

Derivation of single-scattering formulas for x-ray-absorption and high-energy electron-loss spectroscopies

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Derivations of formulas for the efficiency of single-electron excitation from deep core levels to the continuum are presented. Permitting the excited electron to backscatter at most once from the neighboring atoms yields tractable equations that are useful at any energy above threshold and which reduce to the conventional theory of extended fine structure far above threshold.

I. INTRODUCTION

In a recent report,¹ Müller and Schaich presented a simple single-particle theory of x-ray absorption which reproduced well the results of more sophisticated single-particle calculations. The purpose of this paper is to present a full derivation of the formula they used as well as some generalizations of it. Since similar information is contained in high-energy electron-loss experiments, the theory is also extended to treat such spectra. The formulas obtained provide a relatively simple scheme for calculating gross single-particle features at all energies above a core-level threshold.

The focus of the theory is on producing tractable expressions for the final states of such excitations. The scattering of the excited electron from the absorbing atom is treated exactly while the influence of neighboring atoms is approximated by retaining only single backscattering events. Thus the theory is similar in spirit to that used in extended x-ray-absorption fine structure^{2,3} (EXAFS) and in fact reduces to the conventional version of EXAFS for energies well above threshold. However, the theory may also be applied close to threshold and has a reasonable success there, too.^{1,4}

In Sec. II I develop the appropriate formulas for x-ray absorption, outlining their derivation and discussing their justification. Considerable simplification results if one may average over the direction of the incident x-ray's polarization or over the orientation of the absorbing atom's environment. Then in Sec. III I extend the theory to high-energy electron-loss spectroscopy, where similar formulas are obtained. Two appendixes contain discussions of more technical points.

To end this introduction I make two remarks that help place this work in context. First, the concern of this paper is with the efficient evaluation of single-electron-excitation strengths. I do not discuss how the effective single-particle potential is to be determined nor do I consider multiple-electron excitations. Second, formulas equivalent to mine have been used before in x-ray absorption at energies well above threshold (see references cited in Ref. 1) and the spirit of my approach has been applied to high-energy electron-loss spectra.⁵ However, to the best of my knowledge, the particularly simple form of my results has not been presented before.

II. X-RAY ABSORPTION

I begin with the standard single-particle theory of x-ray absorption which derives μ_c , the contribution to the x-ray absorption coefficient due to the excitation of a deep core level. One writes $\mu_c = n_c \sigma_c$, where n_c is the density of atoms with the core level of concern and σ_c is the absorption cross section for this level on a single atom. σ_c is found from the golden-rule transition rate per unit photon flux. Using the dipole approximation yields

$$\mu_c = A_1 \hbar \omega \sum_{i,f} |\langle i | \vec{r} \cdot \hat{E} | f \rangle|^2 \delta(\epsilon_i + \hbar \omega - \epsilon_f), \quad (1)$$

where the x-ray frequency (polarization) is ω (\hat{E}) and the initial (final) electron states have energy ϵ_i (ϵ_f). One sums over all degenerate states at the core level and over all final states above the Fermi level. The factor $A_1 = 4\pi^2 n_c (e^2 / \hbar c)$.

The task of determining the final-state sum with the energy-conserving δ function is aided by the introduction of the Green's function

$$\langle \vec{r} \nu | G^+(\epsilon) | \vec{r}' \nu' \rangle = \langle \vec{r} \nu | (\epsilon - h + i0^+)^{-1} | \vec{r}' \nu' \rangle \quad (2a)$$

$$= \sum_f \frac{\langle \vec{r} \nu | f \rangle \langle f | \vec{r}' \nu' \rangle}{\epsilon - \epsilon_f + i0^+}, \quad (2b)$$

where $\vec{r}(\nu)$ describe an electron's position (spin orientation) and h is the effective single-particle Hamiltonian of the final states. I assume that h may be satisfactorily represented by a sum of nonoverlapping muffin-tin potentials, each of which is spherically symmetric. This approximation has the considerable advantage that it allows an exact solution for G^+ . Since this has been shown several times before both in EXAFS theories⁶⁻⁸ and more generally,⁹ I simply write down the answer in my notation:

$$\mu_c = A_2 \hbar \omega N_0 \text{Im} \left[\sum_{\substack{i \\ L, L' \\ \sigma, \sigma'}} \langle i | \vec{r} \cdot \hat{E} | R_L Y_L Z_\sigma \rangle \times \chi_{L\sigma, L'\sigma'} \langle R_{L'} Y_{L'} Z_{\sigma'} | \vec{r}' \cdot \hat{E} | i \rangle \right]. \quad (3)$$

