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Complex Scattering Amplitudes in Elastic Electron Scattering*

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The scattering amplitudes derived from the Molière approximation are compared with those derived from the first- and second-order Born approximations. A numerical analysis applying a Thomas-Fermi potential was performed. In certain ranges of $a=Z/137\beta$ and the scattering angle, the first-order Born approximation rendered amplitudes that can be applied for the more exact modulus of the Molière approximation, and the second-order Born approximation rendered phases of the scattering amplitudes that are comparable with those obtained by the Molière approximation.

I. INTRODUCTION

IN a classic paper Glauber and Schomaker[1] pointed out that scattering amplitudes must be complex in order to conserve the number of particles. Despite this cardinal requirement, which is termed the unitarity condition, many theoretical considerations and interpretations of electron contrast in electron microscopy and electron diffraction work are based on a first-order Born approximation that is real by nature and prone to give erroneous results. For example, in high-resolution electron microscopy the main contribution to contrast stems from interference of the coherently scattered amplitude with the unscattered uniform background (reference beam); in other words, scattering amplitudes are observable, just as they are in holography. The often-heard statement that phase contrast plays a role only when phase shifts are introduced by defocusing is false, since the complex nature of correct scattering amplitudes in itself provides intrinsic phase shifts. Similarly, these intrinsic atomic phase shifts must be considered in the structural analysis of matter by electron diffraction because they add to the phase shifts resulting from the structural arrangement of the atoms. In conclusion, the unitarity of the scattering amplitude is not an esoteric theoretical refinement but an observable fact.

The theoretical calculations are simplified by the fact that for small-angle scattering only screening effects and no spin effects have to be included; that is, the Klein-Gordon wave equation instead of the Dirac wave equation suffices. The only tables of complex scattering amplitudes available, however, are those by Ibers,[2] which are calculated only for an electron energy of 39.5 keV. This is not sufficient for the experimentalist to "get a feel" for the different trends of real and complex amplitudes.

This paper has two purposes. The first is to enable the experimentalist to estimate the errors caused by the use of real amplitudes in a wide range of experimental conditions.

Ibers's calculations are based on WKB approximation of the phase shifts.[3,4] Physically this approximation is equivalent to the Molière approximation,[5] which is used in this paper. Indeed, when the same expression for the potential is used, both approximations give values that agree within the margin of computational errors. In a recent paper[6] we have shown that as long as spin effects can be neglected, the Molière approximation renders values for the elastic scattering cross section that deviate only by small errors from the values of nonapproximated phase-shift calculations by Lin,[7] which in turn were confirmed by experiments.[8] Our paper[6] also shows how spin effects can be accounted for by a multiplicative correction.

Mathematically, however, Ibers's calculations require summation of up to one hundred single terms, each of which consists of an integral that must be computed, whereas the Molière approximation is accomplished by a single integral. Thus the Molière approximation is more economical.

The second purpose of this paper is to demonstrate the feasibility of producing calculations for each particular experiment.

Definitions

Throughout this paper, energies and momenta are measured in units mc^2 and mc, respectively, and lengths in units of the electron Compton wavelength $\lambdabar_0$. The scattering event changes the momentum $\mathbf{p}_1=p\mathbf{e}_1$ of the

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[1] R. Glauber and V. Schomaker, Phys. Rev. **89**, 667 (1953).

[2] J. A. Ibers, in *International Tables for X-Ray Crystallography*, edited by K. Lonsdale (Kynoch Press, Birmingham, England, 1962), p. 222.

[3] J. A. Hoerni and J. A. Ibers, Phys. Rev. **91**, 1182 (1953).

[4] J. A. Ibers and J. A. Hoerni, Acta Cryst. **7**, 405 (1954).

[5] G. Molière, Z. Naturforsch. **2a**, 133 (1947).

[6] E. Zeitler and H. Olsen, Phys. Rev. **136**, A1546 (1964).

[7] S. R. Lin, Phys. Rev. **133**, A965 (1964).

[8] J. W. Motz, R. C. Placious, and C. E. Dick, Phys. Rev. **132**, 2558 (1963).

incoming electron into $\mathbf{p}_2 = p\mathbf{e}_2$ of the outgoing electron, and the momentum $\mathbf{q} = \mathbf{p}_1 - \mathbf{p}_2$ is transferred to the scattering atom; $q = 2p\sin(\theta/2)$. For the scattering amplitude we write

$$f(\mathbf{e}_1\cdot\mathbf{e}_2) = g(\mathbf{e}_1\cdot\mathbf{e}_2) + ih(\mathbf{e}_1\cdot\mathbf{e}_2)$$

indicating real and imaginary parts.

The unitarity condition then becomes

$$h(\mathbf{e}_1\cdot\mathbf{e}_2) = (p/4\pi)\int f(\mathbf{e}_1\cdot\mathbf{e})f^*(\mathbf{e}\cdot\mathbf{e}_2)d\Omega_e\,, \tag{1}$$

which is simplified to the optical theorem upon setting $\mathbf{e}_2 = \mathbf{e}_1$, namely,

$$h(\mathbf{e}_1\cdot\mathbf{e}_1) = (p/4\pi)\sigma\,, \tag{2}$$

directly relating the imaginary part of the scattering amplitude in forward direction to the total cross section σ.

The foundation and basic significance of Eqs. (1) and (2) can be found in any monograph on modern theory of scattering.[9] In applied electron scattering, however, these conditions are seldom appreciated.

For the potential we use a general form

$$V(r) = -\frac{Z}{137r}\sum_{j=1}^{3} a_j e^{-b_j\Lambda r}\,, \tag{3}$$

Λ being $Z^{1/3}/0.885\times137$.

In the demonstration of our approach to the calculation we shall reduce Eq. (3) to one Yukawa potential

$$V(r) = -(Z/137r)e^{-\Lambda r}. \tag{3$'$}$$

II. BORN APPROXIMATION

The scattering amplitude in first-order Born approximation is a real quantity

$$f_1(q) = v(\Lambda^2+q^2)^{-1} \equiv g_1(q)\,, \tag{4}$$

v being the Born parameter $Z/137$ times twice the total energy E.

