# Extended x-ray-absorption fine-structure amplitudes—Wave-function relaxation and chemical effects*

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Experimentally measured amplitudes of the extended x-ray absorption fine structure (EXAFS) are smaller, typically by a factor of 1/2, than results calculated from one-electron theories. We suggest that this reduction factor may be largely accounted for by a theory based on the relaxation of passive electron orbitals accompanying photoemission, which permits a straightforward approximate calculation in terms of a many-body overlap integral. Using *ab initio* Hartree-Fock-Roothaan calculations and estimates for correlation effects, the theory gives reduction factors of 0.60, 0.64, and $0.64 \pm 0.04$ for $F_2$, $Cl_2$, and $Br_2$, respectively, in rough agreement with experiment. These numbers are 7%–14% smaller than those for free halogen atoms, and indicate that chemical effects (in particular, molecular charge transfer) are important in determining the EXAFS reduction factor. This charge transfer also affects the overall EXAFS phase. The reduction in single-electron excitation is made up by multielectron excitations, the "shake-up," and "shake-off" processes. The possible contributions to EXAFS from these channels are discussed and estimated to be about 10% of the total amplitude.

## I. INTRODUCTION

One electron theories of the extended x-ray absorption fine structure (EXAFS)[1,2] have, on the whole, been quite successful in describing the overall shape of the EXAFS spectra both in simple molecules[3] and in a few solids.[2] However, the amplitude of the calculated EXAFS oscillations is invariably larger than that measured experimentally, typically by a factor of about 2. This discrepancy may complicate the utility of EXAFS as a method for determining local coordination numbers and indicates the need for a more complete theory.

In this article we develop a theory for this amplitude-reduction factor based upon certain many-electron aspects of the absorption process. Specifically, we recognize that the total absorption strength at a given photon energy comes not only from the normally considered "primary" or one-electron excitation "channel," but also from the various "shake-up" and "shake-off" multielectron excitation channels. Also, at the energies of interest in EXAFS (100–1000 eV beyond threshold), the reduction of absorption strength in the primary channel can be ascribed to an incomplete overlap between the passive electrons in the ground state and the final (correlated) ionic state of the system.[4] In Sec. II we outline the theory of overlap effects on EXAFS amplitudes. Section III deals with the contributions to EXAFS from secondary channels, and Sec. IV summarizes our conclusions.

## II. EXAFS AMPLITUDES

The normalized EXAFS spectra $\chi$ is defined in terms of the x-ray absorption coefficient $\mu$ by[1]

$$\chi = (\mu - \mu_0)/\mu_0, \tag{1}$$

where $\mu_0$ is the smoothly varying "average absorption" upon which the EXAFS is superimposed. From the golden rule,

$$\mu \sim \omega^3 \sum_f \left| \langle f_N | \sum_{j=1}^{N} \vec{r}_j \cdot \hat{\epsilon} | i_N \rangle \right|^2, \tag{2}$$

where $|i_N\rangle$ and $|f_N\rangle$ refer to the eigenstates of the full $N$-electron electrostatic Hamiltonian $H_0$ with energies $E_i$ and $E_f$, and the dipole approximation has been employed in treating the radiation field, with polarization in the direction $\hat{\epsilon}$. All the final states $|f\rangle$ are degenerate with $E_f = E_i + \hbar\omega$; they are distinguished by the fact that each corresponds to a different ionic channel.

In conventional treatments of EXAFS,[1,2] Eq. (2) is simplified by restricting the sum to a single, *primary* channel. For example, for $K$-edge absorption in $Br_2$, one assumes that the only important process is the $K$ electron → continuum transition in which the ion is left in its fully relaxed "ground state." Equation (2) is then further simplified by making use of the one-electron approximation and by treating the atoms as independent scattering centers. With these approximations, the absorption coefficient is governed by a one-electron matrix element

$$\mu \sim \omega^3 \, |\langle \phi_f + \delta\phi_f \, | \, \vec{r} \, | K \rangle|^2, \tag{3}$$

where $\phi_f$ is the continuum function originating from the $K$ hole and $\delta\phi_f$ is the component originating from backscattering from neighboring atoms. It is at this stage that inconsistencies begin to appear. The function $\phi_f$ is normally associated with an atomic continuum orbital generated in the potential of a *relaxed* 1s hole state. With relaxation in the physical model, however, the many-electron matrix element in (2) can no longer be reduced to a one-electron integral as in Eq. (3). Furthermore, there are substantial extra-atomic relaxation effects in molecules, and the potential seen by the outgoing electron should take this into account.

