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Experimental check of core Compton profiles, calculated using a quasi-self-consistent-field method

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In order to check the validity of our core Compton-profile calculations [quasi-self-consistent-field (QSCF) method] beyond the impulse approximation, measurements have been performed at two different energies E_1 of the incident photons (8.2 and 12.86 keV). Compton profiles are obtained on a beryllium single crystal using the synchrotron radiation of LURE. In this paper, it is shown that the QSCF profile satisfies the two requirements: It converges to the impulse-approximation profile as E_1 increases and the valence profile, deduced from the experimental and QSCF profiles, is independent of the energy E_1 (as required by the impulse approximation). We conclude that the QSCF approach is quite satisfactory for this type of experiment.

I. INTRODUCTION

The Compton profiles, i.e., the Doppler broadening of the inelastically scattered x rays, are particularly sensitive to the behavior of the valence electrons of the target: since these loosely bound electrons are well localized in momentum space, they lead to a sharp contribution to the profile while the core electrons lead to a broader one. Compton scattering is indeed a well-established tool to study the distribution of the electrons involved in bonding in condensed matter.[1] However, the solid-state calculations lead only to the valence profile while all the electrons contribute to the experimental profile. Thus, in order to compare experimental valence Compton profiles with calculated ones, it is necessary to subtract a calculated core profile from the measured profile. An experimental Compton profile is shown in Fig. 1 with the calculated core-electron contribution. One can observe the departure of the core profile corresponding to an energy transfer equal to the initial binding energy e_i of the ejected electron.

In fact, the Compton profile (CP) is easily calculated within the impulse approximation[2] (IA). In this approximation,[3] the collision is assumed to be fast enough for no relaxation to occur. However, this approximation is valid only if the energy ΔE transferred from the photon to the ejected electron is large enough compared with the

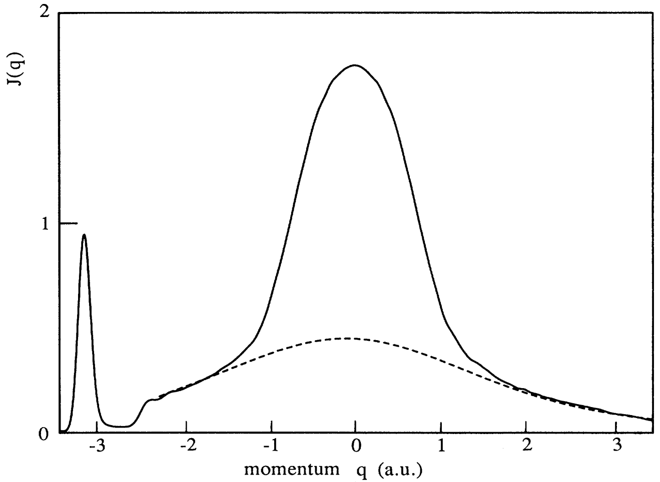

FIG. 1. Total experimental Compton profile of beryllium (solid line) and the QSCF core profile (dashed line). The measurement was done with $E_1 = 12.86$ keV of incident photons with a scattering angle $\Phi = 137°$. e_i is the binding energy of the 1s core electron, ΔE_c the energy transferred by the photon to an electron at rest ($q = 0$).

initial binding energy e_i of this electron.[4] If ΔE is too small and the IA not valid, it has already been shown that the amplitude[5] as well as the symmetry[6,7] of the profiles could be affected.

In the case of x-ray experiments, where the best resolution can be achieved, the energy transfer ΔE is usually of the same order as the binding energy of the core electrons. Therefore, the IA is questionable in that case and a better approximation has to be used. In a previous paper we have described such an approximation—the quasi-self-consistent-field (QSCF) approximation[8]—and used it in the case of the $1s$ electron of C in graphite.[9] It has been found that the QSCF approximation is much more satisfactory than the hydrogenic one.