Utilizing the unitarity condition, we can construct an imaginary part,[1] namely,

$$h_2(q) = v^2(p/4\pi)\int(\Lambda^2+q_1^2)^{-1}(\Lambda^2+q_2^2)^{-1}d\Omega_e. \tag{5}$$

Here $\mathbf{q}_1 = p(\mathbf{e}_1 - \mathbf{e})$ and $\mathbf{q}_2 = p(\mathbf{e} - \mathbf{e}_2)$; the two fixed vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ and the variable vector $\mathbf{e}$ define a spherical triangle on the unit sphere, or

$$\mathbf{q}_2 = \mathbf{q} - \mathbf{q}_1. \tag{6}$$

With the aid of the Feynman identity the integral [Eq. (5)] can be readily evaluated, and we obtain

$$\begin{aligned} h_2(q) &= \tfrac{1}{2}pv^2\int_{-1}^{+1}[\Lambda^4+4p^2\Lambda^2+p^2q^2(1-t^2)]^{-1}dt \\ &= (v^2/p\Lambda^2)A\tanh^{-1}(y^2A)\,, \end{aligned} \tag{7}$$

with A^{-2} being $y^4+4y^2(1+s^2)$; and $y = q/\Lambda$; $s = \Lambda/2p$. Equation (7) represents the imaginary part of the scattering amplitude calculated in the second-order Born approximation.[10]

This approximation gives us the desired estimate of the phase shift inherent in the scattering event. The imaginary part h_2 does not improve the value for the scattering cross section, however, as can be seen by inspecting Eqs. (4) and (5), $h_2(0) = (p/4\pi)\sigma_1$. The optical theorem is fulfilled only when the first-order amplitude is applied for calculating the total cross section; it holds true in general that h_n relates only to σ_{n-1}, thus leaving the contributions of nth order to the real part undetermined. Since the second-order Born approximation must also improve the cross section, we expect it to add second-order terms to the real part g_1 of the scattering amplitude.

We write for the second-order Born approximation

$$f_2 = g_2 + ih_2 = g_1 + g' + ih_2 = f_1 + f'.$$

How can we find the expression g'? Since h_2, the imaginary part of f', is an analytic function in q and p, as can be seen from its integral representation [Eq. (7)], we find the corresponding real part g' of f' as a Hilbert transform of h_2 with respect to p; that is, we apply the Kramers-Kronig dispersion relations.[11]

We obtain

$$\begin{aligned} g'(q) &= \tfrac{1}{2}\Lambda^2v^2\int_{-1}^{+1}[\Lambda^2+\tfrac{1}{4}q^2(1-t^2)]^{-1/2} \\ &\qquad\times[\Lambda^4+4p^2\Lambda^2+p^2q^2(1-t^2)]^{-1}dt \\ &= (v^2/p\Lambda^2)A\tan^{-1}(sy^2A). \end{aligned} \tag{8}$$

Equation (8) represents the real part of the second-order correction to the scattering amplitude, which we could have obtained also in a straightforward evaluation of the second-order Born approximation.[10] We preferred the method sketched above, however, because (a) it reveals the inner connection of the different contributing components and (b) it facilitates computation when the general potential of Eq. (3) is to be applied.

Small Angles, $q \ll 2p$

As noted in the Introduction, our main concern is the small-angle-scattering amplitude. Mathematically the

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[9] T. Wu and T. Ohmura, *Quantum Theory of Scattering* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962).

[10] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 2, p. 1084.

[11] G. R. Screaton, *Dispersion Relations* (Interscience Publishers, Inc., New York, 1961).

region of small-angle scattering is defined by the possibility of replacing the sine of the scattering angle by the angle itself. The physical consequence of this replacement can be seen from the following consideration. The total transferred momentum q_1 equals $2p\sin\frac{1}{2}\theta_1$, whereas the transverse component $q_{1\perp}$, perpendicular to the direction $\mathbf{e}$, equals $p\sin\theta_1$. Hence in small-angle approximation the total transferred momentum is replaced by its transverse component, and the longitudinal component is neglected. This considerably simplifies the condition defined by Eq. (6), since now the angular relation between the various momenta is not determined by the geometry on the unit sphere but by geometry in the tangential plane of the unit sphere at the point e. As a consequence, all integrations must be performed in this plane, in which the element of the solid angle $d\Omega_e$ reduces to $d\varphi\, q_1dq_1/p^2$; otherwise, all the procedures of the previous section hold. The results, however, will change; therefore, it seems justified to develop the pertinent expressions again. We obtain

$$h_2(q)=\frac{v^2}{4\pi p}\int_0^{2\pi}\int_0^{\infty}(\Lambda^2+q_1{}^2)^{-1} \times[\Lambda^2+(\mathbf{q}-\mathbf{q}_1)^2]^{-1}q_1dq_1d\varphi, \tag{9}$$

which again can be written as an integral representation

$$h_2(q)=\tfrac{1}{2}pv^2\int_{-1}^{+1}[4p^2\Lambda^2+p^2q^2(1-t^2)]^{-1}dt. \tag{10}$$

This equation differs from the corresponding Eq. (7) only by the absence of Λ^4, which makes $h_2(q)$ proportional to $1/p$. As an important consequence the Hilbert transform g' of h_2 will be zero; we recall that the principal value of $\int(p-p_0)^{-1}dp$ equals zero. In preparing for the Molière approximation we should like to point out here that h_2 can also be represented by a Bessel transform. First, we can write

$$(\Lambda^2+q_1{}^2)^{-1}=\int_0^\infty J_0(q_1\rho)K_0(\Lambda\rho)\rho d\rho,$$

J_k and K_k being the Bessel and modified Hankel function of kth order. With the aid of the convolution theorem of Bessel transforms, Eq. (9) can be reformulated as

$$\begin{aligned} h_2(q)&=\tfrac{1}{2}(v^2/p)\int_0^\infty J_0(q\rho)[K_0(\Lambda\rho)]^2\rho d\rho \\ &=(v^2/p\Lambda^2)A_0\tanh^{-1}(y^2A_0), \end{aligned} \tag{9'}$$

with $A_0{}^{-2}$ equaling y^4+4y^2, which equals A with $s=0$. Incidentally, the nonappearance of g' in the small-angle approximation can also be achieved by setting $s=0$ in Eq. (8).

Actually the small-angle-approximation amplitudes as $h_2(q)$ of Eq. (9) may be shown to follow from the wave function $\psi=e^{i\mathbf{p}\cdot\mathbf{r}}F$, F satisfying the approximated wave equation

$$[i\hat{p}\cdot\nabla-(1/\beta)V]F=0$$

instead of the correct wave equation

$$[s\nabla'^2+i\hat{p}\cdot\nabla'-(1/\beta)V'+sV'^2]F'=0$$

given in Eq. (10a) of Ref. 6. In the latter equation all lengths are measured in units Λ^{-1}, indicated by the prime added to the symbols, and the potential V is assumed to have the form $V=\Lambda V'$ (as in the case of a Yukawa potential).

