

where

$$U(R) = \int d^3x V(\mathbf{x}-\mathbf{R})\phi^2(x). \quad (13)$$

The cross sections were obtained from

$$\sigma = 2\pi \int_0^\infty b db |I(b)|^4. \quad (14)$$

The multiple integrations implied by Eqs. (11), (12), and (14) were carried out with the aid of an IBM 7094 computer using a total time of about 15 min.

Figure 1 is a plot of the two-particle transfer probability versus impact parameter as obtained from Eqs. (11) and (12) for two different velocities. It is seen that the probability becomes greater than unity for sufficiently small velocity and impact parameter and the calculation loses all validity. It should be noted that  $|I_2|^4 < |I_1|^4$ , so that the modified theory can be extended to lower energies than the usual first Born

theory. In Fig. 2 the maximum value of  $|I|$  is plotted versus velocity for the two theories. Since these probabilities must be less than one, a limit on the range of validity at the low-energy end can be obtained from the curve. Finally, Fig. 3 gives the cross section in units of  $2\pi a_0^2 (= 1.76 \times 10^{-16} \text{ cm}^2)$  versus velocity ( $E_{\text{lab}} = V^2 \times 25 \text{ keV}$ ) for the two results obtained here and the usual first Born approximation of Gerasimenko and Rosentveig.<sup>2</sup> The experimental points of Allison<sup>1</sup> are also shown. Note that all three calculations are for ground-state capture only while the experiments are for total capture. Thus the theories should all lie below the experiment.

Of the two theories presented here the modified one appears to be better. However, we believe that the experiment is not sufficiently good to choose between our modified theory and the first Born approximation of Ref. 2. It is only internal consistency that seems to favor ours. It is desirable that the experiments be redone more directly.

## Electron-Alkali-Atom Interaction Potential and Elastic-Scattering Cross Section\*†

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(Received 23 November 1964)

The potential energy between an incident electron and a neutral alkali atom has been calculated using first-order perturbation theory in the adiabatic approximation. The results are shown to be expressible in terms of a multipole expansion suitably generalized to allow for the penetration of the target-atom wave function by the incident electron. The monopole and dipole contributions have been calculated in detail for cesium. For large separations, the monopole contribution to the potential is small compared to the dipole contribution but becomes increasingly significant at smaller separations. For infinite separation, the calculations can be interpreted to yield the atomic polarizability, and the result for cesium ( $61.0 \text{ \AA}^3$ ) is in reasonable agreement with experimental results. With this interaction potential, the elastic scattering of low-energy electrons from neutral cesium is treated in the adiabatic approximation with exchange. For purposes of comparison, the nonexchange approximation is also treated.

### I. INTRODUCTION

THE elastic scattering of low-energy electrons by neutral atoms may be treated in terms of an effective potential which represents the interaction between the incoming electron and the target atom. This effective potential can be considered as made up of several component parts. At high energies, the dominant component of the scattering potential is a shielded Coulomb field due to penetration by the incident elec-

tron into the electron "cloud" of the target atom. However, at low incident energies, the small polarization forces arising at large separations make an important contribution to the scattering. This polarization component of the potential results from the distortion of the target atom due to the proximity of the incident particle and reacts back on the incident particle as one of the scattering forces. It must vanish for zero separation, since, in this limit spherical symmetry prevails and no nonzero multipole moments can be induced. On the other hand, for asymptotically large separations, the polarization potential varies with the inverse fourth power of the separation and, in this regard, the atom is

\* Based in part on a thesis in preparation by J. C. Crown to fulfill the Ph.D. thesis requirement at the University of Connecticut.

† Jointly supported by Pratt & Whitney Aircraft and the National Science Foundation.

TABLE I. Experiment and theoretical values of polarizability of cesium (in units  $A^3$ ).

Investigator	Method	$\alpha_\infty$
Fues <sup>a</sup>	Experimental	61
Sheffers and Stark <sup>b</sup>	Experimental	42 $\pm$ 2.1
Chamberlain and Zorn <sup>c</sup>	Experimental	36
Salop, Pollack, and Bederson <sup>d</sup>	Experimental	52.5 $\pm$ 6.5
Chamberlain and Zorn <sup>e</sup>	Experimental	48 $\pm$ 6
Haun and Zacharius <sup>f</sup> and Mizushima <sup>g</sup>	Experimental	51
Dalgarno and Kingston <sup>h</sup>	Semiempirical	53.7 $\pm$ 5.4
Sternheimer <sup>i</sup>	Theoretical	67.7
Stone and Reitz <sup>j</sup>	Theoretical	66.5
Present result	Theoretical	61.0

<sup>a</sup> Reference 1.<sup>b</sup> Reference 2.<sup>c</sup> Reference 3.<sup>d</sup> Reference 4.<sup>e</sup> Reference 5.<sup>f</sup> Reference 6.<sup>g</sup> Reference 7.<sup>h</sup> Reference 8.<sup>i</sup> Reference 15.<sup>j</sup> Reference 17.

completely characterized by a single constant, the polarizability  $\alpha_\infty$ .

Direct experimental measurements of polarization effects are at present restricted to asymptotically large separations, and, therefore, determine only the polarizability. The earliest available experimental polarizability data are those of Fues,<sup>1</sup> who determined the polarizability from measurements of the optical Stark effect, and of Scheffers and Stark<sup>2</sup> who measured the electrostatic deflection of an atomic beam in a strong inhomogeneous electric field. These two results bracket more recent measurements, as can be seen from Table I. Chamberlain and Zorn<sup>3</sup> also reported values of polarizabilities obtained from measurements of the deflection of an atomic beam in an electric field. Subsequently, Salop, Pollack, and Bederson<sup>4</sup> measured polarizabilities by balancing the electric and magnetic forces on an atomic beam and obtained results significantly higher than Chamberlain and Zorn.<sup>3</sup> As a result of this, Chamberlain and Zorn repeated their measurements with a revised procedure and obtained results<sup>5</sup> which agree within experimental error with the results of Salop *et al.*<sup>4</sup>

Haun and Zacharius<sup>6</sup> obtained Stark-effect data which Mizushima<sup>7</sup> interpreted to obtain polarizability information. Dalgarno and Kingston<sup>8</sup> derived, from perturbation theory, a relation between oscillator strength and polarizability and then used data on the former to infer the latter. Both these results are in substantial agreement with the two preceding.

