A Wannier orbital based method for resonant inelastic x-ray scattering simulation

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Abstract. We report an algorithm for simulating oxygen $K$-edge RIXS for weakly correlated systems, using maximally localized Wannier functions as the basis set. The $N$-electron wavefunctions are formulated using single Slater determinants, and many-body effects are treated explicitly at the dipole matrix element level. The simulated results for oxygen $K$-edge RIXS from solid state Li$_2$CO$_3$ matches well with the experimental data. Aside from being efficient and reasonably accurate, this algorithm also shows potential to extend to more complex RIXS problems.

1. Introduction
Since its discovery by Wilhelm Roentgen more than a hundred years ago, x-rays have not only improved the quality of life of human beings via chemical imaging and radiotherapy etc., but also provided scientists a powerful tool to directly investigate the microscopic scales of the world. Take transition-metal oxides as an example. X-rays with high photon energy above 5-10 keV, usually called hard x-rays, can be tuned to coincide with the energy difference between specific transition-metal $1s$ core-levels and the valence shell, thus selectively exciting the electronic state of the transition metal in the system. X-rays with lower photon energies, or soft x-rays, can be used to excite transition-metal $2p$ electrons or oxygen $1s$ electrons in a similar fashion. The energy and edge selectivity and their large cross-section are among the main advantages of x-ray spectroscopic techniques. Thanks to the recent development of high-throughput, high-resolution synchrotron light sources and detection instruments, x-ray spectroscopies have become increasingly important in many fields. In physics, x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS) have been employed extensively for understanding electronic structure, generally, and collective excitations, specifically, in strongly correlated systems [1, 2, 3, 4]. In chemistry, x-ray spectroscopy has been used to fingerprint electronic structure and look into static and transient states of matter [5]. Recently, XAS and RIXS also have been used to search for better battery materials by “fingerprinting” the redox process [6, 7].

While x-ray spectroscopies have been used successfully in variety of fields, theoretical understanding remains a great challenge. We lack a universal theoretical scheme to treat different systems and different edges. For strongly correlated systems, correlation effects and localized physics dominate, while for more itinerant systems band dispersion matters more. For many other systems lying between the two extremes, both effects remain non-negligible to some extent. To speak of different edges, the commonly measured ones are transition-metal $K$, $L$, and $M$
edges and the oxygen \( K \) edge. Dipole selection rules guarantee that specific valence orbitals are excited for a certain edge, requiring that one employ the right method to describe the physics of the electrons in those valence orbitals. One of the main theoretical difficulties lies in the choice of basis – how the wavefunction is formulated should be treated very differently between weakly and strongly correlated electronic systems. See Table 1 for a comparison between the single-particle and the many-body methods of constructing the Hilbert space. To treat strongly correlated electronic systems, one has to use the full many-body basis as the starting point. The size of the Hilbert space scales exponentially with the number of available single-particle states, which could represent the number of orbitals for atomic systems, the number of real space lattice sites for single band model Hamiltonians, or a combination of both for a realistic multi-orbital/multi-site system. This exponential scaling leads to a severe limitation of the largest systems one can attempt to simulate. Usually, full band dispersion, which comes along with the inclusion of hoppings at intermediate and long range, cannot be addressed with this construction. On the other hand, for weakly correlated electronic systems, the many-body electronic wavefunction can be expressed as a single Slater determinant of the single-particle states, thus the size of the Hilbert space scales only linearly with the number of single-particle states. Using this basis set and the corresponding construction, we more easily can address the band dispersion by including intermediate and long range hoppings in a supercell with hundreds of atoms. However, many-body effects are “intentionally” missing, as the single Slater determinant wavefunction construction cannot account for the complex response of the remaining \( N – 1 \) electrons when one electron has been perturbed, as in the XAS or RIXS process. For certain systems, such as strongly correlated electronic systems, this missing part proves crucial and not including it usually proves fatal when trying to describe material characteristics. In a word, with current computing power and current algorithms, it has not been possible to address both strong correlations and the intermediate/long range hoppings precisely at the same time.

