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## Rapid Calculation of Electron Scattering Factors

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$C_{33} = 1.417 \times 10^6$  dynes/cm. In zero point motion  $2V = h\nu_1/2$  and we find for  $\nu_1$ :  $\langle S_1^2 \rangle_{\nu_1} = 22.35 \times 10^{-20}$  cm<sup>2</sup>,  $\langle S_2^2 \rangle_{\nu_1} = 6.74 \times 10^{-20}$  cm<sup>2</sup>; and for  $\nu_2$ :  $\langle S_1^2 \rangle_{\nu_2} = 20.52 \times 10^{-20}$  cm<sup>2</sup>,  $\langle S_2^2 \rangle_{\nu_2} = 23.1 \times 10^{-20}$  cm<sup>2</sup>.

One must write  $\delta r = 2S_1$  in terms of the normal modes. If  $\beta$  is the angle between  $N_1$  and  $S_1$ , while  $\gamma$  is the angle between  $N_2$  and  $S_2$ , one has

$$S_1 = N_1 \cos\beta - N_2 \cos\gamma, \quad S_2 = N_1 \sin\beta + N_2 \sin\gamma.$$

Then  $\langle (\delta r)^2 \rangle = 4 \langle N_1^2 \cos^2\beta - N_1 N_2 \cos\beta \cos\gamma + N_2^2 \cos^2\gamma \rangle$ . Now  $\langle N_1 N_2 \rangle = 0$ , and since  $\langle N_1^2 \rangle \cos^2\beta = \langle S_1^2 \rangle_{\nu_1}$  and  $\langle N_2^2 \rangle \cos^2\gamma = \langle S_1^2 \rangle_{\nu_2}$  one has

$$\langle r^{-3} \rangle = r_0^{-6} \{ 1 + [12 \langle (\delta r)^2 \rangle / r_0^2] \} = r_0^{-6} (1 + 0.0755).$$

$S_3^2$  is found to be  $22.9 \times 10^{-20}$  cm<sup>2</sup>. The change in proton-proton vector direction,  $\alpha_A$ , is gotten from  $S_3/\alpha_A = (r_0/2) \cos(109^\circ/2)$ . Then  $\langle \alpha_A^2 \rangle = 1.0 \times 10^{-3}$  rad<sup>2</sup>.

## Rapid Calculation of Electron Scattering Factors\*

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The phase amplitude method is used to reduce the radial Schrödinger equation to two separate differential equations, one for the phase and one for the amplitude. These functions are both smooth as opposed to the rapidly oscillating solution of the radial Schrödinger equation for electron energies in the kilovolt range. The partial-wave phase shifts were obtained rapidly by integrating the differential equations for the phase and amplitude numerically. Hartree-Fock and Thomas-Fermi-Dirac fields were used in the calculation. Results for argon and uranium are given in order to compare with previous results. It was found that the WKB approximation to the partial-wave phase shift is a good approximation for the energies used in electron diffraction. This rapid method of computing electron-scattering factors will make routine analysis of electron diffraction data more rapid as well as more exact.

### I. INTRODUCTION

ACCURATE electron-scattering factors for atoms in the kilovolt energy range are needed in order to analyze electron-diffraction data. Thus the molecular parameters obtained from analysis of electron-diffraction data depend on the accuracy of the electron-scattering factors used in the analyses. Previous calculations have been attempted for these amplitudes.<sup>1-5</sup> The results were limited because of the numerical difficulties involved in a solution of the scattering problem using partial-wave analysis. In some cases this difficulty was also coupled with the lack of a good description of the effective electron atom potential.

Good analytic expressions for the potentials are now available.<sup>6,7</sup> The most significant problem was due to the time required to do one calculation. At these energies the wave function oscillates rapidly and thus the numerical solution to the problem becomes quite difficult. The calculation by Karle and Bonham<sup>5</sup> took some 40 min per partial wave on an IBM 709 and a large number of partial waves are needed to describe the scattering. Using the methods described in the next section, the time has been reduced substantially; namely, to approximately 10 sec per partial wave on an IBM 709.

### II. THEORY

Assuming the electron is elastically scattered from an effective spherically symmetric potential, and neglecting spin and exchange effects, the scattering amplitude is given by<sup>8</sup>

$$f(\theta) = (2ik)^{-1} \sum_{l=0}^{\infty} (2l+1) [\exp(2i\eta_l) - 1] P_l(\cos\theta), \quad (2.1)$$

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<sup>1</sup> R. Glauber and V. Schomaker, *Phys. Rev.* **89**, 667 (1953).

<sup>2</sup> J. A. Hoerni and J. A. Ibers, *Phys. Rev.* **91**, 1182 (1953).

<sup>3</sup> J. A. Ibers and J. A. Hoerni, *Acta Cryst.* **7**, 405 (1954).

