Coexistence of bound and virtual-bound states in shallow-core to valence x-ray spectroscopies

Subhra Sen Gupta,1,* J. A. Bradley,2 M. W. Haverkort,3 G. T. Seidler,2 A. Tanaka,4 and G. A. Sawatzky1
1Department of Physics and Astronomy, University of British Columbia, Vancouver, BC V6T 1Z1, Canada
2Department of Physics, University of Washington, Seattle, Washington 98105, USA
3Max Planck Institute for Solid State Research, Heisenbergstraße 1, D-70569 Stuttgart, Germany
4Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

With the example of the non-resonant inelastic x-ray scattering (NIXS) at the O\text{23} edges (5\text{d} \rightarrow 5\text{f}) of the actinides, we develop the theory for shallow-core to valence excitations, where the multiplet spread is larger than the core-hole attraction, such as if the core and valence orbitals have the same principal quantum number. This involves very strong final state configuration interaction (CI), which manifests itself as huge reductions in the Slater-Condon integrals, needed to explain the spectral shapes within a simple renormalized atomic multiplet theory. But more importantly, this results in a cross-over from bound (excitonic) to virtual-bound excited states with increasing energy, within the same core-valance multiplet structure, and in large differences between the dipole and high-order multipole transitions, as observed in NIXS. While the bound states (often higher multipole allowed) can still be modeled using local cluster-like models, the virtual-bound resonances (often dipole-allowed) cannot be interpreted within such local approaches. This is in stark contrast to the more familiar core-valence transitions between different principal quantum number shells, where all the final excited states almost invariably form bound core-hole excitons and can be modeled using local approaches. The possibility of observing giant multipole resonances for systems with high angular momentum ground states is also predicted. The theory is important to obtain ground state information from core-level x-ray spectroscopies of strongly correlated transition metal, rare-earth, and actinide systems.

DOI: 10.1103/PhysRevB.84.075134 PACS number(s): 78.70.Ck, 78.20.Bh, 78.47.da, 78.70.Dm

I. INTRODUCTION

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 Plutonium2 and the unsolved “hidden-order” phase3 of URu2Si2 below 17.5 K. Their properties interpolate between more itinerant 3\text{d} transition metal (TM) systems and more localized 4\text{f} rare-earth (RE) complexes,4 and exhibit strong interplay between spin, charge, orbital, and lattice degrees of freedom. Thus, versatile experimental techniques are needed to unravel the physics operative in these systems. Core-level spectroscopies, like x-ray absorption spectroscopy (XAS), have been extremely successful in providing information regarding the ground state of TM and RE systems, relying largely on theoretical interpretations based on local correlated models with full multiplet effects5 and atomic selection rules.

The success of such local multiplet models relies strongly on two facts: (1) the electronic structure of these strongly correlated systems is largely governed by local correlation physics and point group symmetry, and (2) the final state core-hole strongly binds the extra \text{d} or \text{f} electron, so that all core-valence multiplet states form excitonic bound states. However, core-valence excitations within the same principal quantum number (n)-shell, like the 5\text{d} \rightarrow 5\text{f} transitions in the actinides (or for that matter the 4\text{d} \rightarrow 4\text{f} transitions in the RE, or the 3\text{p} \rightarrow 3\text{d} transitions in TM compounds), pose a problem because the core-valence multiplet spread is \text{≈}20–25 eV, often much larger than the average core-valence electron-attractive potential (Q) itself. This pushes the higher lying terms of these multiplets up into the conduction band, “autoionizing” the extra \text{f} electron. Such mixing with band-structure or autoionization continua gives rise to very broad, virtual-bound Fano-resonances,6 that cannot be interpreted in terms of local models. We note that this effect is distinct from those involving the decay of the core-hole itself, which have been elegantly described7,8 for these giant dipole resonances (GDR).9

The strong hybridization of the 5\text{f} electrons with conduction band states requires detailed information about inter-atomic interactions and band structure effects, ruling out the usefulness of atomic models. There have been attempts to interpret these broad, so called giant-resonances in terms of broad spin-orbit split multiplets in the final state,11 but this may not be the complete picture. This is because the core-5\text{d} spin-orbit splitting between the 5\text{d}_{3/2} and 5\text{d}_{5/2} states in Th or U is of the order 6–8 eV, whereas the GDR is spread over an energy range of 15–20 eV, and it is hard to imagine that core-hole lifetime effects alone can account for this enormous spread. In this article, we emphasize that the structure of core-level excitations within the same n-shell, is fundamentally different from that between different n-shells, with the example of the 5\text{d} \rightarrow 5\text{f} non-resonant inelastic x-ray scattering (NIXS) in the actinides. We also show that the high-multipole transitions in NIXS to strongly bound core-valence multiplet states, unlike the dipole restricted transitions in XAS and electron energy loss spectroscopy (EELS), can still be treated within local models, but with strongly renormalized parameters, due to very large configuration interaction (CI) in the final state.

