

Dipole approximation in electron-energy-loss spectroscopy: *M*-shell excitations

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By use of analytic expressions for core and excited-state electron wave functions, we examine the validity of the “dipole approximation” in electron-energy-loss spectroscopy (EELS) due to the *M*-shell excitations of atoms up to an atomic number of about 50. We conclude that the dipole approximation is clearly justified for all *M* edges excited by electrons of high primary energy under typical conditions in an electron microscope. For the relatively low primary energies typically used to increase surface sensitivity in reflection EELS, the conditions for the dipole approximation are easily satisfied for all *M*-edge excitations of the lighter elements, and are reasonably well justified even for the heavier elements of our range.

I. INTRODUCTION

The fine structure on electron-energy-loss spectra (EELS) due to the excitation of atomic core electrons on incidence of high-energy electrons in an electron microscope¹ or medium energy electrons for surface studies^{2,3} often shows great similarity to the fine structure on x-ray-absorption spectra (XAS),^{4–6} which are now quite routinely analyzed for crystallographic and electronic structural information. The degree of similarity between the EELS and XAS is governed by the validity of the dipole approximation in EELS.^{7–13}

Using analytic expressions for the core and excited-state wave functions, we have recently made a systematic investigation of the applicability of this approximation for the interpretation of the fine structure on the *K* (Ref. 14) and *L* edges¹⁵ of chemical elements of atomic number *Z* < 50, for a wide range of energies *E_i* of the incident

electrons and those *ε* of the ejected core electrons. In the last-named paper, we concluded that the assumption of the dipole approximation was very questionable for the interpretation of the EELS spectra for *L*_{II-III}-edge excitations of the heavier elements in that range under the typical experimental conditions of reflection EELS. The aim of the present paper is to extend our study to the case of the *M* edges of the same range of chemical elements.

II. THEORY

We begin with the expression¹⁵ for the differential scattering cross section per unit solid angle *Ω* and per unit energy range *E_f* of an electron of primary energy *E_i*, suffering an energy loss to a final energy *E_f*, due to the excitation of an atomic electron of principal quantum number *n* and orbital and total angular momentum quantum numbers *l* and *j*, namely

$$\frac{\partial^2 \sigma^{nj}}{\partial E_f \partial \Omega} = \frac{1}{\pi^2} \frac{k_f}{k_i} \kappa \frac{1}{q^4} (2j+1) \sum_{l'} (2l'+1) \sum_{l''} (2l''+1) [F_{nl,\epsilon l'}^{l''}(q)]^2 \left[\begin{matrix} l' & l'' & l \\ 0 & 0 & 0 \end{matrix} \right]^2, \quad (1)$$

where *k_i* and *k_f* are, respectively, the wave numbers of the primary electron before and after energy loss, *κ* is that of the ejected core electron of angular momentum quantum number *l'*, and we have averaged over all directions of the momentum-transfer vector **q** = **k_i** – **k_f**. Also in (1), the expression within the large parentheses is a Wigner 3-*j* coefficient;¹⁶

$$F_{nl,\epsilon l'}^{l''}(q) = \int_0^\infty \phi_{nl}(r) j_{l''}(qr) R_{l'}(\epsilon, r) r^2 dr \quad (2)$$

is a radial matrix element for the atomic transition, where *φ_{nl}*(*r*) is the radial part of the core wave function; *R_{l'}*(*ε*, *r*) is the radial part of the ejected core electron of energy *ε*; and *j_{l''}* is a spherical Bessel function of order *l''*. From the power-series expansions of the Bessel functions, it is easy to see that the EELS cross section (1) can

be written as a power series in *q*. As pointed out in our previous papers,^{14,15} a convenient expression for the limit of the dipole approximation can be found by comparing the magnitudes of the terms of this power series proportional to *q*² (the dipole term) with that of the next highest power, namely, *q*⁴.

