Coexistence of Bound and Virtual-bound States in Shallow-core to Valence Spectroscopies

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We develop the theory for shallow-core to valence excitations when the multiplet spread is larger than the core-hole attraction, e.g., if the core and valence orbitals have the same principal quantum number. This results in a cross-over from bound to virtual-bound excited states with increasing energy and in large differences between dipole and high-order multipole transitions, as observed in inelastic x-ray scattering. The theory is important to obtain ground state information from x-ray spectroscopies of strongly correlated transition metal, rare-earth and actinide systems.

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The actinides and their compounds are attracting serious attention from the condensed matter community due to their exotic properties.1 Examples of these are the extremely rich phase diagram of Plutonium [2] and the extremely rich phase diagram of Plutonium, rare-earth (RE) and actinide systems, relying largely on theoretical interpretations based on local correlated models with full multiplet effects [5]. On the other hand, we emphasize that the structure of core-level excitations is largely governed by local correlation physics and point group symmetry, and (2) the final state core-hole strongly differs from that between different n-shells, with the example of 5d→f non-resonant inelastic x-ray scattering (NIXS) in the actinides. We also show that the high-multipole (HM) transitions in NIXS to strongly bound CVM states [11], unlike the dipole restricted transitions in XAS and EELS, can still be treated within local models, but with strongly renormalized parameters, due to very large configuration interaction (CI) in the final state.

Unlike dipole restricted XAS, NIXS can access transitions involving high-order multipoles as exemplified by the observation of d-d transitions in TM compounds [12,13]. It also gives us more information of what the true ground state of the system actually was, even for dipole-allowed transitions [11,14]. NIXS uses the first order scattering, off-resonance, due to the (e^2/2mc^2)⃗A·⃗A term in the light-matter coupling [15]. The corresponding double differential cross section is given by [13] the Thompson scattering cross-section, times the material dependent dynamical structure factor:

$$ S(\vec{q}, \omega) = \sum_f |\langle f | e^{i \vec{q} \cdot \vec{r}} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega) $$

where, \( \vec{q} = \vec{k}_i - \vec{k}_f \) is the photon momentum transfer, and \( \hbar\omega = \hbar\omega_i - \hbar\omega_f \) is the energy loss. The transition operator can be multipole expanded [13] as:

$$ e^{i \vec{q} \cdot \vec{r}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^{l} (2l + 1) j_l(qr) C_m^{(l)}(\theta, \phi) C_m^{*(l)}(\theta_i, \phi_i) $$

where, \( j_l(qr) \) are spherical Bessel functions, while \( C_m^{(l)}(\theta, \phi) \) are renormalized spherical harmonics, both of order \( l \). Only terms with \( |l_f - l_i| \leq l \leq (l_f + l_i) \) and \( (l + l_i + l_f) \) even, survive in the infinite sum.

As a relevant illustration we show, in the inset-1 to Fig. 1(a), the radial transition probabilities for the various allowed channels in the 5d-f NIXS of the Th^{4+}...
are sharp and excitonic, while the Fano-like asymmetry seen in the experimental paper \[17\], here we briefly remind the reader of the key results obtained therein, viz.: (i) NIXS data for actinides show the dichotomy that HM features differ from their atomic-like counterparts, (ii) in stark contrast, the calculated low-

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\text{dipolar NIXS spectra are much sharper, intense and similar to the lower energy HM multiplets; (iii) in order to obtain reasonable agreement with experimental spectra in terms of the peak positions, we needed to drastically scale down the 5d-5f Coulomb and exchange Slater integrals (F_k^{(5f)}G_{qy}^{(5f)}) to 60\% (ThO_2) or 50\% (UO_2) of their atomic H-F values! This is hard to justify for these rather atomic-like 5f wavefunctions \[18,19\]. In passing, we note that the dichotomy, discussed in (i) above, is also observed in the 4d→4f NIXS of the RE \[11\] and the 3p→3d NIXS of TM compounds \[14\], and between the “doubly forbidden” pre-edge peak and the GDR, in the O Kα XAS of actinides \[1\], showing that this is a generic feature for shallow core-valence transitions within the same n-shell.

