High Resolution X-Ray Resonant Raman Scattering

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A general formulation of x-ray resonant Raman scattering is presented. Two main results are found. First, it is argued that recent high resolution experiments, displaying the so-called width narrowing, cannot be discussed in the framework of one-electron theory. Inclusion of many-body effects drastically alters the interpretation of the resonances, as demonstrated by numerical calculations. Second, it is shown that, for fast collisions, a symmetry analysis of the cross section provides a simple description of the observable spectra.

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X-ray absorption and resonant (anomalous) diffraction provide a powerful probe of magnetic and low-symmetry crystal structures [1–7]. Both processes are controlled by electric dipole and quadrupole transitions [8–11], and allow for a direct determination of properties of valence (conduction) electron states in transition metals, rare earths, and actinides [12–14].

Notice that, in such experiments, the spectra are recorded by tuning the energy of the ingoing photon across an absorption threshold; severe limitations on energy resolution are therefore brought about by the natural width of the initial excitation. For deep inner shells, the latter can be quite large, attaining the value of about 4 eV, for a $2p$ hole in the heavy rare earths.

In an attempt to overcome the core-hole lifetime broadening of absorption spectra, a new experimental technique was recently put forward by Hämäläinen and co-workers [15]. It consists of performing absorption-followed-by-emission experiments, treated as a single second order process, the resonant Raman scattering (RRS). (The intermediate state is taken to be short-lived, so that no electronic relaxation is allowed.) The process is shown schematically in Fig. 1.

A specific example will help clarify the underlying idea of the method. Given a rare-earth ion, consider $2p \rightarrow 4f$ electric-quadrupole absorption followed by $3d \rightarrow 2p$ electric-dipole emission. Experimentally, the spectrum is recorded as follows. While the energy of the ingoing photon is swept across the $2p$ absorption edge, the energy of the outgoing photon is kept constant, at the $3d \rightarrow 2p$ transition value, and carefully measured with a high resolution analyzer. Interpreted within the framework of one-electron theory, such an experiment is believed to provide a $2p \rightarrow 4f$ absorption spectrum with the much narrower resolution of a $3d$ hole. The observation of a similar effect in Auger electron-yield spectra has also been reported [16].

It is important to observe that, in one-electron theory, valence-electron $\leftrightarrow$ core-hole interactions are neglected; as a consequence, a *frozen valence-electron density of states* is implicitly assumed in the absorption-followed-by-emission process. For narrow bands, this approximation clearly breaks down. As will be seen, when many-body theory is invoked to describe the scattering process, serious difficulties with the above interpretation emerge.

Hämäläinen *et al.* [15] probed the dysprosium L_3 edge in $Dy(NO_3)_3$, where the $2p$-electron initial excitation can be to either the $4f$ ($E2$) or $5d$ ($E1$) unoccupied states. To discuss such an experiment, we have performed a numerical calculation of the isotropic (unpolarized ingoing and outgoing photons) RRS cross section,

$$\frac{d^2\sigma}{d\Omega_{\mathbf{k}'} d\hbar\omega_{\mathbf{k}'}} = \frac{\omega_{\mathbf{k}'}}{\omega_{\mathbf{k}}} \sum_{qq'} \sum_{f} \left| \sum_{n} \frac{\langle f|D_{q'}^{(1)}|n\rangle\langle n|D_{q}^{(2)}|g\rangle}{E_g + \hbar\omega_{\mathbf{k}} - E_n + i\Gamma_n/2} \right|^2 \times \delta(E_f + \hbar\omega_{\mathbf{k}'} - E_g - \hbar\omega_{\mathbf{k}}), \quad (1)$$

at the L_3 edge of the Dy^{3+} ion. Here, $D_q^{(L)}$, with $q = -L, \ldots, L$, denotes the components of the electric 2^L-pole transition operator; $\mathbf{k}$ and $\mathbf{k}'$ identify ingoing and outgoing photons. For the electric quadrupole $\rightarrow$ dipole part of the resonance, ground, intermediate, and final states are, respectively, given by $|g\rangle = |2p^6 3d^{10} 4f^9\rangle$, $|n\rangle = |2p^5 3d^{10} 4f^{10}\rangle$, and

