

Quantum Fisher Information and RIXS

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1 QFI for Non-Hermitian Operator

Let's consider a general operator A and produce its real and imaginary parts

$$A_{\text{Re}} = \frac{1}{2} (A + A^\dagger), \quad A_{\text{Im}} = \frac{1}{2i} (A - A^\dagger) \quad (1.1)$$

Either A_{Re} or A_{Im} will serve as an entanglement-witness. Suppose we have

$$\frac{F_{\text{Re}}}{(\Delta a_{\text{Re}})^2} > N m_{\text{Re}}, \quad \frac{F_{\text{Im}}}{(\Delta a_{\text{Im}})^2} > N m_{\text{Im}} \quad (1.2)$$

corresponding to the two choices of witnesses respectively. Then we detected $\max\{m_{\text{Re}}, m_{\text{Im}}\} + 1$ -partite entanglement. On the other hand, we will have

$$\min\{m_{\text{Re}}, m_{\text{Im}}\} < \frac{F_{\text{Re}} + F_{\text{Im}}}{N(\Delta a_{\text{Re}})^2 + N(\Delta a_{\text{Im}})^2} < \max\{m_{\text{Re}}, m_{\text{Im}}\} \quad (1.3)$$

As a result, we will underestimate the entanglement of the system if we use the normalized ratio. But still, the normalized ratio can serve as an entanglement-witness.

However, to utilize the relation between the quantum Fisher information and the dynamic susceptibility, we need to verify that $\chi''(A, \omega) = \chi''(A_{\text{Re}}, \omega) + \chi''(A_{\text{Im}}, \omega)$. This is not trivial, since

$$\chi(A, t) = -i\Theta(t) \langle [A_{\text{Re}}(t), A_{\text{Re}}(0)] + [A_{\text{Im}}(t), A_{\text{Im}}(0)] - i[A_{\text{Re}}(t), A_{\text{Im}}(0)] + i[A_{\text{Im}}(t), A_{\text{Re}}(0)] \rangle \quad (1.4)$$

The last two cross terms do not cancel each other trivially. Let's also look at the spectral representation:

$$\begin{aligned}\chi''(\omega) &= \frac{1}{Z} \sum_{m,n} (e^{-\beta E_m} - e^{-\beta E_n}) \langle m|A|n\rangle \langle n|A^\dagger|m\rangle \delta(\omega + E_m - E_n) \\ &= \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} (1 - e^{-\beta \omega}) \langle m|A|n\rangle \langle n|A^\dagger|m\rangle \delta(\omega + E_m - E_n)\end{aligned}\tag{1.5}$$

where

$$\begin{aligned}\langle m|A|n\rangle \langle n|A^\dagger|m\rangle &= \langle m|A_{\text{Re}}|n\rangle \langle n|A_{\text{Re}}|m\rangle + \langle m|A_{\text{Im}}|n\rangle \langle n|A_{\text{Im}}|m\rangle \\ &\quad - i \langle m|A_{\text{Re}}|n\rangle \langle n|A_{\text{Im}}|m\rangle + i \langle m|A_{\text{Im}}|n\rangle \langle n|A_{\text{Re}}|m\rangle\end{aligned}\tag{1.6}$$

The last two terms do not cancel each other in general. Unfortunately, we are not able to write the last two terms in terms of yet another hermitian operator. As a result, we have to think about the problem of QFI of non-hermitian operators, which we will do below. However, we mention that the cancellation we wanted above can indeed be implemented under integration over both negative and positive frequencies. This is shown in Robert's note, and the final conclusion will be identical to what we will described in this note.

Let's review the QFI for hermitian operators in a form that can be generalized to non-hermitian operators. For a hermitian operator A , it generates the θ -dependence of the density matrix as

$$\rho(\theta) = \exp(-iA\theta)\rho_0 \exp(+iA\theta) \quad \Rightarrow \quad \frac{\partial \rho}{\partial \theta} = -i[A, \rho]\tag{1.7}$$

To make contact with the classical probability, we usually symmetrize the commutator by introducing an operator $L_\rho(A)$ such that

$$-i[A, \rho] \equiv \frac{1}{2} \{\rho, L_\rho(A)\}\tag{1.8}$$

where the commutator is changed into an anti-commutator. $L_\rho(A)$ is called the symmetric logarithmic derivative, since it is the quantum analog of the logarithmic derivative of the classical probability. It is easy to show that

$$L_\rho(A) = 2i \sum_{k,l} \frac{\lambda_k - \lambda_l}{\lambda_k + \lambda_l} |k\rangle \langle k|A|l\rangle \langle l|\tag{1.9}$$

where λ_k and $|k\rangle$ are eigenvalues and eigenstates of ρ . Also, we can see that $L_\rho^\dagger(A) = L_\rho(A)$, meaning that $L_\rho(A)$ is hermitian.

Now let's forget about Eq. (1.7), and start from

$$\frac{\partial \rho}{\partial \theta} = \frac{1}{2} \{\rho, L_\rho(A)\}, \quad L_\rho(A) = 2i \sum_{k,l} \frac{\lambda_k - \lambda_l}{\lambda_k + \lambda_l} |k\rangle \langle k|A|l\rangle \langle l|\tag{1.10}$$

This is a valid starting point since we have

$$\text{Tr}[\partial_\theta \rho] = \text{Tr}[\rho L_\rho(A)] = 0 \quad (1.11)$$

The quantum Fisher information is then defined as

$$F_Q[\rho, A] = \text{Tr}[\rho L_\rho^2(A)] = 2 \sum_{k,l} \frac{(\lambda_k - \lambda_l)^2}{(\lambda_k + \lambda_l)} |\langle k|A|l \rangle|^2 \quad (1.12)$$

It is defined in this way such that we will have the quantum analog of the Cramér-Rao bound. This is done as follows. By choosing an arbitrary operator X that carries θ -dependence, we can form a classical probability as

$$p(x|\theta) = \text{Tr}[\rho \Pi_x] \quad (1.13)$$

where Π_x is the projector to the eigenstate of X with eigenvalue x . Using Eq. (1.10), we obtain

$$\partial_\theta p(x|\theta) = \text{Re}(\text{Tr}[\rho \Pi_x L_\rho(A)]) \quad (1.14)$$

Then the Cramér-Rao bound is

$$(\Delta\theta)^2 \geq \frac{1}{nF(X, \theta)} \quad (1.15)$$

where n is the number of independent repetitions, and $F(X, \theta)$ is the classical Fisher information:

$$F[X, \theta] = \int dx \frac{1}{p(x|\theta)} [\partial_\theta p(x|\theta)]^2 = \int dx \frac{[\text{Re}(\text{Tr}[\rho \Pi_x L_\rho])]^2}{\text{Tr}[\rho \Pi_x]} \quad (1.16)$$

Then we have the following inequalities:

$$\begin{aligned} F[X, \theta] &\leq \int dx \left| \frac{\text{Tr}[\rho \Pi_x L_\rho]}{\sqrt{\text{Tr}[\rho \Pi_x]}} \right|^2 = \int dx \left| \text{Tr} \left[\frac{\sqrt{\rho} \sqrt{\Pi_x}}{\sqrt{\text{Tr}[\rho \Pi_x]}} \sqrt{\Pi_x} L_\rho \sqrt{\rho} \right] \right|^2 \\ &\leq \int dx \text{Tr}[\Pi_x L_\rho \rho L_\rho] = \text{Tr}[L_\rho \rho L_\rho] = \text{Tr}[\rho L_\rho^2] = F_Q[\rho, A] \end{aligned} \quad (1.17)$$

which gives us the quantum Cramér-Rao bound:

$$(\Delta\theta)^2 \geq \frac{1}{nF_Q[\rho, A]} \quad (1.18)$$

This is actually how the quantum Fisher information in Eq. (1.12) is defined.

