

Multiple-electron excitation in X-ray absorption: a simple generic model. Erratum

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Two typographical errors have been observed in the paper by Roy *et al.* [*J. Synchrotron Rad.* (2001), **8**, 1103–1108]. Equation (16) should read

$$P(\hbar\omega) = P(\infty) \left[\frac{\pi(2n-1)!}{2^{2n}(n-1)!(n+1)!} \right]^{-1} E_B^{n+1/2} \times \int_0^{E_{\max}} \frac{E^{1/2}}{(E_B + E)^{n+2} [1 + t_o^2 (E_B + E)^2]} dE,$$

while the correct form of equation (18) is

$$P(\hbar\omega) = P(\infty) \left[\frac{\pi(2n-1)!}{2^{2n}(n-1)!(n+1)!} \right]^{-1} \times \int_1^{E_p/E_B} \frac{(X-1)^{1/2}}{X^{n+2} [1 + \frac{1}{4}(n-1)^2 (E_B/E_p) X^2]} dX.$$

These typographical errors do not affect our results or conclusions.

References

Roy, M., Lindsay, J. D., Louch, S. & Gurman, S. J. (2001). *J. Synchrotron Rad.* **8**, 1103–1108.

XAFS studies of nitrogenase: the MoFe and VFe proteins and the use of crystallographic coordinates in three-dimensional EXAFS data analysis. Erratum

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One of the authors was omitted in the published version of the paper by Strange *et al.* [*J. Synchrotron Rad.* (2002), **10**, 71–75]. The full author list is given above. Since the acceptance of our paper, an atomic-resolution (1.16 Å) structure of MoFe-protein has emerged [Einsle *et al.* (2002), *Science*, **297**, 1696–1700]. We take this opportunity to update Table 1 of the paper, demonstrating improved agreement of the three-dimensional XAFS refinement with atomic-resolution metrical information.

Table 1

Constrained refinements of the Mo *K*-edge EXAFS using a three-dimensional refinement approach.

In the first refinement, distances are kept at crystallographic values and Debye–Waller (σ^2) values are refined; in the second refinement, the distances are also allowed to vary. A higher value than 0.03 Å² signifies that the atom is incorrectly placed and that little contribution to the EXAFS signal is made. ΔR is the difference in Mo–ligand distance from the crystallographic value averaged over the two independent $\alpha\beta$ units. The final column includes information from a 1.16 Å structure (Einsle *et al.*, 2002).

Ligand	First refinement		Second refinement		ΔR (Å)	1.16 Å structure (Å)
	R (Å)	σ^2 (Å ²)	R (Å)	σ^2 (Å ²)		
Mo–N(His)	2.48	0.11	2.29	0.003	–0.17	2.29
Mo–O5(homocitrate)	2.29	0.11	2.14	0.001	–0.16	2.18
Mo–O7(homocitrate)	2.35	0.11	2.31	0.001	–0.04	2.20
Mo–S1B	2.30	0.001	2.30	0.001	0.0	2.33
Mo–S3B	2.38	0.001	2.37	0.001	–0.01	2.37
Mo–S4B	2.35	0.001	2.35	0.001	0.00	2.33
Mo–Fe7	2.67	0.006	2.67	0.006	0.00	2.67
Mo–Fe6	2.68	0.006	2.67	0.006	–0.01	2.67
Mo–Fe5	2.71	0.006	2.71	0.006	0.00	2.73
Mo–Fe2	5.04	0.01	5.04	0.01	0.00	5.04
Mo–Fe3	5.06	0.01	5.06	0.01	0.00	5.05
Mo–Fe4	5.09	0.01	5.08	0.01	–0.01	5.10
Fit index		12.4		9.5		
<i>R</i> factor	46%		37%			

References

Einsle, O., Tezcan, A., Andrade, S. L. A., Schmid, B., Yoshida, M., Howard, J. B. & Rees, D. C. (2002). *Science*, **297**, 1696–1700.
Strange, R. W., Eady, R. R., Lawson, D. & Hasnain, S. S. (2003). *J. Synchrotron Rad.* **10**, 71–75.

Multiple-electron excitation in X-ray absorption: a simple generic model

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The probability of multiple-electron excitation in X-ray absorption is calculated using a simple generic model. The model permits calculations to be made for all atoms with little input data or computing effort. The high-energy limit of this probability, which gives the usual EXAFS amplitude reduction factor, is calculated in the ‘sudden approximation’ using Slater orbitals. Good agreement with experiment is found. The energy dependence of this probability is also calculated using a simple model form of perturbing potential and found to agree well with experiment for rare gas atoms. The effect on the X-ray absorption coefficient of including multiple-electron excitations is also determined and is found to be small, again in agreement with observation.

Keywords: X-ray absorption; EXAFS; many-body theory.