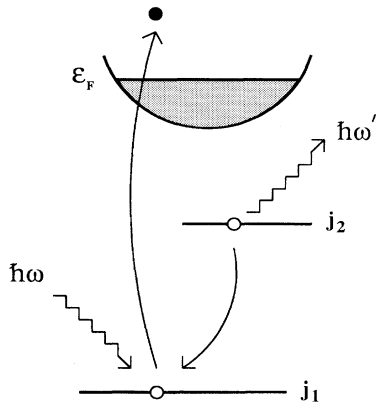

FIG. 1. Resonant Raman scattering in a simple metal.

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$|f\rangle = |2p^6 3d^9 4f^{10}\rangle$. All electric quadrupolar transitions from the $^6H_{15/2}$ Hund's rule ground state of the $2p^6 3d^{10} 4f^9$ configuration of the Dy^{3+} ion, to the full multiplet $2p^5 3d^{10} 4f^{10}$ of the intermediate state were calculated; ditto for all electric dipolar transitions from the intermediate to the final-state multiplet, in the emission matrix element. The results of the calculation are depicted in Fig. 2, as a function of ingoing, $\hbar\omega_{\mathbf{k}}$, and transferred, $\Delta\hbar\omega = \hbar(\omega_{\mathbf{k}} - \omega'_{\mathbf{k}})$, energies; on the vertical axis, the cross section is given in arbitrary units. To account for the finite lifetime of the final states, the energy-conservation δ function was broadened into a Lorentzian of width γ_f. Figure 2 was obtained with $\Gamma_n = 4$ eV and $\gamma_f = 0.3$ eV. A two-dimensional analysis of the spectrum exhibits a variety of effects.

A scan parallel to the $\hbar\omega_{\mathbf{k}}$ axis amounts to moving through the intermediate-state structure. The spectrum has resolution Γ_n, and is obtained by retaining only one final state (selected by the given energy transfer, up to γ_f) in Eq. (1).

Parallel to the $\Delta\hbar\omega$ axis, the final-state structure is scanned, with resolution γ_f. In this case, only a Γ_n-wide set of intermediate states (selected by the fixed ingoing energy) contribute in Eq. (1). For systems with incomplete $4f$ and $5d$ shells, two groups of final states are observed. (i) The $3d^9 4f^{n+1}$ multiplet reached from the intermediate states $2p^5 4f^{n+1}$, as recently observed by Krisch and co-workers [17]; for a suitable choice of photon polarization, the spectrum is equivalent to a $3d \rightarrow 4f$ dipolar absorption, as discussed below. (ii) The $3d^9 4f^n 5d^{m+1}$ final states, reached from the $2p^5 4f^n 5d^{m+1}$ intermediate states, formally equivalent to a $3d \rightarrow 5d$ monopole transition, not observable in absorption.

Keeping $\hbar\omega_{\mathbf{k}'}$ fixed, while varying $\hbar\omega_{\mathbf{k}}$, as performed by Hämäläinen *et al.*, amounts to moving along the 45° line in the $\hbar\omega_{\mathbf{k}}, \Delta\hbar\omega$ plane of Fig. 2. In this case, a superposition of the full set of intermediate and final states is recorded. Considerably different lifetimes, Γ_n and γ_f, determine the particular structure of Fig. 2. When one resolution is rather broad, it is still possible to observe narrow structures; these, however, are entirely due to the other, better resolved set of states. (When $\Gamma_n \gg \gamma_f$, the spectral resolution is controlled by γ_f.)