The procedure presented above has a natural generalization when A is non-hermitian:

$$\frac{\partial \rho}{\partial \theta} = \frac{1}{2} (L_\rho(A) \rho + \rho L_\rho^\dagger(A)), \quad L_\rho(A) = 2i \sum_{k,l} \frac{\lambda_k - \lambda_l}{\lambda_k + \lambda_l} |k\rangle \langle k|A|l\rangle \langle l| \quad (1.19)$$

This makes sense since we still have

$$\text{Tr}[\rho L_\rho(A)] = \text{Tr}[\rho L_\rho^\dagger(A)] = 0 \quad \Rightarrow \quad \text{Tr}[\partial_\theta \rho] = 0 \quad (1.20)$$

Then we just repeat what we have done above, and we arrive at

$$(\Delta\theta)^2 \geq \frac{1}{nF_Q[\rho, A]}, \quad F_Q[\rho, A] = \text{Tr}[\rho L_\rho(A) L_\rho^\dagger(A)] \quad (1.21)$$

so we still have

$$F_Q[\rho, A] = 2 \sum_{k,l} \frac{(\lambda_k - \lambda_l)^2}{(\lambda_k + \lambda_l)} |\langle k|A|l \rangle|^2 \quad (1.22)$$

for non-hermitian operator A .

The next step is to generalize the criteria with respect to multi-particle entanglement. For pure state $\rho_0 = |0\rangle\langle 0|$, we have $\lambda_0 = 1, \lambda_{l \neq 0} = 0$, then

$$\begin{aligned} F_Q[\rho_0, A] &= 2 \sum_{l \neq 0} \frac{(1-0)^2}{(1+0)} |\langle 0|A|l \rangle|^2 + 2 \sum_{l \neq 0} \frac{(0-1)^2}{(0+1)} |\langle l|A|0 \rangle|^2 \\ &= 4 \sum_{l \neq 0} \langle 0|A|l \rangle \langle l|A^\dagger|0 \rangle = 4 \langle 0|A(\mathbb{1} - |0\rangle\langle 0|)A^\dagger|0 \rangle \\ &= 4 (\langle 0|AA^\dagger|0 \rangle - \langle 0|A|0 \rangle \langle 0|A^\dagger|0 \rangle) \equiv 4(\Delta A)_0^2 \end{aligned} \quad (1.23)$$

For mixed state $\rho = \sum_k p_k |k\rangle\langle k|$, the quantum Fisher information is convex:

$$F_Q[\rho, A] \leq \sum_k p_k F_Q[\rho_k, A] = 4 \sum_k p_k (\Delta A)_k^2 \quad (1.24)$$

The variance has an upper bound (we will prove this later):

$$4(\Delta A)_k^2 \leq (a_{\text{Re}, \max} - a_{\text{Re}, \min})^2 + (a_{\text{Im}, \max} - a_{\text{Im}, \min})^2 \quad (1.25)$$

where a_{Re} and a_{Im} are the real and imaginary part of the eigenvalues of A . Finally, let's assume that the system is m -partite:

$$\rho = \sum_k p_k |\Psi_k\rangle\langle \Psi_k|, \quad |\Psi_k\rangle = \prod_{i=1}^m \otimes |\psi_i^{(k)}\rangle \quad (1.26)$$

Then we have

$$F_Q[\rho, A] \leq \sum_{i,k} p_k 4(\Delta A)_{i,k}^2 \leq m [(a_{\text{Re}, \max} - a_{\text{Re}, \min})^2 + (a_{\text{Im}, \max} - a_{\text{Im}, \min})^2] \quad (1.27)$$

As a result, if we have

$$\frac{F_Q[\rho, A]}{(a_{\text{Re}, \max} - a_{\text{Re}, \min})^2 + (a_{\text{Im}, \max} - a_{\text{Im}, \min})^2} > m \quad (1.28)$$

we know that the system is at least $(m+1)$ -partite.

Now let's prove Eq. (1.25). Choose the eigenstate $|i\rangle$ of A with eigenvalue $a_i = \alpha_i + i\beta_i$, where

α_i, β_i are both real. For an arbitrary state $|\psi\rangle = \sum_i c_i |i\rangle$, we can make the choice that all c_i are real. Then we have

$$\begin{aligned}
(\Delta A)_\psi^2 &= \langle \psi | A A^\dagger | \psi \rangle - \langle \psi | A | \psi \rangle \langle \psi | A^\dagger | \psi \rangle \\
&= \sum_i c_i^2 |a_i|^2 - \sum_{ij} c_i^2 c_j^2 a_i^* a_j \\
&= \left(\sum_i c_i^2 \alpha_i^2 - \sum_{ij} c_i^2 c_j^2 \alpha_i \alpha_j \right) + \left(\sum_i c_i^2 \beta_i^2 - \sum_{ij} c_i^2 c_j^2 \beta_i \beta_j \right) - i \sum_{ij} c_i^2 c_j^2 (\alpha_i \beta_j - \beta_i \alpha_j)
\end{aligned} \tag{1.29}$$

The last term vanishes since the summation is over anti-symmetric terms. As a result, we have

$$(\Delta A)_\psi^2 = (\Delta A_{\text{Re}})_\psi^2 + (\Delta A_{\text{Im}})_\psi^2 \tag{1.30}$$

where both A_{Re} and A_{Im} are hermitian operators. Since we know that for hermitian operators B , we have [1]

$$4(\Delta B)_\psi^2 \leq (b_{\text{max}} - b_{\text{min}})^2 \tag{1.31}$$

we then proved Eq. (1.25).

In summary, we can use Eq. (1.22) as the quantum Fisher information for non-Hermitian operator A , and use Eq. (1.28) as the criterion for the multi-particle entanglement.

2 Relation between QFI and Response Function

Consider an arbitrary bosonic operator A , the response function is defined as

$$\chi(\omega) = -i \int_{-\infty}^{\infty} dt e^{i\omega(t-t')} \Theta(t-t') \text{Tr}(\rho [A(t), A^\dagger(t')]) = -i \int_0^{\infty} dt e^{i\omega t} \text{Tr}(\rho [A(t), A^\dagger(0)]) \tag{2.1}$$

where $\rho = e^{-\beta H}/Z$ is the thermal density matrix, $A(t) = e^{iHt} A e^{-iHt}$. The spectral representation for $\chi(\omega)$ is

$$\begin{aligned}
\chi(\omega) &= \frac{1}{Z} \sum_{m,n} \frac{(e^{-\beta E_m} - e^{-\beta E_n}) \langle m | A | n \rangle \langle n | A^\dagger | m \rangle}{\omega + E_m - E_n + i0^+} \\
&= \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} \int_{-\infty}^{\infty} d\omega' \frac{|\langle n | A^\dagger | m \rangle|^2 (1 - e^{-\beta \omega'}) \delta(E_n - E_m - \omega')}{\omega - \omega' + i0^+}
\end{aligned} \tag{2.2}$$

and the spectral representation for $\chi''(\omega)$ is

$$\begin{aligned}
\chi''(\omega) &= \frac{1}{Z} \sum_{m,n} (e^{-\beta E_m} - e^{-\beta E_n}) \langle m | A | n \rangle \langle n | A^\dagger | m \rangle \delta(\omega + E_m - E_n) \\
&= \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} (1 - e^{-\beta \omega}) \langle m | A | n \rangle \langle n | A^\dagger | m \rangle \delta(\omega + E_m - E_n)
\end{aligned} \tag{2.3}$$