<sup>4</sup> R. A. Bonham and J. Karle, *J. Phys. Soc. Japan* **17**, Suppl. B-II, 6 (1962).

<sup>5</sup> J. Karle and R. A. Bonham, *J. Chem. Phys.* **40**, 1396 (1964).

<sup>6</sup> R. A. Bonham and T. G. Strand, *J. Chem. Phys.* **39**, 2200 (1963).

<sup>7</sup> T. G. Strand and R. A. Bonham, *J. Chem. Phys.* **40**, 1686 (1964).

<sup>8</sup> T. Wu and T. Ohmura, *Quantum Theory of Scattering* (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1962).

where  $\eta_l$  is the partial-wave phase shift and  $P_l(\cos\theta)$  is a Legendre function with  $\theta$  as the scattering angle. Also

$$k^2 = (2m/\hbar^2)E, \quad (2.2)$$

where  $E$  is the incident energy of the electron and  $m$  is its mass.

The method used here is essentially one used by Wheeler<sup>9</sup> as an efficient method for calculating Coulomb wavefunctions and can be described as the phase amplitude method. A related method has been described by Lin, Sherman, and Percus.<sup>10</sup> One starts with the radial Schrödinger equation<sup>8</sup>

$$(d^2u_l/dr^2) + \{k^2 - U(r) - [l(l+1)/r^2]\}u_l = 0, \quad (2.3)$$

where

$$U(r) = (2m/\hbar^2)V(r) \quad (2.4)$$

and  $V(r)$  is the effective electron atom potential. Let  $F_l(r)$  be the "regular" solution which vanishes at  $r=0$  and  $G_l(r)$  be the "irregular" solution. These satisfy the condition

$$G_l(dF_l/dr) - F_l(dG_l/dr) = k. \quad (2.5)$$

Now let  $u_l(r) = A_l(r) \exp[i\phi_l(r)]$  and substitute this into the radial Schrödinger equation, Eq. (2.3). Equating both the real part and the imaginary part to zero gives

$$\frac{d^2A_l}{dr^2} - A_l \left( \frac{d\phi_l}{dr} \right)^2 + \left[ k^2 - U(r) - \frac{l(l+1)}{r^2} \right] A_l = 0 \quad (2.6)$$

and

$$A_l(d^2\phi_l/dr^2) + 2(dA_l/dr)(d\phi_l/dr) = 0. \quad (2.7)$$

Equation (2.7) can be integrated once to give

$$A_l^2(d\phi_l/dr) = \text{constant}. \quad (2.8)$$

The constant can be obtained by relating  $A_l$  and  $\phi_l$  to  $F_l$  and  $G_l$ . Since  $F_l$  goes like a sine function as  $r \rightarrow \infty$  and  $G_l$  goes like a cosine function as  $r \rightarrow \infty$ , one has

$$F_l = A_l \sin\phi_l \quad (2.9)$$

and

$$G_l = A_l \cos\phi_l. \quad (2.10)$$

Substituting Eqs. (2.9) and (2.10) into Eq. (2.5) gives

$$A_l^2(d\phi_l/dr) = k. \quad (2.11)$$

Solve Eq. (2.11) for  $d\phi_l/dr$  and insert into Eq. (2.6); letting  $\rho = kr$ , this gives

$$\frac{d^2A_l}{d\rho^2} - \frac{1}{A_l^3} + \left[ 1 - \frac{V(\rho)}{E} - \frac{l(l+1)}{\rho^2} \right] A_l = 0, \quad (2.12)$$

where now  $A_l$  is considered a function of  $\rho$ . Equation (2.11) can be reduced further by letting

$$\phi_l(r) = kr - (l\pi/2) + \eta_l(r), \quad (2.13)$$

where  $\eta_l(0)$  will be the partial-wave phase shift due to the potential  $V(r)$ . The phase shift  $\eta_l(r)$  is defined relative to the origin so that the wavefunction becomes the Bessel function solution for  $r \rightarrow \infty$ , and  $\phi_l \rightarrow kr - (l\pi/2)$  as  $r \rightarrow \infty$ . This is done in order to integrate the equations inwards from infinity. Substituting Eq. (2.13) into Eq. (2.11) and using  $\rho = kr$  gives

$$d\eta_l(\rho)/d\rho = A_l^{-2} - 1. \quad (2.14)$$

Thus Eq. (2.12) must first be solved for  $A_l(\rho)$  and then this can be used to solve for the partial-wave phase shift using Eq. (2.14). These are the equations to be solved numerically. It might appear that the problem of solving these equations would be more difficult than solving the radial Schrödinger equation since the linear second-order radial Schrödinger equation has been replaced by a nonlinear second-order equation for  $A_l(\rho)$  plus the integral that must be evaluated for  $\phi_l(\rho)$ . The advantage of this approach lies in the fact that the amplitude function  $A_l(\rho)$  and the phase function  $\phi_l(\rho)$  are smooth functions of  $\rho$  whereas the radial solution  $u_l(\rho)$  is a rapidly oscillating function, which makes it more difficult to solve numerically. In this particular problem  $k \approx 100 \text{ \AA}^{-1}$  so that  $u_l(\rho)$  is oscillating quite rapidly. This rapid oscillation was the principle difficulty encountered by Karle and Bonham.<sup>5</sup> Because of this they carried out the numerical calculation in double precision which partly accounts for their long computing time.