Lee and Beni[6] have refined the one-electron approximation to include some effects of electron correlation by using a complex, effective one-electron potential. These refined calculations (including, separately, inelastic processes in the absorbing atom and in backscattering) do lead to reductions in the computed amplitude, but it is still much larger than experimentally observed. Also, chemical effects not treatable by varying the zero of energy are essentially ignored. Indeed, Lee and Beni obtain good agreement with experiment by treating fully only the backscattering and lumping the remaining terms into a constant empirical factor, which is 0.62 for $Br_2$ and 0.43 for $GeCl_4$. Lee and Beni have argued that these reduction factors are indicative of the "relative weight in the main peak in photoemission," which was estimated by them to be 0.74 for $Br_2$, and "inelastic processes in the central atom," which gave an average value of 0.75 for Br.

Let us now consider a more precise evaluation of the many-body transition element. The procedure we follow is based on the high- (electron kinetic) energy limit of Eq. (2) and relies on the findings of a detailed study and comparison of photoemission theory and experiment.[7] In this work it was found that for core-excitation in atomic Ne, the transition element can be approximated beyond about 200 eV (or, $k \geq 4$ a.u.) of the absorption edge by

$$\left| \langle f_N | \sum_{j=1}^N \vec{r}_j | i_N \rangle \right|^2 \cong |\langle k \, | \, \vec{r} \, | K \rangle|^2 \, |\langle \Phi'_{N-1} | \Phi_{N-1} \rangle|^2, \tag{4}$$

where $\langle k \, | \, \vec{r} \, | K \rangle$ is the one-electron transition element between a core state $|K\rangle$ and an emitted electron state $|k\rangle$ with wave number $k$, $|k\rangle = |\phi_f + \delta\phi_f\rangle$; and $\langle \Phi'_{N-1} | \Phi_{N-1} \rangle$ is an $N-1$ electron overlap integral between the *passive* electrons in the initial and relaxed final states. The overlap factor,

$$S_0^2 \equiv |\langle \Phi'_{N-1} | \Phi_{N-1} \rangle|^2, \tag{5}$$

arises because the passive electrons in the initial and final states of the system "see" different potentials. This factor is roughly the product of $N-1$ single-particle overlap integrals, so that the net overlap may be significantly less than 1. It has the simple physical interpretation of being the fraction of the total absorption strength which goes into the primary channel. Below 200 eV, corrections to Eq. (4) become important,[8] and a picture as simple as the one described above does not appear to be possible.

The theory developed so far suggests that about 200 eV beyond threshold, the EXAFS as calculated in a single-channel theory including relaxation should be reduced by a *constant* factor of $S_0^2$. In particular, the single-particle transition element could be calculated as in conventional theories,[1,2] including an *ad hoc* factor $e^{-\gamma R}$, which accounts for the lifetime of the final state, and a Debye-Waller factor $e^{-2\sigma^2 k^2}$, for vibrational effects. However, the possibility of molecular charge transfer is an important consideration in calculations of the continuum function. More refined treatments would include a better treatment of lifetime[6] and other effects that determine the width of a given channel. Note that this theory implicitly ignores contributions to EXAFS from the multielectron processes which occur with probability $1 - S_0^2$ (as will be discussed in Sec. III).

