

An alternative multiple scattering approach to the REXS cross-section

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Abstract :

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I. INTRODUCTION

II. GENERAL DERIVATION OF THE REXS CROSS-SECTION

The general approach to the calculation of Resonant Elastic X-ray Scattering cross-section has been derived by many authors [1–5]. We recall here the main points for the sake of consistency and adapt it to the real space multiple scattering framework.

We start by the general expression of Resonant X-ray scattering (RXS) which we will then specialise to the elastic case.

We consider here the interaction of an incoming radiation field (R) with a core electron (E) on an atom immersed into a sample (S) composed of a collection of atoms represented by the potential V_S . The electron is characterised by its mass m , its charge $-e$ and its spin \mathbf{s} . The electromagnetic field representing the photon is defined by its wave vector \mathbf{q} and the direction of its polarisation \mathbf{e}_q . Including the relativistic spin-orbit term, the total Hamiltonian can be written as [4, 5, 5, 6]

$$H = \frac{1}{2m} [\mathbf{p} + e\mathbf{A}]^2 + V_S + g\frac{e}{2m}\mathbf{s} \cdot \mathbf{B} + \frac{e\hbar}{2m^2c^2}\mathbf{s} \cdot (\mathbf{E} \times [\mathbf{p} + e\mathbf{A}]) + H_R \quad (\text{II.1})$$

where \mathbf{A} is the vector potential of this field, and $\dot{\mathbf{A}}$ its time-derivative. The first term is the kinetic energy of the electron in the presence of the electromagnetic field. The second term describes the interaction of the electron with the atoms in the sample. The third term represents the interaction between the spin \mathbf{s} of the particle and the magnetic field \mathbf{B} of the radiation. It leads to the so-called Zeeman scattering [5]. g is the Landé factor of the particle. The fourth term is the spin-orbit term. The Hamiltonian H_R of the excitation field is given by

$$H_R = \sum_{\mathbf{q}, \hat{\mathbf{e}}_q} \hbar\omega_q \left[a_{\mathbf{q}, \hat{\mathbf{e}}_q}^\dagger a_{\mathbf{q}, \hat{\mathbf{e}}_q} + \frac{1}{2} \right] \quad (\text{II.2})$$

Here, $\hat{\mathbf{e}}_q$ is the polarisation of the electromagnetic field of direction \mathbf{q} , $a_{\mathbf{q}, \hat{\mathbf{e}}_q}$ the photon annihilation operator and $a_{\mathbf{q}, \hat{\mathbf{e}}_q}^\dagger$ is the photon creation operator. We neglect all other terms that can enter the full Hamiltonian II.1.

The vector potential of the quantized electromagnetic field can be expressed as

$$\mathbf{A}(\mathbf{r}) = \sum_{\mathbf{q}, \hat{\mathbf{e}}_q} \sqrt{\frac{\hbar}{2\epsilon_0\omega_q\mathcal{V}}} \left[a_{\mathbf{q}, \hat{\mathbf{e}}_q} e^{i\mathbf{q}\cdot\mathbf{r}} \hat{\mathbf{e}}_q + a_{\mathbf{q}, \hat{\mathbf{e}}_q}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}} \hat{\mathbf{e}}_q^* \right] \quad (\text{II.3})$$

with \mathcal{V} the normalisation volume.

Within the Coulomb gauge ($\mathbf{p} \cdot \mathbf{A} = 0$), we can rewrite the Hamiltonian II.1 as

$$H = H_0 + V_I = H_E + H_R + V_I \quad (\text{II.4})$$

where we have defined the electron Hamiltonian as

$$H_E = \frac{\mathbf{p}^2}{2m} + V_S \quad (\text{II.5})$$

and, following Blume [5], we have reduced the photon-electron interaction potential to

$$V_I = \frac{e}{m} \mathbf{p} \cdot \mathbf{A} + \frac{e^2}{2m} \mathbf{A} \cdot \mathbf{A} + \frac{g}{2} \frac{e}{m} \mathbf{s} \cdot \mathbf{B} + \frac{e^2 \hbar}{2m^2 c^2} \mathbf{s} \cdot (\dot{\mathbf{A}} \times \mathbf{A}) \quad (\text{II.6})$$

where $\dot{\mathbf{A}}$ is the time-derivative of the potential vector.

We note that the potential that will give rise to multiple scattering is contained into Hamiltonian H_E .