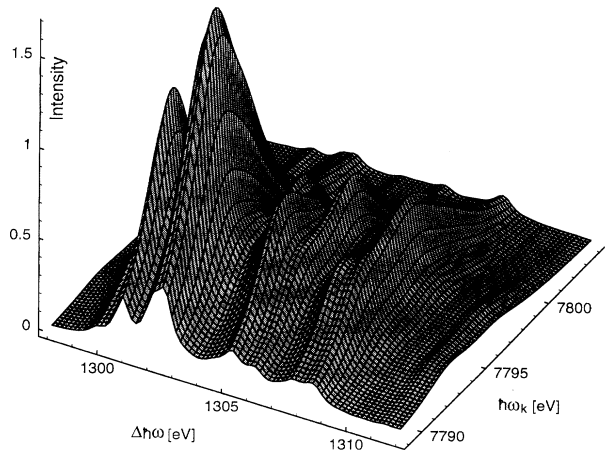

FIG. 2. Numerical calculation of the electric quadrupole → dipole part ($2p_{3/2} \rightarrow 4f$, $3d_{5/2} \rightarrow 2p_{3/2}$) of the RRS cross section at the L_3 edge of Dy^{3+}, as a function of ingoing and transferred photon energies.

In the case of a $2p$-electron excitation into a broad $5d$ band, the interaction with the core hole is believed to be small, and the one-electron picture to provide a good description of the electron density of states; general features of the spectra can then be derived by simple arguments. Consider the resonance $5d^0 \rightarrow 2p^5 5d^1 \rightarrow 3d^9 5d^1$, as described by Eq. (1), with matrix element $\langle f|D^{(1)}|n\rangle\langle n|D^{(1)}|g\rangle$; intermediate and final-state energies can be defined as $E_n = \epsilon_{dn} + \epsilon_{2p}$ and $E_f = \epsilon_{df} + \epsilon_{3d}$, with ϵ_{dn} and ϵ_{df} the one-electron energies of the $5d$ continuum (it could also denote the energy of a state of the d^{m+1} configuration, in a multiplet picture). As $\langle f|D^{(1)}|n\rangle \sim \langle 2p|D^{(1)}|3d\rangle\langle\varepsilon_{dn}|\varepsilon_{df}\rangle$, the band structure $|\langle n|D^{(1)}|g\rangle|^2$ will appear only along the diagonal in the $\hbar\omega_{\mathbf{k}}, \Delta\hbar\omega$ plane. (ε_{dn} changes along $\hbar\omega_{\mathbf{k}}$, whereas ε_{df} changes along $\Delta\hbar\omega$, with $\langle\varepsilon_{dn}|\varepsilon_{df}\rangle = \delta_{dn,df}$ yielding intensity only on the diagonal.)

We note, in passing, that detection of off-diagonal spectral weight yields information on core-hole interactions in transitions to broadbands, therefore providing a stringent test on one-electron (band structure) calculations of x-ray spectra.

Valuable insight into the nature of core-level spectroscopies can be gained by applying the methods of spherical tensor analysis. For the RRS amplitude $f_{L,L'}$, the coupled-multipolar expansion reads

$$f_{L,L'} = 4\pi\lambda \sum_z \sum_{\zeta=-z}^{z} T_\zeta^{(z)*}(\boldsymbol{\epsilon}, \mathbf{k}, \boldsymbol{\epsilon}'^*, \mathbf{k}')\langle f \mid F_\zeta^{(z)}(L,L') \mid g\rangle,$$

where

$$T_\zeta^{(z)*}(L,L') = \sqrt{\frac{2z+1}{2L+1}} \sum_{M,M'} C^{LM}_{L'M';z\zeta} \times [\boldsymbol{\epsilon}\cdot\mathbf{Y}^*_{LM}(\hat{\mathbf{k}})][\boldsymbol{\epsilon}'^*\cdot\mathbf{Y}_{L'M'}(\hat{\mathbf{k}}')]$$

denotes the angular dependence (for photon polarizations $\boldsymbol{\epsilon}$ and $\boldsymbol{\epsilon}'$), and $\lambda = |\mathbf{k}|^{-1}$. The frequency dependent transition operator is given by

$$F_\zeta^{(z)}(L,L') = \sum_{l_z,\sigma,\text{all } m} S_\zeta^{(z)}(L,L') c^\dagger_{j_1 m_1'} c_{j_2 m_2} G(\omega_k) l^\dagger_{l_z\sigma} c_{j_1 m_1},$$