Comparing the two equations, one sees that the correct and the approximate wave functions F' and F differ by terms proportional to s. This explains the absence of s in Eq. (9′).

Since the numerical value of s is small compared to unity (even for the heaviest elements it remains under 0.05, provided the kinetic energy of the electron is beyond 40 keV), the discussion above explains why the small-angle approximation also gives very agreeable results for large angles as long as θ is replaced by $2\sin(\frac{1}{2}\theta)$.

III. MOLIÈRE APPROXIMATION

The Molière approximation is also a small-angle approximation. It is based on the approximate wave function F, as discussed in Ref. 12. Hence the corresponding scattering amplitude will be independent of s [as will be confirmed explicitly in Eqs. (21) and (22) below]. As a result it follows that the validity of the Molière approximation rests on the smallness of s. In this approximation the scattering amplitude assumes the form of a Bessel transform

$$f(q)=\int_0^\infty J_0(q\rho)\tilde{f}(\rho)\rho d\rho. \tag{11}$$

The corresponding space function $\tilde{f}(\rho)$ is determined by the phase shift the electron undergoes when passing through the atomic potential $V(\mathbf{r})$:

$$\tilde{f}(\rho)=\int_0^\infty J_0(q\rho)f(q)qdq=-ip[e^{-i\phi(\rho)}-1]. \tag{12}$$

Here

$$\phi(\rho)=-(1/\beta)\int_{-\infty}^{+\infty}V(\rho,z)dz, \tag{13}$$

the z axis of the cylindrical coordinate system (ρ,z) being along the direction of the incoming electron. This choice of the path of integration is the essence of the Molière approximation. It is permissible provided

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[12] H. Olsen, L. C. Maximon, and H. Wergeland, Phys. Rev. **106**, 27 (1957).

that q is small compared to the total electron energy E, that is, $q/2E\ll 1$.

The total cross section thus becomes

$$\sigma=\frac{2\pi}{p^2}\int_0^\infty f(q)f^*(q)qdq=\frac{2\pi}{p^2}\int_0^\infty \tilde{f}(\rho)\tilde{f}^*(\rho)\rho d\rho. \quad (14)$$

It can easily be seen from Eq. (12) that for the space function the identity

$$\tilde{h}(\rho)=(1/2p)\tilde{f}(\rho)\tilde{f}^*(\rho) \quad (15)$$

holds, which, with the aid of the convolution theorem and Eq. (11), can be transformed into the unitarity condition Eq. (1); or, with the aid of Parseval's theorem [Eq. (14)], into the optical theorem Eq. (2).

It is not surprising that the Molière approximation fulfills all these conditions *a priori* if one recalls the various derivations of this approximation. (a) It can be seen as an approximation of the infinite sum of phase shifts,[5] the latter complying with the unitarity condition. (b) In the small-angle region the Molière approximation constitutes the complete set of Born approximations of all orders.[13] Hence, the connection of h_n with σ_{n-1} becomes immaterial; that is, the unitarity condition is always fulfilled. (c) Specializing for small-momentum transfer at the onset, the Molière approximation evolves from an exact solution of the Klein-Gordon equation,[12] thus conserving the number of electrons *a priori.*

In contrast to the Born approximation, we could show all these relationships to hold without having to specify the kind of potential. When the single Yukawa potential is applied, Eq. (13) becomes

$$\phi(\rho)=(v/p)K_0(\Lambda\rho). \quad (16)$$

Inserted into Eq. (11), we obtain for the scattering amplitude

$$f(q)=-ip\int_0^\infty J_0(q\rho)\{\exp[iv/pK_0(\Lambda\rho)]-1\}\rho d\rho. \quad (17)$$

The relationship of the Molière amplitude to the small-angle Born amplitudes becomes evident upon the expansion of the exponential function in the integrand of Eq. (17). The first member gives the first-order Born approximation; the second leads directly to the second-order Born approximation, Eq. (9′), for small-angle scattering. The correction g' to the real part of the second Born approximation for large-angle scattering cannot be expected from the small-angle Molière approximation. We can readily estimate the contribution of g' to g_1+g', however. Since s is small compared to unity, and since the expression y^2A remains always smaller than unity for all values y, the value of g'/g_1 never exceeds $2sZ/137\beta=\frac{1}{2}\xi$. For small angles the ratio remains even under $\frac{1}{8}\xi$. Values for ξ are tabulated in a previous paper.[6] There the smallness of ξ assured that spin and screening effects do not overlap or influence each other mutually. Thus for two reasons it seems justified to omit the contribution of g' to the second-order scattering amplitude: (a) Its correction is small and also of the wrong sign, as the actual calculations will show, and (b) it does not occur in the consistent small-angle approximation.

This fact is advantageous for presenting the results of this paper, for if s does not appear, all formulas can be written in relative units, so that for a Thomas-Fermi atom neither electron energy nor scattering angle have to be specified explicitly.

General Potential

In this section we state the various expressions derived for three Yukawa potentials and used for the actual computation.

1. *First- and Second-Order Born Approximation*

$$g_1=\frac{v}{\Lambda^2}\sum_1^3 a_j[b_j^2+y^2]^{-1}, \quad (18)$$

$$g'=\frac{v^2}{p\Lambda^2}\sum_1^3\sum_1^3 a_ja_kV\tan^{-1}(QV), \quad (19)$$

$$h_2=\frac{v^2}{p\Lambda^2}\sum_1^3\sum_1^3 a_ja_kV\tanh^{-1}(PV), \quad (20)$$

with the following abbreviations:

$$\begin{aligned}
V^{-2}&=y^4+2y^2(b_j^2+b_k^2+2b_j^2b_k^2s^2)+(b_j^2-b_k^2)^2,\\
Q&=y^2[2s(b_j+b_k)]^{-1}\{s^2(b_j+b_k)^2-[(1+b_j^2s^2)^{1/2}\\
&\quad-(1+b_k^2s^2)^{1/2}]^2\}+(b_j^2+b_k^2)[2s(b_j+b_k)]^{-1}\\
&\quad\times\{s^2(b_j-b_k)^2+[(1+b_j^2s^2)^{1/2}-(1+b_k^2s^2)^{1/2}]^2\},\\
P&=y^2+[b_j(1+b_k^2s^2)^{1/2}-b_k(1+b_j^2s^2)^{1/2}]^2.
\end{aligned}$$

The formulas are written in such a way that for $b_j=b_k=1$, the expression V becomes A; Q and P become sy^2 and y^2, respectively. If $a_1=1$ and all other a_k's$=0$, we obtain the previous results for one Yukawa potential.