However, the comparison of a calculated core CP with the experiment raises the same problem as the comparison of the valence CP: In the latter case one needs a reliable core profile and in the former case, a reliable valence one. And since there are always some approximations that are more or less controlled (mainly concerning the electron correlations) in the calculated valence CP's, no direct comparison is possible.

The aim of the present article is to introduce an indirect test of the QSCF approximation. This test relies on the idea that the IA is valid for the valence electrons and therefore the valence CP should be independent of the energy E_1 of the initial photons. Thus, the indirect test of the calculated core CP consists of checking that the difference profile between the experimental CP and the calculated core CP (so-called valence profile) is independent of E_1.

In order to perform that test, we have performed Compton measurements at two different energies in the regular energy range of LURE (10 keV) using a beryllium sample. Then, we have calculated the core CP within the IA (Ref. 10) and QSCF approximations as a function of E_1 and examine the resulting valence CP.

The case of beryllium was chosen here for the following reasons: its low photoelectric absorption leads to a high counting rate of inelastically scattered photons in this range of energy; its core contains only one type of electrons ($1s$) which makes the calculation easier and the comparison more reliable; its low $1s$ binding energy e_i (Ref. 11) allows one to reach experimentally very different relative values of e_i and ΔE.

There are several interesting features of the valence CP of Be. These features have been discussed previously.[13,14]

In the next two sessions, we briefly recall some aspects of the theory of CP's and describe the experimental procedure. Finally, we discuss the QSCF approximation for the core CP's calculations by examining the quality of the resulting valence CP's.

II. THEORY

The main aspects of the general theory of the Compton profiles of interest here have been outlined previously.[8] The x-ray energy available at LURE enables us to describe the Compton process in the nonrelativistic first Born approximation. Furthermore, if we assume that the independent-particle and frozen-orbital approximations are valid, the Compton profile appears as a sum of one-electron contributions, i.e.,

$$J=\sum_i J_i=\sum_i K\sum_f |\langle \phi_f|e^{i\mathbf{K}\cdot\mathbf{r}}|\phi_i\rangle|^2\delta(e_f-e_i-\Delta E)\ , \quad (1)$$

where e_i and e_f are the initial and final energies of the ith electron; $\mathbf{K}$ and ΔE are, respectively, the momentum and energy transfers from the photon to the ith electron; and ϕ_i and ϕ_f are the initial and final states of one electron.

The above assumptions leading to Eq. (1) mean particularly that we consider here the ionization of a single atom at a time, and that we neglect all interactions between the different ions (excitonic effects). They are generally valid for core profiles except if the transferred energy ΔE is close to an ionization threshold.

Here we will compare the effect of two different additional approximations in the case of core profiles.

A. Impulse approximation (IA)

We assume that ΔE is sufficiently larger than e_i. The Compton profile is then given by

$$J_i^{\mathrm{IA}}(p_z)=\int\int|\chi_i(\mathbf{p})|^2 dp_x dp_y\ , \quad (2)$$

where $\chi_i(\mathbf{p})$ is the Fourier transform of the initial orbital, $\phi_i(\mathbf{r})$, $\mathbf{p}$ is the momentum of an electron in the initial state, and p_z usually labeled q, is the component of $\mathbf{p}$ on the scattering vector $\mathbf{K}$:

$$p_z=q=\frac{\mathbf{K}\cdot\mathbf{p}}{K}=\frac{\Delta E}{K}-\frac{K}{2}\ . \quad (3)$$

Here, the initial state has been described by atomic SCF (Hartree-Fock self-consistent field) orbitals. It is seen in Eq. (2) that, within the IA, the profile $J(q)$ is (a) independent of the experimental conditions, i.e., energy of the incident photon and scattering angle (or, equivalently, momentum transfer for $q=0$); note that we are here within the A^2 approximation. (b) A symmetrical function of q, i.e., the maximum of $J(q)$ (Compton peak) is always obtained for $q=0$ (initial electron at rest). (c) Also, one has

$$\int_0^\infty J(q)dq=n/2\ , \quad (4)$$

where n is the number of electrons under consideration (here core electrons). Impulse CP's are easy to calculate, but the impulse approximation completely ignores the final state[2] of the outgoing electron and the potential where this electron is moving.