### III. NUMERICAL CALCULATIONS

The solution is to be matched onto the "regular" and "irregular" solutions of Bessel's equation which must be obtained. The "regular" and "irregular" solutions are

$$\mathcal{F}_l(\rho) = (\pi\rho/2)^{1/2} J_{l+1/2}(\rho) \quad (3.1)$$

and

$$\mathcal{G}_l(\rho) = (\pi\rho/2)^{1/2} J_{-l-1/2}(\rho) \quad (3.2)$$

which obey the same recurrence relation

$$\begin{pmatrix} \mathcal{F}_{l+1} \\ \mathcal{G}_{l+1} \end{pmatrix} = \frac{2l+1}{\rho} \begin{pmatrix} \mathcal{F}_l \\ \mathcal{G}_l \end{pmatrix} - \begin{pmatrix} \mathcal{F}_{l-1} \\ \mathcal{G}_{l-1} \end{pmatrix}, \quad (3.3)$$

where  $J_{l+1/2}(\rho)$  is a Bessel function. Define

$$\mathcal{F}_l = \alpha_l \sin\Phi_l \quad (3.4)$$

$$\mathcal{G}_l = \alpha_l \cos\Phi_l \quad (3.5)$$

<sup>9</sup> J. A. Wheeler, Phys. Rev. **52**, 1123 (1937).

<sup>10</sup> S. Lin, N. Sherman, and J. K. Percus, Nucl. Phys. **45**, 492 (1963).

which has the same form as Eqs. (2.9) and (2.10). Then the amplitude and phase of the Bessel's solutions are

$$\mathcal{G}_l = [\mathcal{F}_l^2 + \mathcal{G}_l^2]^{1/2} \quad (3.6)$$

and

$$\tan \Phi_l = \mathcal{F}_l / \mathcal{G}_l. \quad (3.7)$$

Setting  $\Phi_l = \rho - (l\pi/2) + \epsilon_l(\rho)$  and using the recurrence relation [Eq. (3.3)] one can obtain explicit formulas for  $\mathcal{G}_l$  and  $\epsilon_l$ . The first few values are

$$\mathcal{G}_0 = 1, \quad \epsilon_0 = 0, \quad (3.8)$$

$$\mathcal{G}_1 = (1+z^2)^{1/2}, \quad \epsilon_1 = \tan^{-1}z, \quad (3.9)$$

$$\mathcal{G}_2 = (1+3z^2+9z^4)^{1/2}, \quad \epsilon_2 = \tan^{-1}[3z/(1-3z^2)], \quad (3.10)$$

where  $z = 1/\rho$ . Note that

$$\mathcal{G}_l \xrightarrow{\rho \rightarrow \infty} 1 \quad \text{and} \quad \epsilon_l \xrightarrow{\rho \rightarrow \infty} 0$$

as they should. Also note that for  $l > 0$ ,

$$\mathcal{G}_l \xrightarrow{\rho \rightarrow 0} \infty.$$

The  $\mathcal{G}_l(\rho)$  and  $\epsilon_l(\rho)$  provide the asymptotic form for the  $A_l(\rho)$  and  $\eta_l(\rho)$  in the phase-amplitude method.

The simplest method was used to integrate Eq. (2.12); namely the second derivative was replaced by a second-order difference formula. This gives

$$A_l(\rho - \Delta\rho) = 2A_l(\rho) - A_l(\rho + \Delta\rho) + (\Delta\rho)^2 \times \left\{ \frac{1}{A_l(\rho)^3} - \left[ 1 - \frac{V(\rho)}{E} - \frac{l(l+1)}{\rho^2} \right] A_l(\rho) \right\}, \quad (3.11)$$

where  $\Delta\rho$  is the interval step size. The iteration scheme is started by taking  $\rho$  large enough so that the potential may be neglected and the first two values of  $A_l(\rho)$  needed to make an iteration are taken to be  $\mathcal{G}_l(\rho)$  and  $\mathcal{G}_l(\rho + \Delta\rho)$ . After  $A_l(\rho)$  is obtained, Eq. (2.14) is integrated for  $\eta_l(\rho)$  using Simpson's rule.<sup>11</sup> Since