with $G(\omega_{\mathbf{k}}) = \sum_n |n\rangle(E_g + \hbar\omega_{\mathbf{k}} - E_n + i\Gamma_n/2)^{-1}\langle n|$, and

$$S_\zeta^{(z)}(L,L') = R_L^{L'}(c_1, l; c_2, c_1)\sqrt{\frac{2z+1}{2L+1}} \sum_{M,M'} C^{LM}_{L'M';z\zeta} \sum_{\gamma_1\gamma_2\gamma_1'\sigma'} \times (-)^{-M'} C^{j_1 m_1'}_{c_1\gamma_1';\frac{1}{2}\sigma'} C^{j_2 m_2}_{c_2\gamma_2;\frac{1}{2}\sigma'} \times C^{j_1 m_1}_{c_1\gamma_1;\frac{1}{2}\sigma} C^{c_1\gamma_1'}_{c_2\gamma_2;L'-M'} C^{ll_z}_{c_1\gamma_1;LM};$$

furthermore,

$$R_L^{L'}(c_1,l;c_2,c_1) = K(c_1,L,l)K(c_2,L',c_1) \times \langle R_{n_1c_1j_1}(r)|r^{L'}|R_{n_2c_2j_2}(r)\rangle \times \langle R_{nl}(r)|r^{L}|R_{n_1c_1j_1}(r)\rangle,$$

and

$$K(c,L,l) = -\frac{e}{\lambda^{L+\frac{1}{2}}} i^L \frac{C^{l0}_{c0;L0}}{(2L+1)!!} \times \left[\frac{(2c+1)(2L+1)(L+1)}{L(2l+1)}\right]^{1/2}.$$

In the fast-collision approximation [14,18,19], $G(\omega_{\mathbf{k}})$ reduces to $\langle G(\omega_{\mathbf{k}})\rangle = (E_g + \hbar\omega_{\mathbf{k}} - \langle E_n\rangle + i\Gamma_n/2)^{-1}$, with $\langle E_n\rangle$ the average energy of the transition, so that $\langle f|c^{\dagger}_{j_1m_1'}c_{j_2m_2}l^{\dagger}_{l_z\sigma}c_{j_1m_1}|g\rangle = \delta_{m_1,m_1'}\langle f|c_{j_2m_2}l^{\dagger}_{l_z\sigma}|g\rangle$, with c_{j_1} and c_{j_2} creating a core hole in the intermediate and final states, respectively; $l^{\dagger}_{l_z\sigma}$ represents the creation operator for conduction electrons. The core electrons have been labeled using spin-orbit coupled states: $j = c \pm \frac{1}{2}, m$; for the conduction band uncoupled orbital l_z and spin σ quantum numbers have been used.

Recoupling $S^{(z)}$ yields

$$S^{(z)}_{\zeta}(L,L') = R_L^{L'}(-1)^{j_1+j_2+1}[j_1][j_2c_1zl]^{1/2} \times \begin{Bmatrix} j_1 & j_2 & L' \\ c_2 & c_1 & \frac{1}{2} \end{Bmatrix} \sum_{jm}[j] \begin{Bmatrix} j_1 & j & L \\ l & c_1 & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} L & L' & z \\ j_2 & j & j_1 \end{Bmatrix} \begin{pmatrix} \frac{1}{2} & l & j \\ \sigma & l_z & -m \end{pmatrix} \begin{pmatrix} j & z & j_2 \\ m & -\zeta & -m_2 \end{pmatrix}, \quad (2)$$

with $[a\cdots b] = (2a+1)\cdots(2b+1)$. The last $3j$ symbol in Eq. (2) shows that, when the collisions are fast, the RRS amplitude contains matrix elements of direct 2^z-pole transitions between the core level j_2m_2 and the valence empty state $(l\,\frac{1}{2})jm$; the value of z results from the coupling between ingoing and outgoing photons, $(LL')z$. In contrast to real absorption, the effective 2^z-pole transition operator is not purely orbital; it also acts on spin, as the spin-orbit coupling in the intermediate state (j_1 level) allows for spin transitions, even in the absence of spin-orbit interaction in the ground and final states.