As pointed out, these relatively direct experimental measurements of polarization effects<sup>1-8</sup> have been made only for essentially infinite separation of incident

and target electrons. However, for scattering calculations, it is necessary to know the variation of the polarization potential at all separations, and, in the most important range, the asymptotic formula is quite inaccurate. Indeed, it diverges in the limit of small separations.

From a theoretical standpoint, the polarization potential of hydrogen as a function of interparticle separation has been approximated by Temkin<sup>9</sup> as one of the series of induced multipole fields. However, for the heavier atoms, the calculations become much more complicated and, consequently, less rigorous approximations are attempted. In fact, several workers have performed scattering calculations using phenomenological potentials which could be justified only for the limiting values of separation. Thus, Robinson<sup>10</sup> assumed, without justification, a polarization potential of the form

$$V_p = -\alpha_\infty / (R^2 + R_c^2)^2, \quad (1)$$

where  $R$  is the distance of the incident electron from the center of the target atom,  $\alpha_\infty$  is the polarizability for infinite separation, and  $R_c$  is a cutoff distance which is taken to be  $(\alpha_\infty/2)^{1/3}$  (all lengths are in units of first Bohr radius and energies in units of rydbergs). While Eq. (1) has the correct asymptotic behavior for large  $R$ , the form of Eq. (1) itself is otherwise unfounded and is incorrect for vanishing separation. Similarly, Garrett and Mann<sup>11</sup> use a polarization potential of the form

$$V_p = -(\alpha_\infty/R^4)[1 - e^{-(R/R_0)^8}], \quad (2)$$

where  $R_0$  is the distance at which "the polarization-induced force disappears" and is taken to be 6.13. Using Eq. (2), Garrett and Mann show that significant variations in scattering cross sections can be obtained from relatively small variations in the cutoff distance  $R_0$ . It is therefore apparent from their calculations that an accurate representation of polarization effects is essential to an accurate calculation of low-energy scattering. While Eq. (2) is qualitatively more realistic than Eq. (1) at small interparticle separations, its form also cannot be justified and is inaccurate as is shown from the present results.

Sternheimer<sup>12-14</sup> treats the electronic polarizability of ions. He extended his method to a consideration of alkaline atoms<sup>15</sup> using wave functions he had previously developed.<sup>16</sup> Rather than calculate each component ( $ns \rightarrow n'p$ ) of the perturbed wave function, Sternheimer obtains the solution for a wave function which represents all components ( $ns \rightarrow p$ ). However, his calculation<sup>15</sup> of the polarizability of neutral cesium for infinite

<sup>1</sup> E. Fues, Z. Physik **82**, 536 (1933).<sup>2</sup> H. Scheffers and J. Stark, Physik Z. **35**, 625 (1934).<sup>3</sup> G. E. Chamberlain and J. C. Zorn, Bull. Am. Phys. Soc. **5**, 241 (1960).<sup>4</sup> A. Salop, E. Pollack, and B. Bederson, Phys. Rev. **124**, 1431 (1961).<sup>5</sup> G. E. Chamberlain and J. C. Zorn, Phys. Rev. **129**, 677 (1963).<sup>6</sup> R. D. Haun and J. R. Zacharius, Phys. Rev. **107**, 107 (1957).<sup>7</sup> M. Mizushima, Natl. Bur. Std. Rept. 6009 (unpublished).<sup>8</sup> A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. (London) **A73**, 455 (1959).<sup>9</sup> A. Temkin, Phys. Rev. **116**, 358 (1959).<sup>10</sup> L. B. Robinson, Phys. Rev. **127**, 2076 (1961).<sup>11</sup> W. R. Garrett and R. A. Mann, Phys. Rev. **130**, 658 (1963).<sup>12</sup> R. M. Sternheimer, Phys. Rev. **96**, 951 (1954).<sup>13</sup> R. M. Sternheimer, Phys. Rev. **107**, 1565 (1957).<sup>14</sup> R. M. Sternheimer, Phys. Rev. **115**, 1198 (1959).<sup>15</sup> R. M. Sternheimer, Phys. Rev. **127**, 1220 (1962).<sup>16</sup> R. M. Sternheimer, Phys. Rev. **78**, 235 (1950).

interparticle separation overestimates the available experimental data<sup>4-8</sup> by about 35%.

Stone and Reitz<sup>17</sup> obtain a polarization potential for cesium using a perturbation technique. However, this result is unexplainedly abandoned in favor of a variational technique. Their calculated value of long-range polarizability is close to that of Sternheimer.<sup>16</sup>

For completeness, it should be pointed out that polarization effects also may be implicitly incorporated into scattering calculations without exhibiting explicitly the polarization component of the potential. Examples of this approach are Burke and Schey,<sup>18</sup> whose analysis is limited to hydrogen as the target atom, and the work of Temkin. Temkin is concerned with polarization and exchange effects in the scattering of electrons by hydrogen<sup>9,19</sup> and oxygen.<sup>20</sup> He uses the method of polarized orbitals (or, equivalently, perturbed stationary states) to describe the adiabatic distortion of the target atom by the incident electron, and his representation of the perturbed wave functions is similar to that of Sternheimer.<sup>12-14</sup> Temkin includes exchange effects with properly antisymmetrized wave functions. However, as will be discussed more fully below, Temkin effectively assumes that the incident electron is always exterior to the valence electron. On the other hand, the present analysis is concerned with a proper representation of the interaction potential for alkaline atoms (in particular, cesium) independent of which electron is exterior to the other. Thus, the effective monopole field is also considered.