NIXS involves first order scattering at photon energies much larger than any typical atomic excitation edge (\text{hv} \sim 6–10 keV), arising from the \text{(e}^2/2mc^2)\vec{A} \cdot \vec{A} term in the light-matter coupling.12 The corresponding double differential cross-section is given by

\[
\frac{d^2\sigma}{d\omega_f d\Omega} = \left(\frac{d\sigma}{d\Omega}\right)_{Th} S(\vec{q},\omega),
\]
where, $\frac{\omega}{2\hbar} r_k$ is the Thompson scattering cross-section for a free electron, while the material dependence is completely contained in the wave-vector ($\vec{q}$) and frequency ($\omega$) dependent dynamical structure factor, $S(\vec{q}, \omega)$, given by:

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

where $\vec{q} = \vec{k}_f - \vec{k}_i$ is the photon momentum transfer, and $\hbar \omega = \hbar \omega_0 - \hbar \omega_f$ is the energy loss, both transferred to the electronic system. Here $|i\rangle$ and $|f\rangle$ are the many-body initial and final states of the system, with energies $E_i$ and $E_f$, respectively. The transition operator can be multipole expanded:\textsuperscript{13,14} as:

$$e^{i \vec{q} \cdot \vec{r}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l (2l+1) j_l(qr) C^l_m(\theta_\tau, \phi_\tau) C^l_m(\theta_r, \phi_r),$$

where, $q = |\vec{q}|$ and $r = |\vec{r}|$, and $j_l(qr)$ are spherical Bessel functions, while $C^l_m(\theta, \phi)$ are renormalized spherical harmonics, both of order $l$. Due to angular momentum and parity selection rules, only terms with $|l_f - l_i| \leq l \leq (l_f + l_i)$ and $(l + l_f + l_i)$, even, survive in the infinite sum. As is evident from Eq. (3), NIXS can access transitions involving high-order multipole channels ($l$), unlike the dipole restricted XAS, the weight of each multipole being decided by the reduced (radial) matrix element ($5f [j_i(qr)] || 5d \rangle = \langle R_{5f}(r) | j_i(qr) | R_{5d}(r) \rangle$). In Eq. (3) the angular part of the operator relating to the electron coordinates is the spherical harmonic $C^l_m(\theta, \phi)$, whereas $C^l_m(\theta_\tau, \phi_\tau)$ is related to the photon momentum direction ($\vec{q}$) and gives rise to natural (crystal field) dichroism in anisotropic systems.\textsuperscript{15} It is to be noted that the sum over $l$ in Eq. (3), enters as a coherent summation into $S(\vec{q}, \omega)$ [Eq. (2)], and this results in interferences between the the various $l$-channels. All this is well exemplified by the observation of $d-d$ transitions in TM compounds by Larson et al.\textsuperscript{16} and its subsequent explanation in terms of excitonic transitions by Haverkort et al.\textsuperscript{13} Even for dipole-allowed transitions like our example of the $5d \rightarrow 5f$ transitions in the actinides, NIXS can access the dipole-forbidden parts of the final state core-valence multiplet and provides a much better representation of the true ground state of the system.\textsuperscript{15,17}

As a relevant illustration we show, in the inset to Fig. 1(c), the radial transition probabilities for the various allowed channels in the $5d \rightarrow 5f$ NIXS of the Th$^{4+}$ ($5f^7$) system (relevant for ThO$_2$), plotted against $q$, as obtained using Cowan’s atomic Hartree-Fock (H-F) code.\textsuperscript{18} From the selection rules, this transition has allowed channels for the dipole ($l = 1$), octupole ($l = 3$) and the triacontadipole ($l = 5$) sectors.\textsuperscript{19} From Fig. 1(c) we find that the transition probabilities for the three channels peak at very different values of $q$, and that with increasing $q$, the cross-section for the dipole transition is suppressed while that for the $l = 3$ first and then for the $l = 5$ sectors are enhanced, at the cost of the dipole. This trend can be understood\textsuperscript{13} on the basis of the behavior of $j_l(x)$ as a function of $(l, x)$. With increasing order $l$, the first largest peak of the spherical Bessel functions occur at progressively larger values of $x$, and with decreasing absolute intensity. Since the range of $r (x = qr)$, that contributes most significantly, is dictated by the range of the associated atomic radial wavefunctions, which is fixed for a given transition, larger values of $q$ are needed to capture peaking at progressively larger $x$.

The rest of the article is organized as follows. In Sec. II, we summarize the salient features of the experimental NIXS spectra in the early actinide oxides ThO$_2$ and UO$_2$. This includes the general $q$-dependent trends that they exhibit and their comparison with simple renormalized atomic multiplet calculations, as detailed by Bradley et al.\textsuperscript{20} This already brings out the key issues which we are to address in this article. In Sec. III, we elucidate the reason for the drastic reduction of the Slater-Condon integrals needed, within a simple renormalized atomic multiplet approach, to account for the experimental lineshapes, in terms of final state CI with higher lying levels like the $6f$. Section IV deals with the mechanism for the formation of the GDR, and the reason for the dichotomy between the dipole and higher multipole transitions. It is further