$$A_l(\rho) \xrightarrow{\rho \rightarrow 0} \infty \quad \text{and} \quad dA_l/d\rho \xrightarrow{\rho \rightarrow \infty} 0 \quad \text{for} \quad l > 0,$$

the amplitude function  $A_l$  starts out with  $A_l = 1$  for  $\rho = \infty$  and rises smoothly as  $\rho$  decreases towards zero. Thus for large  $\rho$ , large intervals can be taken in iterating Eq. (3.11) inward for  $A_l$ . As  $A_l$  starts to rise steeply, smaller interval steps must be taken to maintain numerical accuracy. Also

$$d\eta_l(\rho)/d\rho \xrightarrow{\rho \rightarrow 0} -1 \quad \text{since} \quad A_l(\rho) \xrightarrow{\rho \rightarrow 0} \infty \quad \text{for} \quad l > 0.$$

Thus the integration for  $A_l(\rho)$  may be cut off for  $A_l(\rho)$  large. The value of  $A_l$  used as a cutoff depends on how accurately the partial-wave phase shifts need to be known. In the case  $l=0$ ,

$$A_0 \xrightarrow{\rho \rightarrow 0} \text{constant}$$

which just means the equation for  $A_0$  must be integrated all the way to  $\rho=0$  instead of being cut off.

The Thomas-Fermi-Dirac (TFD) potentials for argon and uranium used in the calculation presented here were the same as those used by Karle and Bonham<sup>5</sup> in order to be able to compare the results of the calculation. Karle and Bonham<sup>5</sup> did not present any numerical integration results using a Hartree-Fock (HF) potential. The TFD<sup>5</sup> and HF<sup>7</sup> potentials used for argon were

$$U(r)^{\text{TFD}} = -(2Z/ar) \{ 0.50529e^{-2.68764r} + 0.43447e^{-9.06392r} + 0.06071e^{-46.4985r} \} \quad (3.12)$$

and

$$U(r)^{\text{HF}} = -(2Z/ar) \{ 1.374e^{-2.0636r/a_0} - 0.374e^{-32.485r/a_0} - (r/a_0)[4.296e^{-4.853r/a_0} + 8.916e^{-19.772r/a_0}] \}. \quad (3.13)$$

The TFD<sup>5</sup> potential used for uranium was

$$U(r)^{\text{TFD}} = -(2Z/ar) \{ 0.3100e^{-2.9802r} + 0.56667e^{-10.564r} + 0.12346e^{-50.463r} \}, \quad (3.14)$$

where  $a$  is the relativistic Bohr radius,

$$a = a_0/[1 - (v/c)^2]^{1/2},$$

$a_0$  is the Bohr radius, and  $Z$  is the atomic number.

#### IV. RESULTS

The exact calculation results have been compared with the results from the Born phase-shift formula<sup>8</sup>

$$\eta_l^{\text{B}} = -k \int_0^\infty dr r^2 U(r) j_l^2(kr), \quad (4.1)$$

where  $j_l(kr)$  is a spherical Bessel function and with those from the WKB approximation<sup>8,12</sup>

$$\eta_l^{\text{WKB}} = \int_{r_0}^\infty dr \left[ k^2 - U(r) - \left( \frac{l + \frac{1}{2}}{r} \right)^2 \right]^{1/2} - \int_{(l+1/2)/k}^\infty dr \left[ k^2 - \left( \frac{l + \frac{1}{2}}{r} \right)^2 \right]^{1/2}, \quad (4.2)$$

<sup>11</sup> See, for instance, J. B. Scarborough, *Numerical Mathematical Analysis* (The Johns Hopkins Press, Baltimore, Md., 1962), 5th ed.

<sup>12</sup> M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964).