## II. INTERACTION POTENTIAL

The interaction Hamiltonian  $H'$  corresponding to a "stationary" incident electron in the field of a neutral target alkali atom of atomic number  $Z$  consists of electron and nuclear components, each of which can be expressed as a sum of two terms designated as the core and valence-electron terms, respectively:

$$H' = H_c' + H_v'. \quad (3)$$

Here,  $H_c'$  is the perturbation term due to the core electrons (i.e., filled shells) plus the potential due to the fraction  $(Z-1)/Z$  of the nuclear Coulomb term:

$$H_c' = \sum_{i=1}^{Z-1} \frac{2}{|\mathbf{R}-\mathbf{r}_i|} - \frac{2}{R} (Z-1), \quad (4)$$

and  $H_v'$  is that due to the valence electron plus the fraction  $1/Z$  of the nuclear Coulomb term:

$$H_v' = (2/|\mathbf{R}-\mathbf{r}|) - (2/R). \quad (5)$$

The decomposition of the nuclear Coulomb energy,  $-2Z/R$ , into two parts is effected for later convenience

and will be discussed below. The position of the incident electron is designated by  $\mathbf{R}$ , that of the  $i$ th atomic electron by  $\mathbf{r}_i$ , and that of the valence electron by  $\mathbf{r}_Z = \mathbf{r}$ .

The energy change of the incident-electron, target-atom system can be obtained from perturbation theory<sup>21</sup> and is

$$E - E^0 = \langle \Psi^0 | H' | \Psi \rangle, \quad (6)$$

where  $\Psi$  is the perturbed wave function of the system and the superscript <sup>0</sup> refers to unperturbed values. From adiabatic perturbation theory,<sup>22</sup> the interaction potential  $V(R)$  is just this change in energy of the system

$$V(R) = E - E^0. \quad (7)$$

In the nonexchange approximation, the wave function for the atom can be written as the product

$$\Psi = \Psi_c(\mathbf{r}_1, \dots, \mathbf{r}_{Z-1}; \mathbf{R}) \psi(\mathbf{r}; \mathbf{R}), \quad (8)$$

where  $\Psi_c$  is the wave function of the core and  $\psi$  is the wave function of the valence electron. The experimentally obtained value for the polarizability of the core is a small fraction of the atomic polarizability ( $\approx 1/20$ ). Thus, to a good approximation, the unperturbed wave function  $\Psi_c^0$  may be used for the core; so that

$$\Psi^0 = \Psi_c^0 \psi^0 \quad (9)$$

and

$$\Psi = \Psi_c^0 \psi. \quad (10)$$

The total interaction potential can be written as a sum of two terms which correspond to the two terms of the interaction Hamiltonian, Eq. (3):

$$V = V_c + V_v. \quad (11)$$

Substituting the wave functions, Eqs. (9) and (10), into Eqs. (6), (7), and (11), and integrating over those coordinates which can be separated out, one obtains

$$V_c = \langle \Psi_c^0 | H_c' | \Psi_c^0 \rangle \quad (12)$$

and

$$V_v = \langle \psi^0 | H_v' | \psi \rangle. \quad (13)$$

Substituting Eq. (4) into Eq. (12), one obtains for the core potential

$$V_c(R) = -2(Z-1)/R + \sum_{i=1}^{Z-1} \int \dots \int \frac{2}{|\mathbf{R}-\mathbf{r}_i|} \Psi_c^{0*} \Psi_c^0 d^3r_1 \dots d^3r_{Z-1}, \quad (14)$$

where it is to be remembered that only a fraction of the nuclear potential (that corresponding to the  $Z-1$  electrons in filled shells) has been included in what is here called the core potential. This was done so that  $V_c$  and  $V_v$  each vanish separately to higher order than  $R^{-1}$  for

<sup>17</sup> P. M. Stone and J. R. Reitz, Phys. Rev. **131**, 2101 (1963).

<sup>18</sup> P. G. Burke and H. M. Schey, Phys. Rev. **126**, 147 (1962).

<sup>19</sup> A. Temkin, Phys. Rev. **121**, 788 (1961).

<sup>20</sup> A. Temkin, Phys. Rev. **107**, 1004 (1957).

<sup>21</sup> E. Merzbacher, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961).

<sup>22</sup> J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. 1.

infinite separation of the incident particle. Thus, comparison of the various terms of the interaction potential is facilitated. Since the core consists of closed shells which are assumed unperturbed,  $V_c$  as given by Eq. (14) represents a monopole or shielded Coulomb potential and can be written

$$V_c = -(2/R)S(R), \quad (15a)$$

where  $S(R)$  represents the screening function and has the limiting values

$$S(0) = Z - 1 \quad \text{and} \quad S(\infty) = 0. \quad (15b)$$

To the order of the independent-particle model, the contribution of the valence electron to the interaction potential is

$$V_v = -\frac{2}{R} + \left\langle \psi^0 \left| \frac{2}{|\mathbf{R} - \mathbf{r}|} \right| \psi \right\rangle. \quad (16)$$

For alkaline atoms, the perturbed valence-electron wave function can be written in the form

$$\psi(\mathbf{r}, \mathbf{R}) = \sum_{l=0}^{\infty} [(2l+1)/4\pi]^{1/2} P_l(\cos\theta) r^{-1} \phi_l(r, R), \quad (17)$$

where the perturbed radial functions can be expanded in terms of the unperturbed radial functions corresponding to vacant shells:

$$\phi_l(r, R) = \sum_{n'=n}^{\infty} C_{n'l}(R) \chi_{n'l}(r). \quad (18)$$

The magnetic quantum number is taken to be zero in all cases and suppressed. The lowest term in the expansions given by Eqs. (17) and (18) corresponds to the unperturbed or ground state  $\chi_{n0}$  of the valence electron, the others being forbidden by the exclusion principle. The coefficients  $C_{n'l}$  are found below to first-order perturbation theory.

The perturbation potential operator in the brackets of Eq. (16) can be expanded in spherical harmonics:

$$\frac{2}{|\mathbf{R} - \mathbf{r}|} = \sum_{l=0}^{\infty} P_l(\cos\theta) \bar{H}_l(r, R), \quad (19a)$$

where

$$\begin{aligned} \bar{H}_l(r, R) &= (2/R)(r/R)^l, & r < R \\ &= (2/R)(R/r)^{l+1}, & r > R, \end{aligned} \quad (19b)$$

so that Eq. (16) reduces, after integration over the angle coordinates, to

$$\begin{aligned} V_v(R) &= -\left(\frac{2}{R}\right) + \left(\frac{2}{R}\right) \sum_{l=0}^{\infty} (2l+1)^{-1/2} \\ &\times \left[ \int_0^R \left(\frac{r}{R}\right)^l \phi_0 \phi_l dr + \int_R^{\infty} \left(\frac{R}{r}\right)^{l+1} \phi_0 \phi_l dr \right]. \end{aligned} \quad (20)$$