Using the fact that

$$\int_{-\infty}^{\infty} d\omega \tanh\left(\frac{\beta\omega}{2}\right) \delta(\omega + E_m - E_n) = \tanh\left(\frac{\beta(E_n - E_m)}{2}\right) = \frac{\lambda_m - \lambda_n}{\lambda_m + \lambda_n} \quad (2.4)$$

where $\lambda_n = \exp(-\beta E_n)/Z$ is the eigenvalue of the density matrix ρ , and the expression for the quantum Fisher information in Eq. (1.22), we obtain

$$F_Q[\rho, A] = 2 \int_{-\infty}^{\infty} d\omega \tanh\left(\frac{\beta\omega}{2}\right) \chi''(\omega), \quad \chi''(\omega) \equiv -\frac{1}{\pi} \text{Im} \chi(\omega) \quad (2.5)$$

For hermitian operator, we can simplify further as

$$F_Q[\rho, A] = 4 \int_0^{\infty} d\omega \tanh\left(\frac{\beta\omega}{2}\right) \chi''(\omega) \quad (2.6)$$

since we have $\chi''(\omega) = -\chi''(-\omega)$. This is not true for a general non-hermitian operator.

3 The RIXS operator

This is based on [2, 3]. In RIXS, the solid is taken from a ground state with energy E_g to a final state with excitations and an energy E_f . The energy and momentum of the excitation are determined by the difference in photon energy $\hbar\omega_{\mathbf{k}} - \hbar\omega_{\mathbf{k}'}$ and momentum $\hbar\mathbf{k}' - \hbar\mathbf{k}$, respectively. The RIXS intensity can in general be written in terms of a scattering amplitude as

$$I(\omega, \mathbf{k}, \mathbf{k}', \epsilon, \epsilon') = \sum_f |\mathcal{F}_{fg}(\mathbf{k}, \mathbf{k}', \epsilon, \epsilon', \omega_{\mathbf{k}})|^2 \delta(E_f + \hbar\omega_{\mathbf{k}'} - E_g - \hbar\omega_{\mathbf{k}}) \quad (3.1)$$

where the delta function enforces energy conservation and the amplitude $\mathcal{F}_{fg}(\mathbf{k}, \mathbf{k}', \epsilon, \epsilon', \omega_{\mathbf{k}})$ reflects which excitations are probed and how, for instance, the spectral weights of final-state excitations depend on the polarization vectors ϵ and ϵ' of the incoming and outgoing x rays, respectively.

The material first absorbs the photon. The system is then in a short-lived intermediate state, from which it relaxes radiatively. In an experiment, one studies the X-rays emitted in this decay process. This two-step process cannot be described simply by using Fermi's golden rule, but requires a higher-order treatment, known as the Kramers-Heisenberg equation [4]. Since absorption and emission are single-photon processes, the interactions between the X-rays and the material are dominated by the terms in the cross section proportional to $\mathbf{p} \cdot \mathbf{A}$, where \mathbf{p} is the momentum of the electrons in the material and \mathbf{A} is the vector potential of the photon. The interaction between the X-rays and the material depends on external quantities, such as wave vector \mathbf{k} and polarization vectors ϵ of the X-rays, and operators, such as \mathbf{p} and \mathbf{r} . As a result the electronic transitions are intermingled. The scattering amplitude can be split into an angular and polarization dependence $\mathbf{T}^x(\hat{\mathbf{k}}, \hat{\mathbf{k}}', \epsilon, \epsilon')$ related to the experimental geometry and spectral functions $\mathbf{F}^x(k, k', \omega_{\mathbf{k}})$ that reflect the properties of the material:

$$\mathcal{F}_{fg}(\mathbf{k}, \mathbf{k}', \epsilon, \epsilon', \omega_{\mathbf{k}}) = \sum_x \mathbf{F}^x(k, k', \omega_{\mathbf{k}}) \mathbf{T}^x(\hat{\mathbf{k}}, \hat{\mathbf{k}}', \epsilon, \epsilon') \quad (3.2)$$

This separation can be done exactly. It is important to note that there are only a finite number of fundamental scattering amplitudes $\mathbf{F}^x(k, k', \omega_{\mathbf{k}})$ and that the RIXS scattering amplitude is a

linear combination of these fundamental scattering amplitudes weighted by the angular functions $\mathbf{T}^x(\hat{\mathbf{k}}, \hat{\mathbf{k}}', \boldsymbol{\epsilon}, \boldsymbol{\epsilon}')$.

The RIXS amplitude \mathcal{F}_{fg} can be represented as

$$\mathcal{F}_{fg} = \langle f | \mathcal{D}'^\dagger G \mathcal{D} | g \rangle, \quad G(z_{\mathbf{k}}) = \frac{1}{z_{\mathbf{k}} - H_n}, \quad H_n = H_0 + H_c, \quad z_{\mathbf{k}} = E_g + \hbar\omega_{\mathbf{k}} + i\Gamma_c \quad (3.3)$$

where $G = G_0 + G_0 H_c G$ is the intermediate state propagator, H_0 is the initial Hamiltonian and H_c is the core-hole Hamiltonian. The transition operator \mathcal{D} corresponds to the incoming X-rays, and \mathcal{D}' corresponds to the outgoing X-rays. The expression for \mathcal{D} is

$$\mathcal{D} = \frac{1}{im\omega_{\mathbf{k}}} \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \boldsymbol{\epsilon} \cdot \mathbf{p}_j \quad (3.4)$$

where \mathbf{R}_j is position of the j -th site and \mathbf{p}_j is momentum of the electron bound to the j -th site. Under the dipole approximation, we will have

$$\langle n | \mathcal{D} | g \rangle \approx \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \langle n | \boldsymbol{\epsilon} \cdot \mathbf{r}_j | g \rangle \quad (3.5)$$

where $|n\rangle$ is the eigenstates of the intermediate Hamiltonian H_n , and \mathbf{r} is the position operator of the electron bound to the j -th site.

Finally, the RIXS cross-section at finite temperature and with finite final-state lifetime is described by the Kramers-Heisenberg formula:

$$I_{\text{RIXS}}(\omega_{\text{in}}, \omega, \mathbf{k}_i, \mathbf{k}_o, \boldsymbol{\epsilon}_i, \boldsymbol{\epsilon}_f) = \sum_g \frac{1}{Z} e^{-\frac{E_g}{k_B T}} \sum_f \left| \frac{\langle f | \mathcal{D}_o^\dagger | n \rangle \langle n | \mathcal{D}_i | g \rangle}{\omega_{\text{in}} - E_n + E_g + i\Gamma_c} \right|^2 \frac{\Gamma/\pi}{(\omega - E_f + E_g)^2 + \Gamma^2} \quad (3.6)$$

where $|g\rangle$ are the ground states of the initial Hamiltonian H_0 describing the valence electrons. T is the temperature and k_B is the Boltzmann factor. Z is the partition function. $|f\rangle$ are the excited eigenstates of the initial Hamiltonian H_0 . $|n\rangle$ are the eigenstates of intermediate Hamiltonian H_n which includes a deep core-hole and one more electron in the valence shell after the X-ray absorption process. ω_{in} is the energy of the incident X-ray which is tuned to be at a specific resonant edge. ω is the X-ray energy loss, i.e., the energy difference between the incident and scattered X-ray. Γ_c and Γ are the lifetime broadening of the intermediate (with a core hole) and final states, respectively. The transition operators \mathcal{D}_i and \mathcal{D}_o^\dagger can be generally written as

$$\mathcal{D}_i = \sum_a P_a^i T_a^i, \quad \mathcal{D}_o^\dagger = \sum_a P_a^{o*} T_a^{o\dagger} \quad (3.7)$$