Instead of directly tackling this hard problem, and trying to find a universal theory for understanding x-ray spectroscopies of both strongly and weakly correlated systems, scientists in the theoretical x-ray spectroscopy community have taken another route: looking at each problem carefully and developing a number of different methods, each suitable for a specific set of problems. \textit{Ab initio} based methods such as FEFF [8] and OCEAN [9] have been developed to target weakly correlated systems and oxygen \( K \)-edge spectra. Many-body techniques such as exact diagonalization have been used for strongly correlated systems and transition-metal \( K/L \)-edges [10, 11, 12].

In this study, we will report on a newly developed method that adds to the existing algorithm “zoo” for x-ray spectroscopy simulations. We target the oxygen \( K \)-edge for weakly correlated systems or at least “not too” strongly correlated systems. We will use a single Slater determinant to construct the \( N \) electron wavefunction, and treat many-body effects explicitly on the matrix element level. The main advantage of this method is that instead of using a plane-wave basis, a typical choice in the \textit{ab initio} methods for spectroscopy simulations of solid state materials, we use Wannier orbitals as the single-particle basis. As shown in Table 1, for the single-particle construction there is a one-to-one correspondence between each building block (Wannier orbital in our method or plane-wave for solid state DFT simulations) and Hilbert space basis vector, thus we will use the two terms, Wannier orbitals and basis set, interchangeably in the discussion of our algorithm. One can demonstrate that the most compact basis set for valence electrons is a basis constructed from Wannier orbitals, thus largely accelerating the algorithm and enhancing the numerical accuracy. Moreover, since Wannier orbitals are very similar to atomic orbitals in the solid state systems, by construction it is easier to extend the current algorithm to include correlation effects. Aside from these advantages, we will demonstrate the effectiveness of this algorithm by showing numerical results for RIXS and comparison with experiments on an example material. The numerical simulations show reasonably good agreement and even catch
Table 1. Comparison of single-particle and many-body constructions for a spinless four-orbital system. In both cases, each Hilbert space basis vector can be written as a 4-bit binary number. In the single-particle construction, each Hilbert space basis vector has a one-to-one correspondence to the orbital. Thus, the size of the Hilbert space scales linearly with the number of orbitals. In the many-body construction, each bit can be either 0 or 1. This gives a total Hilbert size of $2^N$, where $N$ is the number of orbitals. If we confine the total number of electrons to be 2, then we have 6 different basis vectors as shown in the table, where 6 is given by $C_4^2$.

| Hilbert space basis set | single-particle construction | many-body construction |
|-------------------------|-----------------------------|------------------------|
|                         | $b_1 \rightarrow$ 1 0 0 0 | $b_1 \rightarrow$ 1 1 0 0 |
|                         | $b_2 \rightarrow$ 0 1 0 0 | $b_2 \rightarrow$ 1 0 1 0 |
|                         | $b_3 \rightarrow$ 0 0 1 0 | $b_3 \rightarrow$ 1 0 0 1 |
|                         | $b_4 \rightarrow$ 0 0 0 1 | $b_4 \rightarrow$ 0 1 1 0 |
|                         |                           | $b_5 \rightarrow$ 0 1 0 1 |
|                         |                           | $b_6 \rightarrow$ 0 0 1 1 |

The remainder of the manuscript is organized as follows: In section 2, we will talk about the methods by showing the derivation of the algorithm for XAS and RIXS cross-sections. In section 3, we will show the numerical results of RIXS and its comparison with experimental data for Li$_2$CO$_3$ at the oxygen $K$-edge. In section 4, we will conclude this paper with a summary and discussion.

