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## A new spherical-wave approximation for photoelectron diffraction, EXAFS and MEED

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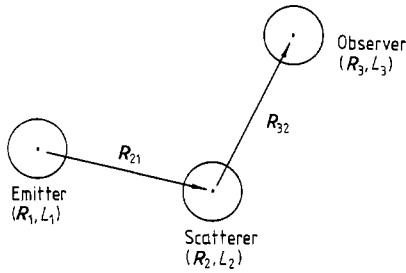
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**Abstract.** An exact formula for the expansion of an outgoing spherical electron wave around another centre is presented from which new approximations for spherical-wave scattering are derived. These expressions allow a considerably higher accuracy in high-speed numerical multiple-scattering calculations than methods existing hitherto. This is demonstrated for tungsten in the energy range from 50 to 5000 eV. The improvements of the given formulae over earlier approaches are greater the higher the energy. In particular the errors in the forward scattering direction are very small.

### 1. Introduction

Elastic scattering processes of electrons can be used to probe the geometrical structure of solids, provided that the wavelength of the electrons is of the same order of magnitude as the interatomic distances. In addition to the well established electron diffraction techniques LEED, MEED and RHEED structure investigation methods are now also applied, which make use of electrons created by excitation processes inside the sample (EXAFS, XANES, photoelectron diffraction, Auger electron diffraction, etc). In the latter four spectroscopies the final state is essentially formed by multiple-scattering processes of the excited electrons at the atoms in the surroundings of the emitter.

In order to obtain the structural data from the energy-dependent or angle-dependent modulations in the measured quantities (x-ray absorption coefficient, photoelectron intensity, etc) one has to study the scattering effects of spherical electron waves in a rather large cluster of atoms, the size of which is mainly determined by the inelastic mean free path of the excited electrons. For electrons with kinetic energies above 50 eV exact calculations within the framework of the partial-wave expansion are prohibitively expensive due to the large number of scattering phase shifts which must be included in the expansion. Therefore the analysis of experimental data was often carried out on the basis of a plane-wave approximation (PWA). However, it is now generally acknowledged that in many systems spherical-wave effects play an important role and that the accuracy of the commonly applied PWA is not sufficient for profound investigations and reliable conclusions. Several attempts have been made in order to develop more sophisticated approximations which on the one hand guarantee adequate accuracy of the theoretical description and which on the other hand are numerically much faster than a full partial-wave expansion [1–7]. The aim of the present paper is to continue this work.



**Figure 1.** Arrangement of emitter, scattering potential and observer.

In § 2 we set up a formula for the coefficients which describe the expansion of an outgoing spherical electron wave around a new centre. From this expression we straightforwardly derive in § 3 very effective approximations for numerical multiple-scattering calculations, which may be considered as a generalisation of the reduced angular momentum expansion (RAME) [4, 6, 7]. The quality of the approximations can be systematically increased by including higher order terms in the asymptotic formula applied for the spherical Hankel functions. In § 4 the accuracy of the given approximations is discussed and compared to that of earlier methods on the basis of error parameters defined in [7].

## 2. Scattering of spherical waves

The key quantities for a quantum mechanical description of spherical-wave scattering are the coefficients which describe the expansion of a given spherical wave around a new centre (figure 1). The general expression for a spherical wave emitted from an atom  $\mathbf{R}_1$  is given by a linear combination of outgoing partial waves with arbitrary coefficients  $C_{L_1}$ ,

$$\varphi(\mathbf{r}) = \sum_{L_1} C_{L_1} h_{l_1}(k|\mathbf{r} - \mathbf{R}_1|) Y_{L_1}(\mathbf{r} - \mathbf{R}_1) \quad (1)$$

where  $h_l(x)$  are spherical Hankel functions,  $k$  is the wavenumber, and  $L$  is an abbreviation for  $L = (l, m)$ . This wavefunction can be expanded into a series of partial waves with another centre  $\mathbf{R}_2$  by means of

$$h_{l_1}(k|\mathbf{r} - \mathbf{R}_1|) Y_{L_1}(\mathbf{r} - \mathbf{R}_1) = \sum_{L_2} G_{L_2 L_1}(\mathbf{R}_{21}) j_{l_2}(k|\mathbf{r} - \mathbf{R}_2|) Y_{L_2}(\mathbf{r} - \mathbf{R}_2) \quad (2)$$

which holds for  $|\mathbf{r} - \mathbf{R}_2| < R_{21} = |\mathbf{R}_2 - \mathbf{R}_1|$ . Assuming that  $\mathbf{R}_2$  is the centre of a spherical scattering potential we obtain for the scattered wave (see, e.g., [4])

$$\psi(\mathbf{r}) = \sum_{L_2} h_{l_2}(k|\mathbf{r} - \mathbf{R}_2|) Y_{L_2}(\mathbf{r} - \mathbf{R}_2) T_{l_2} \sum_{L_1} G_{L_2 L_1}(\mathbf{R}_{21}) C_{L_1} \quad (3)$$

with

$$T_l = i \sin \delta_l \exp(i\delta_l) \quad (4)$$

where the  $\delta_l$  are the scattering phase shifts of the potential.