In the dipole approximation, we have

$$\begin{aligned} P_a^i &= \epsilon_a^i, \quad P_a^o = \epsilon_a^o, \quad a = x, y, z \\ T_x^i &= e^{i\mathbf{k}_i \cdot \mathbf{R}_j} x_j, \quad T_y^i = e^{i\mathbf{k}_i \cdot \mathbf{R}_j} y_j, \quad T_z^i = e^{i\mathbf{k}_i \cdot \mathbf{R}_j} z_j \\ T_x^o &= e^{i\mathbf{k}_o \cdot \mathbf{R}_j} x_j, \quad T_y^o = e^{i\mathbf{k}_o \cdot \mathbf{R}_j} y_j, \quad T_z^o = e^{i\mathbf{k}_o \cdot \mathbf{R}_j} z_j \end{aligned} \quad (3.8)$$

where j labels the site, and x_j, y_j, z_j are position operators of electrons bound to site- j . Note that there is an implicit summation over site label j inside the absolute value in Eq. (3.6). In practical calculations, we will construct the matrix element

$$\langle n | \mathcal{D}_i | g \rangle = \sum_a P_a^i \langle n | T_a^i | g \rangle = \sum_a P_a^i e^{i\mathbf{k}_i \cdot \mathbf{R}_j} \langle n | r_j^a | g \rangle, \quad \mathbf{r}_j = (x_j, y_j, z_j) \quad (3.9)$$

The nonzero matrix element $\langle n | r^a | g \rangle$ is given by the selection rule, which effectively plays with the Clebsch-Gordon coefficients including orbital and spin degrees of freedom (they are collectively called orbitals in practice).

4 Relation to QFI

By comparing the RIXS signal in Eq. (3.6) with the dynamic susceptibility in Eq. (2.3), we can just take

$$A^\dagger = \mathcal{D}_o^\dagger \frac{1}{\omega_{\text{in}} - H_n + H_0 + i\Gamma_c} \mathcal{D}_i \quad (4.1)$$

[Update: Actually, it should be

$$\langle f | A^\dagger | g \rangle = \sum_n \langle f | \mathcal{D}_o^\dagger | n \rangle \frac{1}{\omega_{\text{in}} - E_n + E_g + i\Gamma_c} \langle n | \mathcal{D}_i | g \rangle \quad (4.2)$$

It is not quite the same as the operator form stated above since we have both H_n and H_0 in the denominator, which have different sets of eigenstates. But this modification does not affect the calculation of QFI in the actual code, since the code implements the correct form.] and the Eq. (2.5) should be modified as

$$F(A) = 2 \int_{-\infty}^{\infty} d\omega \tanh\left(\frac{\beta\omega}{2}\right) (1 - e^{-\beta\omega}) I_{\text{RIXS}}(\omega) \quad (4.3)$$

The operator in Eq. (4.1) can be numerically constructed using EDRIXS. In this way, there is no need to find the χ matrix as in the case of a single site problem.

For the integration over the negative frequency, firstly, we indeed have access to the negative frequency; secondly, the negative frequency can be related to the positive frequency via the spectral representation in Eq. (2.3):

$$\begin{aligned} \chi''(\omega) &= \frac{1}{Z} \sum_{m,n} (e^{-\beta E_m} - e^{-\beta E_n}) \langle m | A | n \rangle \langle n | A^\dagger | m \rangle \delta(\omega + E_m - E_n) \\ &= \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} (1 - e^{-\beta\omega}) \langle m | A | n \rangle \langle n | A^\dagger | m \rangle \delta(\omega + E_m - E_n) \\ \chi''(-\omega) &= \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} (1 - e^{\beta\omega}) \langle m | A | n \rangle \langle n | A^\dagger | m \rangle \delta(-\omega + E_m - E_n) \\ &= \frac{1}{Z} \sum_{m,n} e^{-\beta E_m} (1 - e^{\beta\omega}) \langle m | A | n \rangle \langle n | A^\dagger | m \rangle \delta(\omega - E_m + E_n) \\ &= \frac{1}{Z} \sum_{n,m} e^{-\beta E_m} (e^{-\beta\omega} - 1) \langle n | A | m \rangle \langle m | A^\dagger | n \rangle \delta(\omega - E_n + E_m) \end{aligned} \quad (4.4)$$

If $A^\dagger = A$, we would have

$$\chi''(-\omega) = -\chi''(\omega) \quad (4.5)$$

but for $A^\dagger \neq A$, we don't have anything.

Returning back to the RIXS signal, due to the large factor $(1 - e^{-\beta\omega})$ at negative frequency, RIXS signal at negative frequency will be extremely small, which is far below the detectable threshold. Consequently, it is not a good idea to detect or calculate the RIXS signal at negative frequency. However, the contribution from the negative frequency cannot be ignored, since the χ'' itself is finite, with magnitude comparable to the contribution from the positive frequency. As a result, we should replace the detection or calculation of the RIXS signal at negative frequencies with that at positive frequencies. According to Eq. (4.4), we could calculate the RIXS signal at positive frequency with the conjugate of the RIXS operator. Further, according to Eq. (4.1), we could detect or calculate the RIXS signal at positive frequencies with exchanging the incident and scattering polarization and exchanging the incident and scattering momentum. Then Eq. (4.3) is modified as

$$\begin{aligned} F(A) &= 2 \int_0^\infty d\omega \tanh\left(\frac{\beta\omega}{2}\right) (1 - e^{-\beta\omega}) (I_{\text{RIXS}}(\omega) + I_{\text{RIXS,conjugate}}) \\ &= 2 \int_0^\infty d\omega \tanh\left(\frac{\beta\omega}{2}\right) (1 - e^{-\beta\omega}) (I_{\text{RIXS}}(\omega) + I_{\text{RIXS,exchange}}) \end{aligned} \quad (4.6)$$

5 Spin and Orbital Degrees of Freedom

We want to investigate the entanglement between different spins or orbitals. The first step is to write the RIXS operator in terms of spin and orbital degrees of freedom. Firstly, we have at site j

$$\mathcal{D}_i \equiv \sum_a e^{i\mathbf{k}_i \cdot \mathbf{R}_j} P_a^i \mathcal{D}^a, \quad \mathcal{D}_o \equiv \sum_a e^{i\mathbf{k}_o \cdot \mathbf{R}_j} P_a^o \mathcal{D}^a \quad (5.1)$$