We take the analytic expressions

$$\phi_{30}(r) = NZ^{*3/2} (27 - 18Z^*r + 2Z^{*2}r^2) e^{-Z^*r/3}, \quad (3)$$

$$\phi_{31}(r) = NZ^{*3/2} (6 - Z^*r) Z^*r e^{-Z^*r/3}, \quad (4)$$

and

$$\phi_{32}(r) = N3^{-1/2} Z^{*3/2} Z^{*2}r^2 e^{-Z^*r/3} \quad (5)$$

for the *M*-shell core wave functions, where *N* is a normal-

ization constant and Z^* the effective nuclear charge for that subshell.¹⁷ We represent the excited states by the Coulomb wave functions $R_l(\epsilon, r)$ (Ref. 18) for the Coulomb potential due to the same effective charge Z^* .

Following the method described in detail in our two earlier papers,^{14,15} an explicit expression for q_d , the maximum value of q consistent with the dipole approximation for M_{I-III} -shell excitations is found to be

$$q_d = k \frac{A}{\sqrt{B}}, \quad (6)$$

where

$$A = |1 - i\alpha| \left\{ F(2 + i\alpha, 5, 4; z) - 10 \frac{\alpha}{\alpha + i3} F(2 + i\alpha, 6, 4; z) + 20 \frac{\alpha^2}{(\alpha + i3)^2} F(2 + i\alpha, 7, 4; z) \right\}, \quad (7)$$

$$A = 36[F(1 + i\alpha, 5, 2; z)]^2 - 180 \frac{\alpha}{\alpha + i3} F(1 + i\alpha, 5, 2; z) F(1 + i\alpha, 6, 2; z) + 225 \left[\frac{\alpha}{\alpha + i3} \right]^2 [F(1 + i\alpha, 6, 2; z)]^2 + 162 \frac{|2 - i\alpha|^2 |1 - i\alpha|^2}{(\alpha + i3)^4} \left\{ 36[F(3 + i\alpha, 7, 6; z)]^2 - 252 \frac{\alpha}{\alpha + i3} F(3 + i\alpha, 7, 6; z) F(3 + i\alpha, 8, 6; z) + 441 \left[\frac{\alpha}{\alpha + i3} \right]^2 [F(3 + i\alpha, 8, 6; z)]^2 \right\}, \quad (12)$$

and

$$B = 165 \frac{|1 - i\alpha|^2}{(\alpha + i3)^2} \left\{ 4[F(2 + i\alpha, 7, 4; z)]^2 - 28 \frac{\alpha}{\alpha + i3} F(2 + i\alpha, 7, 4; z) F(2 + i\alpha, 8, 4; z) + 49 \frac{\alpha^2}{(\alpha + i3)^2} [F(2 + i\alpha, 8, 4; z)]^2 \right\} + 41472 \frac{|3 - i\alpha|^2 |2 - i\alpha|^2 |1 - i\alpha|^2}{(\alpha + i3)^6} \left\{ 4[F(4 + i\alpha, 9, 8; z)]^2 - 36 \frac{\alpha}{\alpha + i3} F(4 + i\alpha, 9, 8; z) F(4 + i\alpha, 10, 8; z) + 81 \left[\frac{\alpha}{\alpha + i3} \right]^2 [F(4 + i\alpha, 10, 8; z)]^2 \right\} - 400 \left\{ 4F(1 + i\alpha, 5, 2; z) F(1 + i\alpha, 7, 2; z) - 14 \frac{\alpha}{\alpha + i3} F(1 + i\alpha, 5, 2; z) F(1 + i\alpha, 8, 2; z) - 10 \frac{\alpha}{\alpha + i3} F(1 + i\alpha, 6, 2; z) F(1 + i\alpha, 7, 2; z) + 35 \left[\frac{\alpha}{\alpha + i3} \right]^2 F(1 + i\alpha, 6, 2; z) F(1 + i\alpha, 8, 2; z) \right\} - 120960 \frac{|2 - i\alpha|^2 |1 - i\alpha|^2}{(\alpha + i3)^4} \left\{ 4F(3 + i\alpha, 7, 6; z) F(3 + i\alpha, 9, 6; z) - 18 \frac{\alpha}{\alpha + i3} F(3 + i\alpha, 7, 6; z) F(3 + i\alpha, 10, 6; z) - 14 \frac{\alpha}{\alpha + i3} F(3 + i\alpha, 8, 6; z) F(3 + i\alpha, 9, 6; z) + 63 \left[\frac{\alpha}{\alpha + i3} \right]^2 F(3 + i\alpha, 8, 6; z) F(3 + i\alpha, 10, 6; z) \right\}. \quad (13)$$