The coefficients  $G_{L'L}(\mathbf{R})$ , which describe the free electron propagator in a two-centre angular momentum expansion, are given by

$$G_{L'L}(\mathbf{R}) = 4\pi \sum_{L''} i^{l'-l+l''} h_{l''}(kr) Y_{L''}^*(\mathbf{R}) \int d\Omega Y_{L''}^* Y_L Y_{L'}. \quad (5)$$

For high angular momenta  $l'$  and  $l$  a numerical calculation of these coefficients along the lines given by (5) is very involved and time consuming. Therefore it is well worth looking for a proper expression for the  $G_{L'L}(\mathbf{R})$  which is computationally faster than (5).

Our starting point is the following integral representation for the  $G_{L'L}(\mathbf{R})$ :

$$G_{L'L}(\mathbf{R}) = i^{l'-l+1} \frac{2}{\pi} \int d^3K \frac{j_{l'+l}(Kr) Y_{L'}^*(\mathbf{K}) Y_L(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{R}}}{kj_{l'+l}(kr) k^2 - K^2 + i\varepsilon}, \quad (6)$$

where  $\varepsilon \rightarrow 0$  and  $r$  is an auxiliary quantity which has to fulfil the condition  $0 < r < R$ . Equation (6) can be proved by expanding the plane wave into an angular momentum series

$$e^{i\mathbf{K}\cdot\mathbf{R}} = 2\pi \sum_{L''} i^{l''} [h_{l''}^{(1)}(KR) + h_{l''}^{(2)}(KR)] Y_{L''}(\mathbf{K}) Y_{L''}^*(\mathbf{R}). \quad (7)$$

The remaining integral over  $dK$  can be calculated by closing the contour in the complex  $K$  plane (for  $h_{l''}^{(1)}(KR) = h_{l''}(KR)$  in the upper half-plane and for  $h_{l''}^{(2)}(KR)$  in the lower half-plane) and using Cauchy's residue theorem

$$\frac{i}{2\pi} \int_{-\infty}^{+\infty} dK \frac{j_{l'+l}(Kr) K^2}{kj_{l'+l}(kr) k^2 - K^2 + i\varepsilon} [h_{l''}^{(1)}(KR) + h_{l''}^{(2)}(KR)] = h_{l''}(kr). \quad (8)$$

For vectors  $\mathbf{R}$  which lie on the positive  $z$  axis it can be shown that the expansion coefficients  $G_{L'L}(\mathbf{R})$  vanish for  $m' \neq m$ . Following [4] we denote these special coefficients by

$$G_{L'L}(R\mathbf{e}_z) = g_{l'lm}(R) \delta_{m,m'}. \quad (9)$$

The coefficients  $G_{L'L}(\mathbf{R})$  corresponding to an arbitrary position of  $\mathbf{R}$  can be expressed by the  $g_{l'lm}(R)$  using rotations of the coordinate system (see the appendix).

From (6) it follows that

$$g_{l'lm}(R) = i^{l'-l-2m+1} \sqrt{(2l'+1)(2l+1)} \sqrt{\frac{(l'+|m|)!(l-|m|)!}{(l'-|m|)!(l+|m|)!}} \\ \times \frac{1}{\pi} \int_0^\infty dK \frac{j_{l'+l}(Kr) K^2}{kj_{l'+l}(kr) k^2 - K^2 + i\varepsilon} \int_{-1}^{+1} d\xi P_{l'}^{-|m|}(\xi) P_l^{|m|}(\xi) e^{iKR\xi} \quad (10)$$

where the integral over  $d\xi$  can be calculated straightforwardly. After that the integral

over  $dK$  is solved by closing the contour in the complex  $K$ -plane and applying Cauchy's residue theorem:

$$g_{l'm}(R) = i^{l'-l-2m} \sqrt{(2l'+1)(2l+1)} \sqrt{\frac{(l'+|m|)!(l-|m|)!}{(l'-|m|)!(l+|m|)!}} \\ \times \frac{e^{ikR}}{ikR} \sum_n \frac{1}{n!(n+|m|)!} \left(\frac{i}{2kR}\right)^{2n+|m|} d_l^n(kR) d_l^{n+|m|}(kR) \quad (11)$$

where  $d_l^n(x)$  is an abbreviation for

$$d_l^n(x) = \sum_s \frac{(l+s)!}{(l-s)!(s-n)!} \left(\frac{i}{2x}\right)^{s-n}. \quad (12)$$

