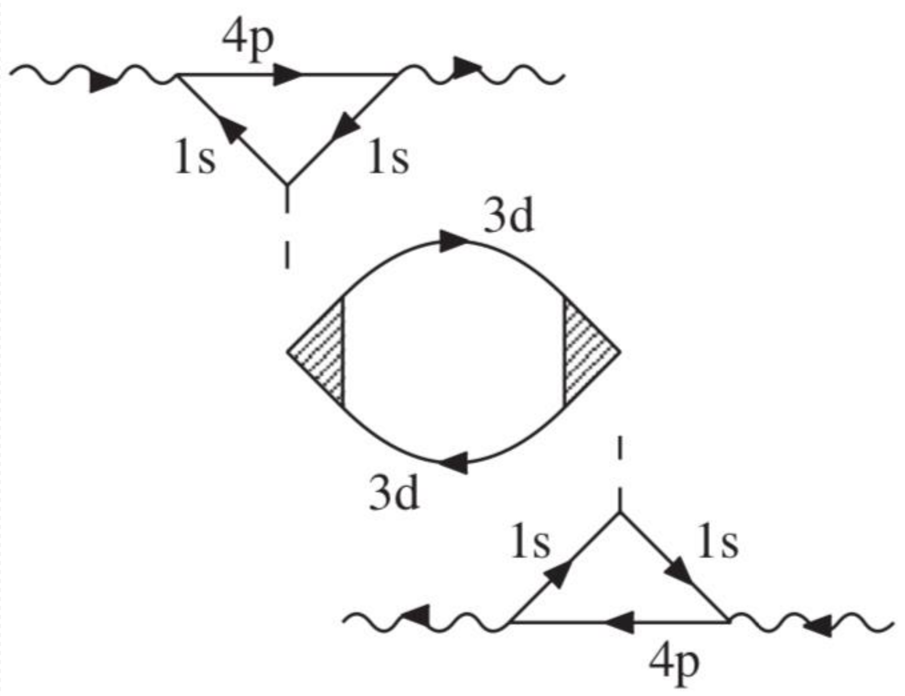
Ament *et al.*, Rev. Mod. Phys. **83**, 705 (2011)

Indirect RIXS

- Core-hole excitation creates local perturbation
- Leads to secondary excitations
  - Charge-transfer
  - d-d*
  - Phonons

Indirect RIXS

- Core-hole excitation creates local perturbation
- Leads to secondary excitations
  - Charge-transfer
  - d-d*
  - Phonons



Ament *et al.*, Rev. Mod. Phys. **83**, 705 (2011)

OCEAN approach to RIXS

OCEAN RIXS

- Valence, direct RIXS
- Core-to-core is in development

OCEAN RIXS

- Start with cross-section

$$\sum_f \left| \sum_m \left[\frac{\langle f|\hat{d}_2|m\rangle\langle m|\hat{d}_1|i\rangle}{E_m - E_i - \omega_1} \right] \right|^2 \delta(E_f - E_i + \omega_2 - \omega_1)$$

- Two classes of excitonic states
  - *m* have a core hole
  - *f* have a valence-band hole
- OCEAN does both core and valence BSE

OCEAN RIXS

$$\sum_f \left| \sum_m \left[\frac{\langle f|\hat{d}_2|m\rangle\langle m|\hat{d}_1|i\rangle}{E_m - E_i - \omega_1 + i\Gamma_m} \right] \right|^2 \delta(E_f - E_i + \omega_2 - \omega_1)$$

- Excitons have complex energy
  - Primarily driven by core-hole lifetime
  - Conveniently avoids divergences
- Start with the core-level exciton

OCEAN RIXS

$$\sum_f \left| \langle f|\hat{d}_2 \sum_m \left[\frac{|m\rangle\langle m|\hat{d}_1|i\rangle}{E_m - E_i - \omega_1 + i\Gamma_m} \right] \right|^2 \delta(E_f - E_i + \omega_2 - \omega_1)$$

- Don't need intermediate eigenstates $|m\rangle$
  - Need the sum of "all" of them
  - Projected onto by d_1
  - Weighted by resonant energy denominator