Thus,  $V_v(R)$  can be written as a sum over *effective*

multipole components:

$$V_v(R) = \sum_{l=0}^{\infty} V_{vl}(R). \quad (21)$$

The present concern is with the monopole component ( $l=0$  and  $-2/R$  terms) and dipole component ( $l=1$  term). It is, as a matter of fact, convenient for comparison purposes to express each component of this expansion for the interaction potential in terms of an equivalent monopole strength  $\bar{Q}_l(R)$ :

$$V_{vl}(R) = -(2/R)\bar{Q}_l(R). \quad (22)$$

Corresponding to  $l=0$ , the monopole and equivalent monopole strengths are identical. A word about this definition is in order. A multipole expansion is most useful in describing a distribution whose extent is small compared to distance from the field point to the distribution. In that case, the distribution can be completely described by a set of constants, the multipole strengths. One of the main contributions of this paper, however, is the inclusion of the effects due to the extended nature of the atomic charge distribution. This gives rise to "multipole strengths" that vary as functions of the radial coordinate and thus renders the concept of multipole strengths useless. Thus, all of the potentials are here expressed in equivalent monopole strengths, i.e., shielded Coulomb potentials, so that their relative strengths can be readily compared at any value of  $R$ .

The perturbation coefficients  $C_{n'l}$  are found from first-order perturbation theory to be

$$C_{n'l}(R) = -\langle \chi_{n0} | \bar{H}_l | \chi_{n'l} \rangle / [(2l+1)^{1/2} (E_{n'l}^0 - E_{n0}^0)], \quad (23)$$

$|n'l\rangle \neq |n0\rangle.$

In terms of these coefficients, the components of the interaction potential can be written

$$V_{vl} = -\sum_{n'=n}^{\infty} C_{n'l}^2 (E_{n'l}^0 - E_{n0}^0) - (2/R)\delta_{l0}. \quad (24)$$

The monopole potential, expressed in terms of an equivalent monopole strength  $\bar{Q}_0$  is given by Eq. (22), where  $\bar{Q}_0$  can be obtained from Eq. (20):

$$\bar{Q}_0 = 1 - \left[ \int_0^R \phi_0^2 dr + \int_R^{\infty} (R/r)\phi_0^2 dr \right]. \quad (25a)$$

From this equation, it can be seen that the infinite nature of the charge distribution has been incorporated into the interaction potential. Similarly, the dipole potential  $V_{v1}$  and the *equivalent* dipole strength  $\bar{Q}_1$  can be obtained:

$$\bar{Q}_1 = -3^{-1/2} \left[ \int_0^R \left(\frac{r}{R}\right) \phi_0 \phi_1 dr + \int_R^{\infty} \left(\frac{R}{r}\right)^2 \phi_0 \phi_1 dr \right]. \quad (25b)$$

The dipole term  $V_{v1}$  in the expansion for  $V_v$  given by

Eq. (24) is the result of a quantum-mechanical calculation which takes into consideration the penetration of the valence electron distribution by the incident electron. To a certain extent, this potential can be interpreted in terms of an induced dipole field reacting back on the incident electron. However, one must be careful in making this interpretation. Although the dipole moment induced in the atom may well be large *as viewed by an observer far removed from both*, not all of this dipole moment is sensed by the incident electron. Effectively, (but not exactly) the incident electron senses only that fraction of the over-all dipole moment which is due to the fraction of the valence electron distribution interior to it. It is this fact which causes the polarization potential to vanish, instead of blowing up as  $R^{-4}$ , as  $R \rightarrow 0$ .

Thus, two opposite forms of error must be avoided in considering the polarization term in the potential. On the one hand, the entire induced dipole does not react on the incident electron. On the other hand, the fraction of the valence-electron exterior to the incident electron should not be entirely neglected. Both forms of error are avoided in the correct quantum-mechanical expression (25b).

Although, strictly speaking, the notion of a polarizability is invalid at any finite separation, it is expected to be a good approximation for those values of  $R$  which are very much larger than atomic dimensions. In this region,  $V_{v1}$  reduces to the customary "polarization potential." It is instructive to pursue this point and to calculate the polarizability, since a calculation of the polarizability is the only direct check that can be made, at this time, on the exactness of the valence-electron wave function used in the calculation. The polarizability  $\alpha$  is defined as the ratio of the dipole moment  $\bar{Q}_1$  to the ambient electric field  $e/R^2$  (in Gaussian units):

$$\alpha = (e/R^2)^{-1}\bar{Q} = (e/R^2)^{-1} \int \rho(\mathbf{r})\mathbf{r}d\tau. \quad (26)$$

Using inner-product notation, this can be expressed in the form

$$\alpha = -R^2 \langle \psi | \mathbf{r} | \psi \rangle. \quad (27)$$

The result, Eq. (27), is valid as long as the extent of the charge distribution represented by  $\psi$  is small compared with  $R$ . The form of Eq. (27) permits a simple translation from Gaussian to present atomic units. It should be noted that  $\alpha$  is defined in terms of  $\bar{Q}_1$ , which is *not* just  $R$  times the integral representing the *equivalent* dipole moment  $\bar{Q}_1$ , given by Eq. (25b). It must be remembered that  $\bar{Q}_1$  is the static dipole moment, while  $\bar{Q}_1$  (and, correspondingly,  $Q_1 = R\bar{Q}_1$ ) follows from an adiabatically induced dipole potential.<sup>23</sup> In this connection, note that Eq. (27) has  $\psi$ , instead of  $\psi^0$ , as the left-

hand member of the matrix element. Thus, to first order, a factor of 2 is introduced relating  $\bar{Q}_1$  to  $Q_1$ . This factor of 2 just cancels another factor of 2 which arises in expressing the radial coordinate  $r$  in terms of  $\bar{H}_1$ . Substituting from Eqs. (17), (18), and (19) into (27), one can write

$$\alpha = \sum_{n'=n}^{\infty} \alpha_{n'} = \sum_{n'=n}^{\infty} R^4 C_{n'1}{}^2 (E_{n'1}{}^0 - E_{n0}{}^0). \quad (28)$$

In the asymptotic region, where Eq. (27) is meaningful and valid,

$$V_{v1} = V_p = -\alpha/R^4. \quad (29)$$

This is just the expression for the potential due to an induced dipole.<sup>23</sup> As pointed out previously,<sup>1</sup> while  $\alpha(\infty)$  may be useful in evaluating the accuracy of the wave functions used in the theoretical calculations,  $\alpha(R)$  does not provide an accurate representation of the polarization force.