Here $A_2 = 2\pi A_1$, Im denotes "imaginary part," and $N_0 = mk/\pi^2 \hbar^2$ is the free-electron density of states, with k determined by the final-state kinetic energy $\epsilon = \hbar^2 k^2 / 2m$. The interesting structure in μ_c comes from the matrix elements. Within the muffin tin of the absorbing atom the final-state wave function is written as a linear combination of products of radial, angular, and spin- $\frac{1}{2}$ eigenfunctions, $R_l Y_L Z_\sigma$, which are indexed by (and to be summed over) the quantum numbers l for orbital angular momentum, L for (l, m) where m is the projection of the orbital angular momentum on a particular axis, and σ for the projection of the spin angular momentum on the same axis. The R_l are regular solutions of the radial Schrödinger equation at energy ϵ in the central

muffin tin. They are normalized so that beyond this potential

$$\langle r | R_l \rangle \rightarrow j_l(kr) \cos \delta_l' + n_l(kr) \sin \delta_l', \quad (4)$$

where the j_l and n_l are spherical Bessel functions¹⁰ and δ_l' is the l -wave phase shift of the absorbing atom—distinguished from that of its neighbors by a prime. The matrix $\chi_{L\sigma, L'\sigma'} = \delta_{\sigma, \sigma'} \chi_{L, L'}$ is diagonal in spin indices by my assumption of no spin-dependent scattering in the final state. Although one can write an exact equation for $\chi_{L, L'}$,⁶ I show only the result that includes all scattering from the absorbing (central) atom plus one backscattering from each neighbor,

$$\chi_{L, L'} = i \delta_{L, L'} + \sum_L \sum_{\vec{R} (\neq \vec{0})} [e^{i\delta_l'} (i)^l C_{L \vec{0}, \vec{L} \vec{R}} t_l^+(\vec{R}) C_{\vec{L} \vec{R}, L' \vec{0}} (-i)^{l'} e^{i\delta_{l'}'}] + \dots, \quad (5)$$

where $i = \sqrt{-1}$. The (isolated) absorbing atom contribution comes from the Kronecker $\delta_{L, L'}$ while the effect of the neighbors located at various \vec{R} is described by the dimensionless t matrices

$$t_l^+(\vec{R}) = e^{i\delta_l'} \sin \delta_l', \quad (6)$$

where the phase shifts may depend on \vec{R} , and by the dimensionless propagators

$$C_{\vec{L} \vec{R}, L' \vec{R}'} = 4\pi \sum_{L''} (i)^{l''} h_{l''}^+(kr) Y_{L''}^*(\hat{r}) \langle Y_L | Y_{L''} Y_{L'} \rangle, \quad (7)$$

where $\vec{r} = \vec{R} - \vec{R}'$, $h_{l''}^+$ is an outgoing spherical Bessel function,¹⁰ and the matrix element is an angular integral of three spherical harmonics.

The muffin-tin approximation to the effective single-particle potential that I used above is reasonable in close-packed systems, but is less so in open systems. One way to remove some of its deficiencies is to include a surrounding sphere that encloses all of the scattering atoms in the cluster or molecule.¹¹ Then Eq. (5) must be augmented by a term $\chi_{L, L'}$ to represent the single backscattering of an outgoing wave from the absorbing atom by the surrounding sphere. Formulas for this extra contribution are derived in Appendix B, but are not discussed further in the text.

The higher-order terms omitted in (5) contain further powers of tC , representing multiple-scattering paths. Numerical work^{1,4} has shown that the truncated, single-scattering expression of (5) reproduces well in close-packed systems the results for μ_c from the complete $\chi_{L, L'}$, when both are sufficiently (and identically) broadened in energy. I briefly consider here some *a priori* arguments for this success. The multiple-scattering terms omitted from (5) are negligible if tC is small compared to unity. Far above threshold the scattering is weak so one can justify the neglect of such terms. Indeed, with some further approximations noted below, the standard EXAFS formulas follow from (5). Near threshold, however, the scattering is quite strong so this argument fails. Yet there is

another way in which the net effect of high powers of tC may be neglected. This arises from the need to energy average the single-particle calculation in order to approximately account for various decay processes. In essence one replaces in (2)

$$(\epsilon - h + i0^+)^{-1} \rightarrow \int \frac{d\bar{\epsilon}}{2\pi} \frac{\Gamma}{(\epsilon - \bar{\epsilon})^2 + \Gamma^2/4} \frac{1}{\bar{\epsilon} - h + i0^+} \\ = (\epsilon - h + i\Gamma/2)^{-1}, \quad (8)$$