FIG. 1. (Color online) Calculated $q$-dependent NIXS spectra [$S(\vec{q}, \omega)$] within a simple renormalized atomic multiplet model for the $5f^0$ system Th$^{4+}$ (a), compared with the corresponding experimental NIXS spectra\textsuperscript{20} for ThO$_2$ (c); and for the $5f^2$ system U$^{4+}$ (b), compared with the corresponding experimental NIXS spectra\textsuperscript{20} for UO$_2$ (d). The respective component spectra (calculated) for the $l = 1, 3, 5$ channels are shown at the bottom of panels (a) and (b). Also, in each case, the calculated spectra with high resolution (dashed lines) is shown below the calculated spectra with experimental resolution (thick solid lines), to bring out the finer details of the multiplet structure. The inset to panel (c) shows the relative variation of the cross-sections (transition probabilities) for the different multipole channels as a function of $q$. 

075134-2
COEXISTENCE OF BOUND AND VIRTUAL-BOUND STATES . . .

II. 5d-5f NIXS IN THE ACTINIDES: Experiment versus Renormalized Atomic Multiplet Theory

A detailed description of the experimental trends in the O K edge (5d – 5f) NIXS of Th (5d105f0 → 5d5f0) and U (5d5f2 → 5d5f5), with a brief account of their simulation within a simple renormalized atomic multiplet approach has been provided for various fillings of the 5f shell (in the 5f0 systems ThO2 and Cs2UO2Cl4, the 5f2 system UO2, and the mixed-valent system U3O7) in our earlier article. The calculations were based on an atomic many-body Hamiltonian, \( \hat{H}_{5d-5f} \), consisting of the onsite energies of the atomic core-5d \((\varepsilon_{5d})\) and valence-5f \((\varepsilon_{5f})\) levels, spin-orbit coupling \((\xi_{5f})\) and full multiplet Coulomb interactions within the 5f manifold [expressed in terms of the non-mixing Slater-Condon integrals \((F_{ij}^{k}, F_{ij}^{*}, F_{ij}^{*}, F_{ij}^{*})\), spin-orbit interaction within the core-5d level \((\xi_{5d})\), and the final state full multiplet core-valence Coulomb interactions [expressed in terms of the non-mixing Slater-Condon integrals \((F_{ij}^{k}, F_{ij}^{*}, F_{ij}^{*}, F_{ij}^{*})\)]. The spin-orbit and Slater-Condon integrals were computed using Cowan’s atomic H-F code and scaled as described below. The qualitative trends are very similar in the two systems and following points summarize the main conclusions:

(i) For low-q, the main feature appears at relatively higher energies and following the trend in the transition probabilities for the various channels, we conclude that it corresponds mainly to dipole transitions. This is also consistent with the fact that for small q, the NIXS operator \( e^{i\vec{q} \cdot \vec{r}} \approx 1 + i\vec{q} \cdot \vec{r} \), where the first term does not contribute due to the orthogonality of \(|i\rangle \) and \(|f\rangle\), while the second term mimics the usual dipole term \( \vec{\kappa} \cdot \vec{r} \), with \( \vec{q} \) playing the role of the polarization \( \vec{\kappa} \). With increasing q, spectral weight is transferred from the dipole feature to the “pre-absorption edge” higher multipole features at lower energy just as in the inset to Fig. 1(c). The component pure dipole (\( l = 1 \)), octupole (\( l = 3 \)) and the triakontadipole (\( l = 5 \)) features are also shown at the bottom of Figs. 1(a) and 1(b). These, together with the theoretical NIXS spectra plotted with high resolution for each q (dashed lines), show that the apparent shift of the broad peak at about 93 eV is actually a spectral weight transfer from the \( l = 3 \) to the \( l = 5 \) feature with increasing q. These high resolution spectra also make it amply clear that although the qualitative trends are similar for both the systems, the detailed spectral shape is very different between the two. Thus UO2 being a 5f-1 system has additional \( f-f \) multiplet interactions in the final state, absent in the 5f0 system ThO2, which yields a more complicated final state multiplet structure for the former, as seen.

(ii) The important point is that the experimental NIXS data for actinides show the dichotomy that the high multipole features are sharp and excitonic, while the Fano-like asymmetric dipole feature is broad, relatively featureless and spread out over a very large energy range.

(iii) In stark contrast, the calculated low-q dipolar NIXS spectra are much sharper and much more intense, just like the lower energy high multipole terms. Thus, the dichotomy mentioned in (ii) above is not captured by the present level of theory.

(iv) Also very importantly, in order to obtain reasonable agreement with experimental peak positions (the dipole peak position is especially extremely sensitive) and relative intensities of the various features within this conventional renormalized atomic multiplet calculation, one needs to drastically scale down the 5d-5f Coulomb and exchange Slater-Condon integrals \((F_{ij}^{kk}, G_{ij}^{kk})\), to 60% (ThO2) and 50% (UO2) of their atomic H-F values. For UO2 the 5f-5f Slater-Condon integrals \((F_{ij}^{kk})\) were also scaled similarly (i.e., to 50%) but the spectrum was found to be much less sensitive to this compared to the 5d-5f scaling. This is hard to justify for these rather atomic-like 5f wavefunctions. Although the 5f orbitals are expected to be more covalent than the 4f, they are definitely more localized than the 3d orbitals in the TM compounds for which normally an 80%-85% scaling works very well.