2. Methods

2.1. Hamiltonians

The tight-binding Hamiltonian of the multi-orbital system can be expressed as:

$$H_0 = \sum_{i,j,\alpha_i,\alpha_j,\sigma} t_{i,j,\alpha_i,\alpha_j} c_{i,\alpha_i,\sigma}^\dagger c_{j,\alpha_j,\sigma}$$  \hspace{1cm} (1)

where index $i/j$ is the atom index, $\alpha_i$ represents the orbital index at atom $i$, $\sigma$ represents spin. $t_{i,j,\alpha_i,\alpha_j}$ represents the hopping between orbital $\alpha_i$ at atom $i$ and orbital $\alpha_j$ at atom $j$. When $i = j$ and $\alpha_i = \alpha_j$, $t_{i,i,\alpha_i,\alpha_i}$ represents the site energy. This Hamiltonian applies to both the RIXS/XAS initial state and RIXS final state without core-hole.

For electronic states with a core-hole, the Hamiltonian with one core-hole can be written as:

$$H_i = \sum_{i,j,\alpha_i,\alpha_j,\sigma} t_{i,j,\alpha_i,\alpha_j} c_{i,\alpha_i,\sigma}^\dagger c_{j,\alpha_j,\sigma} - \sum_{\alpha_0,\sigma} U_0 n_{i_0,\alpha_0,\sigma} n_{i_0,\sigma}^h + \epsilon(O_h)n_{i_0,\sigma}^h$$  \hspace{1cm} (2)
where $n_{i_0, \sigma'}^h$ is the number operator for the core-hole with spin $\sigma'$ at site $i_0$, $\epsilon(O_h)$ is the core-hole site energy, $U_c$ is the core-hole potential which only applies to the orbitals on the same site $i_0$, $n_{i_0, \alpha_{i_0}, \sigma}$ is the electron number operator for orbital $\alpha_{i_0}$ at site $i_0$. This Hamiltonian applies to the RIXS intermediate state or XAS final state, under the assumption that the only interaction term brought in by the core-hole is the monopole term of the Coulomb interaction. Please note that systems with higher order interactions such as multiplet interactions can not be described by the above Hamiltonian. For this reason, the Wannier orbital based RIXS algorithm, which we propose here, is suitable for simulating XAS and RIXS at the oxygen K-edge (sulfur K-edge etc), but not transition-metal L-edges where the $3d - 2p$ multiplet interaction on the transition metal atom typically plays an important role.

There are a number of ways to obtain the tight-binding model Hamiltonian for a material specific problem. What we use here is the maximally localized Wannier functions method implemented in Wannier90 [13], by projecting \textit{ab initio} density functional theory (DFT) results onto the maximally localized Wannier basis set to obtain the Hamiltonian of interest. Compared with directly fitting the DFT bandstructure, each basis element obtained in the Wannier method has a physical meaning, thus it naturally preserves the symmetries of the problem.

2.2. XAS

The general XAS formalism in the single Slater determinant construction has been discussed previously by Liang \textit{et al} [14]. Here, we rederive this for XAS, and extend the derivation to RIXS.

The initial state of the $N+1$ electron wavefunction for XAS is the ground state of the electronic system of $N$ valence electrons plus one core-electron. Without loss of generality, we only consider one core-electron in the initial state or one core-hole in the final state of XAS. This $N+1$ electron wavefunction can be expressed as $|\Phi_0\rangle = \prod_{v=1}^{N} b_v^{|0\rangle}$, where $|0\rangle$ is the empty state, $h$ is the core-electron creation operator (or core-hole annihilation operator), $b_v$ annihilates a valence hole (or creates a valence electron) with single particle index $v$. $|\Phi_0\rangle$ should be understood as the single Slater determinant of the $N+1$ one-electron wavefunction.