where Γ may be energy dependent but is typically several electron volts. The consequence for the free-space Green's function is that the dependence

$$e^{ikR}/R \rightarrow \frac{1}{R} \exp[i(\epsilon + i\Gamma/2)^{1/2} R (2m/\hbar^2)^{1/2}] \quad (9)$$

so that in effect the electron amplitude is continuously damped as it propagates from one scattering center to another. This leads to the suggestion that the energy average of higher powers of tC may be small due to the accumulated decay of the C 's over a long multiple-scattering path. The above qualitative argument also implies that even single scattering from distant shells may be suppressed by energy averaging. Thus as Γ in (8) is increased, the average of the exact μ_c should become a smoother function of energy whose remnant structure is due to atomic variations (e.g., white lines) and to single backscatterings from the nearest neighbors. This trend is apparent in the calculations.⁴ Note that a similar idea has been explored in low-energy electron-diffraction theory, but with less justification.^{12,13}

To complete this section I show some simplifications of my formulas that are possible when sufficient symmetry exists. I also exhibit their relation to the standard EXAFS formulas. Begin by assuming that the absorbing atom is in a cubic environment or that one has a polycrystalline sample. For these cases μ_c is independent of x-ray polarization and an average of (3) over the direction of \hat{E} yields

$$\mu_c = A_3 \hbar \omega N_0 \text{Im} \left[\sum_{\substack{i, \bar{m} \\ L, L', \sigma}} \langle i | r Y_{1\bar{m}}^* | R_l Y_L Z_\sigma \rangle \right. \\ \left. \times \chi_{L, L'} \langle R_{l'} Y_{L'} Z_{\sigma'} | r' Y_{1\bar{m}} | i \rangle \right], \quad (10)$$

where $A_3 = 8\pi^2 A_1/9$. If I further assume that the initial-state wave functions can be written as

$$|i\rangle = |R_{l_0} Y_{L_0} Z_{\sigma_0}\rangle \equiv |R_{l_0} L_0 \sigma_0\rangle, \quad (11)$$

with the $R_{l_0}(r)$ real valued, then the matrix elements in (10) may be separated into

$$\mu_c^{l_0} = 2A_3 \hbar \omega N_0 \text{Im} \left[\sum_{L, L'} M_{l_0, l} B_{L, L'}(l_0, 1) \chi_{L, L'} M_{l_0, l'} \right], \quad (12)$$

where the factor of 2 comes from the sum on σ_0 and the $M_{l_0, l}$ are radial matrix elements:

$$M_{l_0, l} = \int dr r^2 R_{l_0}(r) r R_l(r) \quad (13)$$

with the integration limited to the central muffin tin by the presumed short range of the initial state R_{l_0} . The matrix B is defined by

$$B_{L, L'}(l_1, l_2) = \sum_{m_1, m_2} \langle Y_{L'} | Y_{L_1} Y_{L_2} \rangle \langle Y_{L_2} Y_{L_1} | Y_L \rangle \quad (14)$$

and is in fact diagonal in L, L' . This and some other properties are derived in Appendix A. Using these I obtain

$$\mu_c^{l_0} = A \hbar \omega N_0 [l_0 M_{l_0, l_0-1}^2 \chi_{l_0-1} + (l_0+1) M_{l_0, l_0+1}^2 \chi_{l_0+1}], \quad (15)$$

where $A = (16\pi^3/3)n_c(e^2/\hbar c)$ and

$$\chi_l = \frac{1}{2l+1} \text{Im} \sum_m \chi_{L, L} \quad (16)$$

Equation (15) has a simple generalization when spin-orbit scattering is important for the initial core level, but negligible for the final states. One replaces (11) with

$$|i\rangle = |R_{J_0} J_0 M_0\rangle, \quad (17)$$

where $R_{J_0}(r)$ is again real valued and $|J_0 M_0\rangle$ is an eigenstate of the total angular momentum. Using standard equations¹⁰ for the addition of orbital and spin angular momenta, I find in place of (15)

$$\mu_c^{J_0} = A \hbar \omega N_0 \frac{J_0 + \frac{1}{2}}{2l_0 + 1} [l_0 M_{J_0, l_0-1}^2 \chi_{l_0-1} \\ + (l_0+1) M_{J_0, l_0+1}^2 \chi_{l_0+1}], \quad (18)$$

where for each core level, except those with $l_0=0$, there are two values of J_0 : $l_0 \pm \frac{1}{2}$. The details of this derivation are also in Appendix A. Equation (18) allows one to give the proper weight to the absorption structure of core levels split by the spin-orbit interaction.