In passing, we note that the dichotomy, discussed in (iv) above, is also observed in the Ni5s (4d → 4f) NIXS of RE systems13 and the Mn23 (3p → 3d) NIXS of TM compounds,14 and between the “doubly forbidden” pre-edge peak and the GDR, in the O5s XAS or EELS of actinides,11 showing that this is a generic feature of shallow-core to valence transitions, i.e., within the same n-shell. Below we address each of these issues, starting with the issue of the drastic reduction in the Slater-Condon integrals. From now on we shall focus our attention on the 5f0 system ThO2 alone, treating it as a model system where the core-valence multiplet structure in the final state is not unnecessarily complicated by the presence of additional f-f multiplet interactions. This helps bring out the essential physics which is robust and is expected to hold also for other actinide systems, at least the early ones. We shall come back to the case of a late actinide later.

III. POSSIBLE REASON FOR THE DRAMATIC REDUCTION OF THE SLATER-CONDON INTEGRALS: CI WITH THE 6f

To understand the origin of the apparent large reductions in the Slater integrals, we plot in the top inset of Fig. 2(a), the 5d,
5f and the 6f radial wavefunctions, obtained from an atomic H-F calculation for ThO$_2$ (Th$^{4+}$, ground configuration 5f$^3$). The 5d and 5f orbitals (same n-shell) overlap very strongly, which accounts for the large values of the atomic $(F_{df}^{k}, G_{df}^{k})$ integrals. In contrast, the more diffuse 6f orbital, with an additional radial node, overlaps only weakly with the 5d. Hence, if the final state Hilbert space is augmented to include both the 5d$^5$5f$^1$ and 5d$^6$6f$^1$ configurations, then a CI via the CI(5f$^5$-6f$^1$) matrix elements, would effectively expand the radial part of the 5f wavefunction, which undermines its overlap with the 5d, in turn reducing the 5d-5f Slater integrals. Now, the mixing depends also on the energy separation, $\Delta E$, between the center-of-gravities of configurations involved, which is smaller in the heavier actinides, than between 4d$^4$4f$^1$ and 4d$^5$5f$^1$ in the lighter RE ions, for example. This results in a strong multiplet-dependent CI, because the core-valence multiplet splitting of 5d$^0$5f$^1$ is much larger than that of 5d$^6$6f$^1$, as shown schematically in Fig. 2(b), and which will be discussed in detail below. To illustrate this point, the NIXS spectra for ThO$_2$ (Th$^{4+}$) are calculated (using the XTLS8.3 code) on the basis of the aforesaid CI model, for which the Hamiltonian has the structure:

$$\hat{H}_{CI} = \begin{pmatrix} \hat{H}_{5d-5f} & CI(5f-6f) \\ CI(5f-6f) & \hat{H}_{5d-6f} \end{pmatrix},$$

where $\hat{H}_{5d-6f}$, for the 5d$^0$6f$^1$ configuration, has basically the same form as $\hat{H}_{5d-5f}$ for the 5d$^5$5f$^1$ configuration, discussed earlier, except that the 5f level is now replaced by the 6f level, and CI(5f$^5$-6f$^1$) are the configuration interaction Coulomb integrals, which mix the above two configurations. $S(\hat{q}, \omega)$ is then calculated as a coherent combination of the NIXS transitions $5f^0 \rightarrow 5d^55f^1$ and $5f^0 \rightarrow 5d^66f^1$. Here we leave the $(F_{df}^{k}, G_{df}^{k})$ integrals unaltered at their atomic H-F values, while the scaling of CI(5f$^5$-6f$^1$) 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 in this minimal model that just serves to bring out the basic physics. The full q-dependent spectra, at the optimized 60% scaling of CI(5f$^5$-6f$^1$) [Fig. 2(a)], is spread over a wide energy range and consists of 5f-like and 6f-like regions (marked in the figure), though most of the spectral weight lies in the 5f-like region due to dominance of radial transition 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 high multipole peaks, in good agreement with experiments. Also the component spectra for the $l = 1, 3, 5$ channels plotted at the base of Fig. 2(a) (vertical scale not to be compared with the actual spectra above) clearly show that it also reproduces the mild shift of the high multipole peak at $\sim 93$ eV, due to a q-dependent weight transfer between the $l = 3$ and $l = 5$ channels, as seen in experiments or in the renormalized atomic multiplet calculations (c.f. Fig. 1). The dipole states, in general, mix much more and respond much more sensitively to the CI than the high multipole states. This also means that there is a substantial amount of interference between the 5f-like and 6f-like dipole transitions. All of this helps to transfer a finite part of the spectral weight from the 5f-like dipole feature to the 6f-like one, as seen from Fig. 2(a), but the effect is very small for the high multipole part, which is desirable as it was already in agreement with experiments. However, this is still far from what is needed to convert the very sharp and intense dipole peak in the calculation into the very broad and diffuse GDR seen in the experiments. All of this physics is absent in a simple renormalized atomic multiplet approach as described above.