Temkin<sup>19,20</sup> used only the inner ( $r < R$ ) portion of the perturbation Hamiltonian, so that his wave functions are a meaningful approximation only in the asymptotic region. He<sup>19</sup> makes the further assumption that the magnitude of the perturbed wave function vanishes when the incident electron becomes interior to the valence electron ( $r > R$ ). While Sternheimer<sup>12-15</sup> obtains a wave function which represents all components ( $ns \rightarrow p$ ), he, like Temkin, uses only that part of the perturbation Hamiltonian which corresponds to constraining the incoming electron to be exterior to the valence electron. Thus, Sternheimer's perturbed wave functions also lose significance at small separations. Consequently, the validity of these analyses is limited to the asymptotic region.

Rather than define an "effective" polarizability so that the dipole potential can be written in the form of Eq. (29), it is more convenient, for comparison purposes, to express  $V_{v1}$  in terms of an equivalent *monopole* strength  $\bar{Q}_1$ ; thus, from Eq. (22),

$$V_{v1} = -(2/R)\bar{Q}_1, \quad (30)$$

where  $\bar{Q}_1$  is given by Eq. (25b).

The scattering potential (to the order of the dipole approximation) can now be written

$$V(R) = V_c + V_{v0} + V_{v1} = -(2/R)(S + \bar{Q}_0 + \bar{Q}_1), \quad (31)$$

where each term turns out to be an attractive potential. For a repulsive potential, the penetration of an incident electron depends upon its energy. However, for an attractive potential, the strength of the potential at *all* separations, not just the asymptotic region, is important in scattering calculations.

### III. COMPARISON OF POLARIZABILITIES

The evaluation of the perturbation coefficients  $C_{n'1}$  was effected using approximate analytic shielded-Coulomb wave functions which seemed to represent a

<sup>23</sup> J. C. Slater and N. H. Frank, *Introduction to Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1933).

TABLE II. Components of polarizability (in units  $\text{\AA}^3$ ).

Contributing state ( $ns-n'p$ )	$\alpha_{n'}(\infty)$
6s-6p	60.3
6s-7p	0.1
6s-8p	0.6

convenient compromise between accuracy and ease of computation. Calculations of the 6s-6p contribution to the polarizability of neutral unexcited cesium were based on the wave functions of Ref. 24. The 6s-7p and 6s-8p contributions were based on the more approximate wave functions of Ref. 25. The results obtained are given in Table II.

It can be seen from Table I that the present result overestimates the experimental values by only about 15%. The calculated values of  $\alpha_7$  and  $\alpha_8$  should be taken as estimates, since the valence-electron wave functions for cesium are highly localized, so that any error in the wave functions produces an exaggerated effect on quantities which, like polarization, are determined mainly by the overlap of wave functions. Hydrogen, on the other hand, has wave functions which are more diffuse, so that there is more overlap. Thus, the 1s-2p contribution to the polarizability of hydrogen is found to be 66% of the total, while the 1s-3p contribution is 9%. In the case of hydrogen, Temkin's analysis is appropriate in using a 1s-p representation. However,

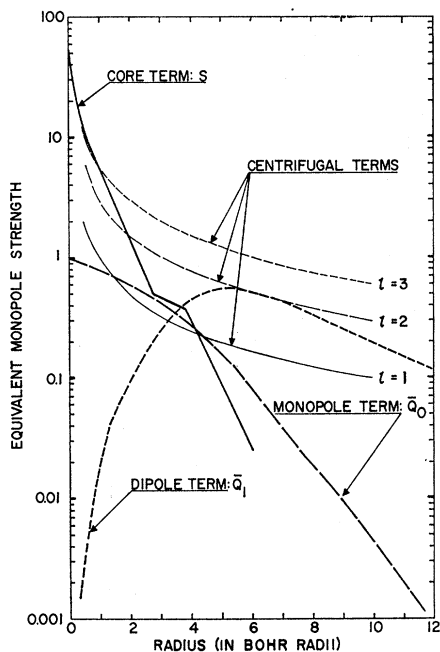


FIG. 1. Comparison of core and induced potentials.

<sup>24</sup> H. A. Moses and A. Russek, Phys. Rev. **135**, A1547 (1964).

<sup>25</sup> A. Russek, C. H. Sherman, and D. E. Flinchbaugh, Phys. Rev. **126**, 573 (1962).

in neutral cesium, it is apparent that the dominant contribution to the polarizability is the 6s-6p term. This tends to corroborate the result of Salmona and Seaton,<sup>26</sup> who found that for sodium the 3s-3p coupling accounts for 99.4% of the atomic polarizability.

The induced monopole and dipole fields were next calculated for cesium using the wave functions of Ref.

TABLE III. Equivalent monopole components of scattering potential [see Eq. (31)].

R (in Bohr radii)	S	$\bar{Q}_0^a$	$\bar{Q}_1^b$
0.0	54.0	1.0	0.0
0.05	42.025	0.98964	0.000075499
0.10	34.365	0.97936	0.000041288
0.20	24.645	0.95892	0.00026962
0.30	18.695	0.93872	0.00076126
0.40	14.935	0.91860	0.0016801
0.50	12.105	0.89852	0.0030437
0.60	9.80	0.87860	0.0048059
0.70	8.65	0.85896	0.0070450
0.80	7.55	0.83948	0.0099370
0.90	6.60	0.81989	0.013668
1.0	5.85	0.79999	0.018344
1.2	4.375	0.75923	0.030351
1.4	3.35	0.71834	0.044748
1.6	2.55	0.67883	0.060191
1.8	1.935	0.64132	0.076256
2.0	1.48	0.60548	0.094398
2.2	1.135	0.57050	0.11603
2.4	0.865	0.53564	0.14126
2.6	0.65	0.50050	0.17167
2.8	0.50	0.46501	0.20724
3.0	0.47	0.42956	0.24711
3.2	0.445	0.39466	0.28989
3.4	0.425	0.36076	0.33378
3.6	0.40	0.32815	0.37689
3.8	0.38	0.29716	0.41730
4.0	0.30	0.26806	0.45319
4.5	0.17	0.20401	0.51911
5.0	0.09	0.15228	0.54842
5.5	0.05	0.11178	0.54524
6.0	0.027	0.080767	0.51817
6.5	0.015	0.057307	0.47661
7.0	0.008	0.039767	0.42886
7.5	0.0043	0.027438	0.38005
8.0	0.0024	0.019354	0.33380
9.0	0.0007	0.0096780	0.25424
10.0	0.0002	0.0045051	0.19355
11.0	0.00005	0.0020868	0.14879
12.0	0.00002	0.0009287	0.11601
13.0	0.000006	0.0004090	0.091823
14.0	0.000002	0.0001760	0.073763
15.0	0.0	0.0000745	0.060074
16.0	0.0	0.0000312	0.049541
17.0	0.0	0.0000129	0.041329
18.0	0.0	0.0000051	0.034804