The structure in μ_c due to the neighboring atoms rests in the χ_l since replacing $\chi_l \rightarrow 1$ gives only the contribution of an isolated (muffin-tin) atom. Using the single-scattering approximation for $\chi_{L, L'}$, Eq. (5), I obtain with the help of (7) and simple properties of spherical harmonics¹⁰

$$\chi_l - 1 = \frac{(4\pi)^2}{2l+1} \text{Im} \left[\sum_{\substack{\vec{R} (\neq \vec{0}) \\ L', L''}} e^{2i\delta_l'} \left[(i)^{l'} h_{l'}^{l'}(kR) Y_{L'}^*(-\hat{R}) \left[\sum_{\vec{T}} t_{\vec{T}}^{l'}(\vec{R}) B_{L', L''}(l, \vec{T}) \right] (i)^{l''} h_{l''}^{l''}(kR) Y_{L''}(\hat{R}) \right] \right]. \quad (19)$$

Then with (6) and the results of Appendix A for the diagonal matrix B I find

$$\chi_l = 1 + \text{Im} \left[\sum_{\vec{R} (\neq \vec{0})} e^{2i\delta_l'} \sum_{\vec{T}} (2\vec{T}+1) e^{i\delta_{\vec{T}}} \sin \delta_{\vec{T}} H(l, \vec{T}; kR) \right], \quad (20)$$

where

$$H(l, \vec{T}; \rho) = \sum_{l'} (2l'+1) \left[\begin{matrix} l & \vec{T} & l' \\ 0 & 0 & 0 \end{matrix} \right] h_{l'}^{l'}(\rho) \quad (21)$$

with the first factor in the square brackets being a 3j symbol.¹⁰ Explicit formulas for these are given in Appendix A. If the neighboring atoms can be arranged in shells of N_j identical atoms all at distance R_j , then (20) may be rewritten as a sum over shells:

$$\chi_l = 1 + \sum_j N_j \text{Im} \left[e^{2i\delta_l'} \sum_{\vec{T}} (2\vec{T}+1) e^{i\delta_{\vec{T}}} \sin \delta_{\vec{T}} H(l, \vec{T}; kR_j) \right], \quad (22)$$

which further simplifies its calculation.

Indeed Eq. (22) is close to the standard EXAFS result, which approximates χ_l by

$$\chi_l = 1 + (-1)^l \sum_j N_j \text{Im} \left[e^{2i\delta_l'} \frac{e^{2ikR_j}}{kR_j^2} f_j(\pi) \right], \quad (23)$$

where $f_j(\pi)$ is the backscattering amplitude of a plane wave off a single atom in the j th shell:

$$f(\pi) = \frac{1}{k} \sum_{\bar{l}} (2\bar{l}+1) (-1)^{\bar{l}} e^{i\delta_{\bar{l}}} \sin \delta_{\bar{l}}. \quad (24)$$

To pass from (22) to (23) requires only the additional approximation of replacing

$$(i)^l h_l^+(\rho) \sim e^{i\rho}/\rho, \quad (25)$$

which is its asymptotic dependence for $\rho \gg l$. Thus the only difference between the exact single-scattering theory and the conventional EXAFS theory rests in the former's proper treatment of the scattered wavelets. I remark that Lee and Pendry⁸ have suggested an approximate formula for the analog of χ_l whose validity depends on a "small atom" limit. Since the exact single-scattering theory for a muffin-tin model, Eqs. (5), (20), or (22), has no reference to atom size except for the implicit constraint that muffin-tin potentials do not overlap, I feel that their intermediate formula is *ad hoc*. Their exact and EXAFS results are, however, equivalent to mine. The point I emphasize is that invoking (25) alone takes one from (22) to (23).