The origin of the higher sensitivity of the dipole compared with the higher multipoles is explained schematically in Fig. 2(b). Before CI (left), the difference ($\Delta E$) in the center-of-gravity energies for the two final state multiplet families, 5d$^5$5f$^1$ (width $W_{\text{mult}}$) and 5d$^6$6f$^1$ (width $w_{\text{mult}}$),
is \(\sim 23-24\) eV, from H-F calculations. Although both the multiplets involve exactly the same terms, \(W_{\text{mult}}(\sim 25\) eV) is much larger than \(w_{\text{mult}}(\sim 7\) eV), demonstrating the difference between states involving the same versus different principle quantum numbers. Also, for a less-than-half-filled system which typically has a low angular momentum \((J)\) ground state, the highest multiplets (red) are generally dipole-allowed, while the lowest ones (blue) are the high multipole allowed terms. This can be understood with the example of ThO\(_2\), which is a 5\(f^6\) system in the atomic limit, and has a \(1S\) \((J = 0)\) ground state. Thus in the final state configuration 5\(d^75f^1\), which involves Coulomb and exchange interactions between a 5\(d\) hole and a 5\(f\) electron, with angular momenta \(l_d = 2, l_f = 3\) and spin-\(\frac{1}{2}\) each, as the dominant effect (neglecting the spin-orbit coupling especially of the core-5\(d\), for the time being), one has the possible terms \(1^3\)P, \(1^3\)D, \(1^3\)F, \(1^1\)G, and \(1^3\)H. From the \(1S\) ground state, a dipole transition is possible only to the \(1^1\)P state, which by virtue of Hund’s rules, is one of the highest energy states of the core-valence multiplet structure. On the other hand, the state \(1^3\)H which is one of the lowest energy terms by virtue of Hund’s rules, is reachable from the ground state only by a triakontadipole \((l = 5)\) transition. Although normally forbidden, most of the triplet states can be reached because of the perturbation by the core-5\(d\) spin-orbit coupling.\(^{11}\) Now \(CI(5f-6f)\) (which consists of the mixing direct and exchange Coulomb integrals \((R_1^0, R_2^0, R_3^0, R_4^0, R_5^0, R_6^0)\), the largest of which is \(\sim 2\) eV, even after a reduction to 60\% of its atomic value) only mixes terms of the same symmetry,\(^{18}\) e.g., the red (blue) states at the top (bottom) of 5\(d^75f^1\), mix only with the red (blue) states at the top (bottom) of 5\(d^66f^1\). The result after mixing is shown in the right panel of Fig. 2(b). Since \(w_{\text{mult}} \ll W_{\text{mult}}\), the effective energy denominator for mixing of the red (dipole) terms \([\sim \Delta E - \frac{1}{2}(W_{\text{mult}} - w_{\text{mult}})]\) is much smaller than that for the blue (high multipole) terms \([\sim \Delta E + \frac{1}{2}(W_{\text{mult}} - w_{\text{mult}})]\), causing the observed differences in the shifts. Because of these strong correlation effects, the effective “screening” becomes highly term dependent, explaining the strong asymmetry in the behavior of the dipole and the high multipole terms, which is not captured by a uniform reduction of the Slater integrals.\(^{20}\)

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

FIG. 3. (Color online) (a) Experimental \(q\)-averaged NIXS for ThO\(_2\), compared with the component \((l = 1, 3, 5)\) summed calculated spectra for atomic values of \((F_{lj}^{jk}, G_{lj}^{jk}),\) 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 \(CI(5f-6f)\) scaling (b) \((5f-6f)\), and (c) \((F_{lj}^{jk}, G_{lj}^{jk})\). While the latter shows a simple linear trend, the former shows a parabolic behavior with signs of saturation.

IV. ORIGIN OF THE GIANT DIPOLE RESONANCE (GDR) : MIXING WITH CONTINUA AND THE FANO EFFECT

A. Why different transitions behave differently?

We now turn to the problem of the experimentally observed low relative amplitude, large width and non-lorentzian line shape of the GDR. To begin with, we address the question as to why edges involving transitions within the same principal quantum number \((n)\) shell behave very differently from edges that involve transitions between different \(n\)-shells. We note that although for the former case, the dominant interaction in the final state is the multiplet core-valence Coulomb interaction which is larger than the core-hole spin-orbit coupling, for the latter case, the core-hole spin-orbit coupling is the largest energy, followed by the core-valence Coulomb interaction.