Let's look at the transition operator \mathcal{D}^a :

$$\begin{aligned} \mathcal{D}^x &= -0.40824829d_1^\dagger p_1 - 0.40824829d_2^\dagger p_2 + 0.70710678d_3^\dagger p_5 + 0.70710678d_4^\dagger p_6 \\ &\quad + 0.70710678d_7^\dagger p_1 + 0.70710678d_8^\dagger p_2 + 0.70710678d_9^\dagger p_3 + 0.70710678d_{10}^\dagger p_4 \\ \mathcal{D}^y &= -0.40824829d_1^\dagger p_3 - 0.40824829d_2^\dagger p_4 + 0.70710678d_5^\dagger p_5 + 0.70710678d_6^\dagger p_6 \\ &\quad - 0.70710678d_7^\dagger p_3 - 0.70710678d_8^\dagger p_4 + 0.70710678d_9^\dagger p_1 + 0.70710678d_{10}^\dagger p_2 \\ \mathcal{D}^z &= +0.81649658d_1^\dagger p_5 + 0.81649658d_2^\dagger p_6 + 0.70710678d_3^\dagger p_1 + 0.70710678d_4^\dagger p_2 \\ &\quad + 0.70710678d_5^\dagger p_3 + 0.70710678d_6^\dagger p_4 \end{aligned} \quad (5.2)$$

The ordering of the orbitals are

$$\begin{aligned} &d_{3z^2-r^2,\uparrow}, \quad d_{3z^2-r^2,\downarrow}, \quad d_{zx,\uparrow}, \quad d_{zx,\downarrow}, \quad d_{zy,\uparrow}, \quad d_{zy,\downarrow}, \quad d_{x^2-y^2,\uparrow}, \quad d_{x^2-y^2,\downarrow}, \quad d_{xy,\uparrow}, \quad d_{xy,\downarrow} \\ &p_{x,\uparrow}, \quad p_{x,\downarrow}, \quad p_{y,\uparrow}, \quad p_{y,\downarrow}, \quad p_{z,\uparrow}, \quad p_{z,\downarrow}, \end{aligned} \quad (5.3)$$

In summary, we have

$$\begin{aligned}
\mathcal{D}^x &= \sum_{\sigma} \left[\left(-0.4d_{3z^2-r^2,\sigma}^{\dagger} + 0.7d_{x^2-y^2,\sigma}^{\dagger} \right) p_{x,\sigma} + 0.7d_{zx,\sigma}^{\dagger} p_{z,\sigma} + 0.7d_{xy,\sigma}^{\dagger} p_{y,\sigma} \right] \\
\mathcal{D}^y &= \sum_{\sigma} \left[\left(-0.4d_{3z^2-r^2,\sigma}^{\dagger} - 0.7d_{x^2-y^2,\sigma}^{\dagger} \right) p_{y,\sigma} + 0.7d_{zy,\sigma}^{\dagger} p_{z,\sigma} + 0.7d_{yx,\sigma}^{\dagger} p_{x,\sigma} \right] \\
\mathcal{D}^z &= \sum_{\sigma} \left[0.8d_{3z^2-r^2,\sigma}^{\dagger} p_{z,\sigma} + 0.7d_{zx,\sigma}^{\dagger} p_{x,\sigma} + 0.7d_{zy,\sigma}^{\dagger} p_{y,\sigma} \right]
\end{aligned} \tag{5.4}$$

and eventually, we have

$$\begin{aligned}
\mathcal{D}_i &= e^{i\mathbf{k}_i \cdot \mathbf{R}_j} \sum_{\sigma} \left[P_x^i \left(-0.4d_{3z^2-r^2,\sigma}^{\dagger} + 0.7d_{x^2-y^2,\sigma}^{\dagger} \right) + P_y^i 0.7d_{xy,\sigma}^{\dagger} + P_z^i 0.7d_{zx}^{\dagger} \right] p_{x,\sigma} \\
&\quad + \left[P_x^i 0.7d_{xy,\sigma}^{\dagger} + P_y^i \left(-0.4d_{3z^2-r^2,\sigma}^{\dagger} - 0.7d_{x^2-y^2,\sigma}^{\dagger} \right) + P_z^i 0.7d_{zy,\sigma}^{\dagger} \right] p_{y,\sigma} \\
&\quad + \left[P_x^i 0.7d_{zx,\sigma}^{\dagger} + P_y^i 0.7d_{zy,\sigma}^{\dagger} + P_z^i 0.8d_{3z^2-r^2,\sigma}^{\dagger} \right] p_{z,\sigma}
\end{aligned} \tag{5.5}$$

and

$$\begin{aligned}
\mathcal{D}_o &= e^{i\mathbf{k}_o \cdot \mathbf{R}_j} \sum_{\sigma} \left[P_x^o \left(-0.4d_{3z^2-r^2,\sigma}^{\dagger} + 0.7d_{x^2-y^2,\sigma}^{\dagger} \right) + P_y^o 0.7d_{xy,\sigma}^{\dagger} + P_z^o 0.7d_{zx}^{\dagger} \right] p_{x,\sigma} \\
&\quad + \left[P_x^o 0.7d_{xy,\sigma}^{\dagger} + P_y^o \left(-0.4d_{3z^2-r^2,\sigma}^{\dagger} - 0.7d_{x^2-y^2,\sigma}^{\dagger} \right) + P_z^o 0.7d_{zy,\sigma}^{\dagger} \right] p_{y,\sigma} \\
&\quad + \left[P_x^o 0.7d_{zx,\sigma}^{\dagger} + P_y^o 0.7d_{zy,\sigma}^{\dagger} + P_z^o 0.8d_{3z^2-r^2,\sigma}^{\dagger} \right] p_{z,\sigma}
\end{aligned} \tag{5.6}$$

Let's look at the RIXS operator:

$$\langle f | A^{\dagger} | g \rangle = \sum_n \langle f | \mathcal{D}_o^{\dagger} | n \rangle \frac{1}{\omega_{\text{in}} - E_n + E_g + i\Gamma_c} \langle n | \mathcal{D}_i | g \rangle \tag{5.7}$$

where we have obtained the structure of \mathcal{D}_o^{\dagger} and \mathcal{D}_i , and E_n is the eigenvalue corresponding to $H_n |n\rangle = E_n |n\rangle$, E_g is the eigenvalue corresponding to $H_0 |g\rangle = E_g |g\rangle$.

Spin degree of freedom - Due to the spin-orbital coupling, neither H_0 nor H_n conserves the spin degree of freedom. This can be checked by looking at the eigenstates of H_0 and H_n to see if they are also eigenstates of the spin operator. The answer is no. On other other hand, both \mathcal{D}_i and \mathcal{D}_o has no selective feature between the two spin projections, thus it is impossible to choose a suitable polarization to make A^{\dagger} expressible as $A_{\uparrow}^{\dagger} + A_{\downarrow}^{\dagger}$. This means that RIXS cannot serves as a entanglement witness for the spin degree of freedom.

We may think of some pseudospin degree of freedom. A linear combination of the spin projections would not work, due to the spin-orbital coupling and the fact that \mathcal{D}_i and \mathcal{D}_o has no selective feature between the two spin projections. We then think of certain type of total angular momentum as combination of spin and orbital. However, due to the electron-electron interaction and crystal splitting field, the orbitals are also mixed, see below.

Orbital degree of freedom - By observing \mathcal{D}_o and \mathcal{D}_i we can learn that the orbits are grouped into

two sets: the e_g orbitals and t_{2g} orbitals. We then want to analyze if H_0 and H_n conserve these two sets. Again, we can check the eigenstates of H_0 and H_n to see if they are also eigenstates of the orbital sets. The result is that neither H_0 nor H_n conserves the orbital sets. However, \mathcal{D}_o and \mathcal{D}_i are selective among the orbitals, so it is potentially possible to tune the polarization to make A^\dagger separate into two terms.