1. Introduction

The theory of X-ray absorption is usually described in one-electron terms. This theory gives very good results for the X-ray absorption coefficient (Gurman, 1983). A one-electron theory also gives good results for the extended X-ray absorption fine structure (EXAFS), except for the amplitude. However, it is known from studies on the noble gases (*e.g.* Bartlett *et al.*, 1992) that 20–30% of X-ray absorption processes give rise to multiple-electron excitation. This value is in line with the empirical amplitude reduction factor applied in early EXAFS analyses. In order to describe such processes, and so obtain a correct value for the EXAFS amplitude, we need to use a many-body theory. Such theories are complicated and computationally intensive. We describe here a simple model which correctly gives the multiple-excitation probability (and hence the EXAFS amplitude reduction factor) as a function of photon energy for all atoms with very little computational effort. We also show why the X-ray absorption coefficient is only very slightly altered by the inclusion of these many-body effects, despite the high probability of multiple-electron excitation.

In EXAFS studies, multiple-electron excitation on X-ray absorption (intrinsic losses) is not the only loss process which needs to be considered. There are also the extrinsic losses suffered by the photoelectron during its passage through the material. These are usually described in terms of a mean-free-path factor. We do not consider such losses here. Strictly, the intrinsic and extrinsic losses cannot be separated in this simple way, since they may interfere with one another. This interference is significant at low photoelectron energies (Hedin, 1989). Since it treats only the intrinsic losses, our theory completely neglects these interference processes.

We first consider multiple-electron excitation in the limit of high photon energy, where we use the ‘sudden approximation’ (Schiff, 1968). We need a form for the one-electron wavefunctions of all atomic states and use the Slater form [the single zeta functions of Clementi & Roetti (1974), which are themselves fitted to Hartree–Fock wavefunctions]. The screening parameters which appear in

these wavefunctions are obtained using a modified form of Slater’s rules. Thus we obtain an accurate representation of the atomic wavefunctions without the need for large amounts of input data. The results of the sudden approximation are compared with the values of the EXAFS amplitude reduction factor S_0^2 derived from many EXAFS analyses.

We go on to consider the energy dependence of the multiple-electron excitation probability, using a development of the model proposed by Thomas (1984). We find that an analytic expression for the energy-dependent probability can be obtained which is in good agreement with experimental data from rare gases. This form provides an energy-dependent form for S_0^2 which could be used in EXAFS analysis to avoid the need for calculations using a complex potential.

Finally, we calculate the X-ray absorption coefficient itself, including multiple-electron excitations, and show why these do not greatly alter the results obtained, again in agreement with experiment.

We therefore obtain a model description of multiple-electron processes in X-ray absorption which involves very little computing or input data and which provides an accurate description of the observed phenomena.

2. The high-energy limit

2.1. The sudden approximation

When an atom absorbs an X-ray photon, a photoelectron and a hole in a deep core state are produced. The core-hole/photoelectron system corresponds to a time-dependent change in potential that is, in general, extremely complex. This more general case is considered in the next section. We first consider the limit of extremely high photon energies. In this limit, the photoelectron has a very high kinetic energy and leaves the atom very rapidly. The other electrons, which we shall refer to as passive electrons, then relax under the influence of the core-hole potential alone. Within this approximation, the passive electrons experience an abrupt change in Hamiltonian so that there is a possibility that they too may be excited into the continuum (we neglect the very weak bound–bound transitions) giving rise to a multiple-electron excitation. The effect of the core-hole potential on these electrons can be described in terms of the sudden approximation (Schiff, 1968).

We describe the wavefunction of the electrons in the atom in Hartree form, as a single product of one-electron wavefunctions. Within the sudden approximation, the boundary condition is that the wavefunction shall be continuous across the abrupt change in Hamiltonian. The probability that a given passive electron is then *not* excited is given by

$$P_i = |\langle \psi_i | \psi'_i \rangle|^2, \quad (1)$$

where the unprimed wavefunctions relate to the unperturbed atom and the primed wavefunctions to the atom with a core hole present. The probability that *no* passive electrons are excited is then the product of such terms over all passive electrons. This is the probability that only one photoelectron is produced. The theory of EXAFS (Stern, 1988) shows that this is equal to S_0^2 , the amplitude reduction factor for EXAFS. Thus we have

$$S_0^2 = \prod_i |\langle \psi_i | \psi'_i \rangle|^2, \quad (2)$$

and $1 - S_0^2$ is equal to the probability of a multiple-electron excitation occurring. This expression for S_0^2 was first obtained by Rehr *et al.* (1978). The proportion of multiple-electron events can be measured

from the charge distribution of the ions produced by photoionization (e.g. Carlson *et al.*, 1968). The EXAFS amplitude reduction factor for very many atoms can be obtained from the many early EXAFS analyses, where this parameter had to be fitted to data obtained from a standard sample with known coordination number (usually a metal foil).