The polynomials  $d_l^n(x)$  are closely related to the polynomial parts of the spherical Hankel functions

$$d_l(x) = i^l \frac{h_l(x)}{h_0(x)} = \sum_s \frac{(l+s)!}{(l-s)!s!} \left(\frac{i}{2x}\right)^s \quad (13)$$

and can be expressed by derivatives of the  $d_l(x)$

$$d_l^n(x) = \frac{d^n}{dz^n} d_l\left(\frac{i}{2z}\right) \Big|_{z=i/(2x)}. \quad (14)$$

### 3. Approximations

Now the obtained exact expressions (11) and (14) can be essentially simplified by applying appropriate approximations to the polynomial part of the spherical Hankel functions. The upper limit of the angular momenta which must be included in the partial wave expansion is determined by the behaviour of the scattering phase shifts. It can be roughly estimated from the radius of the scattering potential to be

$$l_{\max} = kR_{\text{MT}}. \quad (15)$$

Therefore in the case of nearest neighbours the approximation used for the spherical Hankel functions  $h_l(x)$  must be valid for  $l \leq x/2$ . An effective formula which fulfils this condition is [8]

$$d_l(x) \approx \exp [il(l+1)/2x]. \quad (16)$$

At the highest angular momenta included in the partial-wave expansion the argument in this phase factor can be considerably larger than 1 for touching scattering potentials. Therefore an approximation  $d_l(x) = 1$ , which is used in the PWA, is doubtful. All further corrections to the modulus and the phase of (16) are at least of second order in the small parameter  $l/x$  [8].

Inserting (16) into (14) and (11) gives

$$g_{l'm}(R) \approx i^{l'-l-|m|} \sqrt{(2l'+1)(2l+1)} (e^{ikR}/ikR) \times d_{l'}(kR) d_l(kR) J_{|m|}(\sqrt{l'(l'+1)l(l+1)}/kR) \quad (17)$$

where

$$J_m(z) = \sum_n \frac{(-1)^n}{n!(n+m)!} \left(\frac{z}{2}\right)^{2n+m} \quad (18)$$

are the Bessel functions. Due to the last term  $J_{|m|}(z)$  in (17) the absolute values of the expansion coefficients  $g_{l'm}(R)$  strongly decrease for  $z \leq 1$  as the absolute value of the magnetic quantum number increases. This behaviour makes it possible to neglect the coefficients  $g_{l'm}(R)$  with higher  $|m|$  in multiple-scattering calculations, which lessens the numerical effort for the calculation of the rotation matrices considerably (see the appendix).

The accuracy of the presented approximation for the  $g_{l'm}(R)$  can be further increased by taking into account terms of higher order in the description of the spherical Hankel function. Using, for instance

$$d_l(x) \approx \sqrt{1+l(l+1)/2x^2} \exp\{i[l(l+1)/2x][1+l(l+1)/12x^2]\} \quad (19)$$

we obtain

$$g_{l'm}(R) \approx i^{l'-l-|m|} \sqrt{(2l'+1)(2l+1)} (e^{ikR}/ikR) d_{l'}(kR) d_l(kR) \times \{[1+(i/2kR)(z^2/2-|m|^2-|m|)]J_{|m|}(z) + (iz/2kR)J_{|m|+1}(z)\} \quad (20)$$

with

$$z = (1/kR)\sqrt{l'(l'+1)l(l+1)}\sqrt{1+l'(l'+1)/(2kR)^2}\sqrt{1+l(l+1)/(2kR)^2}.$$

Starting from (17) various previously published results can be recovered and classified. In the reduced angular-momentum expansion (RAME) [4, 6, 7], which includes only contributions from the coefficients  $g_{l'm}(R)$  with  $|m| \leq 1$ , the Bessel function in (17) is approximated by the leading terms

$$J_{|m|}(z) \approx [1 - (z/2)^2]\delta_{m,0} + (z/2)\delta_{|m|,1}. \quad (21)$$

In a slightly better version, called the spherical-wave approximation (SWA) [5],

$$J_{|m|}(z) \approx J_0(z)\delta_{m,0} + (z/2)\delta_{|m|,1} \quad (22)$$

is used.