To this end we perform a simple gedanken experiment, as illustrated in Figs. 4(a)–4(d). For both XAS and NIXS, if the initial valence state was \(nl^m\) \((e.g., 5f^m)\), with \(m\) electrons in the valence shell (principal quantum number \(n\), and sub-shell \(l\)), then the final state valence configuration is \(nl^{m+1}\) \((e.g., 5f^{m+1})\), in the presence of a core-hole \(n'(l - 1)\) \((e.g., 5d^4 \equiv 5d^0\) or \(4d^7 \equiv 4d^0\)), the underline denoting a hole state. Although NIXS can access dipole forbidden edges also in general, we have here restricted ourselves to dipole-allowed edges in taking \(l' = l - 1\), as we want to bring out the dichotomy between the
dipole-allowed and high multipole terms under the special circumstance when \( n' = n \). The aforesaid state is shown in Fig. 4(a), but in the absence of the core-hole (formally identical with the final state of inverse photoemission on a \( nl^{m} \) state), when it is positioned below or just inside a continuum (the continuum could relate to band-structure or autoionization continua etc.). Now, suppose the core-hole is created at this site [Fig. 4(b)]. To start with, we assume that its only effect is to provide an attractive scalar potential, that pulls down the \( nl^{m+1} \) level by an amount \( Q \), on the average, and this is now referred to as the \( [n'(l - 1)nl^{m+1}] \) (e.g., \( 5d^{-5}f^{m+1} \)) state. The potential \( Q \) is often strong enough to pull down this level below the continuum. However, this is not the sole effect of the core-hole and the multipole part of the core-valence Coulomb interaction gives rise to a fanning out of this state into a multiplet structure of width \( W_{\text{mult}} \). The level \( [n'(l - 1)nl^{m+1}] \) is now understood to be the center-of-gravity of this newly formed multiplet structure. Now, two disparate situations can arise as is illustrated in Figs. 4(c) and 4(d), viz.: (i) where transitions occur between subshells belonging to two different principal shells (Fig. 4(c) where \( n > n' \), e.g., \( 4d^{-5}f^{m+1} \)). Here, the Slater-Condon integrals that decide \( W_{\text{mult}} \) are relatively small as the core and the valence levels belong to different \( n \)-shells, and hence \( W_{\text{mult}} < Q \). Then, as shown in Fig. 4(c), all the final-state multiplets (both dipole and high multipole) are situated well below the continuum and form bound core-hole excitonic states, that can be treated within local models. Such is the case for the celebrated \( 2p \rightarrow 3d \) transitions in the TM oxides or \( 3d \rightarrow 4f \) transitions in the RE compounds, where XAS works so very well. (ii) More interesting is the case where they belong to the same \( n \)-shell [Fig. 4(d), where \( n = n' \), e.g., \( 5d^{-5}f^{m+1} \)]. In this case, the Slater-Condon integrals are very large due to the large overlap between these orbitals, and \( W_{\text{mult}} > Q \). Then, as in Fig. 4(d), the high multipole terms toward the bottom of the multiplet, still form excitonic bound states, but the dipole-allowed terms in the highest part of the spectrum are pushed up by a large amount, offsetting the attractive effect of \( Q \), and now lie well within the continuum. Once they are degenerate with some of the continuum states, they can easily mix with them, and this gives rise to very broad and asymmetric excitonic resonances with characteristic Fano lineshapes. This physical picture clearly demonstrates why the dipole and the high multipole states show a crossover from virtual-bound to bound excitonic character, at edges involving transitions within the same \( n \)-shell. This is the case for the \( 5d \rightarrow 5f \) edges in the actinides, the \( 4d \rightarrow 4f \) edges in the RE compounds, or the \( 3p \rightarrow 3d \) edges in TM compounds.

B. A model calculation illustrating the formation of the GDR

With this understanding of the origin of the dichotomy between the dipole and the high multipole features, we shall now try to understand, in some more detail, the lineshape of the GDR. As we have already pointed out, the GDR has a typical Fano-like asymmetric lineshape. A Fano line-shape arises when there coexists a discrete state which is degenerate with a continuum and one considers transitions to both of these states from a third (discrete) state. Due to the mixing of the former discrete state with the continuum, these two transitions can interfere giving rise to a very broad and asymmetric lineshape.

Thus, to simulate the \( 5d^{-5}f^{-1} \) NIXS of ThO\(_2\), we consider the model shown in Fig. 5(a), which is an extension of our earlier model for the CI. As shown, it consists of the core \( 5d \), the valence \( 5f \) and the empty \( 6f \) levels on Th. The interaction of the \( 5f \) with the \( 6f \) and the transitions to the \( 6f \) are not shown in the figure, although included in the calculation, as it has been discussed before and does not shed any extra light on the physics we are about to discuss. Instead we just show the fanning out of the renormalized \( 5d^{-5}5j^{-1} \) multiplet structure after the CI with \( 5d^{-6}6f^{1} \) has been taken into account. However, now in addition we also include in the calculation, a fictitious discretized \( 7p^{-1} \) band spreading over an energy range of 7 eV. The discretization step used was 0.2 eV, so that the degeneracy was \( N_p = 36 \). The band is positioned to start below the high energy dipole term, but above the high multipole terms, as shown. We consider NIXS transitions from the \( 5d \) core-level to the \( 5f \) level (denoted by \( T_{5d^{-5}5f} \) and has allowed transitions in the \( l = 1,3,5 \) channels) as well as to the states in the \( 7p \)-like continuum (denoted by \( T_{5d^{-7}p} \) and has allowed transitions in the \( l = 1,3 \) channels). The terms in the
5d⁰5f¹ multiplet mix (hybridize) with the continuum states via the C1(5f⁻⁷p) Coulomb matrix elements which are similar to the C1(5f⁻⁶f) matrix elements introduced earlier. Both the transition matrix elements, T₅d⁻⁶f, as well as the mixing matrix elements C1(5f⁻⁷p) were scaled using the usual 1/√Nₚ factor. An overall additional scaling factor was used to optimize the mixing matrix elements C1(5f⁻⁷p) to obtain good agreement with experiments. From the definition of the Fano-effect in the last paragraph, it is apparent that the l = 1,3 channels, present in both the transitions, can interfere via the C1(5f⁻⁷p) matrix elements, and give rise to a Fano-effect.⁶