And for the M_{IV-V} edge,

$$q_d = 2|1 - i\alpha| k \sqrt{7A/6B}, \quad (14)$$

$$B = \frac{3}{4} \left\{ [F(1 + i\alpha, 5, 2; z)]^2 + 100 \left[\frac{\alpha}{\alpha + i3} \right]^2 [F(1 + i\alpha, 6, 2; z)]^2 + 400 \left[\frac{\alpha}{\alpha + i3} \right]^4 [F(1 + i\alpha, 7, 2; z)]^2 \right\}, \quad (8)$$

and

$$\alpha = \frac{Z^*}{k}, \quad (9)$$

and

$$z = \frac{6}{3 - i\alpha}. \quad (10)$$

Likewise, we find for the M_{II-III} edge:

$$q_d = 80k(\alpha + i3) \left[\frac{A}{7776B} \right]^{1/2}, \quad (11)$$

where

where

$$A = 25[F(2+i\alpha, 7, 4; z)]^2 + 648 \frac{|3-i\alpha|^2 |2-i\alpha|^2}{(\alpha+i3)^4} [F(4+i\alpha, 9, 8; z)]^2 \quad (15)$$

and

$$B = 35[F(1+i\alpha, 7, 2; z)]^2 + 75852 \frac{|2-i\alpha|^2 |1-i\alpha|^2}{(\alpha+i3)^4} [F(3+i\alpha, 9, 6; z)]^2 \\ + 29160 \frac{|4-i\alpha|^2 |3-i\alpha|^2 |2-i\alpha|^2 |1-i\alpha|^2}{(\alpha+i3)^8} [F(5+i\alpha, 11, 10; z)]^2 - 11760 \frac{|1-i\alpha|^2}{(\alpha+i3)^2} F(2+i\alpha, 7, 4; z) F(2+i\alpha, 9, 4; z) \\ - 163296 \frac{|3-i\alpha|^2 |2-i\alpha|^2 |1-i\alpha|^2}{(\alpha+i3)^6} F(4+i\alpha, 9, 8; z) F(4+i\alpha, 11, 8; z), \quad (16)$$

where the hypergeometric functions F may be evaluated from the usual power series,¹⁹ which is convergent if $|z| < 1$. From (9) and (10) it is easy to see that this is equivalent to the condition that $k < Z^*/27$ or that

$$\epsilon < Z^{*2}/54 \quad (17)$$

in Hartree atomic units. Thus, at least within these limits, Eqs. (6) to (16) show that q_d is a function of just two variables, namely, the effective nuclear charge Z^* for that subshell and the wave number κ of the ejected core electrons.

III. RESULTS

In Fig. 1 the variation of q_d with the atomic number Z for $\kappa=1$ a.u. ($\epsilon=0.5$ Hartrees or 13.6 eV), corresponding to the near-edge region on an EELS spectrum, is plotted for the M_I , M_{II-III} , and M_{IV-V} edges. Since our theory is nonrelativistic, we have restricted ourselves to a range of chemical elements with atomic number, Z , up to about 50. The figure shows that for all these absorption edges, q_d increases nearly linearly with Z , but that for the M_I edge the gradient is rather steeper than for the M_{II-III}