Hartree-Fock-Roothaan $\Delta$ self-consistent field (SCF) calculations, as detailed in Ref. 5, give values for $S_0^2$ of 0.68, 0.72, and 0.72, for the diatomic molecules $F_2$, $Cl_2$, and $Br_2$, respectively. These numbers are comparable to, but somewhat larger than the value 0.58 calculated by Bagus *et al.*[9] for $O_2^+$, indicating the importance of overall molecular structure. Since we assume that Hartree-Fock calculations may overestimate the actual reduction factor by $(4-12)\%$ as they do in inert gas atoms,[10] our estimates for the total reduction factor in $F_2$, $Cl_2$, and $Br_2$ are 0.60, 0.64, and 0.64, $\pm 0.04$, respectively, which is in accord with the empirical factor of 0.62 used by Lee and Beni to match experimental results for $Br_2$.

By comparison, similar $\Delta$ SCF calculations (plus our estimate for correlation effects) for the free F, Cl, and Br *atoms* give reduction factors of 0.74, 0.71, and $0.72 \pm 0.04$, respectively. The substantially smaller overlap factor in the molecules is due to extra-atomic relaxation: In an atom the passive electrons can only relax inward following $K$ excitation, thus decreasing the overlap somewhat but leaving the net atomic charge fixed. In $F_2$, $Cl_2$, and $Br_2$, however, the valence molecular orbitals can relax substantially, and

the natural tendency is to *transfer* charge to the atom with the $K$ hole. Examination of the molecular orbitals contributing to $S_0^2$ shows that this molecular charge transfer roughly accounts for the additional (7–14%) reduction. This implies that EXAFS amplitudes may be strongly dependent on the local chemical environment and suggests a way of interpreting amplitude differences in terms of charge transfer. For example, in KBr, the electrons surrounding the $K^+$ ion are in an inert gas configuration, and one would expect relatively little charge transfer to accompany $K$ excitations of the $Br^-$ ion. Thus, we expect a reduction factor for KBr to be more like that of a Br atom. In more general molecular (or condensed matter) environments, the above argument can be made semiquantitative by considering the electronegativities of the molecular constituents.[11]

## III. EXAFS FROM MULTIPLE-ELECTRON EXCITATIONS

It is far from obvious that the EXAFS should simply be reduced by the overlap factor $S_0^2$. In the usual definition of the normalized EXAFS spectra [Eq. (1)], one divides by the average absorption at each energy, so it might appear that the overlap factor simply cancels out. This would be the case if only the primary channel contributed to x-ray absorption. However, this cancellation is ruled out by the sum rule on the total absorption integrated over all energies, which implies that multiple-electron excitations must also contribute to x-ray absorption. Furthermore, this raises the possibility that multiple excitations also contribute to EXAFS.

In consideration of this possibility, let us write the total absorption coefficient [see Eqs. (2) and (4)] in terms of contributions from individual channels, each representing a particular final ionic state labeled by a "channel index $n$":

$$\mu \sim \omega^3 \sum_n |\langle k_n | \vec{r} | K \rangle|^2 S_n^2 , \qquad (6)$$

where $S_n^2$ is defined in a manner similar to Eq. (5). Thus, each channel contributes to the total absorption with a different overlap factor $S_n^2$ and with a somewhat modified transition element. By unitarity the sum of the weights $S_n^2$ is unity, and in principle they may be determined empirically from photoemission experiments. If we approximate the single-particle transition element as

$$\omega^3 |\langle k_n | \vec{r} | K \rangle|^2 \cong M_0^2 (1 + \chi_n), \qquad (7)$$

where $\chi_n$ takes into account the backscattering from neighboring atoms, we deduce from Eq. (1) that the

total normalized EXAFS spectra $\chi$ is given by

$$\chi \cong \sum_n S_n^2 \chi_n. \qquad (8)$$

Thus, each channel gives rise to its own oscillatory structure of amplitude $S_n^2$, which may be phase shifted from the "primary" term. Equation (8) is presumably valid only beyond roughly 200 eV of each threshold; however, we may expect a similar expression to hold at *any* energy, with $S_n^2$ simply replaced by the probability of excitation into channel $n$ at *that energy*, which we shall denote by $\tilde{S}_n^2$.[12]

In order to estimate the contribution to the EXAFS from a given channel $\chi_n$, several important effects on the single-electron matrix element must be considered. First, because in an inelastic channel the ionized molecule is left in an excited state, the kinetic energy of the ejected electron must be reduced by the excitation energy, $\Delta E_n$. Second, the effective one-electron potential differs from one channel to another, so there will be a corresponding phase shift $\delta_n$ in the outgoing wave function of the emitted electron. Other factors (for example, the lifetime, the Debye-Waller factor, etc.) may also change significantly from one channel to the next.