In Fig. 5(b) we show the calculated S(q,ω) for Th⁴⁺, from this model (lines). 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 in the last section. Interestingly, a dipole-allowed peak present at lower energy (∼89 eV) is not broadened into a resonance, but appears as an excitonic feature just like the high multipole terms.

C. A more-than-half-filled system can behave differently:

Example of giant multipole resonances in Tm⁹⁺

In the last section we showed that the position within the multiplet, rather than the symmetry of the state, decides its fate. Here we elucidate this further with the example of a more-than-half-filled model rare-earth system Tm⁹⁺+, which is relevant for the oxide Tm₂O₅. The ionic configuration in the ground state is 4f¹² and the Nᵢ₅ NIXS involves the transition 4d¹⁰4f¹² → 4d⁰⁴f¹⁺. This makes the final state particularly simple (a two-hole state), hence the choice. The 4f¹² system has a high J ground state given by the term 3H₆ (J = 6). However, the final state configuration 4d⁰⁴f¹⁺ has the same terms as the final state for the 5f⁰ system, viz. 13P, 13D, 13F, 13G, and 13H (L = 1,2,3,4,5; S = 0,1). Starting from the J = 6 ground state, dipole transitions can occur only to final states with J = 5 (no J = 7 state is possible here), which could either be a state like 3G₅ (L = 4, S = 1) or to the states 13H₅ (L = 5, S = 0,1). These terms with relatively high L and S values, are expected to be some of the low lying states of the multiplet, by Hund’s rules. On the other hand, some of the highest terms are expected to be the ones like 1³P or 1³D etc., which can be reached only by triakontadipole (l = 5) or octupole (l = 3) transitions. This is indeed borne out by actual calculations as shown in Fig. 6(a), where we show calculated component spectra for the three (l = 1,3,5) channels from a renormalized atomic multiplet calculation (f⁻⁷f and d⁻⁷f Slater-Condon integrals reduced to 80% of atomic values). We find that in the multiplet

FIG. 5. (Color online) (a) Schematic showing the model used to simulate the O₄ NIXS of ThO₂ (Th⁴⁺), which captures both the excitonic high multipole features as well as the GDR. It includes a Fano-effect of the mixing of the atomic 5d⁻⁵f transition, with that to a fictitious 7p-like rectangular broad band, via the C1(5f⁻⁷p) matrix elements. (b) The calculated S(q,ω) from the model (lines) resulting in a broad, asymmetric lineshape for the high-energy dipole term, that agrees well with the experimental q-dependent NIXS for ThO₂ (symbols). A dipole term at lower energy (∼89 eV) is not broadened into a resonance, but appears as an excitonic feature just like the high multipole terms.

FIG. 6. (Color online) Calculated Nᵢ₅ NIXS for a model more-than-half-filled rare-earth system Tm⁹⁺+. (a) The bare component spectra for the l = 1,3,5 channels. (b)-(g) Calculated NIXS spectra [S(q,ω)] plotted as a function of increasing q, for q = 4,8,12,16,20, and 24 Å⁻¹. The vertical scales in the different panels are not to be compared.
structure which is spread out over 25 eV or more, the dipole channel indeed reaches some of the lowest states between 175-179 eV and even the highest dipole term lies at about 184 eV, which is still much lower in energy than the octupole and triakontadipole allowed terms lying between 188-196 eV.

In Figs. 6(b)–6(g), we show the full NIXS spectra $[S(q, \omega)]$ plotted as a function of $q$. Note that compared to the $5f_1$ actinide systems, we need much higher $q$ values to reach the predominantly $l = 3$ or $l = 5$ transitions. This has to do with the fact that the $4f$ has a much smaller radial extent ($r$) compared to the $5f_1$, and hence much higher $q$ values are needed to reach the peaks of $j_3(qr)$ and $j_5(qr)$. From Fig. 6, it is clear that the aforesaid dichotomy between the dipole and the high multipoles (as seen in the early actinides), may be reversed in cases where the dipole allowed states are lower in energy than the high multipoles, like for more-than-half-filled systems, which have large ground state $J$ values. In such cases one can expect sharp, excitonic peaks for the dipole terms, while some of the high multipole allowed terms at higher energies may be broadened into resonances, due to mixing with continuum states. This opens up the possibility of observing giant octupole or triakontadipole resonances instead of the more common GDR.