B. QSCF approximation

We no longer use the IA. Instead, we determine ϕ_f numerically, assuming a simple form for the potential where the outgoing electron is moving. In the case of Be, this potential is written as

$$V(r)=-\frac{Z}{r}+\mathcal{J}_{1s}(r)+2\mathcal{J}_{2s}(r)\ , \quad (5)$$

where Z is the nuclear charge ($Z=4$ for Be).

The Coulomb operator $\mathcal{J}_k(r)$ of orbital ϕ_k is defined by

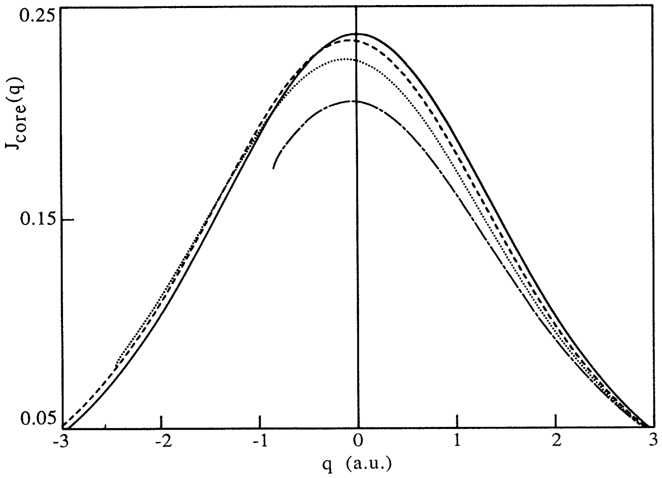

FIG. 2. Calculated core Compton profiles: Solid line is the impulse approximation profile. The QSCF core profiles calculated for different incident energies E_1 are shown as dash-dotted line ($E_1=8.2$ keV), dotted line ($E_1=12.86$ keV), and dashed line ($E_1=25$ keV).

$$\mathcal{J}_k(r)=\int\frac{|\phi_k(r')|^2}{|r-r'|}dr' \ , \tag{6}$$

where ϕ_k ($k=1s$ or $2s$) is the atomic SCF function, and r is the electron position related to the nucleus.

The most important aspect of such a potential is that it is close to ($-Z/r+$ const) for small r and increases as ($-1/r$) for large r. On the other hand, no exchange or correlation effects are included. Computational details for evaluating ϕ_f and the CP [through Eq. (2)] are given in Ref. 8.

In the QSCF approximation, the CP depends on the initial energy E_1 of the photon; it is not necessarily symmetrical with respect to $q=0$, and the integral of Eq. (1) is not necessarily equal to half the number of core electrons.

The core CP, evaluated within the QSCF approximation, for different values of E_1 and for the same scattering angle (137°) is given in Fig. 2. The energy ΔE_c transferred to an electron at rest (i.e., Compton shift) is equal to 2 and 5 times e_i when E_1 is equal to 8.2 and 12.86 keV, respectively. The core profile depends significantly on E_1. When E_1 and, as a consequence, ΔE_c increases, the QSCF core profile converges to the IA core CP. A profile calculated for $E_1=25$ keV (i.e., $\Delta E_c \cong 1900$ eV larger than 15 times e_1) is shown in order to point this convergence out for $q<0$ as well as for $q>0$.

III. EXPERIMENT

The synchrotron beam of LURE-DCI has been monochromatized in order to perform Compton measurements successively with an incident energy equal to 8.2 and 12.86 keV. The two CP's have been measured with the use of the three-axis focusing spectrometer described in Ref. 12.