TABLE I. Partial-wave phase shifts for argon  $Z=18$ .<sup>a</sup>

| $l$ | $\eta_l^{\text{B}_{\text{TFD}}}$ <sup>b</sup> | $\eta_l^{\text{WKB}_{\text{TFD}}}$ <sup>c</sup> | $\eta_l^{\text{KB}_{\text{TFD}}}$ <sup>d</sup> | $\eta_l^{\text{Numerical}_{\text{TFD}}}$ | $\eta_l^{\text{WKB}_{\text{HF}}}$ <sup>e</sup> | $\eta_l^{\text{Numerical}_{\text{HF}}}$ |
|-----|---|---|--|--|--|---|
| 0   | 1.2840  | 1.3224  | 1.2898   | 1.2898                                   | 1.3292   | 1.2967                                  |
| 1   | 0.9379  | 0.9548  | 0.9486   | 0.9487                                   | 0.9611   | 0.9549                                  |
| 2   | 0.7691  | 0.7801  | 0.7754   | 0.7777                                   | 0.7859   | 0.7836                                  |
| 3   | 0.6598  | 0.6677  | 0.6644   | 0.6666                                   | 0.6735   | 0.6725                                  |
| 4   | 0.5801  | 0.5862  | 0.582  | 0.5858                                   | 0.5921   | 0.5917                                  |
| 5   | 0.5182  | 0.5231  | 0.519  | 0.5231                                   | 0.5290   | 0.5291                                  |
| 6   | 0.4681  | 0.4721  | 0.468  | 0.4724                                   | 0.4780   | 0.4782                                  |
| 7   | 0.4264  | 0.4298  |  | 0.4301                                   | 0.4354   | 0.4358                                  |
| 8   | 0.3910  | 0.3938  |  | 0.3942                                   | 0.3993   | 0.3996                                  |
| 9   | 0.3604  | 0.3629  |  | 0.3632                                   | 0.3680   | 0.3683                                  |
| 10  | 0.3337  | 0.3358  |  | 0.3361                                   | 0.3408   | 0.3411                                  |

<sup>a</sup> Incident electron energy is 40 keV.<sup>b</sup> Calculated from Eq. (4.1).<sup>c</sup> Calculated from Eq. (4.2).<sup>d</sup> KB stands for Karle and Bonham (Ref. 5).

where  $r_0$ , the classical turning point, is the zero of the function  $k^2 - U(r) - [(l + \frac{1}{2})/r]^2$ . The results of the calculation for the partial-wave phase shifts are presented in Tables I and II along with the results obtained by Karle and Bonham.<sup>5</sup> The partial-wave phase shifts calculated numerically by Karle and Bonham<sup>5</sup> do not agree with the results obtained here. They integrated the radial wavefunction until it assumed its asymptotic form as a sine function instead of matching onto the Bessel function solution. They found it necessary to make a linear extrapolation from one partial-wave phase shift to another since their integration stopped at  $r=8$  Å and the  $\eta_l$  had not quite reached its asymptotic limit. It was also found that their results for the WKB approximation were not valid because they failed to integrate the region from  $r_0$  to  $(l + \frac{1}{2})/k$  in Eq. (4.2) accurately enough. Therefore their numerically integrated partial-wave phase shifts did not converge to the WKB partial-wave phase shifts. The erroneous results of Karle and Bonham<sup>5</sup> plus the lengthy computing time indicated a need for a better approximation. The results presented here show that the calculation can be done rapidly and that the partial-wave phase shifts converge rapidly to the WKB partial-wave phase

shifts. Both of these facts indicate that a better approximation is not needed.

It can be seen from Tables I and II that the WKB partial-wave phase shifts converge to the numerically calculated phase shifts fairly rapidly. They converge at  $l=5$  for argon for both the TFD case and the HF case and at  $l=11$  for uranium. There is only a small difference between the TFD and HF phases, however this difference will show up more strongly in the expression for the scattering amplitude  $f(\theta)$ . The calculation required  $\sim 10$  sec per partial-wave phase shift on the IBM 709 and  $\sim 1$  sec per partial-wave phase shift on the CDC 3600. This is to be compared with the calculation of Karle and Bonham<sup>5</sup> which required  $\sim 40$  min per partial-wave phase shift on the IBM 709.

The partial-wave phase shifts used in the sum for  $f(\theta)$  were as follows: the numerically integrated partial-wave phase shifts were used until they converged to

TABLE II. Partial-wave phase shifts for uranium  $Z=92$ .<sup>a</sup>

| $l$ | $\eta_l^{\text{B}_{\text{TFD}}}$ <sup>b</sup> | $\eta_l^{\text{WKB}_{\text{TFD}}}$ <sup>c</sup> | $\eta_l^{\text{KB}_{\text{TFD}}}$ <sup>d</sup> | $\eta_l^{\text{Numerical}_{\text{TFD}}}$ |
|-----|---|---|--|--|
| 0   | 5.7234  | 5.2753  | 5.2557   | 5.2555                                   |
| 1   | 3.9818  | 4.1384  | 4.1211   | 4.1228                                   |
| 2   | 3.1518  | 3.3477  | 3.3355   | 3.3376                                   |
| 3   | 2.6261  | 2.7907  | 2.7822   | 2.7845                                   |
| 4   | 2.2514  | 2.3822  | 2.3737   | 2.3785                                   |
| 5   | 1.9662  | 2.0700  | 2.0627   | 2.0678                                   |
| 6   | 1.7399  | 1.8229  | 1.8147   | 1.8217                                   |
| 7   | 1.5549  | 1.6221  | 1.6158   | 1.6214                                   |
| 8   | 1.4004  | 1.4554  | 1.4468   | 1.4550                                   |
| 9   | 1.2694  | 1.3147  | 1.3068   | 1.3145                                   |
| 10  | 1.1567  | 1.1944  | 1.1859   | 1.1943                                   |
| 11  | 1.0589  | 1.0905  | 1.083  | 1.0905                                   |
| 12  | 0.9733  | 0.9999  | 0.991  | 0.9999                                   |
| 13  | 0.8978  | 0.9203  | 0.912  | 0.9203                                   |
| 14  | 0.8307  | 0.8499  | 0.841  | 0.8500                                   |
| 15  | 0.7709  | 0.7872  | 0.780  | 0.7874                                   |
| 16  | 0.7173  | 0.7313  | 0.724  | 0.7314                                   |