We will treat first the effect of V_I within perturbation theory, and then the effect of V_S . We note the initial state and final state solutions of $H_0 = H_E + H_R$

$$\begin{cases} |\Phi_i\rangle = |\phi_i\rangle \otimes |\mathbf{q}_i, \hat{\mathbf{e}}_{\mathbf{q}_i}\rangle \\ |\Phi_f\rangle = |\phi_f\rangle \otimes |\mathbf{q}_f, \hat{\mathbf{e}}_{\mathbf{q}_f}\rangle \end{cases} \quad (\text{II.7})$$

The eigenvalues of H_0 are given by

$$\begin{cases} H_0 |\Phi_i\rangle = \mathcal{E}_i |\Phi_i\rangle \text{ with } \mathcal{E}_i = E_i + \hbar\omega_{\mathbf{q}_i} \\ H_0 |\Phi_f\rangle = \mathcal{E}_f |\Phi_f\rangle \text{ with } \mathcal{E}_f = E_f + \hbar\omega_{\mathbf{q}_f} \end{cases} \quad (\text{II.8})$$

and E and $\hbar\omega_{\mathbf{q}}$ are the eigenvalues associated respectively to $|\phi\rangle$ and $|\mathbf{q}, \hat{\mathbf{e}}_{\mathbf{q}}\rangle$.

We are interested here more specifically in the transition from $|\Phi_i\rangle$ to $|\Phi_f\rangle$ resulting from the action of the interaction term V_I , *i.e.* in the one photon-in one photon-out spectroscopy.

Using perturbation theory [7], we can write the transition probability per unit time from state $|\Phi_i\rangle$ to state $|\Phi_f\rangle$ under the effect of the perturbation V_I as

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle \Phi_f | T_I | \Phi_i \rangle|^2 \rho_f \quad (\text{II.9})$$

where ρ_f is the density of final states of the detected particle and T_I is the transition operator associated to the interaction potential V_I . T_I can be obtained from V_I through the relation

$$T_I = V_I + V_I G^+(\mathcal{E}_i) V_I \quad (\text{II.10})$$

where $G(\mathcal{E}_i)$ is the resolvent (also called propagator or Green operator) of the total Hamiltonian H at the energy of the initial state (or of the final state as the energy \mathcal{E} of the total system is conserved). This resolvent is defined by

$$G^\pm(\mathcal{E}_i) = \lim_{\epsilon \rightarrow 0^+} \frac{1}{\mathcal{E}_i - H \pm i\epsilon} \quad (\text{II.11})$$

At the lowest order in V_I , the transition operator can be approximated by the perturbation V_I . When inserted in (II.9), this gives Fermi's Golden Rule No. 2 [7]. To second order in V_I , it can be replaced by

$$T_I \approx V_I + V_I G_0^+(\mathcal{E}_i) V_I \quad (\text{II.12})$$

which gives Fermi's Golden Rule No. 1 [8]. $G_0(\mathcal{E}_i)$ is the unperturbed resolvent and is obtained from (II.11) by replacing H by H_0 . Note that H_0 contain not only the free electron and the free photon Hamiltonians $\mathbf{p}^2/2m$ and H_R , but also the sample potential V_S with which excited electrons can interact.

The cross-section is then obtained from (II.9) by dividing by the flux I_0 of incoming particles.

If we replace V_I by its expression II.6 into II.12 and truncate to the second order in e/m , we obtain

$$T_I^{(2)} = \left(\frac{e}{m}\right) \mathcal{O} + \left(\frac{e}{m}\right)^2 \left[\frac{m}{2} \mathbf{A} \cdot \mathbf{A} + \frac{\hbar}{2c^2} \mathbf{s} \cdot (\dot{\mathbf{A}} \times \mathbf{A}) + \mathcal{O} G_0^+(\mathcal{E}_i) \mathcal{O} \right] + \mathcal{O} \left(\frac{e^3}{m^3} \right) \quad (\text{II.13})$$

where we have introduced $\mathcal{O} = \mathbf{p} \cdot \mathbf{A} + g/2 \mathbf{s} \cdot \mathbf{B}$ in order to simplify the notation.