The photons scattered at an angle of $\Phi=137°$ are energy analyzed through a curved crystal and are collected with a position-sensitive detector. The full width at half maximum (FWHM) of the measured resolution is 0.17 atomic units (a.u.) of momentum. The beryllium sample is a 3-mm-thick single crystal cut perpendicular to the direction corresponding to the fourth-nearest neighbor, i.e., the (10.l) with $l=1.23$ in the hexagonal system. The choice of a particular direction has no consequence on the problem considered in this work, but to keep the same data processing, the same geometry is conserved for the two measurements. Two million counts were collected in the Compton profile for each measurement leading to a statistical accuracy equal to ±0.5% at the Compton peak ($q=0$). The background has been subtracted out and corrections are made for sample and analyzer absorption, detector efficiency, and cross-section energy dependence.[13]

Then one has to normalize the experimental CP before comparing with the calculated one, using the momentum scale q defined by Eq. (3).

The normalized CP is defined by the condition

$$\int_O^b J_{\text{exp}}(q)dq=\int_O^b J_{\text{val}}(q)dq+\int_O^b J_{\text{core}}(q)dq \ , \tag{7}$$

where b is the limit of the experimental spectrum. Here we have $b=5.5$ a.u. of momentum, due to the detector extent. We can assume that the whole valence profile is contained in the measured spectrum: the Fermi momentum of beryllium is $p_F=1.027$ a.u. and we have already demonstrated that the valence profile, including correlation effects of the conduction gas,[14] is restricted to 2.15 a.u. Furthermore the valence electrons fulfill the IA, so

$$\int_O^{5.5} J_{\text{val}}(q)dq=1 \ . \tag{8}$$

The integrals of the core profiles are determined numerically. In the case of the impulse approximation, we have found

$$\int_O^{5.5} J_{\text{core}}^{\text{IA}}(q)dq=0.9827 \ .$$

In the case of the QSCF approximation, we have found (with $\Phi=137°$):

$$\int_O^{5.5} J_{\text{core}}^{\text{QSCF}}(q)dq=\begin{cases}0.8222 & \text{for } E_1=8.20 \text{ keV} & \text{(9a)}\\ 0.9180 & \text{for } E_1=12.86 \text{ keV} \ . & \text{(9b)}\end{cases}$$

It is seen that the area of the core profile, in this approximation, depends slightly on the incident energy. Table I summarizes the experimental conditions and the related discrepancies between the QSCF core profiles and the IA one. This variation of the core area is reported in column 5 and its effect on the deduced valence CP is discussed in the next section. We notice that the same relative difference between the amplitude at $q=0$ of the QSCF and IA-CP's (about 13%) have been found for graphite[9] and beryllium when ΔE_c is close to $2e_i$ (see Table I).

Finally, it should be noted that no correction has been made here for the experimental resolution function. So the calculated core profile J_{1s} has been convoluted by the measured resolution function to be subtracted from the total profile.

TABLE I. Differences between the QSCF and IA core profiles. $e_i = 112$ eV and $e_i' = 284$ eV are the 1*s* electron binding energies of beryllium and carbon, respectively.

Sample	Incident energy E_1 (keV)	Compton shift (ΔE_c)	$\dfrac{J^{\mathrm{IA}}_{\mathrm{core}}(0) - J^{\mathrm{QSCF}}_{\mathrm{core}}(0)}{J^{\mathrm{IA}}_{\mathrm{core}}(0)}$	$\dfrac{\int_0^{5.5} J^{\mathrm{IA}}_{\mathrm{core}} dq - \int_0^{5.5} J^{\mathrm{QSCF}}_{\mathrm{core}} dq}{\int_0^{5.5} J^{\mathrm{IA}}_{\mathrm{core}} dq}$
Be	8.2	222 eV$\cong 2e_i$	13.5%	16.3%
Be	12.86	532 eV$\cong 5e_i$	5.2%	6.6%
C	12.86	532 eV$\cong 2e_i'$	13%	

The experimental profile, obtained with 12.86-keV incident photons and normalized using the data processing just described [condition (7) and relations (8) and (9)], is shown in Fig. 1. The QSCF core profile is plotted in the same figure. We can observe the departure of the core electron profile at $q = -2.55$ a.u., corresponding to an energy transfer equal to e_i.