V. CONCLUSIONS

In conclusion, we have shown that the modeling of same $n$-shell NIXS is complicated by the simultaneous presence of virtual-bound and bound states within the same final-state multiplet. The complex virtual-bound 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. We also explain the apparent strong reduction of the atomic Slater integrals in the final state, which effectively become term dependent, by invoking CI with higher lying empty levels. For less-than-half-filled systems with low $J$ ground states, the dipole allowed terms form virtual-bound resonances giving rise to the GDR, while the high multipole terms form excitonic bound states. In contrast, we show with an example, that for more-than-half-filled systems with high $J$ ground states, it is possible that this trend is reversed to yield excitonic dipole terms and giant multipole resonances. It would be interesting to observe this experimentally.

The excitonic high multipole transitions and especially their angular dependence in single crystal studies\cite{Fano, Ogasawara, Richter} 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$_2$ [Ref. 3]. The term “hidden order” refers normally to ordering of high angular momentum, many-body wave-functions in the compounds of heavier elements, which could be of “pure orbital” or of “mixed spin-orbital” origin. Such ordering is usually invisible to techniques like XAS, involving pure dipole transitions. For example, a dipole transition measured on a material with local cubic symmetry shows no linear dichroism. This is related to the fact that a transition of angular momentum $l = 1$ in spherical symmetry, has only one irreducible representation in cubic symmetry, namely $t_{1u}$. With a dipole transition, one thus cannot see a difference between the cubic [111] and [001] directions. An $f$ ground-state wave-function, however, might be very different in these two directions. The $f$ states branch down to states of $a_{2u}$, $t_{1u}$ and $t_{2u}$ symmetry, which are inherently very anisotropic. Similarly, an octupole transition ($l = 3$) branches down to transitions of $a_{2u}$, $t_{1u}$ and $t_{2u}$ symmetry. Thus, there are three different fundamental spectra and there might very well be a difference between the inelastic scattering with $q$ in the [111] and [001] directions. With the use of higher multipole transitions in NIXS, it is thus possible to observe higher multipole ordering, not observable with a dipole transition. Such studies are under progress.

Finally, the virtual-bound resonances are modeled with an additional term, mixing the $5f$ states with a model conduction band continuum, resulting in their broad and Fano-like line shapes. More realistic approaches to the latter would involve an energy-dependent hybridization with a realistic density of states, and the inclusion of explicit core-hole decay processes. This is a topic of future investigations.

ACKNOWLEDGMENTS

SSG and GAS acknowledge funding from the Canadian agencies NSERC, CFI and CIFAR. GTS and JAB acknowledge support from University of Washington, and the US Department of Energy.

\begin{thebibliography}{9}
\end{thebibliography}
COEXISTENCE OF BOUND AND VIRTUAL-BOUND STATES...  


19. We would like to stress that the pole of the transition and the change of angular momentum of the one particle wave functions are not one-to-one equivalent. In the examples shown in Fig. 1, the initial orbital is a $5d$ orbital and thus $l_i = 2$. The final state orbital is a $5f$ orbital, so that $l_f = 3$. We find that $\Delta l = l_f - l_i = 1$, is possible not only for the dipole transition, but also for the octupole and triakontadipole transitions. The relation that has to be fulfilled is that the vectorial sum of the angular momentum of the initial orbital, final orbital and pole of the transition has to be zero. In our case one has to be able to make a closed triangle (triangle relations) of a vector of length 2 [for the initial state orbital with $l_i = 2$ ($d$ orbital)], a vector of length 3 [for the final state orbital with $l_f = 3$ ($f$ orbital)], and a vector of the length of the pole of the transition. This can be done for $|l_f - l_i| \leq l \leq (l_f + l_i)$, which together with conservation of parity leads to the selection rules that a $d$ to $f$ transition can be made with only a dipole, octupole or triakontadipole transition.


22. Note that this Taylor expansion of $e^{i\vec{q}\cdot\vec{r}}$ is not equivalent to the multipole expansion enumerated in Eq. (3) on a term by term basis. This is easily seen from the fact that, e.g., the 1st term of the Taylor expansion yields the matrix element $\langle f | 1 | i \rangle$ which is zero except for the case $|i\rangle = |f\rangle$, whereas the first term of the multipole expansion involves the matrix element $\langle f | j_0(qr) | i \rangle$, where $j_0(x) = \sin x/x$ is not a constant but a function of $x$, and this allows transitions between the states $nl$ and $n'l$ (with the additional selection rules $\Delta l = 0$, $\Delta m = 0$). It also turns out that the constant and the quadratic terms of the Taylor expansion are linear combinations of the monopole and quadrupole terms from the multipole expansion, etc. For small $q$, the dipole term of the multipole expansion however coincides with the linear term of the Taylor expansion.


25. In our case, the $C_{I}(\alpha-\beta)$ matrix elements refer to the Slater-Condon Coulomb mixing integrals $R^0(5d,\alpha,5d,\beta)$.


27. The mixing with continua is the most important effect, while the Fano effect is secondary. We find that linenshapes do not change much when transitions to the continuum are switched off.