2.2. Wavefunctions

In order to be able to calculate the multiple-electron probability we need to know the form of the atomic wavefunctions. Accurate wavefunctions are available, derived from self-consistent Hartree–Fock calculations (Clementi & Roetti, 1974). In order to obtain a generic form, we use wavefunctions of the Slater type, fitted to these accurate wavefunctions. These are the single zeta functions of Clementi & Roetti (1974). Thus we have

$$\psi = \frac{(2\zeta)^{n+1/2}}{(2n!)^{1/2}} r^{n-1} \exp(-\zeta r) Y_{lm}. \quad (3)$$

The quantity ζ which appears in these wavefunctions can be written in terms of a screening factor σ ,

$$\zeta = (Z - \sigma)/n, \quad (4)$$

where we use atomic units, such that r is given in terms of the Bohr radius. The values of σ , obtained from the tables of Clementi & Roetti (1974), can be fitted by a modified version of Slater's rules. In this way we obtain a generic form for the wavefunctions of all electrons in all atoms. Our modification of Slater's rules is described in Appendix A: they give a good fit to the tabulated zeta values and so give good wavefunctions for the calculation of multiple-electron excitation probabilities in the high-energy limit.

The Slater wavefunctions give, for the probability of a given passive electron remaining unexcited, the expression

$$P_i = (4\zeta\zeta')^{2n+1} / (\zeta + \zeta')^{4n+2}, \quad (5)$$

where, once again, unprimed values relate to the unperturbed atom and primed values to the atom with a core hole present. Since the perturbation is due to a deep core hole, Slater's rules give

$$\sigma' = \sigma + 1, \quad (6)$$

unless the passive electron state is either below, the same as or next above the core-hole state. For hard X-ray excitation, none of these conditions apply for passive electrons which have an appreciable probability of excitation. Thus equation (6) corresponds to the commonly used $Z + 1$ approximation for the relaxed final states used when calculating atomic scattering factors in EXAFS.

ζ is fairly large for all atomic states. Thus we can approximate the result given in (5) to give

$$P_i = 1 - \frac{2n + 1}{4n^2\zeta^2}. \quad (7)$$

Since the energy E_i of the state is approximately given by the square of ζ (in atomic units) we see that the probability of excitation of a passive electron falls off roughly as E_i^{-1} . Thus only weakly bound passive electrons are likely to be excited, as we would expect. We actually use the full form, equation (5), in our calculations.

We note that our calculation is appropriate to an isolated atom in that we take the atomic states to be discrete levels. We can extend the calculation to include bonding effects in the tight-binding approximation (Roy, 1999). For full bands this extended calculation gives the same results as the atomic calculation, while for partially filled bands

the correction is always less than 10% (Roy *et al.*, 1997). Thus we use the simpler atomic calculations in our comparison with EXAFS data.

2.3. The EXAFS amplitude reduction factor

We may compare our results with experiment in the form of the EXAFS amplitude reduction factor S_0^2 , which is assumed to be energy independent, or the high-energy limit of ion charge data in photoionization.

First of all we note that the amplitude reduction factor will be very similar for K and L edges of the same element, since it only differs in the two cases by the excitation probability of the $1s$ state, which is very small for X-ray photons.

Using the modified Slater's rules to obtain ζ and ζ' we can easily calculate P for any orbital and S_0^2 for any atom, using equations (2) and (5). The values of S_0^2 obtained in this way are shown in Fig. 1. The calculated amplitude reduction factor has a characteristic dependence on atomic number, essentially following the ionization potential as we argued it would following equation (7). For $Z > 10$, the region of interest for EXAFS, it lies between 0.65 and 0.80. Our calculated values for S_0^2 are very similar to those calculated (Roy *et al.*, 1997) using the full tabulated wavefunctions of Clementi & Roetti (1974). Thus it appears that the Slater wavefunctions, fitted to the single zeta function approximations of these wavefunctions, give a sufficiently accurate form for the wavefunction.

Fig. 1 also shows values of the amplitude reduction factor obtained from many EXAFS data analyses (Roy *et al.*, 1997) which used the real $X\alpha$ scattering potential (and hence required empirical amplitude factors) in early versions of the data-analysis program *EXCURV*. Also shown on Fig. 1 are the results obtained by Carlson (1967) using Hartree–Fock wavefunctions and some data from ion charge measurements (Carlson *et al.*, 1968; Holland *et al.*, 1979; Armen *et al.*, 1985; Bartlett *et al.*, 1992). We note that our results are in fairly good agreement with the full calculation and essentially always agree with experiment to within the experimental uncertainties. The poorest agreement occurs for the $3d$ and $4d$ elements: we believe this is due to the lower accuracy of the single zeta form for these orbitals, which have two large components in their full form (Clementi & Roetti,

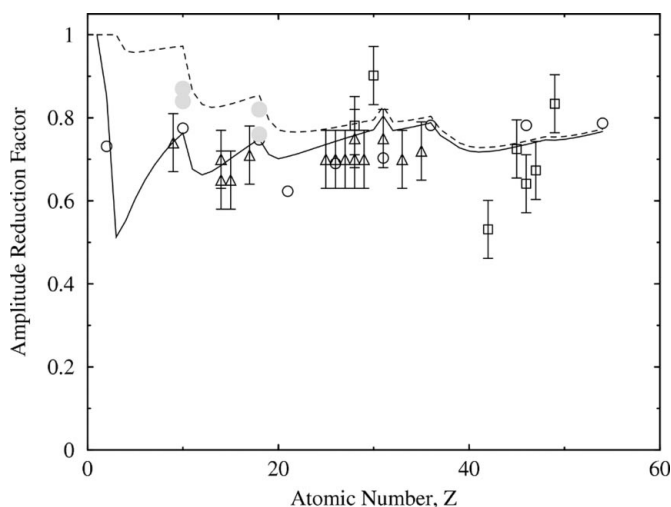


Figure 1 High-energy limit of multiple-electron excitation probability. Solid line: calculated values for the K edge. Dashed line: calculated values for the L_3 edge. Points: calculated values from Carlson *et al.* (1968). Points with error bars: experimental data from K -edge EXAFS fits (S_0^2). Large points: experimental data from ion charge measurements.