2. *Molière Approximation*

For the numerical evaluation it is opportune to perform a partial integration on Eq. (17). Furthermore, a change of the variables q and ρ into $y=q/\Lambda$ and $x=\rho\Lambda$ is indicated. We obtain

$$g=\frac{v}{\Lambda^2}\sum_1^3 a_jb_j\int_0^\infty J_1(yx)K_1(b_jx)\cos\chi(x)xdx, \quad (21)$$

and

$$h=\frac{v}{\Lambda^2}\sum_1^3 a_jb_j\int_0^\infty J_1(yx)K_1(b_jx)\sin\chi(x)xdx, \quad (22)$$

where

$$\chi(x)=\frac{v}{p}\sum_1^3 a_kK_0(b_kx).$$

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[13] L. I. Schiff, Phys. Rev. **103**, 443 (1956).

TABLE I. Moduli of scattering amplitudes in forward direction, $y=0$, in units $2pa/\Lambda^2$.

a	f	f_1	f_2 $s=0$	f_2 $s=0.05$
0.01	4.272	4.272	4.272	4.272
0.1	4.268	4.272	4.274	4.277
0.2	4.252	4.272	4.279	4.285
0.3	4.227	4.272	4.287	4.296
0.4	4.195	4.272	4.299	4.311
0.5	4.157	4.272	4.313	4.328
0.6	4.115	4.272	4.331	4.349
0.7	4.056	4.272	4.353	4.374
0.8	4.024	4.272	4.377	4.401
0.9	3.977	4.272	4.405	4.431
1.0	3.931	4.272	4.435	4.464
1.2	3.839	4.272	4.505	4.540
1.4	3.752	4.272	4.586	4.626
2.4	3.381	4.272	5.141	5.201
4.8	2.794	4.272	7.140	7.226
9.6	2.101	4.272	12.214	12.312

IV. ERROR OF FIRST- AND SECOND-ORDER BORN APPROXIMATION

The numerical analysis can be accomplished in a rather straightforward manner by comparing the results calculated from Eqs. (18) to (22). As to the potential, we feel that the application of a Thomas-Fermi potential is justified because its generality permits the desired synoptic survey of the problem; in terms of the constants a_j and b_j [Eq. (3)], it means using the values $a_j=0.10$, 0.55, 0.35, $b_j=6.0$, 1.2, and 0.30, according to Molière.[5] Since the formulas were introduced in a general form, they can be applied to any particular potential as long as it is given as a series of Yukawa potentials. The only problem remaining is the manner of presenting these data. We performed all computations in Fortran on an IBM 7090 Computer.

Modulus of Scattering Amplitude

Instead of having the two parameters v and p describe the experimental variables in all the formulas, we change to $a=Z/137\beta=v/2p$ and p. It was found appropriate to discuss the influence of the parameter a on the modulus of the scattering amplitude in two steps, namely, (1) on the modulus $|f(0)|$ in forward direction, $y=0$, and (2) on the ratio $r(y)=|f(y)|/|f(0)|$. The normalization procedure will make apparent the more subtle dependence of f on a by eliminating the obvious factor a.

In Table I the moduli of the various scattering amplitudes in the forward direction are listed for a wide range of a. The unit is v/Λ^2, which equals the Rutherford amplitude for $y=1$.

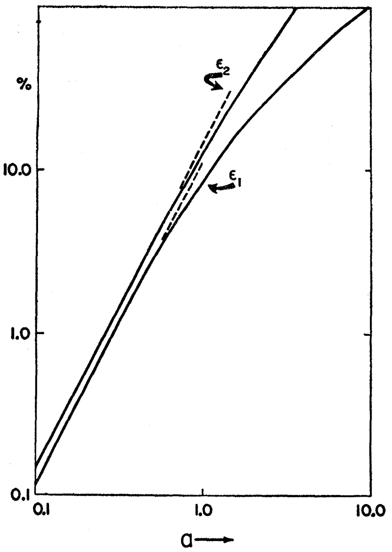

FIG. 1. Deviation ϵ_1 and ϵ_2 of the first- and second-order Born approximation from the Molière scattering modulus in forward direction as a function of $a=Z/137\beta$ (double logarithmic presentation). Broken lines are quadratic approximations.

The most important result of this table is found in the last column, where the complete second-order Born modulus $|f_2|=[(g_1+g')^2+h_2^2]^{1/2}$ [Eqs. (18), (19), and (20)] is shown for $s=0.05$. Instead of choosing any particular energy and element for determining s, we used the maximum value occurring in usual electron-scattering experiments in order to find an upper limit for the influence of s on the result. Comparing these values with those for $s=0$, we see that the differences are negligible for any practical purpose. This result is the numerical proof for the fact that the second-order Born approximation can be replaced by the expansion of the Molière approximation to the second order. We have already seen this to be a consequence of a consistent small-angle approximation. The first-order Born and first-order Molière approximation are identical in any case, whereas the respective second-order contributions differ by the parameter s being finite and small in the one case and zero in the other. From now on we deal only with computations for $s=0$ and hence speak only of first-order and second-order approximations in contrast to the Molière approximation.

For small a the agreement of all three approximations is as good as expected. For large a values, however, the deviations of the second-order approximation from the Molière approximation exceed those of the first-order approximation. In this presentation the modulus in first-order approximation remains at least independent of a, while the second-order modulus increases with increasing a, in contrast to the decreasing result of the Molière approximation.

