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## Charge transfer excitations in VUV and soft X-ray resonant scattering spectroscopies

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## ABSTRACT

The utility of resonant scattering for identifying electronic symmetries and density distributions changes dramatically as a function of photon energy. In the hard X-ray regime, strong core hole monopole potentials tend to produce X-ray absorption features with well-defined electron number on the scattering site. By contrast, in the vacuum ultraviolet (VUV), resonant scattering from Mott insulators tends to reveal spectra that are characteristic of only the nominal valence, and are insensitive to deviations from nominal valence brought on by metal-ligand hybridization. Here, atomic multiplet simulations are used to investigate the interplay of monopolar and multipolar Coulomb interactions in the VUV and soft X-ray regimes, to identify how charge transfer thresholds and other signatures of mixed valence can manifest in this low photon energy regime. The study focuses on the Mott insulator NiO as a well-characterized model system, and extrapolates interactions into non-physical regimes to identify principles that shape the spectral features.

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## 1. Introduction

The incident energy dependence of resonant X-ray scattering tends to be determined by very different physical processes in the hard and soft X-ray regimes. Deeply bound core holes created by hard X-rays provide a very strong monopolar Coulomb perturbation to the valence level, splitting X-ray absorption (XAS) spectra into features with rather well-defined valence on the scattering site [1,2], and often causing charge transfer states to be lower in energy than the nominal-valence resonance peaks (see Fig. 1(b)). In soft X-ray experiments, this monopolar core hole potential is a relatively weak perturbation, and direct wavefunction overlap between a shallow core hole and valence orbitals causes higher order angular momentum interactions to become significant (see Fig. 1(c)). The resulting peak structure can be analyzed to obtain detailed information about ground state symmetries and energetics, but the strong overlapping of features and loss of energetic dominance from the core hole potential make it difficult to quantitatively determine charge density on the scattering site.

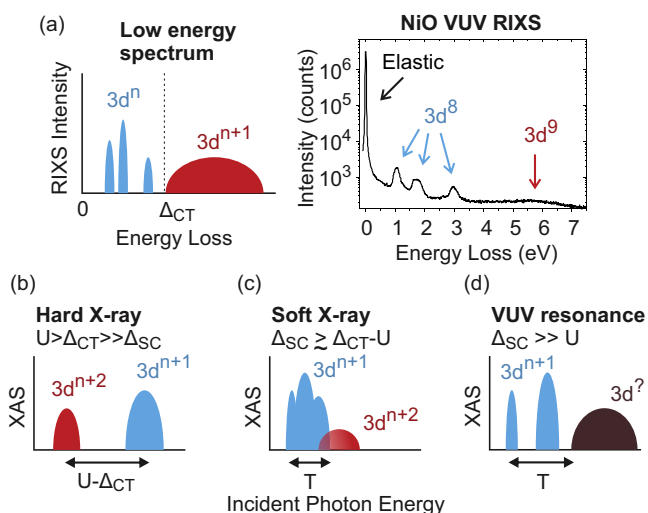
This ambiguity is further accentuated for the even shallower core holes accessed in the vacuum ultraviolet (VUV). RIXS and XAS spectra of Mott insulators measured in the VUV tend to be well reproduced by renormalized nominal-valence models that completely neglect charge transfer from ligands. This is true even in cases where ligand hybridization is known to significantly increase valence electron density on the scattering atom (e.g. from 8 to 8.2 in NiO [3]). For example, the M-edge VUV resonant inelastic X-ray scattering (RIXS) spectrum of NiO in Fig. 1(a, right), shows a far weaker charge transfer peak than L-edge soft X-ray RIXS [4–8], and M-edge XAS from NiO has no obvious charge transfer derived spectral feature. Here, we will explore the question of how charge transfer states manifest in the VUV by varying the core hole modeling parameters of an atomic multiplet (AM) simulation for NiO, augmented by ligand hybridization treated in the single Anderson impurity model (SAIM).

## 2. Methods

The basic parameters of the AM calculation are similar to those used in Refs. [4,8,9]. The crystal field is described by the parameter  $10Dq = 0.56$  eV, and the Slater–Condon parameters that govern 2-particle angular momentum coupling are set to atomic values (80% of bare Hartree–Fock values). Spin orbit coupling of core and

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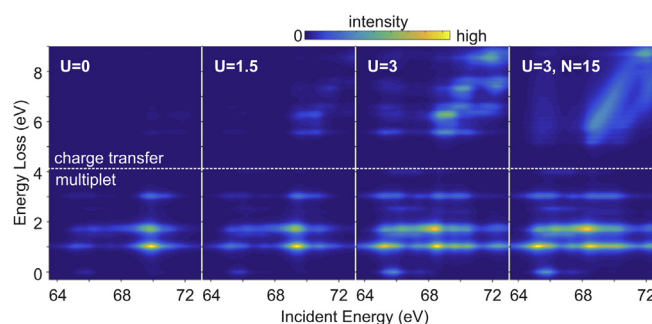


**Fig. 1.** Energetic regimes for resonance. (a) (Left) Energetically separated (blue) multiplet and (red) charge transfer excitations are illustrated next to (Right) the nickel M-edge VUV RIXS spectrum of Mott insulating NiO, measured at  $h\nu = 71.5$  eV. As analyzed in Ref. [4], features above the charge transfer gap ( $\Delta_{CT}$ ) are extremely weak at the M-edge, in spite of a nominal nickel valence state of 8.2. (b–d) Schematics of X-ray absorption features are shown for the hard X-ray, soft X-ray and VUV regimes. The charge transfer threshold  $T$  is the energy gap between the first dipole allowed resonance state and the charge transfer continuum, and is given an empirical definition in the discussion of Fig. 4. In the VUV case, nominal valence multiplet features can appear above the charge transfer threshold, possibly with a mixed valence character (“ $3d^n$ ” peak). We note that though RIXS and XAS spectra can both often be interpreted in terms of features that preserve or change nominal valence, RIXS provides spectroscopic information that cannot be obtained from XAS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