1974). There is also a problem when the hole is located in the outermost orbital (*e.g.* Ne L edge). This is due to electron correlation and occurs in all calculations. It is of no significance for X-ray studies, but is rather a problem for UV photoemission.

Thus we conclude that we can successfully model the high-energy limit of the multiple-electron excitation probability in a way which requires little input data or computing.

3. The energy dependence of the multiple-electron excitation probability

In the previous section the sudden approximation was used to calculate the multiple-electron excitation probability in the limit of extremely high photon energies. In this section we consider the photon energy dependence of this probability. The core-hole/photoelectron system is considered using a spatially and temporally varying model potential and analyzed using standard time-dependent perturbation theory. The temporal variation of the perturbation arises because the photoelectron takes a finite time to leave the atom, this time depending on the size of the atom and the energy of the photoelectron. This gives rise to an energy dependence of the excitation probability. At very high photoelectron energies, the results of this calculation should tend to those found using the sudden approximation, and we use this to normalize our results, so avoiding much computation.

The problem of multiple-electron excitation in photoionization has been studied by many authors. Most of these calculations are extremely complex (*e.g.* Chang & Poe, 1975; Carter & Kelly, 1977) and computationally intensive. They also require much input data. Here we seek a simple model which will describe the energy dependence of the multiple electron probability with reasonable accuracy and with little input or computation. Such a model has been described in outline by Thomas (1984) and we use this as the basis of our work.

Following Gadzuk & Sunjic (1975), we first approximate the time- and position-dependent perturbation $V(r, t)$ due to the core-hole/photoelectron system as a product of time-dependent and position-dependent parts,

$$V(r, t) = V(r)f(t), \quad (8)$$

with a time dependence of the form

$$f(t) = 1 - \exp(-t/t_0). \quad (9)$$

t_0 is a characteristic time which we write as

$$t_0 = R/v, \quad (10)$$

where R is a characteristic distance in the atom and represents the size of the orbital of the passive electron; v is the speed of the photoelectron. With this form, the passive electron sees the full core-hole potential $V(r)$ as $t \rightarrow \infty$, when the photoelectron has left the atom.

Time-dependent perturbation theory gives the probability amplitude of a passive electron being excited from an atomic orbital $|i\rangle$ to a propagating state $|k\rangle$ due to the perturbation $V(r, t)$ as

$$a_{ik} = \langle i|V(r)|k\rangle \int_0^\infty \exp[i(E_i - E_k)t] f(t) dt. \quad (11)$$

Using the form of perturbation given above we can evaluate the integral if we include a convergence factor $\exp(-\delta t)$ in $V(r, t)$. This convergence factor physically represents the finite core-hole lifetime. We then find a transition probability

$$|a_{ik}|^2 = \frac{|\langle i|V|k\rangle|^2}{(E_i - E_k)^2 [1 + t_0^2(E_i - E_k)^2]}. \quad (12)$$

In order to obtain the total excitation probability we must sum over all final states which are accessible, *i.e.* which obey energy conservation. Replacing the sum by an integral and introducing a density of final states we find a total probability

$$P(\hbar\omega) = A \int_0^{E_{\max}} E^{1/2} \frac{|\langle i|V|k\rangle|^2}{(E_B + E)^2 [1 + t_0^2(E_B + E)^2]} dE, \quad (13)$$

with E the energy of the final state $|k\rangle$ and E_B the (positive) binding energy of the initial passive electron state $|i\rangle$. E_{\max} is given by energy conservation as $E_p - E_B$, where E_p is the energy of the primary photoelectron, equal to $\hbar\omega - E_{\text{edge}}$. The factor A includes all the constants.