The final $N+1$ electron wavefunction for XAS can be presented in the following:

$$|\Phi_1\rangle = \prod_{\mu=1}^{N+1} \phi_{\mu}^+ \prod_{v=1}^{N} b_v^{|0\rangle} |\Phi_0\rangle = \prod_{\mu=1}^{N+1} \left( \sum_c \xi_{i_{\mu},c} a_c^+ + \sum_v \xi_{i_{\mu},v} b_v \right) \prod_{v=1}^{N} b_v^{|0\rangle} |\Phi_0\rangle$$

where $|\Phi_0\rangle$ is the initial state $N+1$ electron wavefunction, $a_c^+$ creates an electron with index $c$ in the conduction band, and $\prod_{v=1}^{N} b_v^{|0\rangle} |\Phi_0\rangle$ represents the state with empty electrons in the valence and one core-hole. $\phi_{\mu}^+$ creates an electron with state index $i_{\mu}$ for the XAS final state Hamiltonian with core-hole, and $\phi_{\mu}$ is connected with the initial single particle eigenstates without core-hole by the relation: $\phi_{i_{\mu}}^+ = \sum_c \xi_{i_{\mu},c} a_c^+ + \sum_v \xi_{i_{\mu},v} b_v$.

The XAS cross-section can be expressed using Fermi’s Golden rule:

$$I(\omega) = \sum_i \left| \langle \Phi_1 | \epsilon \cdot \mathbf{R} | \Phi_0 \rangle \right|^2 \delta(E_i - E_0 - \omega)$$

Here $|\Phi_1\rangle$ is the $N+1$ electron final state wavefunction and $|\Phi_0\rangle$ is the $N+1$ electron initial state wavefunction. $E_0$ is the sum of the $N$ lowest single-particle energies in the valence $E_0 = \sum_{v=1}^{N} \epsilon_v$, and $E_i$ is the sum of the single-particle energies for final state $i$: $E_i = \sum_{\mu=1}^{N+1} \tilde{\epsilon}_{i_{\mu}} + \epsilon_h$. As stated in the introduction, we will treat them in the Slater determinant of the single particle basis, and consider many-body effects by treating the matrix elements explicitly. The matrix elements can be expressed in the single particle basis without core-hole:

$$\langle \Phi_1 | \epsilon \cdot \mathbf{R} | \Phi_0 \rangle = \sum_c \langle A_c^+ \rangle^* \langle \phi_c | \epsilon \cdot r | \phi_h \rangle$$


where $|\phi_h\rangle$ is the single-particle wavefunction of the core-electron and $|\phi_c\rangle$ is the single-particle wavefunction of a conduction electron with index $c$. $(\langle \phi_c|\epsilon \cdot r|\phi_h\rangle)$ shows the dipole of one electron excited from the core up to a conduction state with index $c$; the coefficient $A^i_c$ shows the overlap of the $(N+1)$-electron wavefunction between the initial state and the final state, and can be expressed as:

$$A^i_c = \text{det} \left( \begin{array}{cccc} \xi_{i_1,v=1} & \xi_{i_1,v=2} & \cdots & \xi_{i_1,v=N} \\ \xi_{i_2,v=1} & \xi_{i_2,v=2} & \cdots & \xi_{i_2,v=N} \\ \vdots & \vdots & \ddots & \vdots \\ \xi_{i_{N+1},v=1} & \xi_{i_{N+1},v=2} & \cdots & \xi_{i_{N+1},v=N} \end{array} \right)$$ (6)

### 2.3. RIXS

The RIXS cross-section, as expressed in the Kramer’s Heissenberg formula [1]:

$$I(\omega_{in},\omega_{loss}) = \sum_f \left| \sum_i \langle \Phi_f | \epsilon \cdot R | \Phi_i \rangle \frac{1}{E_f - E_0 - \omega_{in} - \Gamma} \langle \Phi_f | \epsilon \cdot R | \Phi_0 \rangle \right|^2 \delta(E_f - E_0 - \omega_{loss})$$ (7)

The RIXS intermediate state wavefunction $|\Phi_i\rangle$ has the same form as the XAS final state wavefunction. The RIXS final state $N+1$ electron wavefunction can be expressed as:

$$|\Phi_f\rangle = a^\dagger_{i_1}b^\dagger_{i_2}|\Phi_0\rangle + a^\dagger_{i_1}a^\dagger_{i_2}a^\dagger_{i_3}b^\dagger_{i_4}|\Phi_0\rangle + \cdots \approx a^\dagger_{i_1}b^\dagger_{i_2}|\Phi_0\rangle$$ (8)