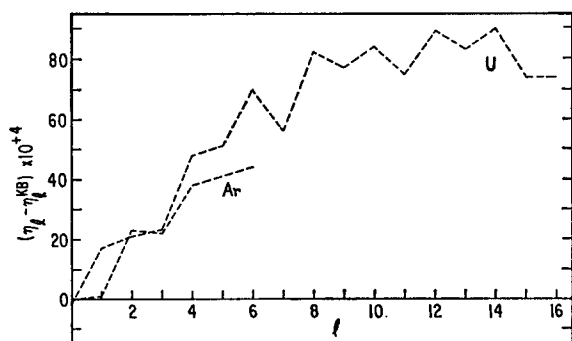
<sup>a</sup> Incident electron energy is 40 keV.<sup>b</sup> Calculated from Eq. (4.1).<sup>c</sup> Calculated from Eq. (4.2).<sup>d</sup> KB stands for Karle and Bonham (Ref. 5).

FIG. 1. Comparison of Karle and Bonham's (Ref. 5) values with the numerical values obtained here for uranium (U) and argon (Ar).

the WKBJ partial-wave phase shifts; then the WKBJ partial-wave phase shifts were used until they converged to the Born partial-wave phase shifts and finally Born partial-wave phase shifts were used until the series for  $f(\theta)$  converged. The real and imaginary parts of  $f(\theta)$  are given by

$$\text{Re}f(\theta) = (2k)^{-1} \sum_{l=0}^{\infty} (2l+1) \sin 2\eta_l P_l(\cos\theta) \quad (4.3)$$

and

$$\text{Im}f(\theta) = (2k)^{-1} \sum_{l=0}^{\infty} (2l+1) (1 - \cos 2\eta_l) P_l(\cos\theta). \quad (4.4)$$

Twice the Born partial-wave phase shift  $\eta_l^B$  was added and subtracted to  $\text{Re}f(\theta)$  in order to make the series converge faster. This gives

$$\begin{aligned} \text{Re}f(\theta) = & k^{-1} \sum_{l=0}^{\infty} (2l+1) \eta_l^B P_l(\cos\theta) \\ & + (2k)^{-1} \sum_{l=0}^{\infty} (2l+1) [\sin 2\eta_l - 2\eta_l^B] P_l(\cos\theta). \end{aligned} \quad (4.5)$$

The first sum can be performed by substituting Eq. (4.1) for  $\eta_l^B$  into the sum and using<sup>3</sup>

$$\sum_{l=0}^{\infty} (2l+1) j_l^2(kr) P_l(\cos\theta) = \frac{\text{sins}r}{sr}, \quad (4.6)$$

where  $s = 2k \sin(\theta/2)$ . It is just the first Born approximation

$$f^B(\theta) = - \int_0^{\infty} dr r^2 U(r) \frac{\text{sins}r}{sr}. \quad (4.7)$$

Thus  $\text{Re}f(\theta)$  becomes

$$\begin{aligned} \text{Re}f(\theta) = & f^B(\theta) + (2k)^{-1} \sum_{l=0}^{\infty} (2l+1) \\ & \times [\sin 2\eta_l - 2\eta_l^B] P_l(\cos\theta). \end{aligned} \quad (4.8)$$

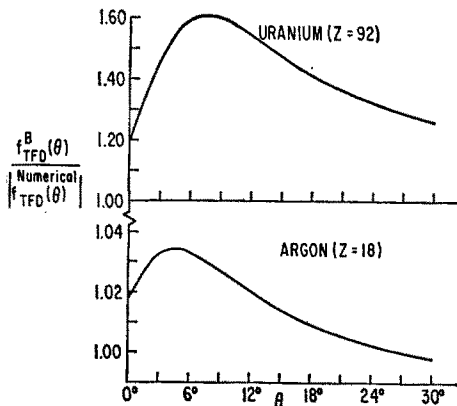


FIG. 2. Ratio of  $f(\theta)^B_{TFD} / |f(\theta)^{\text{Numerical}}_{TFD}|$ .