The above results lead to the following form for the double-differential scattering cross section ($\hbar = 1$):

$$\frac{d^2\sigma}{d\Omega_{\mathbf{k}'}d\hbar\omega_{\mathbf{k}'}} = 8\pi\lambda^2 \int_{-\infty}^{\infty} dt\, e^{i(\omega_{\mathbf{k}}-\omega_{\mathbf{k}'})t} \times \sum_r \sum_{zz'} \mathcal{T}_0^{(zz')r}\langle g|\mathcal{O}_0^{(zz')r}(t)|g\rangle, \quad (3)$$

with the scattering geometry, $\mathcal{T}_0^{(zz')r}$, given by

$$\mathcal{T}_0^{(zz')r} = \sum_{\zeta\zeta'} C^{r0}_{z\zeta;z'\zeta'} T^z_{\zeta} T^{z'}_{\zeta'}; \quad (4)$$

the scattering operator, $\mathcal{O}_0^{(zz')r}(t)$, can be written as

$$\mathcal{O}_0^{(zz')r}(t) = |\langle G(\omega_{\mathbf{k}})|^2 \sum_{\zeta\zeta'} C^{r0}_{z\zeta;z'\zeta'} \times \sum_{m_2m_2'l_zl_z'\sigma\sigma'} S^{(z)\dagger}_{\zeta} S^{(z')}_{\zeta'} c^{\dagger}_{j_2m_2'}(t) l_{l_z'\sigma'}(t) l^{\dagger}_{l_z\sigma} c_{j_2m_2}. \quad (5)$$

For simplicity, expressions (3)–(5) have been derived for $SO_3 \supset SO_2$ symmetry (that of a magnet with a negligible crystal field); in this case, all scattering operators $\mathcal{O}^r$ (i.e., tensors of rank r) branch to the totally symmetric representation [20], usually denoted by 0. The formalism can be extended to the case of an arbitrary point group by applying the methods of Ref. [7].

As observed, Eq. (2) describes an absorption process, induced by an effective photon of energy $\Delta\hbar\omega$. Integrating over $\hbar\omega_{\mathbf{k}'}$, i.e., summing over the final states, leads to an expansion for the integrated cross section in terms of spin and orbital coupled-tensor operators, formally equivalent to the sum rule analysis for x-ray absorption and dichroism [12,13]. In view of the following discussion, the expansion is best performed by working with each photon coupled to itself. [In Eq. (4), ingoing and outgoing photons are coupled together.] This amounts to a redefinition of the geometry factors,

$$\mathcal{T}_0^{(zz')r} \to \tilde{\mathcal{T}}_0^{(zz')r} = \sum_{\zeta\zeta'} C^{r0}_{z-\zeta;z'-\zeta'} \tilde{T}^z_{\zeta}(L)\tilde{T}^{z'}_{\zeta'}(L'),$$

with

$$\tilde{T}^z_{\zeta}(L) = [z]^{1/2}[L]^{-1/2} \sum_{M,M'} C^{LM}_{LM';z\zeta} \times [\boldsymbol{\epsilon}\cdot\mathbf{Y}^*_{LM}(\hat{\mathbf{k}})][\boldsymbol{\epsilon}^*\cdot\mathbf{Y}_{LM'}(\hat{\mathbf{k}})].$$

The scattering operator is transformed accordingly, $\mathcal{O}_0^{(zz')r} \to \tilde{\mathcal{O}}_0^{(zz')r}$, and is then rewritten, using standard diagrammatic methods of angular momentum theory [21]. This is a rather technical part in our derivation, and will not be discussed here. We find

$$\frac{d\sigma}{d\Omega_{\mathbf{k}'}} \cong 8\pi\lambda^2 \sum_{zz'r} \tilde{\mathcal{T}}_0^{(zz')r}(L,L')\langle g|\tilde{\mathcal{O}}_0^{(zz')r}(0)|g\rangle, \quad (6)$$