The first order term involves only one photon as \mathbf{A} occurs only once. It corresponds to the absorption/emission of a photon. This is the term that gives rise to X-ray Absorption Spectroscopy (XAS). We are not interested in this term. The second term involves two photons: it describes photon scattering processes and contains the ingredients that will lead to RXS. Therefore, in order to compute the transition probability II.9 for RXS at second order, the meaningful interaction transition operator is

$$T_I^{RXS} = \left(\frac{e}{m}\right)^2 \left[\frac{m}{2} \mathbf{A} \cdot \mathbf{A} + \frac{\hbar}{2c^2} \mathbf{s} \cdot (\dot{\mathbf{A}} \times \mathbf{A}) + (\mathbf{p} \cdot \mathbf{A} + \mathbf{s} \cdot \mathbf{B}) G_0^+(\mathcal{E}_i) (\mathbf{p} \cdot \mathbf{A} + \mathbf{s} \cdot \mathbf{B}) \right] \quad (\text{II.14})$$

where we have used the fact that $g \approx 2$. This expression contains both the non-magnetic and the magnetic terms for the X-ray Scattering (XS). The first term is the Thomson scattering term while the second term is the non-resonant magnetic scattering term. In the non resonant mode, the third term can be neglected as it is a second order process which involves the excitation of electron. We note that we have $\mathbf{B} = i\mathbf{q} \times \mathbf{A}$, where \mathbf{q} is the momentum of the photon.

If we consider the different physical processes that can involve one photon in, one photon out and possibly one interaction with an electron, we know that we have three possibilities which are sketched in figure 1.

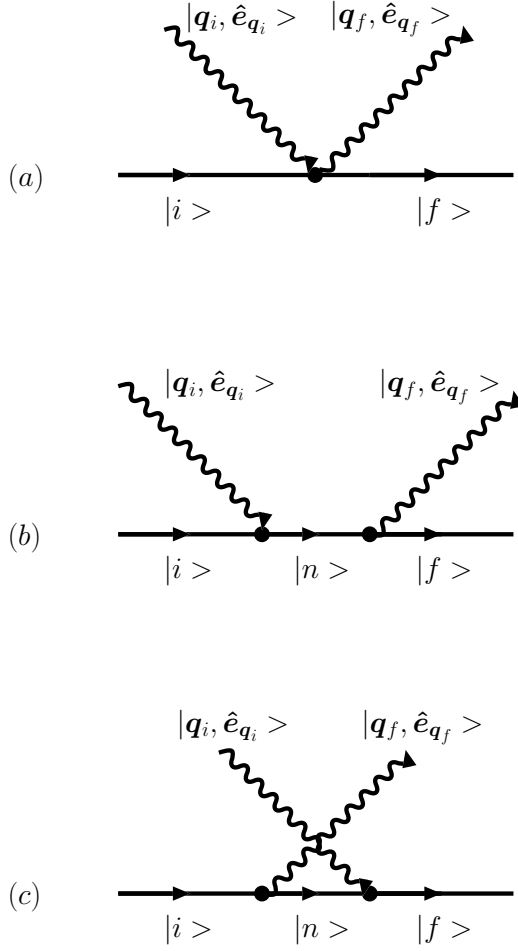


FIG. 1: Feynman diagrams corresponding to the scattering processes

For process (b), the intermediate states $|\Phi_n\rangle$ does not contain any photon while for (c), it contains two photons.

If we replace \mathbf{A} by its expression II.3 and make the creation and annihilation operator act on the photon states, we obtain

$$\left\{ \begin{aligned} \langle \Phi_f | T_{I(a)}^{RXS} | \Phi_i \rangle &= \frac{e^2}{2m} \frac{\hbar}{\epsilon_0 \mathcal{V}} \frac{1}{\sqrt{\omega_{\mathbf{q}_f} \omega_{\mathbf{q}_i}}} \left[(\hat{\mathbf{e}}_{\mathbf{q}_f}^* \cdot \hat{\mathbf{e}}_{\mathbf{q}_i}) \langle \phi_f | e^{-i\mathbf{Q}} | \phi_i \rangle + i \frac{\hbar \omega_{\mathbf{q}_f}}{mc^2} (\hat{\mathbf{e}}_{\mathbf{q}_f}^* \times \hat{\mathbf{e}}_{\mathbf{q}_i}) \cdot \langle \phi_f | \mathbf{s} e^{-i\mathbf{Q}} | \phi_i \rangle \right] \\ \langle \Phi_f | T_{I(b)}^{RXS} | \Phi_i \rangle &= \left(\frac{e}{m} \right)^2 \frac{\hbar}{2\epsilon_0 \mathcal{V}} \frac{1}{\sqrt{\omega_{\mathbf{q}_f} \omega_{\mathbf{q}_i}}} \langle \phi_f | \mathcal{K}_f^\dagger G_E^+(E_i + \hbar \omega_{\mathbf{q}_i}) \mathcal{K}_i | \phi_i \rangle \\ \langle \Phi_f | T_{I(c)}^{RXS} | \Phi_i \rangle &= \left(\frac{e}{m} \right)^2 \frac{\hbar}{2\epsilon_0 \mathcal{V}} \frac{1}{\sqrt{\omega_{\mathbf{q}_f} \omega_{\mathbf{q}_i}}} \langle \phi_f | \mathcal{K}_i G_E^+(E_i - \hbar \omega_{\mathbf{q}_f}) \mathcal{K}_f^\dagger | \phi_i \rangle \end{aligned} \right. \quad (\text{II.15})$$