Basically, we have the following structure. The Hilbert space can be decomposed into two parts: $\mathcal{H} = \mathcal{H}_0 \oplus \mathcal{H}_1$, where \mathcal{H}_0 stands for no core hole, and \mathcal{H} stands for one core hole (let's focus on one of the two sites, the other is just additive). H_0 acts within \mathcal{H}_0 , H_n acts within \mathcal{H}_1 , while $\mathcal{D}_i, \mathcal{D}_o$ connects \mathcal{H}_0 and \mathcal{H}_1 . Finally A^\dagger acts within \mathcal{H}_0 . We want to know if A^\dagger is block-diagonal, meaning that A^\dagger does not connect t_{2g} and e_g orbitals. This cannot be answered by inspecting H_0 or H_n only, since the actual A^\dagger is defined by

$$\langle f | A^\dagger | g \rangle = \sum_n \langle f | \mathcal{D}_o^\dagger | n \rangle \frac{1}{\omega_{\text{in}} - E_n + E_g + i\Gamma_c} \langle n | \mathcal{D}_i | g \rangle \quad (5.8)$$

such that

$$A^\dagger \neq \mathcal{D}_o^\dagger \frac{1}{\omega_{\text{in}} - H_n + H_0 + i\Gamma_c} \mathcal{D}_i \quad (5.9)$$

since H_0 and H_n does not commute. As a result, we have to explicitly construct A^\dagger numerically.

The code has constructed A^\dagger in terms of Eq. (5.8), where the states are eigenstates of H_0 . Let's denote them by $|g_i\rangle$. They are expressed as linear combinations of the basis $|b_i\rangle$:

$$\begin{pmatrix} |g_0\rangle \\ \vdots \\ |g_i\rangle \\ \vdots \end{pmatrix} = P \begin{pmatrix} |b_0\rangle \\ \vdots \\ |b_i\rangle \\ \vdots \end{pmatrix} \Rightarrow \begin{pmatrix} |b_0\rangle \\ \vdots \\ |b_i\rangle \\ \vdots \end{pmatrix} = Q \begin{pmatrix} |g_0\rangle \\ \vdots \\ |g_i\rangle \\ \vdots \end{pmatrix} \quad (5.10)$$

where $Q = P^{-1} = P^\dagger$. Here P is just the Numpy array storing the eigenstates $|g_i\rangle$. Consequently, we have

$$A_{ji}^b \equiv \langle b_j | A^\dagger | b_i \rangle = \sum_{lk} Q_{jk}^* Q_{il} \langle g_k | A^\dagger | g_l \rangle \equiv \sum_{lk} Q_{jk}^* Q_{il} A_{kl}^g = (Q^* A^g Q^T)_{ji} = (P^T A^g P^*)_{ji} \quad (5.11)$$

Now A^b is the RIXS operator define in terms of the basis. We know that $|b_i\rangle$ with $i = 0, \dots, 65$ correspond to the t_{2g} sector, while $|b_i\rangle$ with $i \geq 66$ correspond to the e_g sector. We have 9 A^b matrices, due to 3 incoming polarizations and 3 outgoing polarizations, let's denote them as $c_{ab} = (P_a^o)^* P_b^a$, $a, b = x, y, z$. To realize separation of t_{2g} and e_g sectors, we need

$$A_{ji}^b \equiv \sum_{a,b} c_{ab} A_{ji}^{ab} = 0, \quad \text{for } j \geq 66, \quad i \leq 65 \quad (5.12)$$

Let's choose $i = 0, j = 66, \dots, 74$ to form a set of linear equations for c_{ab} . Solving it gives us c_{ab} , then we check if other choices of i, j fulfills the condition:

$$\begin{pmatrix} A_{66,0}^{00} & A_{66,0}^{01} & \cdots & A_{66,0}^{22} \\ A_{67,0}^{00} & A_{67,0}^{01} & \cdots & A_{67,0}^{22} \\ \vdots & \vdots & \vdots & \vdots \\ A_{74,0}^{00} & A_{74,0}^{01} & \cdots & A_{74,0}^{22} \end{pmatrix} \begin{pmatrix} c_{00} \\ c_{01} \\ \vdots \\ c_{22} \end{pmatrix} = 0 \quad (5.13)$$

and

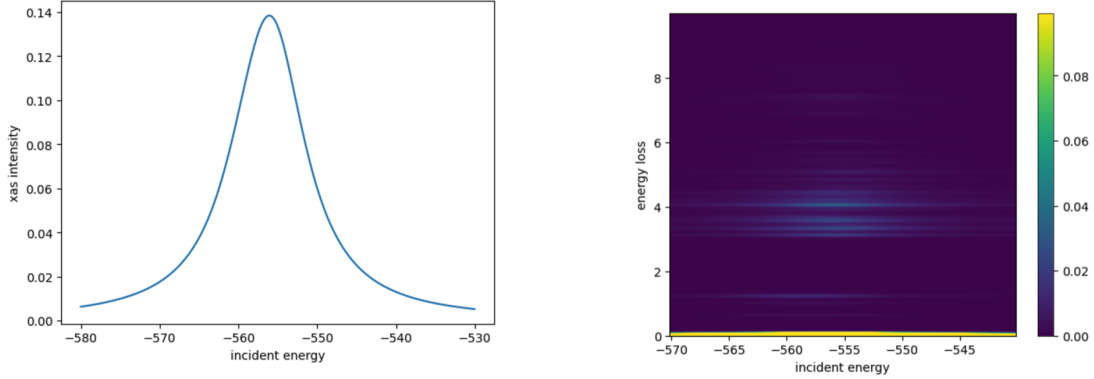
$$\mathbf{v} = (A_{ji}^{00} \ A_{ji}^{01} \ \cdots \ A_{ji}^{22}), \quad \mathbf{v} \cdot \mathbf{c} = 0 \quad (5.14)$$

In actual implementation, we compute the eigenvalues and eigenvectors of the matrix in Eq. (5.13), and take the eigenvector with the smallest eigenvalue (in terms of modulus) as the solution. Also we need to normalize the solution such that it has modulus one. Let's denote the solution as \mathbf{c} . We then take \mathbf{v} from the off-diagonal ($t_{2g}-e_g$) and from the diagonal ($t_{2g}-t_{2g}$ or e_g-e_g), and compute & compare $\mathbf{v} \cdot \mathbf{c}$. Unfortunately, the result is that the off-diagonals have the same order of magnitude as the diagonals. This means that we cannot tune the polarizations to make the RIXS operator decompose into different orbital sectors.

6 Material Parameters

HKL corresponds to the reciprocal lattice sites, whose lattice constants are $a^* \sim 1.22$, b^* not known, $c^* \sim 0.426$. In experiments, we have $H = 0.5$, $K = 0$, and varying L . The momenta Q are obtained from HKL , the angles are obtained from the momenta, and polarizations are obtained from the angles. We have $\alpha = 0, \beta = 0, \pi/2, \phi = 10$. Also the wavelength is $\lambda = 1.105483$.