Other approaches take into account only the coefficients  $g_{l'm}(R)$  with  $m = 0$ . The most effective of them is the modified small-scattering-centre approximation (MSSCA) [4, 6, 7], which is obtained from (17) by applying

$$J_{|m|}(z) \approx \delta_{m,0}. \quad (23)$$

If the resulting expression is further simplified by setting  $d_{l'}(kR) = 1$  and  $d_l(kR) = 1$ , we will arrive at the commonly used PWA. An intermediate version between the MSSCA and the PWA is the small-atom approximation [9], in which the exact expression for  $d_l(kR)$  is used, whereas  $d_{l'}(kR)$  is replaced by 1.

Another well established formalism for spherical-wave scattering is the Taylor-series magnetic-quantum-number expansion [2, 3], which is based on the following exact expression for the  $g_{l'm}(R)$ :

$$g_{l'm}(R) = i^{l'-l-2m} \sqrt{(2l'+1)(2l+1)} \sqrt{\frac{(l'+|m|)!(l-|m|)!}{(l'-|m|)!(l+|m|)!}} \frac{e^{ikR}}{ikR} \\ \times \sum_s \sum_t \frac{(l'+t)!}{(l'-t)!t!} \left(\frac{i}{2kR}\right)^t \frac{(l+s)!}{(l-s)!s!} \left(\frac{i}{2kR}\right)^s \frac{(t+s)!}{(t+|m|)!(s-|m|)!}. \quad (24)$$

For large values of  $l$  and  $l'$  the first terms in this double sum are proportional to

$$\frac{1}{t!} \left(\frac{l'^2}{2kR}\right)^t \frac{1}{s!} \left(\frac{l^2}{2kR}\right)^s. \quad (25)$$

Since the behaviour of the scattering phase shifts ensures only that  $l/(kR)$  and  $l'/(kR)$  are small quantities, the first terms in this double sum can considerably increase with  $s$  and  $t$  for the largest values of  $l$  and  $l'$  included in the partial-wave expansion. In such a case a truncation of the double sum after a few terms can produce errors in the scattered wave which are much larger than that of the pWA [6, 7]. A similar behaviour is known from the polynomial part of the spherical Hankel functions. In (17) such difficulties are removed, because the cumbersome terms of (24) are pulled out from the summation as prefactors  $d_{l'}(kR)$  and  $d_l(kR)$ . Then the remaining part, which describes the coupling between  $l$  and  $l'$ , i.e. the coupling between  $s$ - and  $t$ -sum, is a rapidly convergent sum (Bessel function in (17)).

#### 4. Discussion of accuracy

In [7] error parameters were introduced in order to obtain a comprehensive assessment of the quality of the various approximations for spherical-wave scattering. In these parameters the errors are averaged over the emitter-scatterer direction  $\mathbf{R}_{21}$  and the scatterer-observer direction  $\mathbf{R}_{32}$  (figure 1):

$$X = \left( \int d\Omega_e \int d\Omega_{e'} |\psi_{\text{ap}}(\mathbf{R}_{21}\mathbf{e}, \mathbf{R}_{32}\mathbf{e}') - \psi_{\text{ex}}(\mathbf{R}_{21}\mathbf{e}, \mathbf{R}_{32}\mathbf{e}')|^2 \right) \\ \times \left( \int d\Omega_e \int d\Omega_{e'} |\psi_{\text{ex}}(\mathbf{R}_{21}\mathbf{e}, \mathbf{R}_{32}\mathbf{e}')|^2 \right)^{-1} \quad (26)$$

where  $\mathbf{e}$  and  $\mathbf{e}'$  are unit vectors.  $\psi_{\text{ex}}(\mathbf{R}_{21}, \mathbf{R}_{32})$  is the exact scattered wave  $\psi(\mathbf{R}_3)$  from (3) and  $\psi_{\text{ap}}(\mathbf{R}_{21}, \mathbf{R}_{32})$  is the approximate one. The physical background of the proposed averaging procedure in the error parameters is the nature of multiple-scattering processes in a cluster of atoms, where the total wavefunction is given by a superimposition of a large number of individual scattering events. The error parameter is normalised in such a way that for  $X = 1$  the averaged errors in the scattered wave have the same magnitude as the averaged scattered wave itself.