where, in order to simplify the notation, we have introduced the effective photon-electron interaction operator \mathcal{K} acting only on electron states

$$\mathcal{K} = [\hat{\mathbf{e}}_{\mathbf{q}} \cdot \mathbf{p} + i \mathbf{s} \cdot (\mathbf{q} \times \hat{\mathbf{e}}_{\mathbf{q}})] e^{i\mathbf{q} \cdot \mathbf{r}} = \hat{\mathbf{e}}_{\mathbf{q}} \cdot [\mathbf{p} + i \mathbf{s} \times \mathbf{q}] e^{i\mathbf{q} \cdot \mathbf{r}} \quad (\text{II.16})$$

and the momentum transfer vector $\mathbf{Q} = \mathbf{q}_f - \mathbf{q}_i$.

G_E is the resolvent corresponding to the electron Hamiltonian H_E alone.

We can now add the three terms together, multiply by the density of photons in the final state (see equation (II.9)) given by [9], and divide by the incoming photon flux c/\mathcal{V} to obtain the corresponding cross-section

$$\left(\frac{d\sigma}{d\Omega_f}\right)_{RXS} = r_o^2 \frac{\omega_{\mathbf{q}_f}}{\omega_{\mathbf{q}_i}} \left| \hat{\mathbf{e}}_{\mathbf{q}_f}^* \cdot \hat{\mathbf{e}}_{\mathbf{q}_i} \langle \phi_f | e^{-i\mathbf{Q} \cdot \mathbf{r}} | \phi_i \rangle + i \frac{\hbar\omega_{\mathbf{q}_f}}{mc^2} (\hat{\mathbf{e}}_{\mathbf{q}_f}^* \times \hat{\mathbf{e}}_{\mathbf{q}_i}) \cdot \langle \phi_f | \mathbf{s} e^{-i\mathbf{Q}} | \phi_i \rangle + \right. \\ \left. \frac{1}{m} \left[\langle \phi_f | \mathcal{K}_f^\dagger G_E^+(E_i + \hbar\omega_{\mathbf{q}_i}) \mathcal{K}_i | \phi_i \rangle + \langle \phi_f | \mathcal{K}_i G_E^+(E_i - \hbar\omega_{\mathbf{q}_f}) \mathcal{K}_f^\dagger | \phi_i \rangle \right] \right|^2 \quad (\text{II.17})$$

Here $d\Omega_f$ is a solid angle about \mathbf{q}_f and $r_o = e^2/(4\pi\epsilon_0 mc^2)$ is the classical radius of the electron. This is the Kramers–Heisenberg cross-section for the scattering of light by electrons within condensed matter. It only involves electron states which are coupled to the radiation field through the $\exp[-i\mathbf{Q} \cdot \mathbf{r}]$ and \mathcal{K} operators.

This expression further simplifies for REXS. Indeed, in this case, only elastic processes are taken into account. This implies that must have $\hbar\omega_{\mathbf{q}_f} = \hbar\omega_{\mathbf{q}_i}$ and therefore $|\phi_f\rangle = |\phi_i\rangle$. \mathcal{K}_f only coincides with \mathcal{K}_i in the forward scattering direction. We have then

$$\left(\frac{d\sigma}{d\Omega_f}\right)_{REXS} = r_o^2 \left| \hat{\mathbf{e}}_{\mathbf{q}_f}^* \cdot \hat{\mathbf{e}}_{\mathbf{q}_i} \langle \phi_i | e^{-i\mathbf{Q} \cdot \mathbf{r}} | \phi_i \rangle + i \frac{\hbar\omega_{\mathbf{q}_i}}{mc^2} (\hat{\mathbf{e}}_{\mathbf{q}_f}^* \times \hat{\mathbf{e}}_{\mathbf{q}_i}) \cdot \langle \phi_f | \mathbf{s} e^{-i\mathbf{Q}} | \phi_i \rangle + \right. \\ \left. \frac{1}{m} \left[\langle \phi_i | \mathcal{K}_f^\dagger G_E^+(E_i + \hbar\omega_{\mathbf{q}_i}) \mathcal{K}_i | \phi_i \rangle \langle \phi_i | \mathcal{K}_i G_E^+(E_i - \hbar\omega_{\mathbf{q}_i}) \mathcal{K}_f^\dagger | \phi_i \rangle \right] \right|^2 \quad (\text{II.18})$$