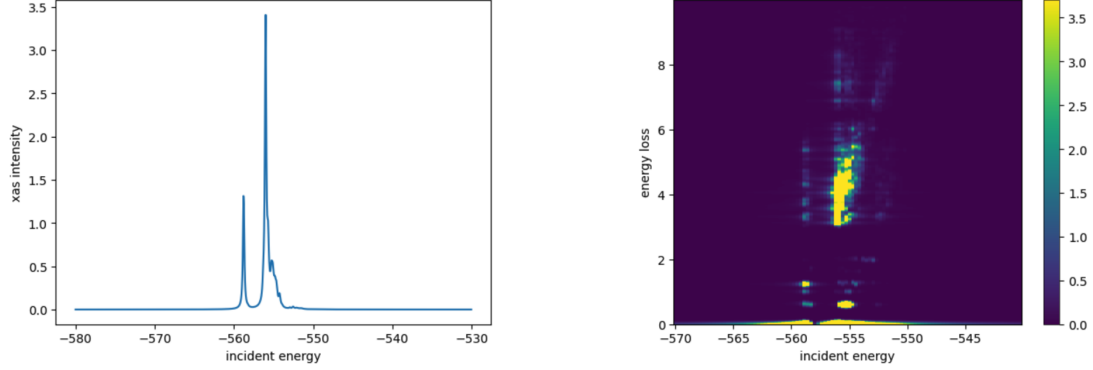
7 Tuning Parameters



$$\Gamma_c = 5.0, \Delta_{10Dq} = 3.5$$

Figure 1: The case of normal parameters.

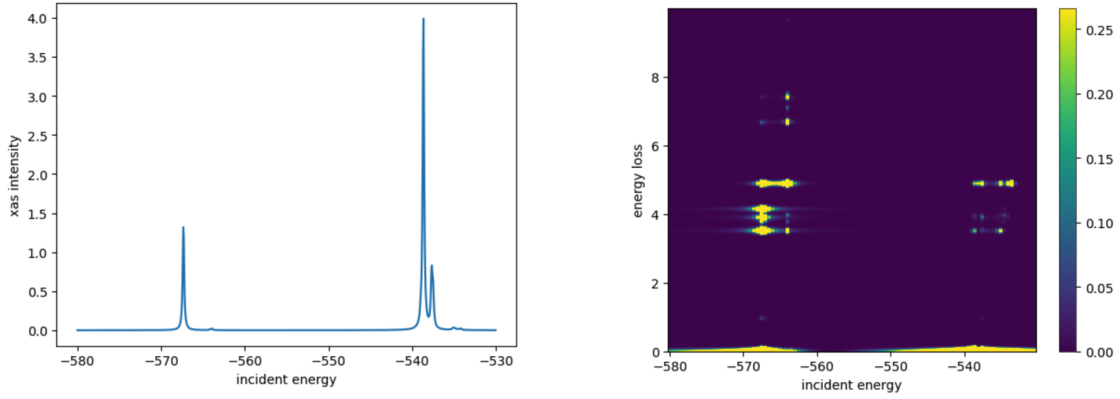
From the results shown in Figs. 2 to 5, we learn that the mixing of t_{2g} and e_g orbitals persist even in large crystal splitting field. We can further looking into this issue by inspecting the eigenstates of H_0 and H_n . For a specific eigenstate, we can expand it in terms of orbital-eigenstates, which we



$$\Gamma_c = 0.1, \Delta_{10Dq} = 3.5; \quad \frac{\text{offdiag}}{t_{2g}\text{diag}} \sim 0.32, \quad \frac{e_g\text{diag}}{t_{2g}\text{diag}} \sim 0.50$$

at t_{2g} resonance

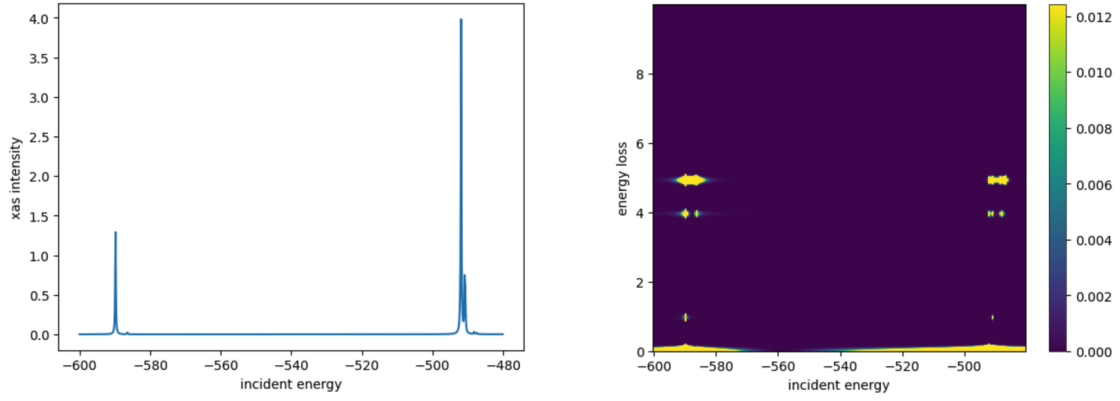
Figure 2: The case of new parameters set 1.



$$\Gamma_c = 0.1, \Delta_{10Dq} = 30; \quad \frac{\text{offdiag}}{t_{2g}\text{diag}} \sim 0.068, \quad \frac{e_g\text{diag}}{t_{2g}\text{diag}} \sim 0.49$$

at t_{2g} resonance

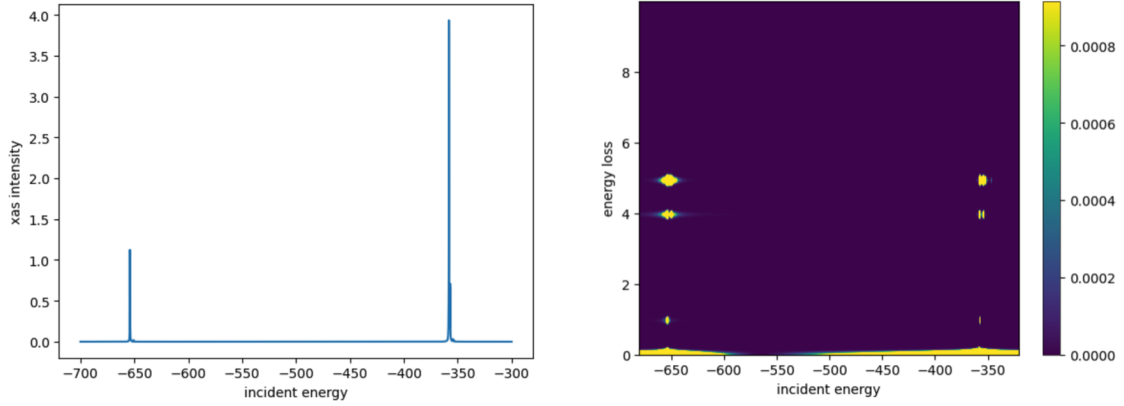
Figure 3: The case of new parameters set 2.



$$\Gamma_c = 0.1, \Delta_{10Dq} = 100; \quad \frac{\text{offdiag}}{t_{2g}\text{diag}} \sim 0.067, \quad \frac{e_g\text{diag}}{t_{2g}\text{diag}} \sim 0.34$$

at t2g resonance

Figure 4: The case of new parameters set 3.



$$\Gamma_c = 0.1, \Delta_{10Dq} = 300; \quad \frac{\text{offdiag}}{t_{2g}\text{diag}} \sim 0.061, \quad \frac{e_g\text{diag}}{t_{2g}\text{diag}} \sim 0.29$$

at t2g resonance

Figure 5: The case of new parameters set 4.

symbolically write as

$$|g\rangle = g_0 |t_{2g}\rangle + g_1 |e_g\rangle, \quad |n\rangle = n_0 |t_{2g}\rangle + n_1 |e_g\rangle \quad (7.1)$$

where $|g\rangle$ is the eigenstate of H_0 , and $ketn$ is the eigenstate of H_n . For experimentally relevant $\Delta_{10Dq} = 3.5$, g_0 and g_1 are on the same order, n_0 and n_1 are on the same order. For $\Delta_{10Dq} = 30, 100, 300$, g_1 becomes increasing suppressed below g_0 , being several orders of magnitude smaller than g_0 . However, n_1 will stay on the same order of n_0 , indicating significant mixing of t_{2g} and e_g sectors when a core-hole is present.