This approximation only keeps the first term (or a single electron-hole pair) in the final state. For intermediate states $|\Phi_i\rangle = \prod_{\mu=1}^{N+1} (\sum_c \xi_{\mu,c}a^\dagger_{i_1} + \sum_v \xi_{\mu,v}b_{i_2}) \prod_{i=1}^{N} b^\dagger_{i_3}|\Phi_0\rangle$ and final states $|\Phi_{f=(v,c)}\rangle = a^\dagger_{i_1}b^\dagger_{i_2}|\Phi_0\rangle$, the matrix element can be expressed as:

$$\langle \Phi_{f=(v,c)} | \epsilon \cdot R | \Phi_i \rangle = A^i_c \langle \phi_h | \epsilon \cdot r | \phi_v \rangle$$ (9)

By expanding the matrix elements with single-particle wavefunction overlaps, the above RIXS cross-section can be expressed as:

$$I(\omega_{in},\omega_{loss}) = \sum_{f=(v,c)} \left| \sum_i \langle A^i_c | \phi_h | \epsilon_{out} \cdot r | \phi_v \rangle \frac{1}{E_f - E_0 - \omega_{in} - \Gamma} \langle A^i_c | \phi_h | \epsilon_{in} \cdot r | \phi_h \rangle \right|^2 \delta(E_f - E_0 - \omega_{loss})$$ (10)

where the final state energy $E_{f=(v,c)} = \sum_{v'=1}^{N} \epsilon_{v'} - \epsilon_{v} + \epsilon_{c}$.

The preceding formulation is a general expression for the RIXS cross-section with single electron-hole pair excitations in the final state. In the following, we will make an additional approximation: for the XAS final state or RIXS intermediate state $|\Phi_i\rangle$, we only will consider those many-body states with the $N$ lowest single-particle levels occupied (the remaining electron can occupy any unfilled single-particle state at arbitrary energy):

$$|\Phi_i\rangle = \hat{\phi}_h^\dagger \prod_{l=1}^{N} \hat{\phi}_h^\dagger \prod_{v=1}^{N} b^\dagger_{i_1}b^\dagger_{i_2}|\Phi_0\rangle.$$ (11)

For large band gap insulators, intermediate states with one or more electron-hole pairs corresponds to a much larger excitation energy. [14] As we will show in the next section, these approximations give reasonable results for the incident energy range near the excitation edge.
3. Results

In this section, we show the numerical simulation of O $K$-edge RIXS spectra for the example material Li$_2$CO$_3$. Experimental RIXS spectra of Li$_2$CO$_3$ at the oxygen $K$-edge have been measured by Zhuo and his colleagues [16]. This material is interesting because of its connection with Li-ion battery materials and possible explanations of anionic redox. The crystal structure of Li$_2$CO$_3$ has been shown in Figure 1(a) and (b). Each primitive cell has four Li$^+$ and two CO$_2^-$.

Solid state Li$_2$CO$_3$ is an insulator with band gap $\sim 5$eV, with its band structure and partial density of states shown in Figure 1(c). The bandstructure and density of states were calculated with the density functional theory package Quantum Espresso [17] using a PBE exchange-correlation functional, norm-conserving pseudopotentials, and a $4 \times 4 \times 4$ momentum sampling.

The Wannier downfolding using Wannier90 [13] was implemented with the initial projection onto carbon $pz$ orbitals, oxygen $px/py/pz$ orbitals, Li $s$ orbitals and ten $s$-like orbitals at random starting positions (a 34-orbital model). Oxygen $K$-edge RIXS was calculated using Eq. (10) with a $4 \times 4 \times 4$ supercell. Both the incoming and outgoing x-ray photons were taken to be non-polarized. We used core-hole lifetime broadening $\Gamma = 0.25$eV, core-hole potential $U_c = 3.5$eV and $\epsilon(O_{1s}) = 534$eV (relative to $E_f$) in the calculation.