III. STANDARD PRACTICAL FORMULATIONS

In the literature, the derivation of the REXS cross-section is usually not performed in terms of the propagators G_E . Instead, these propagators are replaced by their expression in terms of a set of eigenstates

$$G_E^\pm(E) = \lim_{\epsilon \rightarrow 0^+} \sum_n \frac{|\phi_n\rangle \langle \phi_n|}{E - E_n \pm i\epsilon} \quad (\text{III.19})$$

Doing this transformation into the cross-section II.18 leads to the more familiar expression

$$\left(\frac{d\sigma}{d\Omega_f}\right)_{REXS} = r_o^2 \left| \hat{\mathbf{e}}_{\mathbf{q}_f}^* \cdot \hat{\mathbf{e}}_{\mathbf{q}_i} \langle \phi_i | e^{-i\mathbf{Q} \cdot \mathbf{r}} | \phi_i \rangle + i \frac{\hbar\omega_{\mathbf{q}_i}}{mc^2} (\hat{\mathbf{e}}_{\mathbf{q}_f}^* \times \hat{\mathbf{e}}_{\mathbf{q}_i}) \cdot \langle \phi_f | \mathbf{s} e^{-i\mathbf{Q}} | \phi_i \rangle \right. \\ \left. + \frac{1}{m} \lim_{\epsilon \rightarrow 0^+} \sum_n \left[\frac{\langle \phi_i | \mathcal{K}_f^\dagger | \phi_n \rangle \langle \phi_n | \mathcal{K}_i | \phi_i \rangle}{E_i - E_n + \hbar\omega_{\mathbf{q}_i} + i\epsilon} + \frac{\langle \phi_i | \mathcal{K}_i | \phi_n \rangle \langle \phi_n | \mathcal{K}_f^\dagger | \phi_i \rangle}{E_i - E_n - \hbar\omega_{\mathbf{q}_i} + i\epsilon} \right] \right|^2 \quad (\text{III.20})$$

When the energy $\hbar\omega_{\mathbf{q}_i}$ of the incoming wavefield goes through the absorption edge ($E_n - E_i$) of a core state, the denominator of the second term will become very small making this term produce a strong enhancement in the cross section, and become much larger than the third term. This is the resonant mode. Therefore, to a good approximation, we can neglect the third term and write the REXS cross-section as

$$\left(\frac{d\sigma}{d\Omega_f}\right)_{REXS} \approx r_o^2 \left| \hat{\mathbf{e}}_{\mathbf{q}_f}^* \cdot \hat{\mathbf{e}}_{\mathbf{q}_i} \langle \phi_i | e^{-i\mathbf{Q} \cdot \mathbf{r}} | \phi_i \rangle + \frac{1}{m} \lim_{\epsilon \rightarrow 0^+} \sum_n \frac{\langle \phi_i | \mathcal{K}_f^\dagger | \phi_n \rangle \langle \phi_n | \mathcal{K}_i | \phi_i \rangle}{E_i - E_n + \hbar\omega_{\mathbf{q}_i} + i\epsilon} \right|^2 \quad (\text{III.21})$$

where we have further neglected the non-resonant magnetic term.

From this well-know equation, two different approaches can be found in the literature. One consists in replacing the infinitesimal imaginary part ϵ by a phenomenological broadening Γ_n accounting for the finite lifetime of the intermediate electron state $|\phi_n\rangle$. We obtain then an expression such as [10]

$$\left(\frac{d\sigma}{d\Omega_f}\right)_{REXS} \approx r_o^2 \left| \hat{\mathbf{e}}_{\mathbf{q}_f}^* \cdot \hat{\mathbf{e}}_{\mathbf{q}_i} \langle \phi_i | e^{-i\mathbf{Q} \cdot \mathbf{r}} | \phi_i \rangle + \frac{1}{m} \sum_n \frac{\langle \phi_i | \mathcal{K}_f^\dagger | \phi_n \rangle \langle \phi_n | \mathcal{K}_i | \phi_i \rangle}{E_i - E_n + \hbar\omega_{\mathbf{q}_i} + i\frac{\Gamma_n}{2}} \right|^2 \quad (\text{III.22})$$

where the sum, which is continuous in general [3], extends over all suitable intermediate states of the virtual electron.