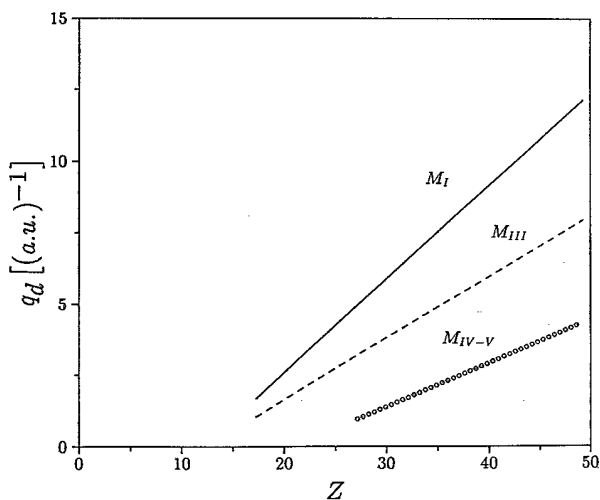


FIG. 1. Plot of q_d vs atomic number Z for EELS with $\epsilon=13.6$ eV [$k=1$ (a.u.)⁻¹]: (a) M_I edge, (b) M_{II-III} edge, and (c) M_{IV-V} edge.

edge, which in turn is steeper than that for the M_{IV-V} edge.

The observations may be understood by noting from (2) that the linear (dipole) term in qr in the series expansion of the Bessel function will be dominant if $qr_c \ll 1$, where r_c is the radial extent of the core wave function.¹⁴ This implies that $q_d \approx 1/r_c$. Thus the observed increase in q_d with Z on Fig. 1 may be attributed to the fact that the radii of inner electronic shells tend to decrease as Z increases, due to the increase in the nuclear charge, and the fact that the outer shells do not contribute significantly to the screening of that charge.

On Figs. 2 and 3 we plot the calculated values of q_d as functions of the energy ϵ of the ejected core electron, over the accessible range (17), for the elements Ni ($Z=28$) and Ag ($Z=47$) in the first and second rows, respectively, of transition metals. The parts (a) of the figures consider the M_I edge, the parts (b) the M_{III} edge, and the parts (c) the M_{IV-V} edge. The solid curves of these figures indicate that q_d does not vary strongly with ϵ , but that, for the M_I and M_{II-III} edges, q_d decreases slightly with increasing ϵ and that this trend is reversed for the M_{IV-V} edges of both elements.

IV. DISCUSSION AND CONCLUSIONS

In a typical EELS experiment the incident primary electron may suffer much multiple scattering both before and after the inelastic scattering event.²⁰⁻²⁶ As a result, the magnitude and direction of the momentum transfer vector q is generally not simply related to the wave vectors of the incident and detected electrons. In fact the observed signal may be regarded as an aggregate of inelastic scattering events involving many different inelastic scattering events. Fortunately from the point of view of theoretical analysis, as has been pointed by several authors (e.g., Refs. 27, 9, 14), the existence of the squared inverse of q outside the sum over l' in (1) implies that the dominant contributors to the measured EELS signal are those loss events with the smallest q , which correspond to forward inelastic scattering. This minimum value of q can be shown to be equal to^{28,29,21,22}