III. HIGH-ENERGY ELECTRON LOSS

Excitation of core-level electrons into the continuum can be accomplished by both photons and electrons. If the latter are at sufficiently high energy, their impact scattering may be satisfactorily treated in first Born approximation which yields the following differential cross section for the probe electron to lose energy E and momentum $\hbar\vec{K}$ via a Coulomb interaction with a single atom:

$$\frac{d^2\sigma_c}{d\Omega dE} = 4 \frac{v_s/v_0}{(Ka_0)^2} \times \sum_{i,f} \left| \left\langle i \left| \frac{e^{-i\vec{K}\cdot\vec{r}}}{K} \right| f \right\rangle \right|^2 \delta(\epsilon_i + E - \epsilon_f), \quad (26)$$

where v_0 (v_s) is the probe electron's initial (final) speed, a_0 is the Bohr radius, and $d\Omega$ describes the range of solid angle into which the probe electron is scattered. The other notation in (26) is the same as in (1). Comparing these two formulas reveals that the only difference, aside from slowly varying prefactors, is the absence in (26) of a dipole selection rule. Even this distinction is essentially removed if one considers near-forward scattering where K approaches (but never reaches) zero. Hence it is clear that the theory developed for x-ray absorption will have a straightforward analog for high-energy electron-loss spectra. I briefly summarize these equations here.

If I define $\mathcal{A}_1 = 4(v_s/v_0)/(Ka_0)^2$, the analog of (3) is

$$\frac{d^2\sigma_c}{d\Omega dE} = \mathcal{A}_2 N_0 \text{Im} \left[\sum_{\substack{i \\ L,L', \\ \sigma,\sigma'}} \left\langle i \left| \frac{e^{-i\vec{K}\cdot\vec{r}}}{K} \right| R_l Y_L Z_{\sigma} \right\rangle \chi_{L\sigma,L'\sigma'} \times \left\langle R_{l'} Y_{L'} Z_{\sigma'} \left| \frac{e^{i\vec{K}\cdot\vec{r}}}{K} \right| i \right\rangle \right], \quad (27)$$

where $\mathcal{A}_2 = 2\pi\mathcal{A}_1$. If again one ignores spin-dependent scattering in the final state and retains only a single backscattering contribution from the neighbors, Eq. (5) for the matrix χ will result, subject to the same justifying remarks given before.

The formulas can be simplified when sufficient symmetry is present to justify an average over the direction of \vec{K} . Then I find as the analog of (12) for excitation of the l_0 core level

$$\frac{d^2\sigma_c^{l_0}}{d\Omega dE} = \mathcal{A}_3 N_0 \text{Im} \left[\sum_{L,L'} M_{l_0,l}(\bar{l}) B_{L,L'}(l_0,\bar{l}) \chi_{L,L'} M_{l_0,l}(\bar{l}) \right], \quad (28)$$

where B is defined in (14), $\mathcal{A}_3 = (4\pi)^2 \mathcal{A}_1$, and

$$M_{l_0,l}(\bar{l}) = \int dr r^2 R_{l_0}(r) [j_{\bar{l}}(Kr)/K] R_l(r), \quad (29)$$

which reduces to $\delta_{\bar{l},l} M_{l_0,l}/3$ when $K \rightarrow 0$ if R_{l_0} and R_l are orthogonal. Using the results of Appendix A for the matrix B , (28) may be rewritten as

$$\frac{d^2\sigma_c^{l_0}}{d\Omega dE} = \mathcal{A} (2l_0+1) N_0 \sum_{\bar{l}} (2\bar{l}+1) \chi_{\bar{l}} \mathcal{M}_{l_0,\bar{l}}^2 \quad (30)$$

with $\mathcal{A} = 16\pi(v_s/v_0)/(Ka_0)^2$ and

$$\mathcal{M}_{l_0,\bar{l}}^2 = \sum_{l'} (2l'+1) \begin{pmatrix} l_0 & \bar{l} & l' \\ 0 & 0 & 0 \end{pmatrix}^2 M_{l_0,\bar{l}}^2(l'). \quad (31)$$

Together (30) and (31) are the analog of (15). Note that in the formal limit

$$K \rightarrow 0, \mathcal{M}_{l_0,\bar{l}}^2 \rightarrow \frac{1}{3} \begin{pmatrix} l_0 & \bar{l} & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 M_{l_0,\bar{l}}^2,$$

which yields in turn

$$\frac{d^2\sigma_c^{l_0}}{d\Omega dE} \rightarrow \frac{\mathcal{A}}{3} N_0 [l_0 M_{l_0,l_0-1}^2 \chi_{l_0-1} + (l_0+1) M_{l_0,l_0+1}^2 \chi_{l_0+1}], \quad (32)$$

a result identical in content to (15).

One may also derive an analog of (18) when spin-orbit coupling is important in the core level:

$$\frac{d^2\sigma_c^{J_0}}{d\Omega dE} = \mathcal{A} (J_0 + \frac{1}{2}) N_0 \sum_{\bar{l}} (2\bar{l}+1) \chi_{\bar{l}} \mathcal{M}_{J_0,\bar{l}}^2. \quad (33)$$

The proof is outlined in Appendix A.