The other approach makes use of the relation [11]

$$\lim_{\epsilon \rightarrow 0^+} \frac{1}{x - x_0 \pm i\epsilon} = \mathcal{P} \left(\frac{1}{x - x_0} \right) \mp i\pi\delta(x - x_0) \quad (\text{III.23})$$

where \mathcal{P} stands for Cauchy principal part which can be defined as

$$\mathcal{P} \left(\frac{1}{x - x_0} \right) = \frac{1}{2} \lim_{\epsilon \rightarrow 0^+} \left[\frac{1}{x - x_0 + i\epsilon} + \frac{1}{x - x_0 - i\epsilon} \right] \quad (\text{III.24})$$

This relation allows to rewrite the cross-section as [1]

$$\left(\frac{d\sigma}{d\Omega_f}\right)_{REXS} \approx r_o^2 \left| \hat{\mathbf{e}}_{\mathbf{q}_f}^* \cdot \hat{\mathbf{e}}_{\mathbf{q}_i} \langle \phi_i | e^{-i\mathbf{Q} \cdot \mathbf{r}} | \phi_i \rangle + f'(\hbar\omega_{\mathbf{q}_i}) + if''(\hbar\omega_{\mathbf{q}_i}) \right|^2 \quad (\text{III.25})$$

with the imaginary part given by

$$f''(\hbar\omega_{\mathbf{q}_i}) = -\frac{\pi}{m} \sum_n \langle \phi_i | \mathcal{K}_f^\dagger | \phi_n \rangle \langle \phi_n | \mathcal{K}_i | \phi_i \rangle \delta(E_i - E_n + \hbar\omega_{\mathbf{q}_i}) \quad (\text{III.26})$$

The advantage of this formulation becomes clear in the case of forward scattering, *i.e.* when $\mathbf{q}_f = \mathbf{q}_i$ and $\hat{\mathbf{e}}_{\mathbf{q}_f} = \hat{\mathbf{e}}_{\mathbf{q}_i}$. Indeed, we have then

$$f''_{FS}(\hbar\omega_{\mathbf{q}_i}) = -\frac{\pi}{m} \sum_n |\langle \phi_n | \mathcal{K}_i | \phi_i \rangle|^2 \delta(E_i - E_n + \hbar\omega_{\mathbf{q}_i}) \quad (\text{III.27})$$

where we recognise a quantity proportional to the XAS cross-section σ_{abs} [1], namely

$$f''_{FS}(\hbar\omega_{\mathbf{q}_i}) = -\frac{2m}{\hbar^2} \frac{\hbar\omega_{\mathbf{q}_i}}{8\pi\alpha} \sigma_{abs} \quad (\text{III.28})$$

where α is the fine structure constant.

Once the function $f''_{FS}(\hbar\omega_{\mathbf{q}_i})$ has been calculated, the function $f'(\hbar\omega_{\mathbf{q}_i})$ can be obtained using the Kramers-Kronig relation [12]

$$f'(E) = \frac{2}{\pi} \mathcal{P} \int_0^{+\infty} E' \frac{f''(E')}{E'^2 - E^2} dE' \quad (\text{III.29})$$

where $\mathcal{P} \int_0^{+\infty}$ stands for $\lim_{\epsilon \rightarrow 0^+} \left[\int_0^{\omega-\epsilon} + \int_{\omega+\epsilon}^{+\infty} \right]$.

Both approaches allow to compute the cross-section of REXS, but they involve an integration over the energy variable.

IV. ALTERNATIVE FORMULATION

We propose here an alternative approach which does not involve any energy integration in the calculation. Our starting point is our resolvent formulation (II.18) of the cross-section of REXS. Using the argument developed in the previous section, we can neglect the third term to obtain

$$\left(\frac{d\sigma}{d\Omega_f} \right)_{REXS} \approx r_o^2 \left| \hat{\mathbf{e}}_{\mathbf{q}_f}^* \cdot \hat{\mathbf{e}}_{\mathbf{q}_i} \langle \phi_i | e^{-i\mathbf{Q} \cdot \mathbf{r}} | \phi_i \rangle + \frac{1}{m} \langle \phi_i | \mathcal{K}_f^\dagger G_E^+(E_i + \hbar\omega_{\mathbf{q}_i}) \mathcal{K}_i | \phi_i \rangle \right|^2 \quad (\text{IV.30})$$

We recall that G_E is the propagator (we switch now from the mathematical vocabulary to the multiple scattering vocabulary) corresponding to the electron Hamiltonian $H_E = \mathbf{p}^2/2m + V_S$, where V_S is the potential representing the effect of the cluster of atoms with which the electron can interact.