<sup>a</sup> For  $R > 18$ ,  $\bar{Q}_0$  extrapolated with a decaying exponential.

<sup>b</sup> For  $R > 18$ ,  $\bar{Q}_1$  extrapolated using asymptotic equation.

24. In presenting the results, rather than plotting the actual potential, it is more illustrative to plot  $VR/2$  [see Eq. (31)]. The three components are presented graphically in Fig. 1 and numerically in Table III, where the core term  $S$  [see Eq. (15)] was obtained from Ref.

<sup>26</sup> A. Salmona and M. J. Seaton, Proc. Phys. Soc. (London) **77**, 617 (1961).

27. The monopole term  $\bar{Q}_0$  vanishes for infinite separation and becomes unity as the incident electron approaches the origin (nucleus). At large separations, the induced dipole contribution dominates the induced monopole contribution, which, in turn, is appreciably greater than the core potential. At intermediate range the three terms are of comparable magnitude, while at short range the dipole contribution vanishes as expected.

A comparison of the present results with the polarization potentials used by other authors is presented in Fig. 2. For large  $R$ , the polarization potential approaches

$$V_{v1} \sim -\alpha_\infty/R^4, \quad (32)$$

where  $\alpha_\infty$  is taken equal to  $60.3 \text{ \AA}^3$  (or 406 a.u.), as obtained in the present calculations. For small separations, the present polarization potential varies approximately as  $R^{3/2}$ . For comparison, the polarization potential of Robinson, Eq. (1), has been computed using

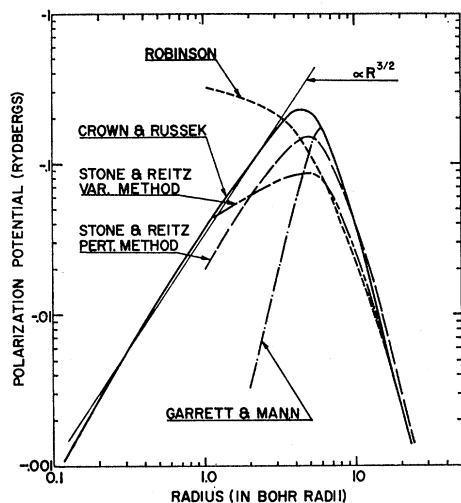


FIG. 2. Comparison of various approximations to the polarization potential.

$\alpha_\infty = 406$  a.u. It can be seen that for small separations, Eq. (1) is not only formally wrong in not vanishing as the separation vanishes, but yields values which involves substantial numerical error. Similarly, the polarization potential of Garrett and Mann, Eq. (2), has been computed using  $\alpha_\infty = 406$  a.u. For small separations, this potential varies as  $R^4$ , thus vanishing far too rapidly, so that here, too, substantial numerical error is incurred.

Stone and Reitz<sup>27</sup> begin a perturbation calculation of the polarization potential but claim that their numerical results are not "justified" at intermediate separations and hence adopt a variational approach. This latter procedure yields a polarizability close to that of Sternheimer (see Table I). Both these polarization potentials of Stone and Reitz are shown in Fig. 2.

<sup>27</sup> P. M. Stone, Phys. Rev. **127**, 1151 (1962).

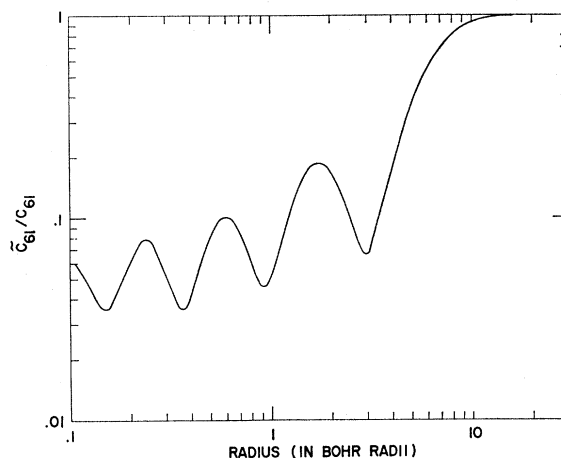


FIG. 3. Ratio of inner component to total value of polarization potential.

As has been pointed out previously, the present analysis allows for the infinite extent of the charge distribution and is not restricted to a consideration of only that portion of the charge distribution which is interior to the position of the incident particle. In order to obtain an estimate of the magnitude of the difference implied by these two approaches, consider the ratio

$$\frac{\tilde{C}_{61}}{C_{61}} = \frac{\langle \chi_{60} | \bar{H}_1 | \chi_{61} \rangle_{r < R}}{\langle \chi_{60} | \bar{H}_1 | \chi_{61} \rangle} \sim \frac{V_{v1}^{(int)}(R)}{V_{v1}(R)}.$$

Here  $\tilde{C}_{61}$  is defined as in Eq. (23), except that the integration in the inner product is extended only over the domain  $r < R$ . By the same token,  $V_{v1}^{(int)}$  represents the polarization potential computed using only that portion of the valence electron charge interior to the incident electron. In this connection, it is to be noted that although  $V_{v1}$  depends on  $C_{61}^2$  [see Eq. (24) to the order  $6s-6p$ ], the ratio  $V_{v1}^{(int)}/V_{v1}$  is taken to depend linearly on the ratio  $\tilde{C}_{61}/C_{61}$ . This is because one of the factors  $C_{61}$  in (24) describes the effect of the dipole distribution on the incident electron, while the other factor  $C_{61}$  describes the effect of the incident electron in setting up the dipole distribution. It is therefore assumed, in this comparison, that in the interior electron approximation, the correct dipole distribution is obtained by perturbation theory, but that the inner portion only is used in evaluating the polarization potential. However, Temkin<sup>19</sup> (in the terminology of the present work) uses only the interior portion of the valence electron distribution both in setting up the dipole as well as ascertaining the effect on the incident electron. Thus, in that case,  $(\tilde{C}_{61}/C_{61})^2$  would be a better comparison.