TABLE III. Magnitude and phase of scattering amplitude for argon  $Z = 18$ .<sup>a</sup>

| $\theta$ | $s (\text{\AA}^{-1})^a$ | $f(\theta)^B_{TFD}{}^b$ | $ f(\theta)^{\text{KB}}_{TFD}{}^c$ | $\eta(\theta)^{\text{KB}}_{TFD}{}^c$ | $\eta(\theta)^{\text{KB}}_{TFD}{}^c$ | $ f(\theta)^{\text{Numerical}}_{TFD}$ | $\eta(\theta)^{\text{Numerical}}_{TFD}$ | $f(\theta)^B_{HF}{}^b$ | $ f(\theta)^{\text{Numerical}}_{HF}$ | $\eta(\theta)^{\text{Numerical}}_{HF}$ |
|----------|-------------------------|-------------------------|------------------------------------|--------------------------------------|--------------------------------------|---------------------------------------|---|------------------------|--------------------------------------|--|
| 0°       | 0.00                    | 5.521                   | 5.417                              | 0.117                                | 0.118                                | 5.428                                 | 0.118                                   | 4.929                  | 4.933                                | 0.135                                  |
| 3°       | 5.47                    | 1.285                   | 1.237                              | 0.359                                | 0.361                                | 1.245                                 | 0.361                                   | 1.343                  | 1.300                                | 0.361                                  |
| 6°       | 10.93                   | 0.453                   | 0.434                              | 0.633                                | 0.633                                | 0.438                                 | 0.633                                   | 0.437                  | 0.425                                | 0.661                                  |
| 9°       | 16.38                   | 0.227                   | 0.219                              | 0.845                                | 0.844                                | 0.221                                 | 0.844                                   | 0.227                  | 0.221                                | 0.853                                  |
| 12°      | 21.83                   | 0.135                   | 0.131                              | 1.018                                | 1.014                                | 0.133                                 | 1.014                                   | 0.137                  | 0.134                                | 1.015                                  |
| 15°      | 27.26                   | 0.090                   | 0.088                              | 1.161                                | 1.154                                | 0.088                                 | 1.154                                   | 0.091                  | 0.089                                | 1.158                                  |
| 18°      | 32.67                   | 0.064                   | 0.063                              | 1.282                                | 1.272                                | 0.063                                 | 1.272                                   | 0.064                  | 0.063                                | 1.282                                  |
| 21°      | 38.06                   | 0.048                   | 0.047                              | 1.386                                | 1.374                                | 0.047                                 | 1.374                                   | 0.048                  | 0.047                                | 1.388                                  |
| 24°      | 43.42                   | 0.037                   | 0.037                              | 1.477                                | 1.463                                | 0.037                                 | 1.463                                   | 0.037                  | 0.037                                | 1.479                                  |
| 27°      | 48.75                   | 0.029                   | 0.030                              | 1.557                                | 1.543                                | 0.030                                 | 1.543                                   | 0.029                  | 0.029                                | 1.559                                  |
| 30°      | 54.05                   | 0.024                   | 0.024                              | 1.628                                | 1.614                                | 0.024                                 | 1.614                                   | 0.024                  | 0.024                                | 1.630                                  |

<sup>a</sup> Incident electron energy is 40 keV and  $s = 2k \sin(\theta/2)$ . <sup>b</sup> Calculated from Eq. (4.7). <sup>c</sup> KB stands for Karle and Bonham (Ref. 5).

TABLE IV. Magnitude and phase of scattering amplitude for uranium  $Z=92$ .<sup>a</sup>

| $\theta$ | $s(\text{\AA}^{-1})^a$ | $f(\theta)^B_{\text{TFD}}^b$ | $ f(\theta)^{\text{KB}} _{\text{TFD}}^c$ | $\eta(\theta)^{\text{KB,TFD}}^c$ | $ f(\theta)^{\text{Numerical}} _{\text{TFD}}$ | $\eta(\theta)^{\text{Numerical}}_{\text{TFD}}$ |
|----------|------------------------|------------------------------|--|----------------------------------|---|--|
| 0°       | 0.00                   | 15.008                       | 12.411                                   | 0.329                            | 12.550  | 0.329  |
| 3°       | 5.47                   | 4.518                        | 3.040                                    | 1.010                            | 3.119   | 0.988  |
| 6°       | 10.93                  | 1.843                        | 1.174                                    | 1.887                            | 1.159   | 1.827  |
| 9°       | 16.38                  | 0.995                        | 0.671                                    | 2.572                            | 0.624   | 2.535  |
| 12°      | 21.83                  | 0.616                        | 0.440                                    | 3.122                            | 0.400   | 3.140  |
| 15°      | 27.26                  | 0.417                        | 0.305                                    | 3.603                            | 0.283   | 3.661  |
| 18°      | 32.67                  | 0.301                        | 0.222                                    | 4.048                            | 0.213   | 4.119  |
| 21°      | 38.06                  | 0.228                        | 0.169                                    | 4.464                            | 0.167   | 4.528  |
| 24°      | 43.42                  | 0.178                        | 0.134                                    | 4.853                            | 0.135   | 4.897  |
| 27°      | 48.75                  | 0.144                        | 0.111                                    | 5.215                            | 0.111   | 5.234  |
| 30°      | 54.05                  | 0.118                        | 0.095                                    | 5.544                            | 0.094   | 5.544  |