8 5d Orbitals and Basis for Dimer

There are in total 10 5d orbitals (including spin degrees of freedom):

$$\begin{aligned} 0 : d_{3z^2-r^2, \uparrow}, m = 2, & \quad 1 : d_{3z^2-r^2, \downarrow}, m = 2 \\ 6 : d_{x^2-y^2, \uparrow}, m = 1, & \quad 7 : d_{x^2-y^2, \downarrow}, m = 1 \\ 2 : d_{zx, \uparrow}, m = -1, & \quad 3 : d_{zx, \downarrow}, m = -1, \quad J = 3/2 \\ 4 : d_{zy, \uparrow}, m = 0, & \quad 5 : d_{zy, \downarrow}, m = 0, \quad J = 1/2 \\ 8 : d_{xy, \uparrow}, m = -2, & \quad 9 : d_{xy, \downarrow}, m = -2, \quad J = 3/2 \end{aligned} \quad (8.1)$$

where $d_{3z^2-r^2}$ is often abbreviated as d_{z^2} . The crystal field (octahedral complex) splits them into two sets, the higher energy level is called e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}), and the lower energy level is called t_{2g} orbitals (d_{xy} , d_{zx} , d_{zy}).

For the dimer system, we then have 20 5d orbitals in total (including spin degrees of freedom, 10 on each site), among which 12 belong to the t_{2g} manifold (6 on each site). For the case of $Ba_3CeIr_2O_9$, there are 10 electrons in total, then we have the following possibilities for the t_{2g} manifold:

- 5 electrons on each site - there are $C_6^5 \cdot C_6^5 = 36$ states in total.
- 6 electrons on site-1 and 4 electrons on site-2 - there are $C_6^4 = 15$ states in total.
- 4 electrons on site-1 and 6 electrons on site-2 - there are $C_6^4 = 15$ states in total.

As a result, the t_{2g} manifold has 66 states.

Now let's see how they are implemented in EDRIXS. In the module `witness_utils` we define the function `get_fock_bin_by_N_S`. It takes in the argument of possible levels and number of electrons and produces the basis. For example, the following code will produce the basis for the t_{2g} manifold of the dimer:

```
all_states = get_fock_bin_by_N_S(8,0,12,10, dispinfo=False)
```

The resulting shape of `all_states` is `(66, 10)`, meaning that there are 66 states in the t_{2g} manifold, and they are labeled by labels of the occupied single-electron states. Also the convention for the single-electron states, at this stage, is such that number 0 to 7 refer to the e_g states, while number 8 to 19 refer to the 12 t_{2g} states. For example

```
all_states[0] # array([8, 9, 10, 11, 12, 13, 14, 15, 16, 17])
```

If you want to obtain the basis with fixed electron numbers on each site, you can use the following code:

```
states_55 = get_fock_bin_by_N_S(8,0,6,5,6,5, dispinfo=False)
```

which corresponds to the states with 5 electrons on site 1 and 5 electrons on site 2. You can check the following

```
states_55.shape # (36,10)
states_55[0] # array([8, 9, 10, 11, 12, 14, 15, 16, 17, 18])
```

In the actual implementation, we also include the valence levels, so the basis of the t_{2g} manifold is obtained as

```
all_states = get_fock_bin_by_N_S(8,0,12,10,6,6,6,6, dispinfo=False)
```

There are also extra processing of the relevant basis, such as rearranging e_g states such that they come after the t_{2g} states, changing from complex harmonics to real harmonics, and so on. Finally, the full basis (occupation of the e_g orbitals can be either 0 or 1) without core hole is stored as `basis_i.npz`, and the full basis with a core hole is stored as `basis_n1.npz` and `basis_n2.npz`.

Using the basis listed above, we can then express the relevant states. For example, the eigenstates of the system without core hole is stored as `evecs_i.npy`, which is a set of vectors, whose components are the normalized coefficients for linear superposition of `basis_i`. The same is true for the eigenstates of the system with core hole, which is stored as `evecs_n1.npy` and `evecs_n2.npy`.

We also want to consider the states with fixed electron numbers, and express them using the basis `basis_i`. This is stored as `states_64.npy`, `states_55.npy`, and `states_46.npy`.

9 RIXS Operators

The RIXS operators are defined by their matrix elements with respect to the states of `evecs_i`. They are denoted as `F_mag_real` and `F_mag_imag` for each choice of $\omega_{\text{in}}, \theta$ and ϵ_i, ϵ_o .

On the other hand, for a pure state, we have

$$F_Q = 4 \left(\langle \psi | A_{\text{Re}}^2 | \psi \rangle - \langle \psi | A_{\text{Re}} | \psi \rangle^2 \right) + 4 \left(\langle \psi | A_{\text{Im}}^2 | \psi \rangle - \langle \psi | A_{\text{Im}} | \psi \rangle^2 \right) \quad (9.1)$$

We will consider three classes of pure states, corresponding to `states_64`, `states_55`, and `states_46`, respectively. For each class, the pure state is represented as

$$|\psi\rangle = \sum_i \alpha_i |\psi_i\rangle \quad (9.2)$$

where $|\psi_i\rangle$ are the states with fixed electron numbers. Then we have

$$F_Q = 4 \left[\sum_{ij} a_i^* a_j A_{\text{Re},ij}^2 - \left(\sum_{ij} a_i^* a_j A_{\text{Re},ij} \right)^2 + \sum_{ij} a_i^* a_j A_{\text{Im},ij}^2 - \left(\sum_{ij} a_i^* a_j A_{\text{Im},ij} \right)^2 \right] \quad (9.3)$$

So we need the matrix elements

$$\begin{aligned} A_{\text{Re},ij} &\equiv \langle \psi_i | A_{\text{Re}} | \psi_j \rangle, & A_{\text{Im},ij} &\equiv \langle \psi_i | A_{\text{Im}} | \psi_j \rangle \\ A_{\text{Re},ij}^2 &\equiv \langle \psi_i | A_{\text{Re}}^2 | \psi_j \rangle, & A_{\text{Im},ij}^2 &\equiv \langle \psi_i | A_{\text{Im}}^2 | \psi_j \rangle \end{aligned} \quad (9.4)$$

For the first step, we have $A_{\text{Re},\alpha\beta}$ and $A_{\text{Im},\alpha\beta}$ in terms of the states in `evecs_i`, then we have

$$\begin{aligned} A_{\text{Re},ij} &= \sum_{\alpha\beta} \langle \psi_i | \psi_\alpha \rangle A_{\text{Re},\alpha\beta} \langle \psi_\beta | \psi_j \rangle = (M A_{\text{Re}} M^\dagger)_{ij} \\ A_{\text{Im},ij} &= \sum_{\alpha\beta} \langle \psi_i | \psi_\alpha \rangle A_{\text{Im},\alpha\beta} \langle \psi_\beta | \psi_j \rangle = (M A_{\text{Im}} M^\dagger)_{ij} \end{aligned} \quad (9.5)$$

where $M_{i\alpha} = \langle \psi_i | \psi_\alpha \rangle$.

10 Data Repository Information

- [Original dimer repository](#)
- [Example repository](#)
- [Data management instructions](#)
- [Figure instructions](#)

References

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