To understand the origin of the apparent large reductions in the Slater integrals, we plot in the inset-2 of Fig. 1(a), the 5d, 5f and the 6f radial wavefunctions, obtained from an atomic H-F calculation for ThO_2 (Th⁴⁺, ground configuration 5f⁰). The 5d and 5f orbitals (same n-shell) overlap very strongly, which accounts for the large values of the atomic (F_k^{(5f)}G_{qy}^{(5f)}) integrals. In contrast, the more diffuse 6f orbital, with an additional radial node, overlaps only weakly with the 5d. Hence, a final state (CI) between 5d^65f^1 and 5d^66f^1, via the CI(5f-6f) matrix elements \[20\], would effectively expand the radial part of the 5f wavefunction, reducing the 5d-5f Slater integrals. Now, the mixing depends also on the energy separation, \(\Delta E\), between the center-of-gravities (CG) of configurations involved, which is smaller in the actinides, than between 4d^4f^1 and 4d^5f^1 in the RE. This results in a strong multiplet-dependent CI, because the multiplet splitting in 5d^65f^1 is much larger than that in 5d^66f^1, as shown schematically in Fig. 1(b). To illustrate this point, the NIXS spectra for ThO_2 (Th⁴⁺) are calculated (using the XTLS8.3 code \[21\]) on the basis of the above model, as a coherent combination of the transitions 5f⁰→5d^65f^1 and 5f⁰→5d^66f^1 \[22\]. Here we leave the (F_k^{(5f)}G_{qy}^{(5f)}) integrals unaltered at their atomic H-F values, while the scaling of CI(5f-6f) is varied to obtain agreement with experimental peak positions. This presents a more natural and physical mechanism for understanding the reduced multiplet spread observed experimentally. The fact that we need to scale the CI integrals merely indicates that the band-like 6f state is poorly approximated by the atomic H-F calculations, and that CI with numerous other states is neglected here. The full \(q\)-dependent spectra, at the optimized 60\% scaling of CI(5f-6f)(Fig. 1(a)), is spread over a wide energy range and consists of 5f-like and 6f-like regions (marked in the figure), although most of the spectral weight lies in the 5f-like region due to dominance of radial matrix elements. The CI serves to reduce the 5d-5f multiplet spread considerably (while enhancing the 5d-6f spread), especially pushing the dipole peak close to the HM peaks, in good agreement with experiments \[17\]. Also the component spectra for the \(l=1, 3, 5\) channels plotted at the

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FIG. 1: (color online) (a) The variation of the radial transition probabilities with \(q\), for the three component channels, \(l=1\) (dipole), \(3\) (octupole) and \(5\) (triakontadipole) (inset-1); plots of the 5d, 5f and 6f atomic H-F radial wavefunctions for Th⁴⁺ (inset-2); and calculated NIXS \(S(q, \omega)\) for Th⁴⁺ (5f⁰) including final-state CI with the 6f level, for 60\% of atomic CI(5f-6f) values (main). Both the 5f-like and 6f-like regions are shown. The bare component \(l=1, 3, 5\) spectra (not to scale) are shown at the bottom. (b) Schematic illustrating the high sensitivity of the dipole term vis-a-vis the HM terms, to the strongly term-dependent CI with the 6f.

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 FIG. 2: (color online) (a) Experimental q-averaged NIXS for ThO₂, compared with the component (l=1, 3, 5) summed calculated spectra for atomic values of \((F^k_d, G^k_d)\), and the CI(5f-6f) varied from a scaling of 20% to their full atomic values. Only peak-positions are relevant. The best agreement is obtained at 60% scaling of CI(5f-6f). Variation of the high-energy dipole peak position with varying scaling of : (b) CI(5f-6f), and (c) \((F^k_d, G^k_d)\). While the latter shows a simple linear trend, the former shows a parabolic behavior with signs of saturation.

The origin of the higher sensitivity of the dipole compared to the HM is explained schematically in Fig. 1(b). Before CI (left), the difference (\(\Delta E\)) in the CG energies for the two multiplets, 5d\(^{10}\)5f\(^1\) (width \(W_{\text{mult}}\)) and 5d\(^{10}\)6f\(^1\) (width \(w_{\text{mult}}\)), is ~23-24 eV, from H-F calculations. Although both the multiplets involve exactly the same terms, \(W_{\text{mult}}\) (~25 eV) is much larger than \(w_{\text{mult}}\) (~7 eV), demonstrating the difference between states involving the same versus different principle quantum numbers. Also, for a less-than-half-filled system with a low J ground state (\(J=0\) for ThO₂), the highest multiplets (red) are generally dipole-allowed, while the lowest ones (blue) are the HM-allowed terms. Now, CI(5f-6f) only mixes terms of the same symmetry \([16]\), e.g., the red (blue) states at the top (bottom) of 5d\(^{10}\)5f\(^1\), mix only with the red (blue) states at the top (bottom) of 5d\(^{10}\)6f\(^1\). The result after mixing is shown in the right panel. Since \(w_{\text{mult}} << W_{\text{mult}}\), the effective energy denominator for mixing of the red (dipole) terms is much smaller than that for the blue (HM) terms, causing the observed differences in the shifts. Due to these strong correlation effects, the effective “screening” becomes highly term dependent, explaining the strong asymmetry in the behavior of the dipole and the HM terms, which is not captured by a uniform reduction of the Slater integrals \([17]\).