Of course, the values for  $X$  depend on the choice of the coefficients  $C_{L_1}$  in (1), which describe the character of the incident spherical wave  $\varphi(\mathbf{r})$ . The most interesting case for us is when  $\varphi(\mathbf{r})$  represents the scattered wave of a preceding scattering process. Then the absolute values of the coefficients  $C_{L_1}$  are essentially determined by the scattering

properties of atom  $\mathbf{R}_1$ , i.e. the  $C_{L_1}$  are roughly proportional to the  $T_{l_1}$  of atom  $\mathbf{R}_1$ . For that reason we define the error parameter for the scattering of a scattered wave  $X_s$  by setting  $|C_{L_1}| = |T_{l_1}|$  in (26) and averaging over all possible phases of the  $C_{L_1}$ . Furthermore we are interested in the case that only one single partial wave is emitted from atom  $\mathbf{R}_1$ . This situation is realised at the atoms where the excitation process takes place. The corresponding error parameter  $X_l$  is defined by setting  $C_{L_1} = \delta_{L_1,L}$  in (26). It can be shown that  $X_l$  is independent of  $m$  due to the averaging procedure.

In the energy range considered forward scattering processes can play an important role. In many cases they have a significant influence on the structures in the above mentioned spectra. Therefore it is useful to investigate the accuracy of the approximations considered in this special direction separately. For this purpose we introduce an error parameter which includes only forward scattering processes in the numerator. In analogy with (26) the errors in the scattered wave are normalised by the intensity of the averaged scattered wave. Explicitly, we define

$$X_f = \left( 4\pi \int d\Omega_e |\psi_{ap}(R_{21}e, R_{32}e) - \psi_{ex}(R_{21}e, R_{32}e)|^2 \right) \times \left( \int d\Omega_e \int d\Omega_{e'} |\psi_{ex}(R_{21}e, R_{32}e')|^2 \right)^{-1} \tag{27}$$

with  $|C_{L_1}| = |T_{l_1}|$ . From a more detailed inspection of (27) with all rotation matrices, it follows that the numerator of  $X_f$  depends only on the coefficients  $g_{l'm}(R)$  with  $m = 0$ .

In the following figures the errors of the above described approximations are compared for tungsten, which has a relatively strong scattering potential due to its large atomic number. The exact scattered wave was calculated with the help of

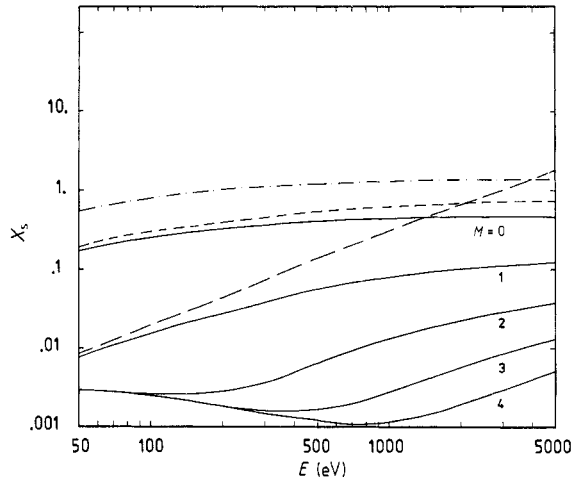
$$g_{l'm}(R) = i^{l'-l} \sqrt{(2l'+1)(2l+1)} \sqrt{\frac{(l'+|m|)!(l+|m|)! e^{ikR}}{(l'-|m|)!(l-|m|)! ikR}} \times \sum_t \frac{(-i)^t (2t)!}{t!(t-m)!(t+m)!} \frac{|(l'-|m|)!|(l-|m|)!|}{(l-t)!(l-t)!} \frac{d_{l'+l-t}(kR)}{(2kR)^t} \tag{28}$$

obtained from [10]. Up to 56 scattering phase shifts were included at the highest energies. For  $R_{21}$  and  $R_{32}$  the nearest neighbour distance in the tungsten lattice (2.74 Å) was chosen, i.e., the approximations are tested in the most unfavourable case. As is shown in [6] the errors decrease considerably as the distance  $R_{21}$  increases, but a variation of  $R_{32}$  has practically no influence on the error parameters.