Figure 1 shows in double logarithmic presentation the errors $\epsilon_k=[|f_k|-|f|]/|f|$ in the forward direction as a function of a. For a smaller than unity the curves can very well be approximated by a quadratic dependence of the forms

$$\epsilon_1=11.5a^2\,\% \quad \text{and} \quad \epsilon_2=15.5a^2\,\%.$$

In principle, all errors are positive because the approx-

TABLE II. Moduli of scattering amplitude r_k, normalized in forward direction, as a function of the angular variable for different values of a.

y	a \ N	0.01		0.1		0.2		0.4		0.6		0.8	
		r	$r_1(\approx r_2)$	r	r_2	r	r_2	r	r_2	r	r_2	r	r_2
0.0063	−3	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.0125	−2	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999
0.025	−1	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994	0.994
0.05	0	0.976	0.976	0.976	0.976	0.976	0.976	0.975	0.976	0.975	0.976	0.974	0.977
0.1	1	0.909	0.909	0.909	0.909	0.909	0.909	0.908	0.910	0.906	0.911	0.905	0.913
0.2	2	0.718	0.718	0.718	0.718	0.717	0.719	0.715	0.721	0.711	0.725	0.706	0.731
0.4	3	0.409	0.409	0.408	0.409	0.407	0.409	0.403	0.417	0.397	0.427	0.390	0.441
0.8	4	0.175	0.175	0.174	0.176	0.174	0.178	0.170	0.188	0.166	0.203	0.160	0.222
1.6	5	0.637 *E*-1[a]	0.637 *E*-1	0.636 *E*-1	0.647 *E*-1	0.632 *E*-1	0.674 *E*-1	0.616 *E*-1	0.773 *E*-1	0.974 *E*-1	0.912 *E*-1	0.570 *E*-1	0.107
3.2	6	0.195 *E*-1	0.195 *E*-1	0.195 *E*-1	0.202 *E*-1	0.193 *E*-1	0.222 *E*-1	0.183 *E*-1	0.290 *E*-1	0.184 *E*-1	0.374 *E*-1	0.178 *E*-1	0.464 *E*-1
6.4	7	0.533 *E*-2	0.534 *E*-2	0.533 *E*-2	0.575 *E*-2	0.532 *E*-2	0.685 *E*-2	0.527 *E*-2	0.101 *E*-1	0.521 *E*-2	0.138 *E*-1	0.515 *E*-2	0.176 *E*-1
12.8	8	0.140 *E*-2	0.140 *E*-2	0.140 *E*-2	0.158 *E*-2	0.140 *E*-2	0.205 *E*-2	0.140 *E*-2	0.329 *E*-2	0.140 *E*-2	0.465 *E*-2	0.140 *E*-2	0.602 *E*-2
25.6	9	0.355 *E*-3	0.355 *E*-3	0.355 *E*-3	0.428 *E*-3	0.356 *E*-3	0.596 *E*-3	0.359 *E*-3	0.102 *E*-2	0.363 *E*-3	0.146 *E*-2	0.367 *E*-3	0.203 *E*-2
51.2	10	0.891 *E*-4	0.891 *E*-4	0.892 *E*-4	0.115 *E*-3	0.895 *E*-4	0.170 *E*-3	0.905 *E*-4	0.302 *E*-3	0.920 *E*-4	0.439 *E*-3	0.937 *E*-4	0.574 *E*-3
102.4	11	0.223 *E*-4	0.223 *E*-4	0.223 *E*-4	0.308 *E*-4	0.224 *E*-4	0.480 *E*-4	0.227 *E*-4	0.875 *E*-4	0.231 *E*-4	0.128 *E*-3	0.236 *E*-4	0.168 *E*-3
204.8	12	0.558 *E*-5	0.558 *E*-5	0.559 *E*-5	0.826 *E*-5	0.561 *E*-5	0.134 *E*-4	0.568 *E*-5	0.249 *E*-4	0.579 *E*-5	0.365 *E*-4	0.592 *E*-5	0.340 *E*-4

y	a \ N	1.0		1.2		2.4		4.8		9.6	
		r	r_2	r	r_2	r	r_2	r	r_2	r	r_2
0.0063	−3	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.0125	−2	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.998	0.999
0.025	−1	0.994	0.994	0.994	0.995	0.993	0.996	0.992	0.997	0.990	0.999
0.05	0	0.974	0.977	0.974	0.978	0.971	0.982	0.967	0.990	0.960	0.995
0.1	1	0.903	0.915	0.901	0.917	0.892	0.934	0.877	0.961	0.850	0.979
0.2	2	0.702	0.738	0.697	0.745	0.671	0.800	0.631	0.879	0.562	0.931
0.4	3	0.383	0.456	0.376	0.474	0.337	0.586	0.289	0.730	0.230	0.816
0.8	4	0.155	0.243	0.149	0.265	0.124	0.391	0.102	0.533	0.912 *E*-1	0.614
1.6	5	0.546 *E*-1	0.124	0.523 *E*-1	0.141	0.432 *E*-1	0.229	0.362 *E*-1	0.323	0.327 *E*-1	0.376
3.2	6	0.173 *E*-1	0.555 *E*-1	0.168 *E*-1	0.644 *E*-1	0.149 *E*-1	0.109	0.131 *E*-1	0.156	0.116 *E*-1	0.182
6.4	7	0.508 *E*-2	0.214 *E*-1	0.502 *E*-2	0.250 *E*-1	0.477 *E*-2	0.432 *E*-1	0.457 *E*-2	0.619 *E*-1	0.436 *E*-2	0.724 *E*-1
12.8	8	0.141 *E*-2	0.735 *E*-2	0.141 *E*-2	0.864 *E*-2	0.143 *E*-2	0.150 *E*-1	0.145 *E*-2	0.216 *E*-1	0.147 *E*-2	0.252 *E*-1
25.6	9	0.372 *E*-3	0.234 *E*-2	0.378 *E*-3	0.275 *E*-2	0.401 *E*-3	0.479 *E*-2	0.433 *E*-3	0.689 *E*-2	0.485 *E*-3	0.806 *E*-2
51.2	10	0.956 *E*-4	0.705 *E*-3	0.975 *E*-4	0.831 *E*-3	0.107 *E*-3	0.145 *E*-2	0.121 *E*-3	0.209 *E*-2	0.144 *E*-3	0.244 *E*-2
102.4	11	0.241 *E*-4	0.206 *E*-3	0.247 *E*-4	0.243 *E*-3	0.277 *E*-4	0.425 *E*-3	0.325 *E*-4	0.612 *E*-3	0.404 *E*-4	0.715 *E*-3
204.8	12	0.606 *E*-5	0.590 *E*-4	0.620 *E*-5	0.696 *E*-4	0.701 *E*-5	0.122 *E*-3	0.837 *E*-5	0.175 *E*-3	0.108 *E*-4	0.205 *E*-3

[a] The decimal exponent *E*-03 means a factor 10^{-3}.

imations do not fully account for the interference phenomena of the scattering event.