with

$$\tilde{\mathcal{O}}_0^{(zz')r}(0) = |\mathcal{A}_L^{L'}(\omega_{\mathbf{k}})|^2(-1)^{j_1+j_2+c_1+c_2}[j_1]^2[j_2] \times [zz']^{1/2}\begin{Bmatrix} j_1 & j_2 & L' \\ c_2 & c_1 & \frac{1}{2} \end{Bmatrix}^2\begin{Bmatrix} L' & L' & z' \\ j_1 & j_1 & j_2 \end{Bmatrix}\sum_{ab}[ab]^{1/2}\left[\sum_x [x]\begin{Bmatrix} a & b & r \\ z & z' & x \end{Bmatrix}\begin{Bmatrix} c_1 & \frac{1}{2} & j_1 \\ c_1 & \frac{1}{2} & j_1 \\ x & a & z' \end{Bmatrix}\begin{Bmatrix} L & l & c_1 \\ L & l & c_1 \\ z & b & x \end{Bmatrix}\right] W_0^{(ab)r}, \tag{7}$$

that is, the cross section expressed as a linear combination of "hole" double-tensor operators

$$W_0^{(ab)r} = -\frac{[ab]^{1/2}}{2[l]^{1/2}}\sum_{\alpha\beta} C^{r0}_{a-\alpha;b-\beta}\sum_{l_z l'_z,\sigma\sigma'} C^{\sigma/2}_{\sigma'/2;a\alpha} C^{ll_z}_{ll'_z;b\beta} l_{l'_z\sigma'} l^{\dagger}_{l_z\sigma},$$

describing the multipole moments of the charge and magnetic distributions of the valence l electrons (shell selectivity). One has [13,14] $W^{(00)} \sim n_h$ (number of holes), $W^{(11)0} \sim \sum_i \mathbf{s}_i \cdot \boldsymbol{l}_i$ (spin-orbit), $W^{(01)} \sim \mathbf{L}$ (orbital angular momentum), $W^{(10)} \sim \mathbf{S}$ (spin); higher order moments are discussed in Ref. [22]. The quantity $\mathcal{A}_L^{L'}(\omega_{\mathbf{k}}) = \langle G(\omega_{\mathbf{k}})\rangle R_L^{L'}$ denotes a dimensionless reduced scattering amplitude. Different values of the tensor rank r are selected by the order of the transitions (L, L') and by photon polarizations, as determined by $\tilde{\mathcal{T}}_0^{(zz')r}(L, L')$.

When the outgoing photon is isotropic ($z' = 0$), expression (6) reduces to

$$\frac{d\sigma}{d\Omega_{\mathbf{k}'}} \cong \lambda^2|\mathcal{A}_L^{L'}(\omega_{\mathbf{k}})|^2[j_2]\begin{Bmatrix} L' & j_1 & j_2 \\ \frac{1}{2} & c_2 & c_1 \end{Bmatrix}^2[j_1]\sum_{abz}[ab]^{1/2}\tilde{T}_0^z(L) \times (-1)^{j_1+c_1+\frac{1}{2}+a}\begin{Bmatrix} \frac{1}{2} & c_1 & j_1 \\ c_1 & \frac{1}{2} & a \end{Bmatrix}\begin{Bmatrix} L & l & c_1 \\ L & l & c_1 \\ z & b & a \end{Bmatrix}\langle g|W_0^{(ab)z}|g\rangle. \tag{8}$$

This case is particularly simple to interpret: absorption and emission are decoupled; for the former, standard sum rules for x-ray absorption and dichroism are recovered [13,22]; the latter yields a multiplicative factor,

$$[j_2]\begin{Bmatrix} L' & j_1 & j_2 \\ \frac{1}{2} & c_2 & c_1 \end{Bmatrix}^2,$$

corresponding to the total intensity of the $2^{L'}$-pole isotropic transitions from j_2 to j_1. (There is a population asymmetry between these two core levels, as they contain $[j_2]$ electrons and one hole, respectively.) The total emission yield simply serves to detect the absorption intensity.

When the angular dependence of the outgoing photon is determined ($z' \neq 0$), other linear combinations of $W^{(ab)r}$ are selected, and higher multipole moments are present. A detailed discussion of Eq. (7) as a function of ingoing and outgoing photon polarizations will be given elsewhere.

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