We know from multiple scattering theory [13] that the propagator $G_E^+(z)$ can be written in terms of the scattering path operator τ at energy z

$$G_E^+(z) = \tilde{\tilde{\Omega}}_j^{(+)}(z) \bar{\tau}^{ji+}(z) \tilde{\tilde{\Omega}}_i^{(-)\dagger}(z) - \tilde{\tilde{\Omega}}_i^{(+)}(z) \delta_{ij} \quad (\text{IV.31})$$

where i and j is any couple of atoms in the cluster used to represent the sample. Here, $\bar{\tau}^{ji+}(z)$ is the scattering path operator describing the propagation of the electron of kinetic energy z from atom i to atom j . $\tilde{\tilde{\Omega}}_i^{(+)}(z)$ is a renormalised Møller wave operator [13] and the corresponding continuum inner state $\langle \mathbf{r} | \tilde{\tilde{\Omega}}_i^{(+)}(z) | L_i \rangle$ matches smoothly to $-\sqrt{\pi/2} t_{l_i}^{-1} i^{l_i} \left[j_{l_i}(kr) + i t_{l_i} h_{l_i}^{(1)}(kr) \right] Y_{L_i}(\hat{\mathbf{r}})$ at the surface of the potential sphere of atom i . k is the wave number.

The bar over the operator or the states indicates that they are centered at the origin of space, and not on the atom considered. So, for any operator A_i centered on site i , we have [13]

$$\bar{A}_i = \mathcal{T}(\mathbf{R}_i) A_i \mathcal{T}(-\mathbf{R}_i)$$

where $\mathcal{T}(\mathbf{R}_i)$ is the translation operator bringing the origin to site i . We have a similar relation for two-site-centered operators A_{ij} .

We consider now the resonant excitation to take place on an atom which we label 0 and choose as the origin of space. We note $|\phi_{L_c}^0\rangle$ the core state which is excited in the resonant process, with L_c standing for the angular momentum variable (l_c, m_c) . With the help of (IV.31), we can rewrite the cross-section, with the suitable sum over the absorbing atoms, as

$$\left(\frac{d\sigma}{d\Omega_f} \right)_{REXS} \approx r_o^2 \left| \sum_{0, m_c} e^{i\mathbf{Q} \cdot \mathbf{R}_0} \left(\hat{\mathbf{e}}_{\mathbf{q}_f}^* \cdot \hat{\mathbf{e}}_{\mathbf{q}_i} \langle \phi_{L_c}^0 | e^{-i\mathbf{Q} \cdot \mathbf{r}} | \phi_{L_c}^0 \rangle + \frac{1}{m} \left[\langle \phi_{L_c}^0 | \mathcal{K}_f^\dagger \tilde{\tilde{\Omega}}_0^{(+)} \tau^{00} \tilde{\tilde{\Omega}}_0^{(-)\dagger} \mathcal{K}_i | \phi_{L_c}^0 \rangle - \langle \phi_{L_c}^0 | \mathcal{K}_f^\dagger \tilde{\tilde{\Omega}}_0^{(+)} \mathcal{K}_i | \phi_{L_c}^0 \rangle \right] \right) \right|^2 \quad (\text{IV.32})$$

where we have added a sum over all possible atoms 0 (located at \mathbf{R}_0) in the cluster and on the unresolved azimuthal quantum number m_c . The scattering path operator and the renormalised Møller wave operators are evaluated at the energy $E_i + \hbar\omega_{q_i}$.

This is our central result. We note that with this type of approach, we could in principle treat also multiresonant phenomena with one electron being excited on atom i and reabsorbed on atom j while at the same time the electron being excited on atom j would be reabsorbed on atom i . This would prompt a τ^{ij} term instead of the τ^{00} term in (IV.36), and we would have now $|\phi_f\rangle \neq |\phi_i\rangle$ as atom i differs from atom j (they would correspond to the same core state, but belonging to two different atoms).