We use the Slater orbitals as our initial states $|i\rangle$ and propagating spherical waves (free electron approximation) normalized to unit amplitude as the final states $|k\rangle$. Taking the core-hole potential as a Coulomb potential we then find

$$|\langle i|V|k\rangle|^2 = B/(k^2 + \zeta^2)^n = B'/(E + E_B)^n, \quad (14)$$

with B and B' constants. The second form of equation (14) is obtained by replacing $k^2/2$ by the final-state energy E (we use atomic units) and $\zeta^2/2$ by the binding energy of the initial state E_B . When we substitute this form into equation (13) the total excitation probability is given by

$$P(\hbar\omega) = A' \int_0^{E_{\max}} \frac{E^{1/2}}{(E_B + E)^{n+2} [1 + t_0^2(E_B + E)^2]} dE. \quad (15)$$

In the high-energy limit, $t_0 \rightarrow 0$ since the velocity of the photoelectron $v \rightarrow \infty$. The integral can then be performed at once (Gradshteyn & Ryzhik, 1980; 3.241.4). Setting the excitation probability to $P(\infty)$ in this limit gives us

$$P(\hbar\omega) = P(\infty) \left[\frac{\pi(2n-1)!}{2^{2n}(n-1)!(n+1)!} \right] E_B^{n+1/2} \times \int_0^{E_{\max}} \frac{E^{1/2}}{(E_B + E)^{n+2} [1 + t_0^2(E_B + E)^2]} dE. \quad (16)$$

$P(\infty)$ is known from the results of the sudden approximation. Thus we have only to evaluate the remaining integral. It is this normalization to the high-energy limit which produces much of the simplicity of our final result.

Equation (16) is obtained using an atomic calculation, with the initial state of the passive electron an atomic level, not a band. As we noted in the previous section, full bands give the same result as atomic levels in the high-energy limit, with partially filled bands changing the result by less than 10%. The integral of (16) remains finite as E_B goes to zero (as occurs when the passive electron lies at the Fermi level) so, at worst, including bonding effects (which will involve an integral over E_B) will only alter the energy dependence of $P(\hbar\omega)$. Such effects are expected to be small (Roy *et al.*, 1997) and so we continue to use the simpler atomic calculation.

t_0 is given by equation (10). We fix R as the radius at which the charge density $|\psi|^2$ peaks, which is easily evaluated using the Slater form. We also calculate the speed of the photoelectron from its kinetic energy. Thus we find

$$t_0^2 = \left(\frac{n-1}{2} \right)^2 \frac{1}{E_B E_p}. \quad (17)$$

We substitute this expression into (16) and scale the integration variable by E_B to obtain a dimensionless integral. Thus our final

result for the probability of exciting a passive photoelectron with a photon of energy $\hbar\omega$ is

$$P(\hbar\omega) = P(\infty) \left[\frac{\pi(2n-1)!}{2^{2n}(n-1)!(n+1)!} \right] \times \int_1^{E_p/E_B} \frac{(X-1)^{1/2}}{X^{n+2} \{1 + [(2n+1)/4]^2 (E_B/E_p) X^2\}} dX. \quad (18)$$

We note that no passive electron can be excited until the energy of the primary photoelectron is greater than its binding energy, as seems reasonable. Thus no secondary electrons are excited until an energy E_B above the absorption edge.

The integral may be evaluated analytically [by splitting it into partial fractions and using Gradshteyn & Ryzhik (1980); 2.216 and 2.225], giving a result in terms of the photon energy and the binding energies of the core hole and the passive electron. We therefore obtain a general result for the multiple-electron excitation probability which involves very little computation or input data. We can compare the predictions of this model with experimental data obtained for rare gases: we do this below. The result also gives the energy-dependent EXAFS amplitude reduction factor which could be used in data analysis. We also note that equation (18) gives P as a function of two parameters, the ratio E_p/E_B , the ratio of the primary photoelectron energy to the binding energy of the passive electron, and n , the principal quantum number of the passive electron orbital. We can therefore plot a canonical form for P as a function of these two variables. This is shown in Fig. 2. We note that P has reached essentially its high-energy limit by a few times E_B above the edge, rising somewhat more slowly for higher values of n . Since only the outermost electrons give a significant contribution to the total multiple electron probability, this means that the EXAFS amplitude reduction factor will reach its full value within a few tens of eV above the edge, with a slower rise for heavier atoms. The rapid rise accounts for the success of simple analyses made using a constant value for the reduction factor.

The results shown in Fig. 2 depend on our value for t_0 , *i.e.* the value we take for R . Values other than the one we use could be tried. However, they all give a very similar form for P . Thus if we choose R as the peak in the radial charge density $r^2|\psi|^2$, we merely replace

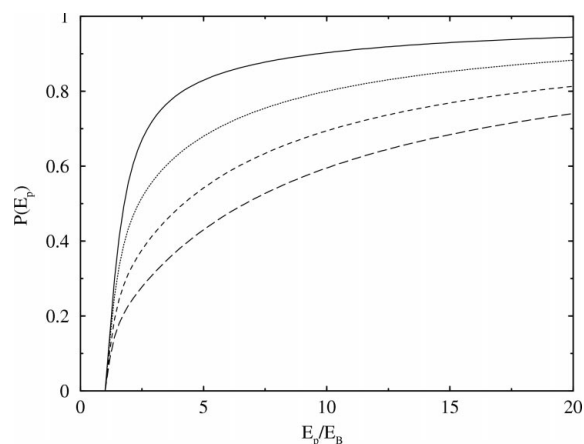


Figure 2 Canonical form for the energy-dependent multiple-electron probability $P(E_p)$. E_p is the primary photoelectron energy, $E_p = \hbar\omega - E_{\text{edge}}$, E_B the binding energy, and n the principal quantum number, of the initial state of the passive electron. Solid line: $n = 2$; dotted line: $n = 3$; short dashed line: $n = 4$; long dashed line: $n = 5$.