Table II lists the various moduli $r_k(y)$, normalized in the forward direction, as a function of the angular variable y for different a values. For orientation, the magnitude of y is given in a few examples, e.g., for $\theta=6°$ and $T=50$ keV, y equals 1.812 for $Z=32$ and 1.347 for $Z=78$; for $T=100$ keV the respective values are 2.622 and 1.949. To cover the desired wide range of y, a geometric division of the form $y=0.05\times 2^N$ was chosen. Table II shows that the normalized modulus $r_1(y)$ reproduces the exact values $r(y)$ in a large (a,y) region with an accuracy high enough to be sufficient for the experimentalist. Note that r_1 itself is independent of a; it can be seen as the limit of r_2 for vanishing a. The region of moderate accuracy of r_2 is smaller than for r_1, the reasons for which are already pointed out in the discussion of ϵ_2. The over-all behavior of the relative deviation $\eta_k=(r_k-r)/r$ can readily be appreciated from Fig. 2.

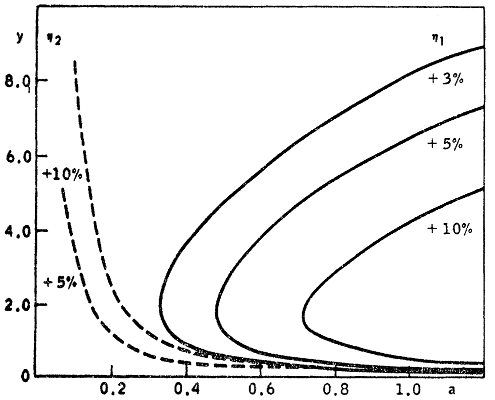

FIG. 2. Topographic presentation of the deviations η_1 and η_2 of the first- and second-order Born approximation from the Molière scattering modulus normalized in the forward direction as a function of the angular variable y and of $a=Z/137\beta$.

Phase

The phase angles $\varphi=\tan^{-1}(h/g)$ and $\varphi_2=\tan^{-1}(h_2/g_1)$ in radians are compiled in Table III; the fact that $\varphi_1=0$ was the primary objection to the first-order Born approximation. A division of the phase angle by a is suggested by the following considerations: (1) For large scattering angles, screening effects are negligible, so that the scattering amplitudes and their phase angles as well should approach the values rendered by the Rutherford formula, i.e., should behave as does $2a\ln y$

TABLE III. Phase angle of scattering amplitude φ_k/a in radians as a function of the angular variable for different values of a.

$N \backslash a$	0.01		0.1		0.2		0.4		0.6		0.8		1.0		1.2		2.4		4.8		9.6	
	φ/a	φ_2/a	φ/a	φ_2/a	φ/a	φ_2/a	φ/a	φ_2/a	φ/a	φ_2/a	φ/a	φ_2/a	φ/a	φ_2/a	φ/a	φ_2/a	φ/a	φ_2/a	φ/a	φ_2/a	φ/a	φ_2/a
−3	0.275	0.279	0.275	0.279	0.272	0.279	0.263	0.278	0.250	0.277	0.236	0.275	0.222	0.272	0.209	0.269	0.155	0.246	0.105	0.194	0.065	0.126
−2	0.275	0.279	0.275	0.279	0.273	0.279	0.263	0.278	0.250	0.277	0.237	0.275	0.223	0.272	0.210	0.269	0.155	0.246	0.105	0.194	0.065	0.126
−1	0.277	0.281	0.276	0.280	0.274	0.280	0.264	0.279	0.251	0.278	0.237	0.276	0.244	0.274	0.211	0.271	0.156	0.247	0.105	0.194	0.065	0.126
0	0.306	0.285	0.281	0.285	0.278	0.285	0.269	0.284	0.256	0.282	0.241	0.280	0.227	0.278	0.214	0.275	0.159	0.250	0.108	0.196	0.066	0.127
1	0.319	0.304	0.299	0.303	0.297	0.303	0.287	0.302	0.272	0.300	0.258	0.298	0.243	0.295	0.229	0.291	0.170	0.262	0.116	0.202	0.073	0.129
2	0.371	0.372	0.367	0.372	0.364	0.371	0.352	0.369	0.336	0.366	0.319	0.361	0.302	0.356	0.285	0.350	0.215	0.304	0.151	0.221	0.099	0.135
3	0.582	0.585	0.581	0.585	0.576	0.583	0.561	0.575	0.538	0.563	0.514	0.547	0.490	0.530	0.468	0.510	0.368	0.397	0.274	0.256	0.203	0.145
4	1.04	1.04	1.04	1.04	1.03	1.03	1.01	0.987	0.976	0.931	0.941	0.868	0.906	0.806	0.587	0.747	0.717	0.496	0.551	0.286	0.482	0.153
5	1.75	1.75	1.75	1.73	1.74	1.69	1.71	1.53	1.66	1.35	1.62	1.19	1.56	1.05	1.51	0.939	1.27	0.557	0.977	0.303	0.697	0.157
6	2.78	2.79	2.78	2.72	2.77	2.54	2.72	2.10	2.66	1.72	2.54	1.44	2.51	1.23	2.43	1.07	2.02	0.593	1.55	0.312	1.12	0.159
7	4.04	4.03	4.03	3.84	4.01	3.40	3.95	2.54	3.86	1.97	3.76	1.59	3.65	1.33	3.54	1.14	2.98	0.612	2.32	0.316	1.60	0.160
8	5.37	5.37	5.37	4.93	5.35	4.11	5.27	2.84	3.17	2.12	5.04	1.68	4.91	1.39	4.76	1.18	4.10	0.622	3.28	0.319	2.15	0.161
9	6.76	6.75	6.75	5.94	6.73	4.67	6.65	3.04	6.53	2.22	6.39	1.73	6.24	1.42	6.10	1.21	5.35	0.629	4.05	0.321	2.78	0.162
10	8.15	8.13	8.14	6.84	8.12	5.10	8.04	3.18	7.92	2.28	7.77	1.77	7.60	1.45	7.44	1.22	6.64	0.633	5.65	0.321	3.58	0.162
11	9.52	9.51	9.51	7.62	9.50	5.44	9.43	3.29	9.32	2.33	9.15	1.80	8.98	1.47	8.82	1.23	8.00	0.636	6.98	0.323	4.15	0.162
12	10.9	10.9	10.9	8.30	10.9	5.71	10.8	3.36	10.7	2.37	10.6	1.82	10.4	1.43	10.2	1.25	9.47	0.639	8.34	0.323	4.91	0.162
	1.99		1.99		1.99		2.00		2.00		2.07		2.08		2.04		2.13		1.97		1.10	