RESULTS AND DISCUSSIONS

We proceed now to the indirect check of the IA and QSCF approximations on the core CP's. To that end, we consider the valence profile obtained by the difference between the experimental profile and the calculated core one. Since the valence electrons are assumed to satisfy the IA, the resulting valence profile must be symmetrical with respect to $q = 0$ a.u. and independent of the energy E_1 of the incident photons. These two properties form a critical test for the QSCF approximation on the core CP calculation.

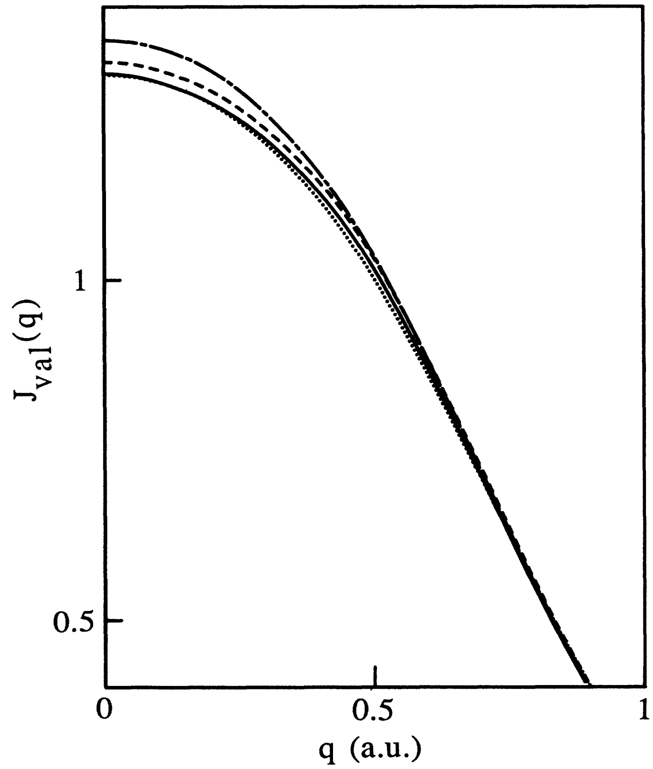

FIG. 3. Experimental valence profiles. The four profiles are obtained from the two measured profiles by subtraction of a core profile calculated under the impulse approximation: dash-dotted line, $J^{\mathrm{IA}}_{\mathrm{val}}$ ($E_1 = 8.2$ keV); dashed line, $J^{\mathrm{IA}}_{\mathrm{val}}$ ($E_1 = 12.86$ keV); or with the QSCF method: dotted line, $J^{\mathrm{QSCF}}_{\mathrm{val}}$ ($E_1 = 8.2$ keV); solid line, $J^{\mathrm{QSCF}}_{\mathrm{val}}$ ($E_1 = 12.86$ keV).

It is seen in Fig. 3 that the valence CP resulting from the QSCF approximation is indeed very weakly dependent on the initial energy E_1 of the photons. On the contrary, the valence CP does depend on E_1 if the IA is used for evaluating the core CP. These two features, appearing in Fig. 3, constitute the main result of the present work. They lead to the conclusion that QSCF is a reliable approximation for evaluating the core CP in the case of the experimental conditions considered here.