I have presented the formulas of this section very concisely since they have such close analogs in Sec. II. No detailed calculations have yet been done with them, although less sophisticated equations with the same basic physics have been treated.⁵ I hope that the success of the x-ray formulas^{1,4} will encourage people to test the electron-loss equations given here.

Note added in proof. After this paper had been submitted the work by S. J. Gurman, N. Binstead, and I. Ross [J. Phys. C **17**, 143 (1984)] appeared. They also derive the single-scattering formulas for x-ray absorption that are obtained here. In addition they present numerical results indicating further the utility of these equations.

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APPENDIX A

Here I present some of the details omitted from the derivations in the text. Most of the manipulations involve standard but cumbersome formulas for spherical harmonics and their integrals.¹⁰

Begin with the matrix B that is defined in Eq. (14). The necessary integrals may be written in terms of $3j$ symbols,¹⁰ e.g.,

$$\langle Y_{L'} | Y_{L_1} Y_{L_2} \rangle = \left[\frac{(2l'+1)(2l_1+1)(2l_2+1)}{4\pi} \right]^{1/2} \times \begin{Bmatrix} l' & l_1 & l_2 \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} l' & l_1 & l_2 \\ -m' & m_1 & m_2 \end{Bmatrix} (-1)^{m'}, \quad (\text{A1})$$

$$H(0, \bar{l}) = (h_{\bar{l}}^+)^2, \quad (\text{A6})$$

$$H(1, \bar{l}) = \frac{\bar{l}+1}{2\bar{l}+1} (h_{\bar{l}+1}^+)^2 + \frac{\bar{l}}{2\bar{l}+1} (h_{\bar{l}-1}^+)^2, \quad (\text{A7})$$

$$H(2, \bar{l}) = \frac{3}{2} \frac{(\bar{l}+2)(\bar{l}+1)}{(2\bar{l}+3)(2\bar{l}+1)} (h_{\bar{l}+2}^+)^2 + \frac{\bar{l}(\bar{l}+1)}{(2\bar{l}+3)(2\bar{l}-1)} (h_{\bar{l}}^+)^2 + \frac{3}{2} \frac{\bar{l}(\bar{l}-1)}{(2\bar{l}+1)(2\bar{l}-1)} (h_{\bar{l}-2}^+)^2, \quad (\text{A8})$$

$$H(3, \bar{l}) = \frac{5}{2} \frac{(\bar{l}+3)(\bar{l}+2)(\bar{l}+1)}{(2\bar{l}+5)(2\bar{l}+3)} (h_{\bar{l}+3}^+)^2 + \frac{3}{2} \frac{(\bar{l}+2)(\bar{l}+1)\bar{l}}{(2\bar{l}+5)(2\bar{l}-1)} (h_{\bar{l}+1}^+)^2 + \frac{3}{2} \frac{(\bar{l}+1)\bar{l}(\bar{l}-1)}{(2\bar{l}+3)(2\bar{l}-3)} (h_{\bar{l}-1}^+)^2 + \frac{5}{2} \frac{\bar{l}(\bar{l}-1)(\bar{l}-2)}{(2\bar{l}-1)(2\bar{l}-3)} (h_{\bar{l}-3}^+)^2, \quad (\text{A9})$$

where for simplicity I have suppressed the argument ρ , both in H and in all the $h_{\bar{l}}^{\pm}$. Note that replacing $(i)^{\bar{l}} h_{\bar{l}}(\rho) \rightarrow e^{i\rho/\rho}$ yields $H(l, \bar{l}; \rho) \rightarrow (-1)^{l+\bar{l}} e^{2i\rho/\rho^2}$ from each of (A6)–(A9). This should always occur due to the sum rule¹¹

$$\sum_{l'} (-1)^{l'} (2l+1) \begin{Bmatrix} l & \bar{l} & l' \\ 0 & 0 & 0 \end{Bmatrix}^2 = (-1)^{l+\bar{l}}, \quad (\text{A10})$$

which ensures that (22) goes to (23) far above threshold. Note that the same expansion coefficients of H in terms of $(h^+)^2$'s, Eq. (20), also apply to the expansion of both \mathcal{M}^2 in terms of (M^2) 's, Eq. (31), and T^s in terms of (t^s) 's, Eq. (B8).