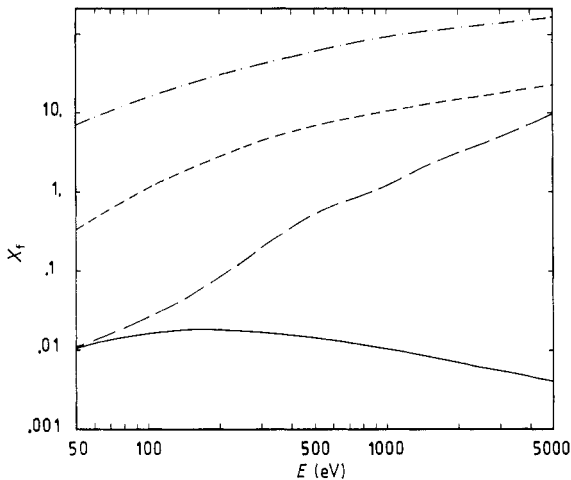
In figure 2 the error parameter for the scattering of a scattered wave is plotted in the energy range from 50 to 5000 eV on a logarithmic scale. The parameter  $M$  determines how many coefficients  $g_{l'm}(R)$  are included in the calculation of the approximate scattered wave. As explained above the modulus of the  $g_{l'm}(R)$  decreases for fixed  $l, l', R$  and  $E$  as  $|m|$  increases. Therefore we can assume all coefficients  $g_{l'm}(R)$  with  $|m| > M$  to be zero. This truncation parameter  $M$  determines mainly the numerical effort for the calculation of the rotation matrices (see the appendix). Within this framework both the PWA and the MSSCA correspond to  $M = 0$ , while the RAME corresponds to  $M = 1$ . Roughly estimated, the numerical work for a full multiple-scattering calculation with the given approximations amounts to  $(M + 1)^2$  times the numerical work of a PWA calculation. For pure single-scattering calculations the numerical effort scales as  $(M + 1)$ .

At first sight it comes out that the accuracy of the approximations does not improve as energy increases unlike what is often expected. The higher accuracy of the new





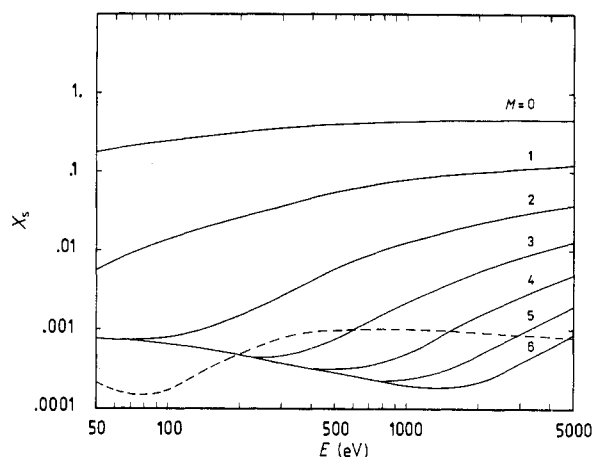
**Figure 2.** Error parameter for the scattering of a scattered wave (tungsten, nearest neighbours): —, new approximation (17) using (19) for the  $d_l(x)$ . The parameter  $M$  determines how many coefficients  $g_{lm}(R)$  are included in the calculation of the approximate scattered wave (see text). — — —, RAME; - - - -, MSSCA; — · — · —, plane-wave approximation.



**Figure 3.** Error parameter for the forward scattering of a scattered wave (tungsten, nearest neighbours): —, new approximation (17) using (19) for the  $d_l(x)$ ; other curves as defined in figure 2.

approximation (17) as against previously published methods can be clearly seen. In particular, the better quality of the new  $M = 1$  version in comparison to the RAME for energies above 300 eV should be noted. It should also be mentioned that the error parameter  $X_s$  for the SWA, which is an intermediate approach between the RAME and the new  $M = 1$  version, lies much closer to that of the RAME than to that of the new  $M = 1$  approximation. For larger distances between emitter and scattering centre the depicted errors decrease as  $R_{21}^{-2}$  in the  $M = 0$  version and as  $R_{21}^{-4}$  in the  $M = 1$  version. For higher values of  $M$  this behaviour is even better.

In figure 3 the error parameter for forward scattering of a scattered wave is shown. This comparison shows that forward scattering processes are very well described by



**Figure 4.** —, error parameter for the scattering of a scattered wave and - - -, error parameter for forward scattering of a scattered wave calculated with the improved version (20) (tungsten, nearest neighbours).  $M$  is as given in figure 2.

the new approximation (17), which is equivalent to the SWA in this special direction. Especially for energies above 500 eV the accuracy achieved is better by several orders of magnitude than that of the PWA, MSSCA or RAME. By means of (17) the essential drawback of earlier approximations—that large errors of a small number of forward scattering processes can have a prevailing influence on the calculated spectra—is successfully removed.