More detailed comparisons are presented in Figs. 4 and 5. It is seen in Fig. 4 that the energy dependence of the valence profile is of same order as the error bar when the core CP is evaluated in the QSCF approximation, while a much larger dependence appears when the IA is used for the core profile. In addition it is seen in Fig. 5 that the difference between the valence profiles deduced from the two approximations on the core profile have no effect (smaller than the error bar) at large ΔE_c ($E_1 = 12.86$ keV): In the present case (beryllium 1*s* core electron), the IA is valid for $\Delta E_c = 5e_i$ in regard to statistical accuracy. But for $E_i = 8.2$ keV leading to a Compton shift $\Delta E_c = 2e_i$, the discrepancy between the valence profiles obtained from the two approximations is significant (larger than two times the error bar).

For the incident energy $E_1 = 12.86$ keV, the QSCF core profile is weakly asymmetrical (see Fig. 2). The core

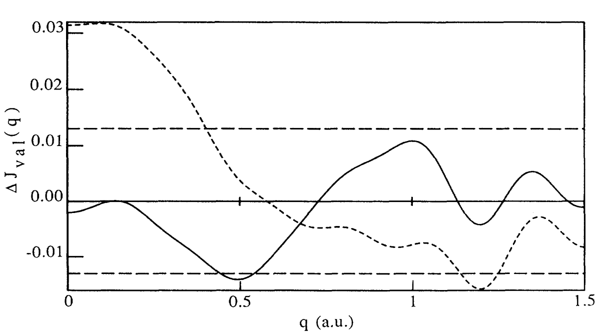

FIG. 4. Difference between valence profiles obtained from two different energy measurements and using the same approximation in the core profile calculation: short-dashed line, $\Delta J^{\mathrm{IA}}_{\mathrm{val}} = J^{\mathrm{IA}}_{\mathrm{val}}$ ($E_1 = 8.2$ keV)$-J^{\mathrm{IA}}_{\mathrm{val}}$ ($E_1 = 12.86$ keV); solid line, $\Delta J^{\mathrm{QSCF}}_{\mathrm{val}} = J^{\mathrm{QSCF}}_{\mathrm{val}}$ ($E_1 = 8.2$ keV)$-J^{\mathrm{QSCF}}_{\mathrm{val}}$ ($E_1 = 12.86$ keV). The long-dashed lines show the error $\Delta J(q) = \pm 1\% J(0)$.

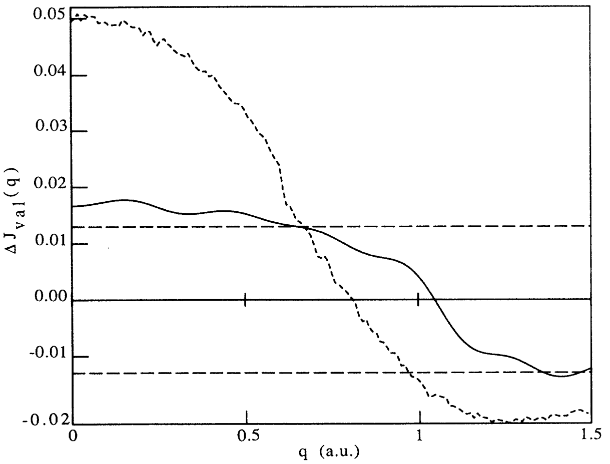

FIG. 5. Difference between valence profiles obtained from two different core approximations (at a given energy measurement): short-dashed line, $\Delta J_{\rm val}$ ($E_1=8.2$ keV) = $J_{\rm val}^{\rm IA}$ (8.2 keV) $-J_{\rm val}^{\rm QSCF}$ (8.2 keV); solid line, $\Delta J_{\rm val}$ (12.86 keV) = $J_{\rm val}^{\rm IA}$ (12.86 keV) $-J_{\rm val}^{\rm QSCF}$ (12.86 keV). The long-dashed lines show the error $\Delta J(q)=\pm 1\% J(0)$.

profile subtraction leads to a symmetrical valence profile with respect to $q=0$, in the region ($q>-1$ a.u.) far enough to the threshold, so that the IA and QSCF approximations were valid for the valence and core electrons, respectively. The fact that the subtraction of the core profile leads to a symmetrical valence profile is consistent with a slight defect observed in the Compton shift of the measured profile, estimated as 10^{-2} a.u. of momentum.