Lastly I turn to the derivation of (18). Using (17) in (10) yields, instead of (12),

$$\mu_c^J = A_3 \hbar \omega N_0 \text{Im} \left[\sum_{L, L'} M_{J_0, L} A_{L, L'}(J_0; l_0, \frac{1}{2}) \chi_{L, L'} M_{J_0, L'} \right], \quad (\text{A11})$$

where

$$A_{L, L'}(J_0; l_0, \frac{1}{2}) = \sum_{M_0, \bar{m}, \sigma} \langle J_0 M_0 | Y_{1\bar{m}}^* | Y_L Z_{\sigma} \rangle \langle Y_{L'} Z_{\sigma} | Y_{1\bar{m}} | J_0 M_0 \rangle. \quad (\text{A12})$$

Introduce complete sets of states and factor the matrix elements

where I have used $Y_{l, m}^* = (-1)^m Y_{l, -m}$. Then one needs the sum rule¹⁰

$$\sum_{m_1, m_2} \begin{Bmatrix} l' & l_1 & l_2 \\ -m' & m_1 & m_2 \end{Bmatrix} \begin{Bmatrix} l & l_1 & l_2 \\ -m & m_1 & m_2 \end{Bmatrix} = \frac{1}{2l+1} \delta_{L, L'}, \quad (\text{A2})$$

which yields

$$B_{L, L'}(l_1, l_2) = \frac{(2l_1+1)(2l_2+1)}{4\pi} \delta_{L, L'} \begin{Bmatrix} l & l_1 & l_2 \\ 0 & 0 & 0 \end{Bmatrix}^2. \quad (\text{A3})$$

To make this more explicit one can apply the formula¹⁰

$$\begin{Bmatrix} l & l_1 & l_2 \\ 0 & 0 & 0 \end{Bmatrix}^2 = \frac{(l_1+l_2-l)!(l_1+l-l_2)!(l_2+l-l_1)!}{(l+l_1+l_2+1)!} \times \left[\frac{p!}{(p-l)!(p-l_1)!(p-l_2)!} \right]^2, \quad (\text{A4})$$

where $2p = l + l_1 + l_2$. Using (A4) I find, for instance,

$$B_{L, L'}(l_0, 1) = \frac{3}{4\pi} \delta_{L, L'} \left[\delta_{l, l_0-1} \left[\frac{l_0}{2l+1} \right] \times \delta_{l, l_0+1} \left[\frac{l_0+1}{2l+1} \right] \right], \quad (\text{A5})$$

which was used in (15). Similarly one may tediously generate the $H(l, \bar{l}, \rho)$'s of Eq. (21):

$$A_{L,L'}(J_0; l_0, \frac{1}{2}) = \sum_{\substack{M_0, \bar{m}, \sigma \\ L_1, L_2}} \langle Y_{L'} | Y_{1\bar{m}} Y_{L_1} \rangle \langle Y_{L_1} Z_{\sigma} | J_0 M_0 \rangle \langle J_0 M_0 | Y_{L_2} Z_{\sigma} \rangle \langle Y_{L_2} Y_{1\bar{m}} | Y_L \rangle. \quad (\text{A13})$$

Since the $|J_0 M_0\rangle$ are sums of direct products of $|Y_{L_0}\rangle$ times $|Z_{\sigma_0}\rangle$, I deduce from the parentheses on the right-hand side in (A13) that $l_1=l_2=l_0$ and $m_1=m_2$. From the form of the Clebsch-Gordan coefficients for adding angular momenta l_0 and $\frac{1}{2}$ to get J_0 , one has for allowed values

$$|\langle Y_{l_0 m} Z_{\sigma_0} | J_0 M_0 \rangle|^2 = \frac{J_0 + \frac{1}{2} + m \operatorname{sgn}[\sigma_0(J_0 - l_0)]}{2l_0 + 1}, \quad (\text{A14})$$

where sgn denotes "sign of." Now most of the sums in (A13) can be done to obtain

$$\begin{aligned} A_{L,L'}(J_0; l_0, \frac{1}{2}) &= 2 \frac{J_0 + \frac{1}{2}}{2l_0 + 1} \sum_{m_0, \bar{m}} \langle Y_{L'} | Y_{1\bar{m}} Y_{l_0 m_0} \rangle \langle Y_{l_0 m_0} Y_{1\bar{m}} | Y_L \rangle \\ &= 2 \frac{J_0 + \frac{1}{2}}{2l_0 + 1} B_{L,L'}(l_0, 1). \end{aligned}$$

Substituting (A15) into (A11) and using (A5) yields (18). An entirely similar approach leads to (33).