To go further and derive a formula that can be implemented in a computer code, we can

express the operator equation (IV.36) into a spherical wave representation. For this, we can choose the normalised spherical waves defined by [13]

$$\langle \mathbf{r} | L \rangle \equiv \langle \mathbf{r} | kL \rangle = k \sqrt{\frac{2}{\pi}} i^l j_l(kr) Y_L(\hat{\mathbf{r}}) \quad (\text{IV.33})$$

as the basis onto which to expand the various operators involved in equation (IV.36). With this basis, the matrix elements of the two main ingredients of multiple scattering theory, the transition operator and the propagator, write as [13]

$$\left\{ \begin{array}{l} \langle L_j | T^+ | L_i \rangle = T_{L_j L_i}^+ = -\frac{2k}{\pi} \sin \delta_{l_i} e^{i\delta_{l_i}} \delta_{L_i L_j} = -\frac{2k}{\pi} t_{l_i} \delta_{L_i L_j} \\ \langle L_j | \mathcal{T}(-\mathbf{R}_{ij}) G_0^+ | L_i \rangle = G_{L_j L_i}^{ji+} = -\frac{2i\pi^2}{k} \sum_L i^l h_l^{(1)}(kR_{ij}) Y_L(\hat{\mathbf{R}}_{ij}) G(L_j L | L_i) \end{array} \right. \quad (\text{IV.34})$$

where $G(L_j L | L_i)$ is the Gaunt coefficient given by

$$G(L_j L | L_i) = \int Y_{L_j}(\hat{\mathbf{r}}) Y_L(\hat{\mathbf{r}}) Y_{L_i}^*(\hat{\mathbf{r}}) d\hat{\mathbf{r}}$$

and $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ is the vector connecting i and j .

We recall that the scattering path operator τ entering the expression of (IV.36) can be written in matrix terms as

$$\tau = \mathbf{T} (\mathbf{I} - \mathbf{G}_0 \mathbf{T})^{-1}$$

where \mathbf{I} is the identity matrix and \mathbf{T} and \mathbf{G}_0 the matrices whose elements are given by (IV.34). We see that due to the choice of the normalised basis (IV.33), the scattering path operator defined here will differ by a factor $-2k/\pi$ from the one usually found in the literature and calculated in computer packages such as MsSpec [14] ($\mathbf{G}_0 \mathbf{T}$ is homogeneous upon the change of normalisation). Likewise, the renormalised Møller wave operator on atom 0 given by [13] $\tilde{\Omega}_0^{(+)} = (I + G_0 T_0) T_0^{-1}$ will differ by a factor $-\pi/2k$.

We are ready now to insert the closure relation $\sum_L |L\rangle \langle L| = I$ of the normalised spherical wave basis functions whenever necessary. Introducing the matrix elements

$$\left\{ \begin{array}{l} M_{LL_c}^{00n} = \langle L | \tilde{\Omega}_0^{(-)\dagger} \mathcal{K}_n | \phi_{L_c}^0 \rangle \\ \mathcal{M}_{LL_c}^{00n} = \langle L | \mathcal{K}_n | \phi_{L_c}^0 \rangle \end{array} \right. \quad (\text{IV.35})$$

we obtain finally for the cross-section of REXS in the spherical wave representation

$$\left(\frac{d\sigma}{d\Omega_f}\right)_{REXS} \approx r_o^2 \left| \sum_{0,m_c} e^{i\mathbf{Q}\cdot\mathbf{R}_0} \left(\hat{\mathbf{e}}_{\mathbf{q}_f}^* \cdot \hat{\mathbf{e}}_{\mathbf{q}_i} \langle \phi_{L_c}^0 | e^{-i\mathbf{Q}\cdot\mathbf{r}} | \phi_{L_c}^0 \rangle - \right. \right. \\ \left. \left. \frac{\pi}{2km} \sum_{L_0, L'_0} \left(M_{L_c L_0}^{00f} \right)^* \left[\tau_{L_0 L'_0}^{00} M_{L'_0 L_c}^{00i} - \mathcal{M}_{L_0 L_c}^{00i} \right] \right) \right|^2 \quad (\text{IV.36})$$

This expression does not involve any energy integration. But, by contrast to the XAS cross-section, the full matrix elements are necessary and not only their imaginary part. This means that despite the fact that $\tilde{\Omega}_0^{(\pm)} = V_0^{-1}$, the term $\mathcal{M}_{L_0 L_c}^{00i}$ will not vanish for real atomic potentials in REXS, as it does for XAS. A similar expression, without this term involving $\mathcal{M}_{L_0 L_c}^{00i}$ was already proposed in [4], where it was mistakenly assumed that it vanishes for real potentials.

V. CONCLUSION

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