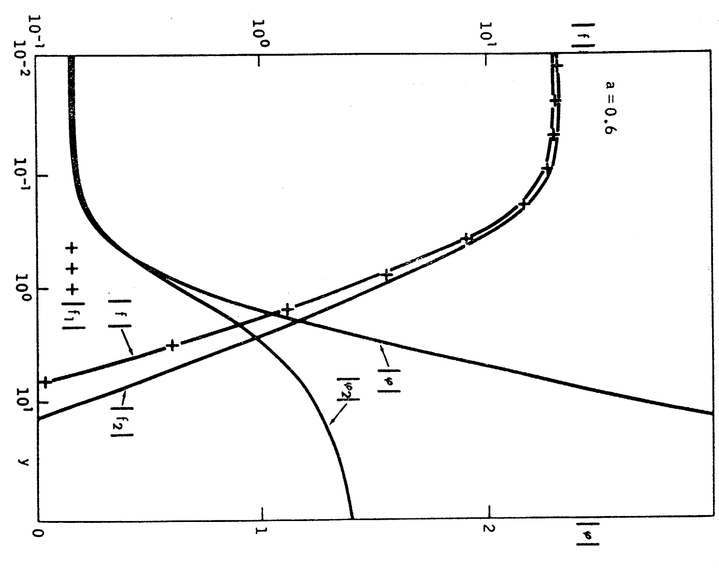

FIG. 3. Scattering amplitude (modulus $|f_k|$ in Compton wavelengths and phase φ_k in radians) in Molière and in first- and second-order Born approximations as a function of the angular variable y for $a=Z/137\beta=0.6$. The suffixes 1 and 2 refer to the first- and second-order Born approximations, respectively.

(Mott and Massey).[14] Table III permits a simple check of this point because

$$\frac{1}{a}\frac{\Delta\varphi}{\Delta \ln y}=\frac{1.443}{a}\frac{\Delta\varphi}{\Delta N}.$$

For the Molière approximation this quotient is not only constant for a wide range of a but also amounts to the correct numerical value of 2, as shown in the last line of Table III. (2) For small scattering angles and small a the phase angles will be small, so they can be expressed by their tangent (i.e., $\varphi=h/g$), and again an over-all proportionality to a can be expected. Furthermore, under these conditions $\varphi_2(0)$ should give a good estimate for $\varphi(0)$. We find

$$\varphi_2(0)=a\Big[\sum_1^3 a_j/b_j^2\Big]^{-1}\sum_1^3\sum_1^3 a_ja_k(b_j^2-b_k^2)^{-1}\ln\frac{b_j}{b_k}=0.2788a, \quad (23)$$

which correlates well with the result of the Molière approximation. It should be pointed out that in the case of a single exponential potential, Eq. (23) becomes $\varphi_2(0)=0.5a$, independent of the screening parameter b_k.

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[14] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, England, 1949), 2nd ed.

TABLE IV. Scattering cross section in the Molière approximation in units of the Rutherford cross section as a function of the angular variable y for different values of $a=Z/137\beta$.

$N \backslash a$	0.01	0.1	0.2	0.4	0.6	0.8	1.0	1.2	2.4	4.8	9.6
−3	0.279 *E*-7	0.278 *E*-7	0.276 *E*-7	0.269 *E*-7	0.258 *E*-7	0.247 *E*-7	0.236 *E*-7	0.225 *E*-7	0.174 *E*-7	0.119 *E*-7	0.674 *E*-8
−2	0.445 *E*-6	0.444 *E*-6	0.440 *E*-6	0.429 *E*-6	0.412 *E*-6	0.394 *E*-6	0.376 *E*-6	0.359 *E*-6	0.278 *E*-6	0.190 *E*-6	0.107 *E*-6
−1	0.705 *E*-5	0.703 *E*-5	0.698 *E*-5	0.679 *E*-5	0.653 *E*-5	0.625 *E*-5	0.596 *E*-5	0.568 *E*-5	0.440 *E*-5	0.300 *E*-5	0.169 *E*-5
0	0.109 *E*-4	0.108 *E*-3	0.108 *E*-3	0.105 *E*-3	0.101 *E*-3	0.961 *E*-4	0.916 *E*-4	0.873 *E*-4	0.674 *E*-4	0.456 *E*-4	0.254 *E*-4
1	0.151 *E*-2	0.150 *E*-2	0.149 *E*-2	0.145 *E*-2	0.139 *E*-2	0.133 *E*-2	0.126 *E*-2	0.120 *E*-2	0.910 *E*-3	0.600 *E*-3	0.319 *E*-3
2	0.151 *E*-1	0.150 *E*-1	0.149 *E*-1	0.144 *E*-1	0.137 *E*-1	0.129 *E*-1	0.122 *E*-1	0.115 *E*-1	0.823 *E*-2	0.497 *E*-2	0.223 *E*-2
3	0.782 *E*-1	0.778 *E*-1	0.768 *E*-1	0.732 *E*-1	0.684 *E*-1	0.632 *E*-1	0.581 *E*-1	0.533 *E*-1	0.333 *E*-1	0.166 *E*-1	0.597 *E*-2
4	0.228	0.227	0.223	0.209	0.190	0.170	0.151	0.135	0.722 *E*-1	0.331 *E*-1	0.174 *E*-1
5	0.486	0.482	0.472	0.437	0.391	0.344	0.302	0.265	0.140	0.670 *E*-1	0.310 *E*-1
6	0.725	0.720	0.707	0.661	0.601	0.540	0.484	0.436	0.266	0.139	0.628 *E*-1
7	0.872	0.868	0.858	0.820	0.770	0.718	0.669	0.623	0.437	0.274	0.141
8	0.956	0.953	0.947	0.923	0.890	0.855	0.820	0.785	0.630	0.439	0.257
9	0.986	0.986	0.984	0.974	0.956	0.936	0.914	0.904	0.791	0.629	0.445
10	0.997	0.997	0.995	0.991	0.985	0.978	0.969	0.963	0.904	0.791	0.629
11	0.999	0.999	0.999	0.997	0.995	0.993	0.990	0.987	0.963	0.904	0.791
12	1.000	1.000	1.000	0.999	0.999	0.998	0.997	0.996	0.987	0.963	0.904

Comparing now the values φ/a and φ_2/a in Table III, it is seen that for small scattering angles ($y \ll 1$) the second-order approximation renders phase angles accurate enough to be taken for the exact values. For large angles, however, the discrepancies are tremendous.