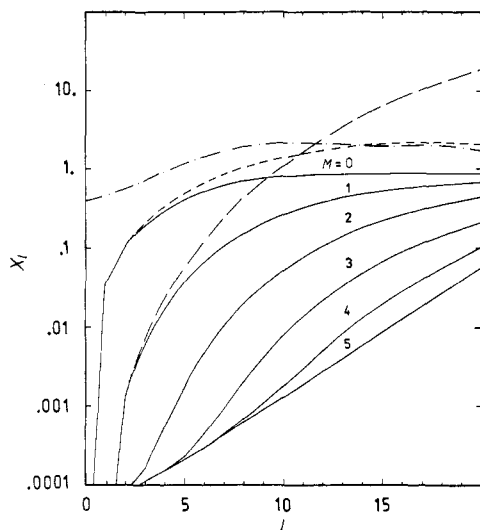
Figure 4 shows the errors for the improved version of our approximation (20). In comparison with figures 2 and 3 it can be seen that the errors for  $M \geq 2$  and also the errors in forward scattering direction are considerably diminished. This figure demonstrates convincingly that a very high accuracy can be achieved within the given approximation scheme. It should also be mentioned that the errors in the backscattering direction are even lower than the ones shown for forward scattering. At 500 eV, for instance, the corresponding errors for backscattering are  $X_b = 0.0002$  with (17) and  $X_b = 0.000\ 003$  with (20).

For energies below 50 eV the errors of the approximations presented increase slightly, because the description of the  $d_l(x)$  by the asymptotic expressions (16) or (19) becomes poorer. In this energy range, therefore, the exact formula (28) should be used. In the same way as above, coefficients  $g_{l'm}(R)$  with large values  $|m|$  can be neglected in the calculation.

Figure 5 illustrates for an energy of 500 eV the dependence of the errors on the angular momentum of the incident wave. In the PWA all incident partial waves are poorly described. The other approximations show a very high accuracy for the lowest angular momenta, but the errors increase considerably with  $l$ . The first statement is quite favourable for the calculation of photoelectron spectra, Auger electron spectra or EXAFS, because the electrons that leave the atom where the excitation process takes place always have a low angular momentum. In this way at least the first scattering process of the excited electrons is described to good accuracy. Especially for the RAME the increase of the errors with  $l$  is extremely large. Such an instability can disturb numerical calculations considerably.

## 5. Conclusions

In the preceding sections we have presented an exact formula for the coefficients  $g_{l'm}(R)$



**Figure 5.** Error parameter for the scattering of a single partial wave  $h_l(kr)Y_l(r)$  as a function of the angular momentum  $l$  (tungsten, nearest neighbours,  $E = 500$  eV). The curves are drawn as guide to the eye: —, new approximation (20).  $M$  is as given in figure 2. Other curves as defined in figure 2.

from which effective expressions for numerical multiple-scattering calculations were derived in a transparent manner by applying approximate descriptions to the polynomial part of the spherical Hankel functions. In the present paper,  $d_l(x) = \exp[i l(l+1)/(2x)]$  was used as the simplest approximation, because this phase factor is not negligible for the largest angular momenta which must be included in the partial-wave expansion. All further corrections to these  $d_l(x)$  are terms of second or higher order in the small quantity  $l/x$ .

The main contributions to the scattered wave come from the coefficients  $g_{l'm}(R)$  with small absolute values of the magnetic quantum number. Therefore we include in our approach only those coefficients with  $|m| \leq M$  in the calculation of the scattered wave. The truncation parameter  $M$  essentially determines the numerical effort that is required to compute the rotation matrices. From this point of view the parameter  $M$  is used to optimise the amount of numerical calculation depending on the accuracy required. For nearest-neighbour scattering in tungsten the  $M = 1$  version gives reasonable results. Only for energies above 1000 eV is the  $M = 2$  version necessary. For larger distances the situation is even more favourable and for a great number of large-distance scattering processes, which occur in cluster calculations, the  $M = 0$  version is quite sufficient. It should be noted that for energies above 300 eV the  $M = 1$  version of the new approximation is much better than the previously published RAME, which requires the same numerical work. The advantages of the new approximation are most obvious for energies above 500 eV. In this sense the results presented here can open a new way to simplify MEED calculations along the lines given in [11]. Furthermore it should be stressed that the new approximation possess a very high accuracy in the forward-scattering region. This is of great importance for the calculation of angle-resolved photoelectron or Auger electron spectra.