$$q_{\min} = \sqrt{2E_i} [1 - (1 - \Delta E/E_i)^{1/2}], \quad (18)$$

where E_i is the energy of the incident electron, ΔE the

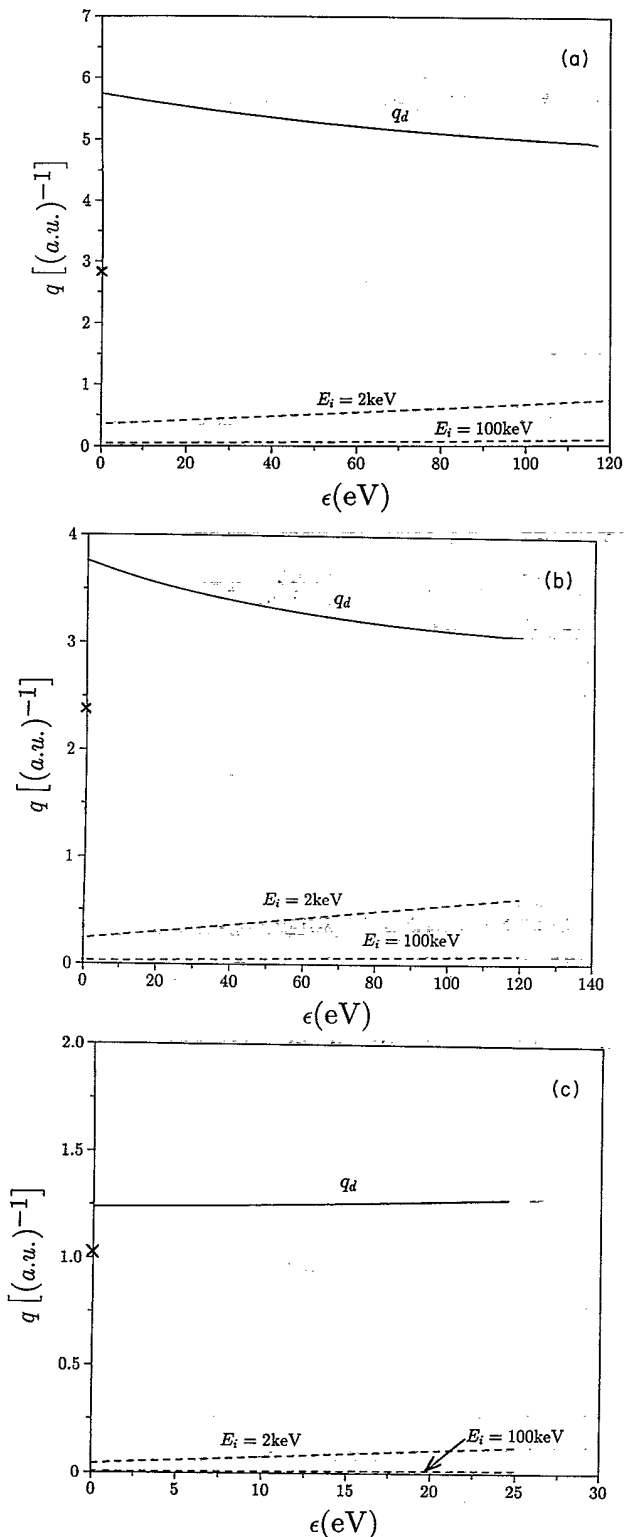


FIG. 2. Comparison of q_d (solid line) and q_{\min} (dashed lines) for Ni ($Z=28$) as a function of the energy ϵ of the ejected core electron. The different dashed lines correspond to different energies E_i of the incident primary electrons. (a) M_I edge ($E_{M_I} = 115.6$ eV); (b) M_{II-III} edge ($E_{M_{II-III}} = 78.3$ eV); (c) M_{IV-V} edge ($E_{M_{IV-V}} = 15.2$ eV). The crosses on the q_d axis mark the limiting values of q_{\min} at the ionization threshold (when $E_i = E_M$).