$n - 1$ by n and so can still use Fig. 2. If we choose the expectation value $\langle r \rangle$ we need to replace $n - 1$ by $n + 1/2$. Both these models give a slower rise in P for a given n . Comparison with experimental data from rare gases (see below) suggests that our present form gives the best agreement.

3.1. Multiple electron probabilities in rare gases

Experimental data on the photon energy dependence of the multiple-electron excitation probability is available for the rare gases. In Fig. 3 we show a comparison between our results, obtained using equation (18), and the value of $P(\infty)$ obtained as in §2, and the experimental data of Armen *et al.* (1985) for the K edge of argon. The argon K edge lies at 3203 eV and we have taken the binding energy of the $n = 3$ state (the passive electron) as 15 eV, the first ionization potential of argon. This is probably a little low, since the core hole will lower the $3sp$ energy somewhat (a relaxation shift). In the energy range of the data, only the $3s$ and $3p$ passive electrons can be excited. We note that the sudden approximation gives a good estimate of the high-energy end of the data, as is clear from Fig. 1 also. The shape of the energy variation is also well reproduced, although the rise is a little too rapid in the calculated values. The data for the K edge of neon (Carlson & Krause, 1965) is similarly well described (Roy, 1999). In the case of the neon L edge (Bartlett *et al.*, 1992) and the argon M edge (Holland *et al.*, 1979) the energy dependence is accurately reproduced (Lindsay, 2000) by equation (18) but the limit $P(\infty)$ is poorly calculated by the sudden approximation owing to problems with electron correlation noted in §2.

The use of the experimental binding energy rather than that given by the screening coefficient calls for some comment. We find much better agreement with experiment, for all rare gases, using the former. It appears that, although the single Slater orbital gives a good representation of the overall wavefunction [and hence good values for $P(\infty)$], it does not give accurate values for the binding energies, $\zeta^2/2$ normally being considerably larger than E_B . Nor does it give a good representation of the energy dependence of the matrix elements (Roy, 1999). The use of experimental energies, which are easily accessible for all levels as the X-ray edge energies, appears to solve both these problems.

In Fig. 4 we plot the K -edge EXAFS amplitude reduction factor $S_0^2 = 1 - P(\hbar\omega)$ for silicon, copper and silver, calculated using this model. The energy dependence agrees with the commonly held view

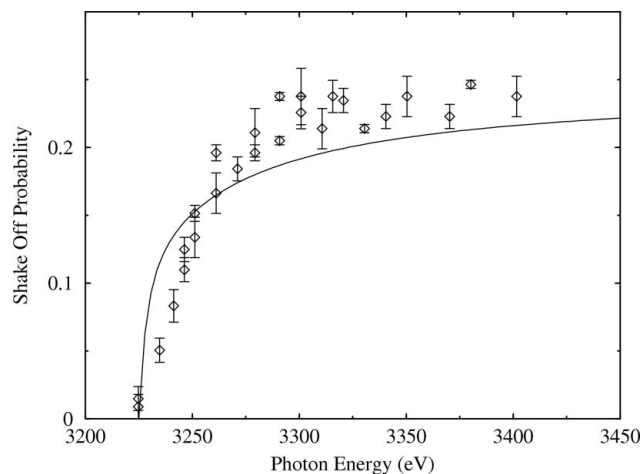


Figure 3 Multiple-electron excitation probability for the K edge of argon. Line: calculation; points: data of Armen *et al.* (1985).

that S_0^2 reaches almost its full magnitude within at most a couple of hundred volts of the edge. The model results also agree closely with those calculated using the local density approximation (LDA) (Roy, 1999; Roy & Gurman, 2001). The LDA calculation is known to give good results for the EXAFS amplitude reduction factor and so we may say that our model will also.

We may also note that the integrand of (16) gives the probability that a passive electron will be excited to an energy E [the primary photoelectron will then have an energy $E_p - (E + E_B)$]. Thus the integrand can be used to predict the secondary electron spectrum in X-ray photoemission. We (Roy, 1999) find reasonable agreement with the experimental data (Carlson, 1967) for this spectrum.

4. The X-ray absorption coefficient

We have noted that a one-electron calculation gives good results for the X-ray absorption coefficient (Gurman, 1983). We have also noted that 20–30% of X-ray absorption events give rise to multiple-electron excitation. We now try to show how these two points may be resolved.

If we take Thomas' (1984) model at face value then there is no problem. In this model the photoelectron is emitted *before* it interacts with the passive electrons, so the absorption process is described solely in one-electron terms. However, this is physically untenable: one-electron and multiple-electron processes form different channels for the excitation of the atom and must be considered as separate processes.