The main effect of the excitation energy, other things being equal, is to shift the zero of energy (or phase) of the EXAFS oscillations by an amount $\Delta E_n$:

$$\chi_n(k) \cong \chi_0(k^2 - 2\Delta E_n)^{1/2}. \qquad (9)$$

Here $\chi_0(k)$ represents the EXAFS in the primary channel, which is conventionally written as[1,2]

$$\chi_0(k) \cong \sum_R \frac{|f_k|}{kR^2} \sin[2kR + 2\delta_0(k)] e^{-\gamma R - 2\sigma^2 k^2}, \qquad (10)$$

where $|f_k|$ is the backscattering amplitude, $R$ is a near-neighbor distance, and $\delta_0(k)$ an appropriate phase shift.

The excitation energies for the diatomic molecule $Br_2$ are illustrated schematically in Fig. 1. In arriving at Fig. 1, we have modeled the spectrum by comparison with the shake-up, shake-off spectrum for Ne,[13] with several parameters chosen to be appropriate for $Br_2$. The $\delta$ functions at 15, 20, and 40 eV represent, respectively, a low-energy satellite, a Rydberg series of shake-up states, and the onset of double electron shake-up. The shake-off spectrum was assumed to have an exponential form beginning at 20 eV with about 25% of the total shake-off intensity in multiple-electron shake-off beginning at 40 eV. Relative intensities were chosen by rough calculation (primary peak and satellite) and by comparison with
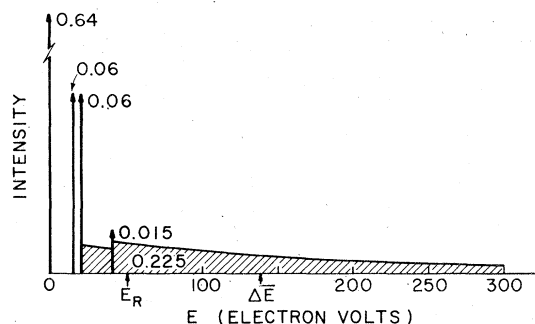
FIG. 1. Model $Br_2$ shake-up, shake-off spectrum (see text). All shake-up channels have been lumped into $\delta$ functions at 15, 20, and (multiple shake-up) 40 eV; the shake-off (and multiple shake-off) spectra were taken to be exponential beginning at 20 (and 40) eV beyond the primary peak. Relative intensities are indicated in the figure. The centroid of the shake-up, shake-off part of the spectrum is at $\Delta \bar{E}$; that of the entire excitation spectrum is at $E_R$.

the spectrum for Ne. At low primary electron energies, we would expect substantial modifications to occur. The average excitation energy,

$$\Delta \bar{E} = \sum_{n=1}^{\infty} \frac{S_n^2 \Delta E_n}{1 - S_0^2} \qquad (11)$$

is estimated to be 139 eV beyond the primary peak based on a numerical calculation[5] of the relaxation energy $\Delta E_R = \langle \Phi'_{N-1} | H | \Phi'_{N-1} \rangle$ $- \langle \Phi_{N-1} | H | \Phi_{N-1} \rangle \cong 50.2$ eV, and a simple argument due to Manne and Aberg[14] that $\Delta \bar{E} = \Delta E_R / (1 - S_0^2)$. The strong "satellite" at 15 eV corresponds to the molecular charge transfer transition $\sigma \rightarrow \sigma^*$.