APPENDIX B

Here I present equations for the extra contributions to the formulas of the text when one allows a sphere of potential to surround all the (muffin-tin) atoms in the cluster or molecule. This additional source of scattering is especially relevant for molecules^{11,14} or other cases where the screening of the core hole on the absorbing atom is not efficient. Formal procedures for including such contributions have been published before;^{9,11,14-16} I followed the methods of Beeby.¹⁷

It is convenient to make a slight change in notation, putting the coordinate origin at the center of the surrounding sphere, whose radius is R_0 , and calling the location of the absorbing atom \vec{R} . Assuming the muffin-tin potential of this atom does not overlap that of the surrounding sphere, one finds an extra contribution to (5) of

$$\chi_{L,L'}^s = \sum_L [e^{i\delta_l^s} (i)^l C_{L\vec{R}}^s t_{LS,L'\vec{R}}^s (-i)^l e^{i\delta_{l'}^s}], \quad (\text{B1})$$

where s denotes surrounding sphere. The propagators are given by

$$C_{L\vec{R},L'S}^s = 4\pi \sum_{L''} (i)^{l''} j_{l''}(kR) Y_{L''}^*(\hat{R}) \langle Y_L | Y_{L''} Y_{L'} \rangle, \quad (\text{B2})$$

where the only changes for $C_{LS,L'\vec{R}}^s$ is that $\hat{R} \rightarrow -\hat{R}$ in (B2). Note that R_0 does not appear explicitly in (B2). Its effect instead lies in t_l^s which is determined by

$$\begin{aligned} t_l^s &\equiv t_l^s(k, k) \\ &= -\frac{2mk}{\hbar^2} \int_{R_0}^{\infty} dx x^2 h_l^+(kx) \int_{R_0}^{\infty} dy y^2 h_l^+(ky) t_l^s(x, y), \end{aligned} \quad (\text{B3})$$

where I have used an angular momentum decomposition of the t matrix of the surrounding sphere:

$$\langle \vec{x} | t^s | \vec{y} \rangle = \sum_L Y_L(\hat{x}) t_l^s(x, y) Y_L^*(\hat{y}). \quad (\text{B4})$$

I stress that the dimensionless t_l^s is not given by an equation like (6) since the conventional phase shifts are determined by scattering from outside a spherically symmetric potential. For the present case of a surrounding sphere the t_l^s arise as parameters in solutions of the form

$$\langle \vec{r} | \psi^+ \rangle = \begin{cases} Y_L(\hat{r}) [h_l^+(kr) + t_l^s j_l(kr)], & r < R_0 \\ Y_L(\hat{r}) a_l h_l^+(kr), & r > \bar{R} \end{cases} \quad (\text{B5})$$

where $\bar{R} > R_0$ is the radius beyond which the surrounding sphere potential stops varying. (A minor generalization is necessary for a Coulomb potential.¹⁴) Hence the t_l^s may be computed by starting with a wave of the form (B5) for $r > \bar{R}$ [call its radial part $R_l(r)$], integrating Schrödinger's equation inward to $r=R_0$, and then matching. This yields

$$t_l^s = -\frac{[h_l^+, R_l]}{[j_l, R_l]}, \quad (\text{B6})$$

where

$$[A, B] = A \frac{d}{dr} B - B \frac{d}{dr} A$$

and all quantities are evaluated at $r=R_0$.

As shown in the text one often only requires a reduced form of $\chi_{L,L'}$: χ_l of (16). The extra contribution to χ_l due to the surrounding sphere is readily obtained from (B1) and the properties of the B matrix proven in Appendix A. I find that one should add to (20)

$$\chi_l^s = \operatorname{Im} \left[e^{2i\delta_l^s} \sum_T (2\bar{l}+1) j_{\bar{l}}^2(kR) T^s(l, \bar{l}; k, R_0) \right], \quad (\text{B7})$$

where

$$T^s(l, \bar{l}; k, R_0) = \sum_{l'} (2l'+1) \begin{bmatrix} l & \bar{l} & l' \\ 0 & 0 & 0 \end{bmatrix}^2 t_{l'}^s. \quad (\text{B8})$$

These equations simplify a lot if the absorbing atom is at the center of the surrounding sphere, i.e., $R=0$ so

$$\chi_l^s(R=0) = \operatorname{Im}(e^{2i\delta_l^s} t_l^s), \quad (\text{B9})$$

which emphasizes that the oscillatory structure lies in t_l^s . Indeed if one represents the potential energy of the surrounding sphere by a spherical average of a shell of muffin-tin potentials, he can show that (B9) yields a contribution identical in form to those summed over in (20).

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