If we consider separate channels, then the measured X-ray absorption coefficient is a sum of one-electron and multiple-electron processes. In the latter, only the sum of the final energies of the two excited electrons is fixed. We can therefore write the total absorption coefficient $\mu(\omega)$ as

$$\mu(\hbar\omega) = \left[1 - \sum |a_{ik}|^2\right] \mu_1(\hbar\omega) + \sum |a_{ik}|^2 \mu_1(\hbar\omega - E_{ik}). \quad (19)$$

The first term is the one-electron channel. In the second term we have the probability of exciting a passive electron to a final state $|k\rangle$ multiplying the absorption coefficient appropriate to a photoelectron of diminished final energy, summed over all available final states. Equation (19) looks physically reasonable and can also be derived using a many-body theory of photon absorption.

We now expand the one-electron absorption coefficient which appears in the second term about the photon energy $\hbar\omega$. We then find

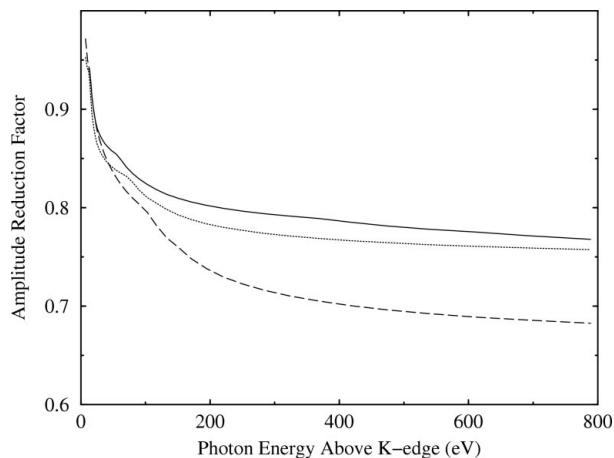


Figure 4
Calculated K-edge EXAFS amplitude reduction factor $S_0^2 = 1 - P(E_p)$. Dashed line: silicon; solid line: copper; dotted line: silver.

$$\mu(\hbar\omega) = \mu_1(\hbar\omega) + \frac{d\mu_1}{dE} \Big|_{\hbar\omega} \sum |a_{ik}|^2 E_{ik}, \quad (20)$$

so that the absorption coefficient is equal to the one-electron value plus a correction term. The one-electron absorption coefficient may be fairly accurately described by a power law form

$$\mu_1(\hbar\omega) = \mu_1(\hbar\omega_e)(E_e/E)^n, \quad (21)$$

with n about 3 or 4 (this is a slightly simplified version of the standard Victoreen form) and $\hbar\omega_e$ the energy of the edge. When we substitute this form into equation (20) we find

$$\mu(\hbar\omega) = \mu_1(\hbar\omega) \left[1 - n \sum |a_{ik}|^2 E_{ik}/\hbar\omega\right]. \quad (22)$$

Now, $|a_{ik}|^2$ is only large for small values of E_{ik} : according to equations (12) and (13) it is effectively the slope of the plot of $P(\hbar\omega)$. Thus the factor $E_{ik}/\hbar\omega$ is very small, of the order of the ratio of the binding energy of the passive electron to that of the core electron. For the argon K-edge data used above, this ratio is 15/3200. Also, the sum rises from zero in a manner very similar to that shown by $P(\hbar\omega)$. [The sum is actually given by equation (16) with the power $n + 2$ replaced by $n + 1$ in the denominator: Fig. 2 shows that this change has little effect.] We therefore expect to see very little change in the X-ray absorption coefficient when multiple-electron excitations become energetically allowed: just a very weak kink as is actually observed (e.g. Deutsch & Hart, 1986; Filipponi, 1995). Such small changes may be expected, since both the one-electron and the many-body calculations of the X-ray absorption coefficient obey the same sum rule, the Thomas–Reiche–Kuhn sum rule.

5. Conclusions

We have described a simple generic model for many-body effects in X-ray absorption. Our major purpose has been to provide a theory which gives the probability of multiple-electron excitation, and hence the EXAFS amplitude reduction factor, in a form which requires little computing or input data. We achieved this by the use of Slater orbitals, with the screening constants fitted to modern wavefunction results (Clementi & Roetti, 1974) and so calculated using a modified form of Slater's rules. For the energy dependence we have used a development of the model originally proposed by Thomas (1984) which gives an analytic result for the energy-dependent probability, normalized to the high-energy limit calculated in the sudden approximation.

The results obtained using this model agree well with experimental data, both for the standard EXAFS amplitude reduction factor S_0^2 (which is assumed constant, so is given by the high-energy limit) and for the energy-dependent probability as measured for rare gases.

One possible application of our results is in EXAFS data analysis. At present the major data-analysis codes use complex potentials derived from the local density approximation (the Hedin–Lundqvist potential). This gives good results for the amplitude reduction in the energy region of interest for EXAFS (photoelectron energies up to about 1 keV), although this is largely fortuitous (Roy & Gurman, 1999, 2001). However, use of this potential involves calculating the photoelectron scattering using a complex potential. It may be more convenient to calculate the EXAFS spectrum using a real potential, such as the energy-dependent Hara potential which is known to give good results (Woolfson *et al.*, 1982) with the intrinsic losses described by S_0^2 included using this model, which requires very little input data. The extrinsic losses also need to be included, but this can be performed in terms of the standard mean-free-path term.