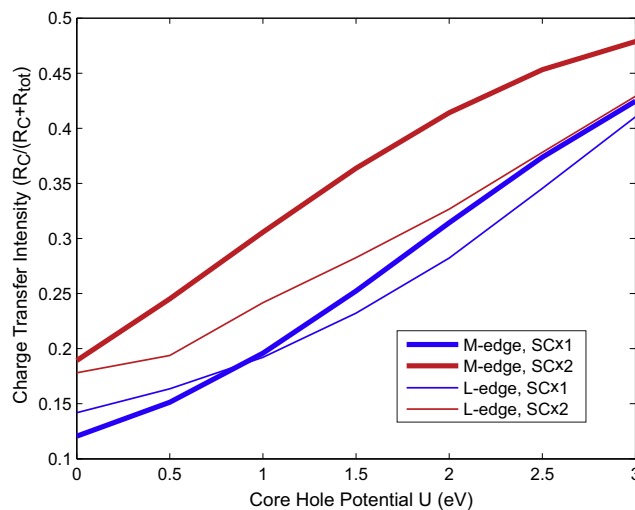
valence Ni electrons is set to Hartree–Fock values. Core hole inverse lifetimes are set to  $\Gamma = 1$  eV at the M-edge,  $\Gamma = 0.6$  eV at  $L_3$  and  $\Gamma = 0.8$  eV at  $L_2$ . Hybridization with oxygen is accounted for in the SAIM model as in Ref. [8], with 0 or 1 ligand holes, a ligand band width  $W = 3$  eV, and ligand states distributed in just 3 discrete energies ( $N = 3$ ). The configuration energy of ligand hole states was set to 3.5 eV, in the absence of a core hole. Hopping between  $e_g$  orbitals and the nearest neighbor ligand states with corresponding symmetry is  $V_{eg} = 2.2$  eV ( $V_{t2g} = -V_{eg}/2$ ), and is reduced by 10% when a core hole is present. The ground state density of oxygen holes within this model matches the experimentally based estimate of 0.2 [3].

The effective core hole potential is defined as  $U = U_{cv} - U_{vv}$ , where  $U_{cv}$  is the core–valence monopole interaction (3p–3d interaction, for the NiO M-edge), and  $U_{vv}$  is the same-site Mott–Hubbard interaction between valence electrons. This potential assumes larger positive values for deeper core holes, as the radial wavefunction of the core electron becomes more compact. For shallow core holes accessed in the VUV, the radial size of core level wavefunctions is quite similar to the radial size of valence orbitals, and the  $U$  potential may be negligible. In the modeling implementation used for this manuscript, the valence configuration energies (average energy for a given 3d electron number) are defined entirely by  $U$ , the crystal field, and the ligand site energy. The dependence of spectra on ‘multiplet’ angular momentum interactions is explored by multiplying the higher order Slater–Condon terms by a factor of 2 in some panels. This is indicated as “ $SC \times 2$ ”, and refers to the  $n > 0$  Slater–Condon terms ( $G^n$  and  $F^n$ ). Though the core hole potential  $U$  is associated with the lowest order Slater–Condon term ( $F^0$ ), an accurate renormalized value of the  $U$  parameter can not be easily obtained from first principles [10], and we adopt the common practice of using the term “Slater–Condon parameters” to reference only the higher order terms with  $n > 0$ .

Simulated RIXS spectra are obtained using the Kramers–Heisenberg equation (see Fig. 2), with exactly



**Fig. 2.** Simulated M-edge RIXS images. The RIXS spectrum of NiO is shown for different values of the core hole potential  $U$ . A dashed horizontal line indicates the partition between low energy multiplet excitations and higher energy charge transfer excitations. The rightmost panel uses a larger number of ligand band states ( $N = 15$ ) to show the well-converged form of the charge transfer features.



**Fig. 3.** Charge transfer shake-up scattering intensity vs. Coulomb potentials. The charge transfer excitation intensity (summed energy loss  $E > 4$  eV RIXS intensity) is plotted as a function of the core hole potential  $U$ . Charge transfer scattering intensity is averaged over incident energy at the M- and L-edges, and plotted as a ratio of total scattering at the relevant edge. Curves are shown for the typical Hartree–Fock derived Slater–Condon multiplet interaction strength ( $SC \times 1$ ) and for a non-physical case in which the interaction strength has been artificially doubled ( $SC \times 2$ ).

diagonalized eigenstates of the model Hamiltonian (as in Ref. [11]). The VUV RIXS measurement in Fig. 1(a, right) was performed at the beamline 4.0.3 (MERLIN) RIXS endstation (MERIXS) at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The data were recorded by a VLS based X-ray emission spectrograph equipped with a commercially available CCD detector [12,13]. A large single crystal of NiO was measured near room temperature at a pressure of  $3 \times 10^{-10}$  Torr. The  $\pi$ -polarized photon beam had a grazing  $25^\circ$  angle of incidence to the cleaved [100] sample face, and scattered photons were measured with a  $90^\circ$  included scattering angle. The RIXS simulations of charge transfer intensity were also performed in this scattering geometry.

### 3. Results and discussion

The degree to which RIXS couples to charge transfer states reflects how the core hole resonance states deviate from the ground state charge density distribution. Fig. 3 evaluates how the total charge transfer intensity in RIXS depends on core hole potential and Slater–Condon interaction strengths, when charge transfer excitations are summed over the M- and L-edge resonances. The RIXS

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