The ratio  $\tilde{C}_{61}/C_{61}$  is shown graphically in Fig. 3. It can be seen that, except for the asymptotic region, the effect of ignoring the part of the charge distribution exterior to the incident particle is large. For attractive potentials, for which the whole potential at all separa-

tions is important in determining scattering characteristics, serious errors can thus arise if proper consideration is not given to the infinite nature of the charge distribution.

The various minima of  $\tilde{C}_{61}/C_{61}$  in Fig. 3 represent the penetration of the incident electron past the various shells of concentration of the valence electron and is characteristic of the polarization potential in the interior electron approximation. As can be seen from Fig. 1, the actual polarization potential Eq. (24) does not possess this characteristic. Thus, not only may quantitative errors be introduced by using only the inner component of the polarization potential, but qualitative errors as well. The present method avoids both these errors.

#### IV. ELASTIC SCATTERING

##### A. Formulation of The Problem

For low-energy incident electrons, the core of an alkaline atom may be assumed, as before, to be essentially unaffected; so that the incident-electron, target-atom system may be treated as a two-electron system in the core potential. Thus, the Schrödinger equation for the system can be written

$$(H_T - E_T)\Psi_T(\mathbf{r}, \mathbf{R}) = 0, \quad (33)$$

where the total energy  $E_T$  is the sum of the energies of the unperturbed valence electron and the incident electron:

$$E_T = E^0 + k^2. \quad (34)$$

The total Hamiltonian  $H_T$  is the sum of two unperturbed Hamiltonians plus an interaction term

$$H_T = H_r^0 + H_R^0 + H'. \quad (35)$$

Here,

$$H_r^0 = -\nabla_r^2 - (2/r)[S(r) + 1] \quad (36)$$

and

$$H_R^0 = -\nabla_R^2. \quad (37)$$

The unperturbed valence-electron wave function is an eigenfunction of  $H_r^0$ :

$$(H_r^0 - E^0)\psi^0(\mathbf{r}) = 0. \quad (38)$$

The interaction term,  $H'$ , in accordance with the assumption of an unperturbed core, may be taken as [see Eqs. (3), (4), (12), and (15a)]:

$$H' = V_c(R) + H_v' \\ = - (2/R)[S(R) + 1] + (2/|\mathbf{R} - \mathbf{r}|). \quad (39)$$

The total wave function is given by

$$\Psi_T(\mathbf{r}, \mathbf{R}) = \psi(\mathbf{r}, \mathbf{R})F(\mathbf{R}), \quad (40)$$

for the adiabatic model without exchange, where  $\psi(\mathbf{r}, \mathbf{R})$  is the perturbed wave function for the valence electron and  $F(\mathbf{R})$  is the perturbed wave function for the incident electron. For the adiabatic model with exchange, the total wave function is given appropriate

symmetry by writing

$$\Psi_T^\pm(\mathbf{r}, \mathbf{R}) = \psi(\mathbf{r}, \mathbf{R})F(\mathbf{R}) \pm \psi(\mathbf{R}, \mathbf{r})F(\mathbf{r}), \quad (41)$$

where the plus sign refers to the symmetric (singlet) state and the minus sign refers to the antisymmetric (triplet) state. Stone and Reitz<sup>17</sup> approximate this symmetrization by replacing  $\psi(\mathbf{R}, \mathbf{r})$  in Eq. (41) by  $\psi^0(\mathbf{R})$  in order to obtain a solution. However, it will be seen that a solution to Eq. (33) can be obtained without having to make this approximation.

Forming the inner product of  $\psi^0(\mathbf{r})$  with Eq. (33), one can write

$$\langle \psi^0 | H_T - E_T | \Psi_T \rangle_r = 0, \quad (42)$$

where the notation indicates that integration is performed only over  $\mathbf{r}$ .

Substituting Eq. (41) for  $\Psi_T$ , one can write

$$\langle \psi^0(\mathbf{r}) | H_T - E_T | \psi(\mathbf{r}, \mathbf{R})F(\mathbf{R}) \rangle_r = \pm \Upsilon(\mathbf{R}). \quad (43)$$

In the nonexchange approximation,  $\Upsilon(\mathbf{R}) = 0$ ; and, for the case with exchange,

$$\Upsilon(\mathbf{R}) = -\langle \psi^0(\mathbf{r}) | H_T - E_T | \psi(\mathbf{R}, \mathbf{r})F(\mathbf{r}) \rangle_r. \quad (44)$$

Substituting  $H_T$  from Eq. (35) and  $E_T$  from Eq. (34) into Eq. (43), one obtains

$$\langle \psi^0(\mathbf{r}) | H_R^0 - k^2 + H_r^0 + H' - E^0 | \psi(\mathbf{r}, \mathbf{R})F(\mathbf{R}) \rangle_r \\ = \pm \Upsilon(\mathbf{R}). \quad (43')$$