In Figure 2, the experimental RIXS data shows three main emission features at x-ray emission energies 519eV, 520.5eV and 526eV respectively. Our theoretical simulation reproduced all the three emission features at 519eV, 520.5eV and 525eV respectively. In simulation we see another emission feature at 526.5eV, which is not seen in the experiment. A probable explanation is that in experiment the 526.5eV emission has merged into the main 526eV emission. Simulation with a larger core-hole lifetime broadening $\Gamma = 0.5$eV also reports merging of these two emissions.

To understand the nature of these excitations, we can make connection with the calculated partial density of states, as shown in Figure 1(c). These four calculated emission lines at 519eV,
520.5eV, 525eV and 526.5eV correspond to the energy for the recombination of valence electrons with oxygen 2p orbital content from \(-8\)eV, -6eV, -2eV and -0.5eV back to the 1s core level.

At incident excitation energy \(\sim 533\)eV, the experimental RIXS spectra show four Raman-like features (with a finite energy loss) at emission energies at \(\sim 518\)eV, 520.5eV, 525eV, and a sharp peak at 526.5eV on the right. Our numerical simulation reports four Raman-like features at \(\sim 533\)eV excitation energy, and with emission energies \(\sim 518.5\)eV, 520.5eV, 525eV, and 526.5eV. The \(\sim 533\)eV incident x-ray energy corresponds to the energy of an electron to be excited from a 1s core level to unfilled electronic states with O 2p orbital content between 5 - 6.5eV, as shown in Figure 1(c). The energy loss of these four Raman-like features corresponds to the energy of the final state with a single electron-hole pair, where the electron resides in the conduction band with oxygen 2p orbital content and the hole resides in one of the four occupied oxygen 2p electronic states. For both the emission lines and the Raman features, some of the calculated energies do not line up perfectly with experimental data, mainly due to missing valence Coulomb interactions and excitonic effects in the calculation. However, overall, our numerically simulated Li2CO3 RIXS spectra well reproduce the main features of the experimental data.

4. Conclusions and discussions
There are several points to discuss about this algorithm. (1) This algorithm is “almost” ab initio, since the only adjustable parameters are \(U_c\) and \(\epsilon(O_{1s})\), both of which potentially can be evaluated in DFT calculations using an appropriate oxygen pseudopotential with a 1s core-hole. In our Li2CO3 calculation, we take \(\epsilon(O_{1s})\) to be adjustable, fit with the experimental
energy scale. The spectral weight only weakly depends on the value of $U_c$. (2) At higher incoming energies (> 537eV) where the emission lines dominate, our algorithm underestimates the spectral weight, compared with the experiment. The possible explanation is that the approximation in Eq.(11) does not include some of the high energy (> absorption edge + band gap) configurations in the intermediate state. [14] Low energy scales, close to absorption edges, dominate the discussion of most RIXS spectra. They capture rich information about the overlap of the ground, intermediate, and final states of the RIXS process. The current approximation works well for simulating RIXS spectra close to absorption edges for large band gap insulators, while remaining computationally efficient. For semiconductors and metals, the approximation can be changed to allow one or more electron-hole pairs in the RIXS intermediate state. In other words, we may need to go beyond the simple approximations as stated in Eq.(11). (3) The current theory does not account for the Coulomb interaction and excitonic effects. However, in the Wannier orbital basis, one can potentially extend the current algorithm by including the Coulomb interaction (both on-site and at short/intermediate distances). (4) Since the Wannier orbital basis is the most compact, complete basis set for valence electrons, this algorithm is very efficient in terms of both time and space computational complexity.

To summarize, we have developed a Kramer’s-Heissenberg-like formulation for the RIXS cross-section by addressing the many-body effects at the matrix element level. Simulated results of oxygen $K$-edge RIXS for solid state $\text{Li}_2\text{CO}_3$ well match the experimental data. Aside from being efficient and reasonably accurate, this algorithm shows potential to extend to more complex RIXS problems.

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