A great advantage of the approximation scheme given here is that the accuracy can be systematically increased by including higher order terms in the description of the spherical Hankel functions [8]. This permits a steady improvement of the quality towards the exact partial wave expansion to be achieved.

For energies below about 50 eV, where the accuracy of the approximations slightly decreases, the exact formula (28) for the  $g_{l'm}(R)$  should be preferred. Also in this case

the numerical effort can be diminished by truncating the sum over the magnetic quantum numbers as discussed above.

**Appendix**

In order to express the coefficients  $G_{L'L}(\mathbf{R})$  for arbitrary vectors  $\mathbf{R}$  by the  $g_{l'm}(\mathbf{R})$  defined in (9) we transform equation (2) into a rotated coordinate system whose  $z$  axis is parallel to  $\mathbf{R}$ . Using the well-known transformation law for spherical harmonics under a rotation we obtain

$$G_{L'L}(\mathbf{R}) = \sum_{\tilde{m}} D_{\tilde{m}m}^{(l')} (0, -\vartheta, -\varphi) g_{l'\tilde{m}}(\mathbf{R}) D_{\tilde{m}m}^{(l)} (\varphi, \vartheta, 0) \tag{A1}$$

where  $\vartheta$  and  $\varphi$  are the spherical polar coordinates of  $\mathbf{R}$  in the basis system. In our notation the rotation matrices are given by

$$D_{m'm}^{(l)}(\alpha, \beta, \gamma) = e^{i(m'\gamma+m\alpha)} \sqrt{(l+m')!(l-m')!(l+m)!(l-m)!} \\ \times \sum_s \frac{(-1)^s [\cos(\beta/2)]^{2l-m'+m-2s} [\sin(\beta/2)]^{m'-m+2s}}{(l-m'-s)!(l+m-s)!s!(m'-m+s)!} \tag{A2}$$

where  $\alpha, \beta$  and  $\gamma$  are the Eulerian angles.

The coefficients  $G_{L'L}(\mathbf{R})$  in the multiple-scattering theory always appear in combinations of the following type:

$$\dots \sum_{L_j} G_{L_k L_j}(\mathbf{R}_{kj}) T_{l_j}(\mathbf{R}_j) G_{L_j L_i}(\mathbf{R}_{ji}) \dots \tag{A3}$$

in which the rotation matrices of neighbouring coefficients  $G_{L'L}(\mathbf{R})$  can be combined with the result

$$\dots \sum_{\tilde{m}_{kj}} D_{\tilde{m}_{kj}m_{kj}}^{(l_k)} (0, -\vartheta_{kj}, -\varphi_{kj}) \sum_{l_j} g_{l_k l_j \tilde{m}_{kj}}(\mathbf{R}_{kj}) T_{l_j}(\mathbf{R}_j) \\ \times \sum_{\tilde{m}_{ji}} D_{\tilde{m}_{ji}m_{ji}}^{(l_j)} (\alpha_j, \beta_j, \gamma_j) g_{l_j l_i \tilde{m}_{ji}}(\mathbf{R}_{ji}) D_{\tilde{m}_{ji}m_{ji}}^{(l_i)} (\varphi_{ji}, \vartheta_{ji}, 0) \dots \tag{A4}$$

where the Eulerian angles are determined by

$$\begin{aligned} \cos \beta_j &= \sin \vartheta_{kj} \sin \vartheta_{ji} \cos(\varphi_{kj} - \varphi_{ji}) + \cos \vartheta_{kj} \cos \vartheta_{ji} \\ \sin \alpha_j \sin \beta_j &= \sin \vartheta_{kj} \sin(\varphi_{kj} - \varphi_{ji}) \\ \cos \alpha_j \sin \beta_j &= \sin \vartheta_{kj} \cos \vartheta_{ji} \cos(\varphi_{kj} - \varphi_{ji}) - \cos \vartheta_{kj} \sin \vartheta_{ji} \\ \sin \gamma_j \sin \beta_j &= -\sin \vartheta_{ji} \sin(\varphi_{kj} - \varphi_{ji}) \\ \cos \gamma_j \sin \beta_j &= -\cos \vartheta_{kj} \sin \vartheta_{ji} \cos(\varphi_{kj} - \varphi_{ji}) + \sin \vartheta_{kj} \cos \vartheta_{ji}. \end{aligned} \tag{A5}$$

Expression (A4) shows that from the rotation matrices between two coefficients  $g_{l'm}(\mathbf{R})$  only those elements that have low magnetic quantum numbers  $|m| \leq M$  need to be calculated ( $M$  is the truncation parameter introduced in § 4).

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