Next we estimate the additional phase shift in a multielectron excitation. Consider, for example, one of the "Rydberg" series of shake-up processes, in which one unit of electron charge is moved, say, from a $4p$ to a $5p$ orbital. This charge redistribution acts roughly as a dipole-layer, so that the potential shift relative to the unexcited ion may be crudely approximated as an *attractive* square well of depth of the order of $\Delta E_n$, and radius $R_n$ of the order of an atomic radius. From the generalized Born approximation,[15] this potential gives rise to the relative phase shift

$$\delta_n - \delta_0 \sim (\Delta E_n / k) R_n. \qquad (12)$$

From Eq. (10) it is seen that such a phase shift has an effect on $\chi$ similar to that from the energy shift, but *smaller* by a factor of $R_n / R < 1$. This argument also applies to molecular shake-up channels, such as the strong $\sigma \rightarrow \sigma^*$ satellite, in which charge is transferred away from the atom with the $K$ hole. These estimates indicate that this phase shift is important, but may be taken into account by shifting the excitation energies somewhat.

An accurate calculation of the relative phase shift in Eq. (12) depends on both $\delta_n$ and $\delta_0$, and there can be substantial chemical effects on both quantities. In particular, our discussion of molecular charge transfer (Sec. II) indicates that the atom containing the $K$ hole in the $Br_2^+$ "ground state" (primary channel) is largely screened by a transferred valence electron. This implies a negative phase shift in the primary channel (relative to an unscreened ion) which is comparable to that in Eq. (12), corresponding to an energy shift of several eV.

An estimate of the other parameters shows them to be comparatively unimportant. In one study[13] the widths of the shake-up peaks were about 1.5 times that in the primary channel, but this will not change the decay factor $e^{-\gamma R}$ for the other channels by more than a few percent in $Br_2$. Weaker bonding in the excited molecular states would change the mean internuclear distance $R$; however, the lifetime of the excited photoelectron state is too short for the nuclear positions to relax. Thus, values for the distance $R$ and rms fluctuation $\sigma$ must be taken as those for the unexcited ground state of the system.

In summary, the total EXAFS from all channels may be obtained by performing a *phasor summation* of the individual channel contributions [Eqs. (8)–(10)]. For purposes of illustration we have performed this summation for our model shake-up, shake-off spectra for $Br_2$ (Fig. 1). For each wave number $k$ (primary channel) we used phasors of relative weights $\tilde{S}_n^2$ as determined by including all multiple excitations in the shake-up, shake-off spectrum $I(k)$, with $k_n < k$

$$\tilde{S}_n^2(k_n) = I(k_n) \Delta k \Big/ \int_0^k I(k) \, dk, \qquad (13)$$

and relative phases $\Phi_n(k_n)$ given by

$$\Phi_n(k_n) \cong 2R \left[ (k^2 - 2\Delta E_n)^{1/2} - k \right], \qquad (14)$$

where $R \cong 4.31 a_0$ is the $Br_2$ nearest-neighbor distance. Thus, we have ignored all effects other than the energy shift in this calculation. After performing the phasor summation, the net EXAFS spectrum can be recast into the conventional form, multiplied by an energy-dependent reduction factor $|A(k)|$ and phase shifted by $\Phi(k)$:

$$\chi = \sum_R |A(k)| \frac{|f_k|}{kR^2}$$
$$\times \sin[2kR + 2\delta_0(k) + \Phi(k)] \exp(-\gamma R - 2\sigma^2 k^2), \qquad (15)$$

where the reduction factor[16] is given by

$$A(k) \equiv |A(k)| e^{i\Phi(k)} = \sum_n \tilde{S}_n^2 e^{i\Phi_n(k)}. \qquad (16)$$
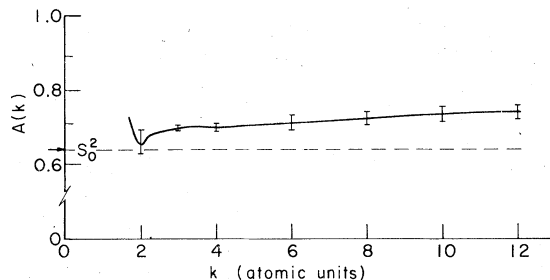
FIG. 2. EXAFS amplitude reduction factor $A(k)$, as computed from Eq. (16) with the model shake-up, shake-off spectrum for $Br_2$. The "error bars" indicate the variation in $A(k)$ with a change of $\pm 2\%$ in the 15-eV satellite intensity: The primary channel value is $S_0^2 = 0.64 \pm 0.04$.