It is also interesting to compare the IA and QSCF profiles for the small values if the transferred energy ΔE (small q) for which the valence electrons give a negligible contribution to the total profile. For q below $\cong -2.2$ a.u. the transferred energy is very close to the ionization threshold; therefore, most of the approximations made here fail and no valid comparison can be made between theory and experiment. On the other hand, while the difference between the IA and the experimental profiles does not vanish, it is seen in Fig. 6 that around $q=-2$ a.u. the QSCF profile is indeed very close to the experimental one.

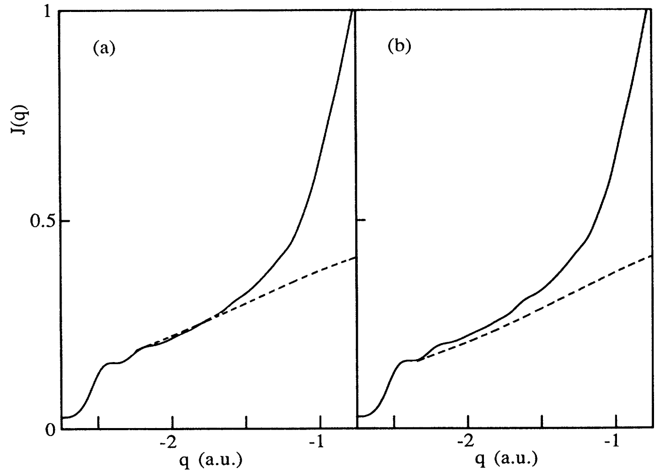

FIG. 6. Small transfer region: experimental profile ($E_1=12.86$ keV) at q just above the ionization threshold (Raman departure) compared with calculated QSCF core profile (a) and IA one (b). Solid line, total experimental Compton profile; dashed line, core profile.

IV. CONCLUSION

We have calculated the core Compton profile of beryllium within two different approximations (IA and QSCF) and for two values of the energy E_1 of the incident photons. It appears that the IA is satisfactory only if the transferred energy for $q=0$ (Compton shift) is at least equal to 5 e_i. On the other hand, the QSCF approximation is quite satisfactory for all the energies considered here. Particularly, the experimental valence profile resulting from this last approximation is stable with respect to the variation of E_1.

It should be emphasized that the wave function ϕ_f of the outgoing electron is ignored only in the IA approximation. Therefore, if the transferred energy for $q=0$ (ΔE_c) is lower than $5e_i$, one has to determine ϕ_f in some way.

The QSCF approximation is—in a sense—the simplest reasonable method for determining ϕ_f. It relies only on the following very general physical conditions.

The potential $V(r)$ seen by the electron in ϕ_f is local and satisfies

$$V(r)\sim\begin{cases}-\dfrac{Z}{r}+\text{ const as } r\to 0\\[2mm] -\dfrac{1}{r}\quad\text{as } r\to\infty\ .\end{cases}$$

Here we determined the constant and the switching function between the two limits of $V(r)$ simply from the isolated atoms.

It is likely that the short-range expression of the potential $V(r)$ is realistic. Particularly, it seems important to use the actual charge Z of the considered atom and not some effective charge leading, for instance, to a good energy in the hydrogenic approximation (see the discussion in Ref. 8).

However, the remaining assumptions (V is always local—i.e., the exchange is always negligible—the switching function is independent of the solid, the limit as $r\to\infty$ is just $-1/r$) seem more questionable.

The present work is a quantitative test of the above considerations on the potential V to be used for describing properly the Compton profile due to core electrons. The good result obtained demonstrates that the assumptions made here (the simplest reasonable ones) are in fact satisfactory in the case of beryllium. It should be interesting to investigate the conditions (various initial potentials: inner shells K, L, or M, and various final ones: insulator or conductive solid, etc.) in which they are valid, by studying other cases.

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