To show that the two approaches are qualitatively different, we compare in Fig. 2(a) the experimental q-averaged NIXS (topmost), with the calculated sum of the three component spectra (l=1, 3 and 5), keeping \((F^k_d, G^k_d)\) fixed at their atomic values, while the CI(5f-6f) are switched on and gradually increased to their atomic value (100%) (top to bottom). For this purpose only the peak positions are relevant. As already noted, a good agreement with HM peak positions is obtained for 60% reduction of CI(5f-6f). But more importantly, with gradual uniform reduction in \((F^k_d, G^k_d)\) we would expect a linear movement of the dipole towards the HM features. On the other hand with changing degree of CI, the dipole moves towards the HM peaks in a nonlinear manner, showing signs of saturation, as governed by level-repulsion physics. This contrasting behavior is shown in Figs. 2(b) and 2(c), where we have plotted the dipole peak position in the two cases, as a function of the scaling of \((F^k_d, G^k_d)\) and of CI(5f-6f), respectively.

We now turn to the problem of the experimentally observed low relative amplitude, large width and non-lorentzian line shape of the GDR. This can be understood on the basis of Figs. 3(a)-(b). Fig. 3(a) shows the NIXS final state, 5f\(^{n+1}\), of a 5f\(^n\) actide system. In the absence of the 5d core-hole, this would be identical to the inverse photoemission final state 5f\(^{n+1}\) (dashed line), and lies just below or within a continuum (shaded). Primarily, the core-hole provides an attractive scalar potential, \(Q\), which is often large enough to pull down the 5d\(^{10}\)5f\(^{n+1}\) state, out of the continuum, forming a bound core-hole exciton. However, in a more complete picture (Fig. 3(b)), the core-hole f-electron multipole interaction, also yields a very broad multiplet structure (width \(W_{\text{mult}}\)) about the CG of 5d\(^{10}\)5f\(^{n+1}\). The Slater integrals are very large for these transitions occurring within the same n-shell, implying \(W_{\text{mult}}>>Q\). Thus while the HM states towards the bottom of the multiplet, still form bound states, the high-lying dipolar terms are pushed up into the continuum, offsetting the effect of \(Q\), and their mixing gives rise to the GDR with characteristic Fano lineshapes, as seen experimentally. This physical picture clearly demonstrates why the dipole and the HM states show a crossover from V-B to bound character, in the 5d→5f (actinides) \([17]\), the 4d→4f (RE compounds) \([11]\), or the 3p→3d (TM compounds) edges \([14]\).
In Fig. 3(c) we show $S(q, \omega)$ from a model calculation for Tb$^{4+}$ (lines) that includes transitions from the 5d core-level to both the (5f, 6f) levels as before (allowed $l=1,3,5$), and to a fictitious $7p$-like discretized band (allowed $l=1,3$). The band is so positioned that it starts below the high energy dipole state, but above the HM states. The $l=1,3$ channels can interfere via the $C1(5f-7p)$ matrix elements $^{20,22}$. We find that while the lower lying $l=3,5$ peaks remain sharp and excitonic, the high-energy dipole feature forms a GDR, just as discussed above. Interestingly, a dipole-allowed peak present at lower energy ($\sim 88$ eV) is not broadened by this mechanism, implying that the position within the multiplet, rather than the symmetry of the state, decides its fate. A fairly good comparison with the experimental $q$-dependent NIXS for ThO$_2$ $^{17}$ (symbols) is obtained if we use a somewhat larger Lorentzian width for the GDR than the HM states, in order to simulate the multiplet dependent core-hole decay probabilities, not included in the present calculation. It is important to note that this dichotomy, between the dipole and the HM, could be reversed in cases where the dipole allowed states are lower in energy than the HM, like for more-than-half-filled systems which have large ground state $J$ values $^{22}$.

In conclusion, the modeling of same n-shell NIXS is complicated by the simultaneous presence of V-B and bound states within the same final-state multiplet. The complex V-B resonances, involving non-local effects, provide insight into the hybridization of the locally excited core-electron with continua, and about core-hole decay processes. The dipole-forbidden bound states (not prominent in XAS) are modeled using a local, atomic CI approach, that provides direct ground state information. It also explains the apparent strong reduction of the atomic Slater integrals, which effectively become term dependent. The HM transitions and especially their angular dependence in single crystal studies $^{12,13}$ are also expected to provide detailed information on the importance of “orbital-ordering” in the ground state and changes at phase transitions in “hidden order” materials like URu$_2$Si$_2$ $^{8}$. The V-B resonances are modeled with an additional term, mixing the 5f states with a conduction band continuum, resulting in their broad and Fano-like line shapes. More realistic approaches to the latter would include an energy-dependent hybridization with a realistic density of states, and explicit core-hole decay processes. This is a topic of future investigations.

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