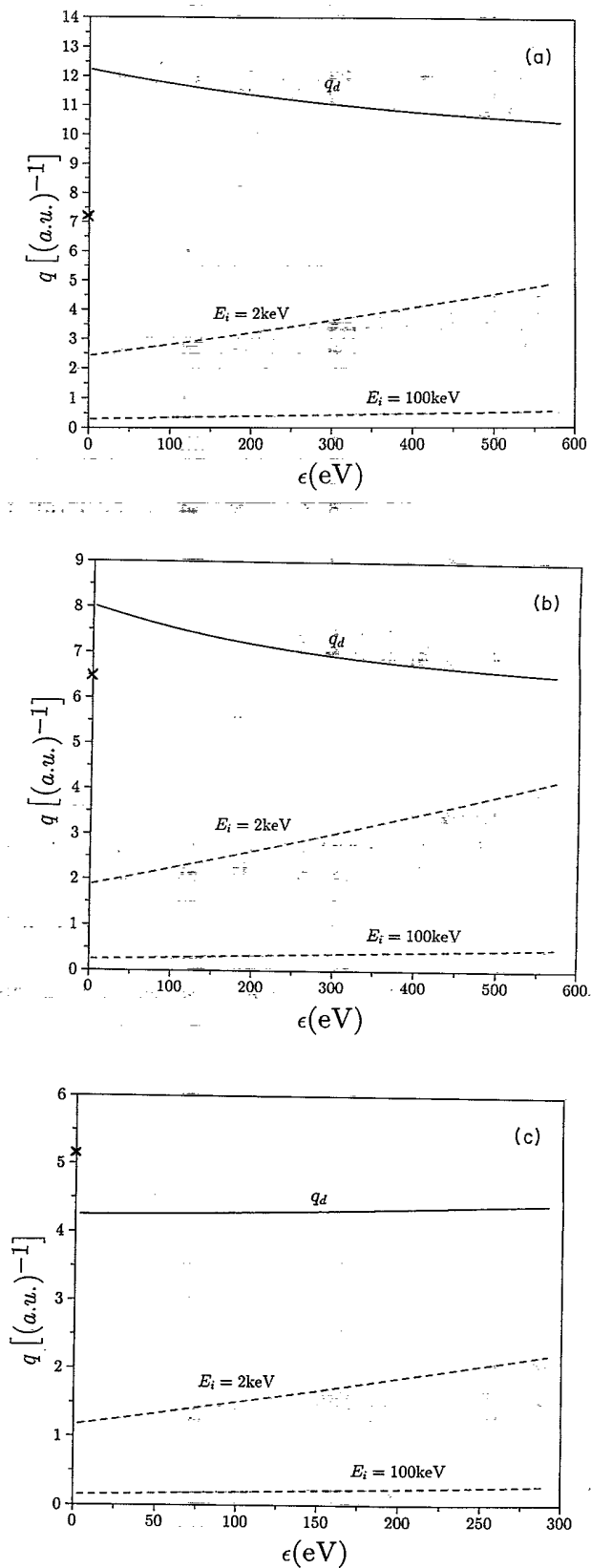


FIG. 3. Same as Fig. 2, except for Ag ($Z=47$). (a) M_I edge ($E_{M_I} = 719.6$ eV); (b) M_{III} edge ($E_{M_{III}} = 573.5$ eV); (c) M_{IV-V} edge ($E_{M_{IV-V}} = 366.7$ eV).

magnitude of the energy loss, and

$$\Delta E = E_M + \varepsilon, \quad (19)$$

where E_M is the core-electron binding energy. The dashed lines in Figs. 2 and 3 show the variation of q_{\min} against ε for the incident electron energy $E_i = 2$ keV, typical of reflection EELS work, and $E_i = 100$ keV, typical of transmission EELS in the electron microscope. The cross on the ordinate axis marks the limiting value of q_{\min} when $E_i = E_M$ in each case.

Figures 2(a)–2(c) show that for typical values of E_i in the case of Ni, q_d is always significantly greater than q_{\min} over the entire range of ε shown. However, Figs. 3(a)–3(c) show that for the higher values of ε , i.e., in the extended electron-energy-loss fine structure (EXELFS)³⁰ region, q_{\min} comes to within a factor of about 2 of q_d for Ag. Small deviations from “dipole” behavior may therefore be expected in these regions of the M energy-loss edges for heavier elements like Ag. Note also the fact that the cross on the ordinate axis on Fig. 3(c) lies above the corresponding value of q_d , which indicates that the dipole approximation also breaks down for the lowest incident electron energies E_i (~ 400 eV) capable of exciting an electron from the M_{IV-V} shell in Ag. However, the

last case is of little consequence for practical EELS even in the reflection geometry, since significantly higher primary energies are typically used.

Overall, it may be concluded that the dipole approximation is well justified for all M energy-loss edges of elements such as Ni, which lie near the lower atomic number end of the range of elements that exhibit all three of the M edges, and that for all practical incident electron energies E_i , it is reasonably well justified even for heavier elements like Ag ($Z = 47$), near the upper end of the range of our nonrelativistic theory. In contrast, we concluded in our earlier paper¹⁵ that the dipole approximation was clearly not justified for the L_{II-III} edges of even an element as light as Ni ($Z = 28$).

Experimental support for these conclusions is found in the successful interpretation of EELS spectra by theories originally developed for extended x-ray-absorption fine structure (EXAFS) in the cases of transmission³¹ and reflection³ experiments on the M_{II-III} and M_{IV-V} edges of Ni.

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