<sup>a</sup> Incident electron energy is 40 keV and  $s=2k \sin(\theta/2)$ .<sup>b</sup> Calculated from Eq. (4.7).<sup>c</sup> KB stands for Karle and Bonham (Ref. 5).

The series was considered converged when

$$|(2l+1)[\sin 2\eta_l - 2\eta_l^B]| \leq 10^{-6}.$$

The absolute value of the scattering amplitude  $|f(\theta)|$  and the phase of the scattering amplitude  $\eta(\theta)$  are presented in Tables III and IV along with some results obtained by Karle and Bonham.<sup>5</sup> As is well known the results for  $|f(\theta)|$  and  $\eta(\theta)$  in the forward direction are quite sensitive to the partial-wave phase shifts used in the sum. In the argon calculation the partial-wave phase shifts obtained by using the TFD potential and those obtained by using the HF potential differ by less than 1% in the worst case ( $l=0$ ). However this gives rise to a difference of  $\sim 10\%$  in  $|f(\theta)|$  and  $\sim 13\%$  in  $\eta(\theta)$  for  $\theta=0^\circ$ . As one goes away from the forward direction the magnitude of the scattering amplitudes calculated from the TFD potential and the HF potential approach each other as is to be expected. It is interesting to note that the result obtained by Karle and Bonham<sup>5</sup> does not differ appreciably from the results presented here for the TFD potential for  $|f(\theta)|$  and  $\eta(\theta)$ . This is because their calculation for the partial-wave phase shifts tends to become worse as  $l$  increases due to their linear extrapolation method. The deviation is shown in Fig. 1. Thus their lower-partial-wave phase shifts agree quite well with the partial-wave phase shifts obtained here. Also after  $l=21$ , they used partial-wave phase shifts obtained from the WKB approximation. Even though their numerical results did not converge to the WKB results, they were in essence using the correct higher- $l$  partial-wave phase shifts since, as was shown, the numerical results

converge fairly rapidly to the WKB results at this high energy, 40 keV. Since their calculation contained fairly good phase shifts for the lower partial waves and essentially the correct ones for the higher partial waves, it is no surprise that their results agree as well as they do with the results presented here.

The ratio  $f^B(\theta)/|f(\theta)|$  is plotted in Fig. 2. This just indicates how well the first Born approximation describes the process and thus what sort of correction the numerical calculation makes to the Born approximation. The curve for uranium shows a larger deviation as expected since it has a large  $Z$  ( $Z=92$ ). These differences in the electron-atom scattering amplitudes can have a significant effect on the molecular parameters determined from the electron diffraction data. The correction to the internuclear distances in the molecule ranges from  $\sim 0.1\%$  for molecules composed of light atoms to  $\sim 12\%$  for molecules composed of heavy and light atoms such as  $\text{UF}_6$ .<sup>1,13</sup> The correction to the mean-square amplitudes of vibration of the molecule ranges from  $\sim 15\%$  to  $\sim 30\%$  even for molecules composed of light atoms.<sup>13</sup> The experimental error in determining the internuclear distances and the mean-square amplitudes of vibration are of the order of  $\sim 0.1\%$  and  $\sim 10\%$ , respectively. The largest corrections to the molecular parameters occur when the parameters involve different atoms (for instance atoms  $i$  and  $j$ ) since the  $\cos[\eta_i(\theta) - \eta_j(\theta)]$  term in the molecular scattering amplitude will then contribute.

The results for the total elastic cross section were obtained by using the optical theorem<sup>8</sup>

$$\sigma_{\text{total}} = (4\pi/k) \text{Im} f(0) \quad (4.9)$$

and these are presented in Table V.

#### ACKNOWLEDGMENT

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<sup>13</sup> T. G. Strand and H. L. Cox, Jr., J. Chem. Phys. **44**, 2426 (1965).

TABLE V. Total elastic cross section for an incident electron energy of 40 keV.<sup>a</sup>

|               |                        |
|---------------|------------------------|
| Argon (HF)    | 0.07999 $\text{\AA}^2$ |
| Argon (TFD)   | 0.07683 $\text{\AA}^2$ |
| Uranium (TFD) | 0.48822 $\text{\AA}^2$ |

<sup>a</sup> Calculated from Eq. (4.9).