OCEAN RIXS

$$\sum_f \left| \langle f | \hat{d}_2 \sum_m \left[\frac{|m\rangle\langle m|\hat{d}_1|i\rangle}{E_m - E_i - \omega_1 + i\Gamma_m} \right] \right|^2 \delta(E_f - E_i + \omega_2 - \omega_1)$$

- Don't need intermediate eigenstates $|m\rangle$
  - Need the sum of "all" of them
  - Projected onto by d_1
  - Weighted by resonant energy denominator
- Instead replace with Hamiltonian

OCEAN RIXS

$$\sum_f \left| \langle f | \hat{d}_2 \sum_m \left[\frac{|m\rangle\langle m|\hat{d}_1|i\rangle}{E_m - E_i - \omega_1 + i\Gamma_m} \right] \right|^2 \delta(E_f - E_i + \omega_2 - \omega_1)$$

- Don't need intermediate eigenstates $|m\rangle$
  - Need the sum of "all" of them

- Instead replace with Hamiltonian

$$\sum_f \left| \langle f | \hat{d}_2 \left[\frac{1}{\hat{H} - E_i - \omega_1} \right] \hat{d}_1 | i \rangle \right|^2 \delta(E_f - E_i + \omega_2 - \omega_1)$$

OCEAN RIXS

$$\sum_f \left| \langle f | \hat{d}_2 \left[\frac{1}{\hat{H} - E_i - \omega_1} \right] \hat{d}_1 | i \rangle \right|^2 \delta(E_f - E_i + \omega_2 - \omega_1)$$

- Approximate the Hamiltonian using the BSE
  - Set $E_i = 0$; Explicit core-hole broadening

$$\sum_f \left| \langle f | \hat{d}_2 \left[\frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1 + i\Gamma} \right] \hat{d}_1 | i \rangle \right|^2 \delta(E_f + \omega_2 - \omega_1)$$

OCEAN RIXS

$$\sum_f \left| \langle f | \hat{d}_2 \left[\frac{1}{\hat{H} - E_i - \omega_1} \right] \hat{d}_1 | i \rangle \right|^2 \delta(E_f - E_i + \omega_2 - \omega_1)$$

- Approximate the Hamiltonian using the BSE
  - Set $E_i = 0$; Explicit core-hole broadening

$$\sum_f \left| \langle f | \hat{d}_2 \left[\frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1 + i\Gamma} \right] \hat{d}_1 | i \rangle \right|^2 \delta(E_f + \omega_2 - \omega_1)$$

- $|x(\omega)\rangle$

OCEAN approach to RIXS

OCEAN RIXS

- $Ax = b$
- $|x(\omega)\rangle \equiv \dfrac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1 + i\Gamma} \hat{d}_1 |i\rangle$
- $\hat{A} = \hat{H}_{\mathrm{BSE}} - \omega_1$
- $|b\rangle = \hat{d}_1 |i\rangle$

OCEAN RIXS

- $Ax = b$

- Use GMRES (Generalized Minimal Residual Method)
  - Y. Saad and M.H. Schultz, SIAM J. Sci. Stat. Comput., 7, 856 (1986)
  - Core-hole broadening
    - Needed for stability (finite precession math)
    - Physically motivated

OCEAN RIXS

- $$\sum_f \left| \langle f | \hat{d}_2 | x(\omega_1) \rangle \right|^2 (E_f - E_i - \omega_1 + \omega_2)$$

- Eliminate sum over final states with Green's function
- Use valence level BSE solver to obtain final state spectrum

- $$\left\langle x(\omega_1) \middle| \hat{d}_2^+ \left[\frac{1}{\hat{H}_{BSE}^{val} - \omega_1 + \omega_2 + i\gamma} \right] \boxed{\hat{d}_2 \middle| x(\omega_1) \right\rangle}$$

- electron in conduction band
- hole is valence band

Limitations of OCEAN (BSE)

- Single electron-hole excitation
  - Only partial multiplet effects
  - Poor for localized open d- and f-shells
- Core-hole screening is *static*
  - No secondary excitations
  - No magnons, d-d*
  - No phonon response

- OCEAN is limited to direct RIXS