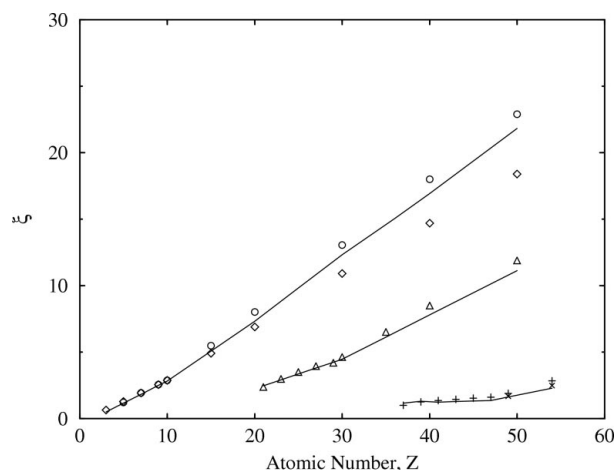


Figure 5
The parameter ζ of the Slater wavefunctions [see equation (3)]. Lines: calculated using the modified Slater rules. Points: \circ , $+$: s states, \diamond , \times : p states, Δ : d states (Clementi & Roetti, 1974).

APPENDIX A Modified Slater's rules

The wavefunctions used in these model calculations were the single zeta functions of Clementi & Roetti (1974), which are the best approximation to full Hartree–Fock wavefunctions when the simple Slater form [equation (3)] is assumed. In order to avoid much input data, the parameter ζ which appears in the formula was written in terms of a screening parameter σ [equation (4)] which was itself calculated using a modified version of Slater's rules.

Slater's rules in their original form were proposed in 1930 (Slater, 1930) on the basis of fitting to some of the earliest calculated wavefunctions. Since that date, wavefunction calculations have been improved and extended, requiring some modification to the rules. We have kept to the spirit of the original rules, but modified them to give the best fit to the screening factors derived from the single zeta functions of Clementi & Roetti (1974).

Slater (1930) first divided the electrons into groups: $1s$, $(2s\ 2p)$, $(3s\ 3p)$, $3d$, $(4s\ 4p)$ etc. The contribution of each electron to the screening factor was then given by:

- Nothing from any shell outside the one considered.
- An amount 0.35 from each other electron in the group considered, except in the $1s$ group where 0.30 is used.
- If the shell considered is an s, p shell, an amount 0.85 from each electron with principal quantum number less by one and an amount 1.00 from each electron still further in; but if the shell is a d or f , an amount 1.00 from every electron inside it.

Slater also used an effective principal quantum number n^* instead of n in equation (3) for all $n > 3$.

In order to obtain a best fit to the single zeta functions of Clementi & Roetti (1974), we need to modify the rules, principally by including a small screening effect from electrons *outside* the shell considered: without this contribution deep shells become underscreened and their contribution to S_0^2 too high (Roy *et al.*, 1997). Thus we use the same grouping of levels but with the following rules:

- For every electron outside the group considered, an amount 0.1 electron for s or p electrons, nothing for d or f electrons.
- For every other electron in the group considered, 0.33 electron, except for $1s$ where 0.30 is used.
- For electrons in groups inside that considered. Electrons with the same principal quantum number as the group considered

contribute 0.45 if s or p ; 0.1 if d or f . For electrons with a principal quantum number less by one than that considered: 0.9 electrons for every d or f electron and an amount $1.00 - 0.2(n - 2)$ for every s and p electron (n is the principal quantum number of the passive electron under consideration), if the group considered is s or p ; 0.55 electrons for every d or f electron and 1.00 for every s or p electron, if the group considered is a d or f electron. Electrons with a principal quantum number more than one less than that of the group considered, a contribution of 1.00 per electron.

The complex form of our rule (c) replaces Slater's effective principal quantum numbers and also more accurately describes the differences between s, p and d, f electrons. These three rules give a good description of the screening of all electrons: three examples are shown in Fig. 5. For these three examples the rules may be written algebraically as

$$\begin{aligned} 2sp : \quad \sigma &= 1.0N_{1s} + 0.33(N_{2sp} - 1) + 0.1(N_{3sp} + N_{4sp} + \dots), \\ 3d : \quad \sigma &= 1.0(N_{1s} + N_{2sp}) + 0.45N_{3sp} + 0.33(N_{3d} - 1), \\ 5sp : \quad \sigma &= 1.0(N_{1s} + N_{2sp} + N_{3sp} + N_{3d}) + 0.4N_{4sp} \\ &\quad + 0.9N_{4d} + 0.33(N_{5sp} - 1). \end{aligned} \quad (23)$$

In order to calculate the screening coefficients σ and σ' , for atoms without and with a core hole, we simply use the appropriate occupancies. It is then clear from equation (23) that, as long as the core hole is much deeper than the passive electron, $\sigma' = \sigma + 1$ as noted in equation (6). Since only the least-bound passive electrons contribute significantly to S_0^2 [equation (7)], this is always the case for hard X-rays, the only case of interest for EXAFS.

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