V. DISCUSSION

The results of the previous section show that neither the first-order nor the second-order Born approximation renders reliable scattering amplitudes when a is not very small compared to unity. This remains true even when the scattering angles are small, as can be seen in Fig. 3, in which, as an example for the whole picture, the scattering amplitude for $a=0.6$ is given. This finding refutes the statement often brought forth in electron microscopic discussion that a first-order Born approximation is applicable despite a large value of a, as long as the scattering angles are small. This result also demonstrates that the optical theorem is a necessary, not a sufficient condition, since regardless of the fact that it fulfills the optical theorem, the second-order approximation is erroneous.

To obtain reasonably exact values, the Molière approximation must be applied, though on the one hand it is more involved than the low-order approximation but on the other hand is less cumbersome than exact or approximated phase-shift calculations. If, however, one is interested in small-angle-scattering events, as in electron diffraction and electron microscopy, the results suggested the following simplified procedure for obtaining rather fair values of the scattering amplitudes: One calculates the modulus $|f(y)|$ as $|f_1(y)| \times |f(0)/f_1(0)|$; i.e., one calculates the scattering amplitude in the first-order Born approximation for whatever potential is requested and performs one integration (numerically) to establish the angle-independent normalization factor. This is why a closed form of $f(0)$ would be desirable. Kessler,[15] in his experiments on electron scattering, applied empirically such an over-all correction factor for the scattering cross section, a procedure that can be justified by the heuristic arguments given above. To obtain the phase angle of the scattering amplitude for small angles one can resort to φ_2. This was proposed previously by Glauber and Schomaker.[1] They, however, calculated φ_2 as h_2/g_1, which for large scattering angles incidentally has the logarithmic behavior demanded by the Rutherford formula, thus obscuring the actually large errors of the true phase $\varphi_2=\tan^{-1}(h_2/g_1)$ in comparison to φ. Furthermore, their statement that the phase angle for small scattering angles is little dependent on the scattering potential cannot be confirmed. It is true that in the case of a single exponential potential $\varphi_2(0)=0.5a$; yet for the Thomas-Fermi potential we find $\varphi_2(0)\approx 0.25a$, which is significantly different.

Haine[16] in his book points out the importance of phase contrast in electron microscopy. This contrast may be shown to be of the order $2a\ln(1+y_0^2)\sin\varphi$ for values of a considerably smaller than unity and for not too large aperture angle y_0. For a single exponential potential this contrast amounts to $a^2\ln(1+y_0^2)$. In a recent paper Zeitler[17] has shown that the contrast of a single atom in an aberration-free electron microscope can exceed the value of 20%. Admittedly a single atom seems a rather academic proposition. It is not unfeasible, however; in a real electron microscope the phase shifts introduced by spherical aberration are "balanced" by optimal defocusing. Since, however, in the image plane the scattered wave is shifted not only by $\pi/2$ with respect to the unscattered wave, as the first-order Born approximation would imply, but by an additional amount depending on the Z of the scatterer, each kind of atom in a specimen requires a different amount of defocusing to exhibit optimal contrast. Heidenreich[18]

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[15] J. Kessler, Z. Physik **182**, 153 (1964).

[16] M. S. Haine, *The Electron Microscope* (E. and F. N. Spon, Ltd., London, 1961).

[17] E. Zeitler, *Electron Microscopy* (Maruzen Company, Ltd., Tokyo, 1966), Vol. 1, p. 43.

[18] R. D. Heidenreich, Bell System Tech. J. **45**, 651 (1966).

has produced electron micrographs of low-Z material with a point-to-point resolution of 2 Å or better that show an overwhelming amount of detail. If heavy atoms were built into this matrix, the phase shifts discussed in this paper would probably bring out these single atoms, while the required defocusing would suppress the matrix.

APPENDIX I

The influence of the screening effect on the scattering cross section is borne out most clearly if the Rutherford cross section is used as the unit, since it is exact when no screening is present. Molière[5] published a set of curves of this ratio for various a values; the usefulness of these curves for discussion is documented by their repeated reprinting.[19,20] Since on the one hand the major part of these curves is based on interpolation only and since on the other hand our calculations automatically rendered the ratio of cross sections in question, we should like to include a table of these values (Table IV).

APPENDIX II

Nigam *et al.*[21] have questioned the validity of the Molière approximation for obtaining the cross section for single electron scattering. Their statement is surprising in view of many papers[6–8,12,13] which either show numerical and experimental agreement between the values of the cross section for single scattering obtained from Molière and exact phase-shift calculations or the physical equivalence between the two theoretical treatments for small scattering angles. Using Dalitz's formula[22] for one Yukawa potential Nigam *et al.* had to adjust the parameter b_1 [our Eq. (3)] from its actual value of 1.12 to 1.80 to obtain agreement with values from multiple scattering experiments.[23] Leaving, however, the potential unchanged, that is retaining $b_1 = 1.12$ but changing from the second-order Born approximation to the Molière approximation alters the results in the same fashion as does the change of parameters. The same holds true when Gorshkov's formula[24] for three Yukawa potentials is compared with the Molière approximation. Hence, multiple scattering experiments and the argument by Nigam *et al.* do not refute the validity of the Molière approximation, whereas single scattering experiments and theoretical considerations confirm it.

APPENDIX III

In some instances[25,26] more exact atomic potentials have been applied to compute the first-order Born scattering amplitude, which in turn has been approximated by best-fit techniques in the form of

$$f_1(q) = \sum c_i e^{-d_i q^2}.$$

The corresponding $h_2(q)$ can be readily found with the aid of Eq. (9):

$$h_2(q) = \frac{1}{p} \sum \sum \frac{c_i c_k}{d_i + d_k} \exp\left[-q^2 \frac{d_i d_k}{d_i + d_k} \right].$$

The two equations suffice to calculate the phase shift. It is obvious that the unitarity condition is fulfilled. For large angles these approximations cannot hold, since the ratio of $f_1(q)$ to the Rutherford amplitude does not approach unity for large values of q, the latter amplitude being proportional to q^{-2}.

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[21] B. P. Nigam, M. K. Sundaresan, and Ta-You Wu, Phys. Rev. **115**, 491 (1959).

[22] R. H. Dalitz, Proc. Roy. Soc. (London) **A206**, 509 (1951).

[23] A. O. Hanson, L. H. Lanzl, E. M. Lyman, and M. B. Scott, Phys. Rev. **84**, 634 (1951).

[24] V. G. Gorshkov, Zh. Eksperim. i Teor. Fiz. **41**, 977 (1961); **43**, 1714 (1962) [English transls.: Soviet Phys.—JEPT **14**, 694 (1962); **16**, 1211 (1963)].

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[26] D. T. Cromer and J. T. Waber, Acta Cryst. **18**, 104 (1965).