The results are plotted in Fig. 2. Remarkably, the reduction factor is roughly constant at about $0.7 \pm 0.04$ in the experimental range of interest $2 < k < 10$. Since $S_0^2 = 0.64$, $\pm 0.04$ the agreement with experiment is not so good as appeared to be the case when only the primary channel was considered, though part of the discrepancy may be due to approximations in evaluating the one-electron transition element. In any case, the calculation indicates that the multiple-electron excitations constitute a non-negligible 10% fraction of the total EXAFS, and that most of the contribution comes from the low-energy excitations which add nearly coherently. The net phase shift $\Phi(k)$ was about $-9°$. Finally, note that for very large energies, $k \gg 2\Delta\overline{E}R$, all channels must add coherently! For $\Delta\overline{E} \cong 140$ eV, this corresponds to $k \gg 40$ (i.e., 20 keV), well outside the experimental range and unobservable for any reasonable value of the Debye-Waller factor.

## IV. DISCUSSION

We have developed a theory for the reduction in EXAFS amplitudes based upon wave-function relaxation accompanying photoemission. In this theory the total EXAFS is given by a phasor summation of contributions from each possible final ionic channel. The dominant term comes from the primary channel and is given by the fraction of single-electron excitations. Above about 200 eV from threshold, this fraction is reduced from unity (as in a one-electron theory) by the square of a many-electron overlap integral $S_0^2$, which we have estimated to be 0.60, 0.64, and $0.64 \pm 0.04$ for $F_2$, $Cl_2$, and $Br_2$, respectively. Retaining only the primary channel yields reasonably good agreement with the observed discrepancy between one-electron theory calculations and experiment,

for which the reduction factor[6] is about 0.62 for $Br_2$. This also gives one possible explanation for the constancy of the reduction factor.

However, we have found no compelling argument for ignoring the possible contributions from the multielectron excitations. A proper calculation of the contributions from the multiexcitation channels requires knowledge of the shake-up, shake-off spectrum for $Br_2$, together with the dependence of the phase shift and final-state width on the form of the final ionic state. The contributions from these channels was estimated from a representative shake-up, shake-off spectrum constructed so as to fit a few known parameters for $Br_2$ (Fig. 1). This calculation indicates that the multiexcitation channels add, predominantly, incoherently over the experimental range of interest $2 < k < 10$ (atomic units). The net contribution from all multiexcitation channels (Fig. 2) was found to be about 10% of the contribution from the primary channel. Most of this 10% is due to the low-energy satellite and the shake-up excitations in the $Br_2$ spectrum. While these conclusions are based on a spectrum which is only semiquantitatively correct, our calculations prove to be sensitive only to the intensities of the low-energy satellite and shake-up peaks; the "error bars" in Fig. 2 indicate the variation in the amplitude reduction factor brought about by a change of $\pm 2\%$ in the intensity assigned to the 15-eV satellite. Thus, we would not expect a more realistic spectrum to alter our conclusions substantially.

Finally, we emphasize that the reduction factors calculated in this theory are quite sensitive to the nature of the local chemical environment. In the diatomic molecules treated here, charge transfer to the atom with the core-hole reduces the amplitude reduction factor by (7–14)% relative to that in free (or unscreened) atoms. Furthermore, this charge transfer alters the potential seen by the photoelectron and hence its phase shift. Thus, calculations of EXAFS, both amplitude and phase, based on models with independent scattering centers may not be adequate. This implies that the determination of both coordination numbers and internuclear distances from EXAFS is dependent on the local chemical environment, and that transferability of amplitudes and phase shifts from one system to another cannot always be taken for granted.

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