Since the operator  $H_r^0 - E^0$  (but not  $H_R^0$ ) is Hermitian for this inner product, and since  $\psi^0(\mathbf{r})$  is an eigenfunction of this operator [see Eq. (38)], these terms do not contribute in (43'). Finally, the perturbed valence-electron wave function is subjected to the normalization condition

$$\langle \psi^0(\mathbf{r}) | \psi(\mathbf{r}, \mathbf{R}) \rangle_r = 1, \quad (45)$$

so that, with Eqs. (6) and (7) which define  $V(R)$ , Eq. (43') can be written in the form

$$(H_R^0 + V(R) - k^2)F(\mathbf{R}) = \pm \Upsilon(\mathbf{R}). \quad (43'')$$

As before,

$$V(R) = \langle \psi^0 | H' | \psi \rangle_r = - (2/R)[S(R) + \sum_{l=0}^{\infty} \bar{Q}_l(R)] \quad (46a)$$

$$= - (2/R)S(R) + \Delta V(R). \quad (46b)$$

At this point,  $V(R)$ , as given above, is replaced by  $\bar{V}(R)$ , given by

$$\bar{V}(R) = - (2/R)[(S(R) + \bar{Q}_0(R)) + P \cdot \bar{Q}_1(R)]. \quad (47)$$

Here,  $P$  is a constant which allows adjustment of the size of the polarization contribution to the potential. It is seen that  $P=0$  corresponds to no polarization correction,  $\alpha_\infty=0$ , and  $P=1$  corresponds to present calculation of polarization potential,  $\alpha_\infty=60.3 \text{ \AA}^3$ . In what follows, the value for  $P$  will be taken as  $P=0.85$  corresponding to a proportional modification of the



$\bar{Q}_1(R)$  term to yield the experimentally measured polarizability,  $\alpha_\infty = 51.3 \text{ \AA}^3$ .

The present polarization potential was calculated using wave functions<sup>25</sup> obtained without consideration of correlation effects. This neglect results in valence wave functions which are too diffuse. As a result, the polarizability is overestimated. Thus, some sort of modification of the polarization potential is justified. In the absence of further information, a linear modification is the simplest appropriate.

In order to simplify the expression for  $\Upsilon(\mathbf{R})$ , Eq. (44a), the equation satisfied by  $\psi(\mathbf{R}, \mathbf{r})$  must be obtained corresponding to that for  $\psi(\mathbf{r}, \mathbf{R})$ . The perturbed valence-electron wave function satisfies the equation

$$(H_r^0 + H' - E)\psi(\mathbf{r}, \mathbf{R}) = 0. \quad (48)$$

By means of Eqs. (36), (37), and (46b), one can obtain, after interchanging the variables  $\mathbf{r}$  and  $\mathbf{R}$ ,

$$[H_R^0 + H' - (2/r) - \Delta V(r) - E^0]\psi(\mathbf{R}, \mathbf{r}) = 0. \quad (49)$$

Making use of this relation, together with Eqs. (34) and (35), one can obtain, from Eq. (44),

$$\Upsilon(\mathbf{R}) = -\langle \psi^0(\mathbf{r}) | H_r^0 - k^2 + (2/r) + \Delta V(r) | \psi(\mathbf{R}, \mathbf{r}) F(\mathbf{r}) \rangle_r. \quad (44')$$

Again making use of the Hermitian property of  $H_r^0 - E^0$  and using Eq. (38), one can obtain for  $\Upsilon(\mathbf{R})$

$$\Upsilon(\mathbf{R}) = \langle \psi^0(\mathbf{r}) | H_x | \psi(\mathbf{R}, \mathbf{r}) F(\mathbf{r}) \rangle_r, \quad (50)$$

where

$$H_x(r) = k^2 - E^0 - [2/r + \Delta V(r)]. \quad (51)$$

It can be seen that  $H_x(r)$  is spherically symmetric. As a consequence of this and the fact that  $\psi^0(\mathbf{r})$  represents a spherically symmetric ground state, it follows that in the expansion

$$F(\mathbf{r}) = \sum_{l=0}^{\infty} F_l(\mathbf{r}) = \sum_{l=0}^{\infty} \frac{1}{r} f_l(r) \left[ \frac{(2l+1)^{-1/2}}{4\pi} \right] P_l(\cos\theta), \quad (52)$$

only the  $l=0$  component of  $F$  survives in  $\Upsilon$ ; i.e.,

$$\Upsilon(\mathbf{R}) = \langle \psi^0(\mathbf{r}) | H_x(r) | \psi(\mathbf{R}, \mathbf{r}) F_0(r) \rangle_r. \quad (53)$$

Let  $\Upsilon(\mathbf{R})$  now be expanded

$$\Upsilon(\mathbf{R}) = \sum_{l=0}^{\infty} (1/R) U_l(R) [(2l+1)/4\pi]^{1/2} P_l(\cos\Theta). \quad (54)$$

Thus, making use of this expansion and Eqs. (17) and (18), one obtains

$$\Omega_l f_l^\pm = \mp U_l^\pm(R), \quad (55)$$

where

$$\Omega_l = (d^2/dR^2) - [l(l+1)/R^2] - V(R) + k^2, \quad (56)$$

$$U_l^\pm(R) = \sum_{n'=n}^{\infty} g_{n'l^\pm}(k) \chi_{n'l}(R), \quad (57)$$

and

$$g_{n'l^\pm} = \langle \chi_{n0}(r) | H_x(r) | C_{n'l}(r) f_0^\pm(r) \rangle. \quad (58)$$

Thus, only the  $l=0$  component requires solution of an integro-differential equation. Once the  $f_0$  term has been found, the other components ( $f_l$ ,  $l \geq 1$ ) can be found by solving a differential equation in which the coupling involves only an independent integration. Furthermore, to the order of the dipole approximation ( $C_{n'l}=0$ ,  $l \geq 2$ ), it follows from Eqs. (57) and (58) that

$$U_l(R) = 0 \quad \text{for } l \geq 2. \quad (59)$$

It can be seen that, to the order of the dipole approximation, for  $l \geq 2$  the  $f_l$  components of the incident-electron wave functions and hence the phase shifts are not affected by exchange.

It was shown in Sec. III (see Table II) that only the  $n'=n$  term contributes appreciably to the polarization, and only this term need be retained in the expansion of  $U_l^\pm$ . The solution of the integro-differential equation (55) for  $l=0$  and  $l=1$  can be accomplished simply by means of the following artifice. First, it will be shown that  $f_l^\pm$  can be written in the form

$$f_l^\pm(R) = \bar{f}_l(R) \mp \gamma_l^\pm(k) \bar{f}_l(R), \quad (60)$$

where  $\bar{f}_l$  is defined by

$$\Omega_l \bar{f}_l(R) = 0 \quad (61)$$

(this is just the nonexchange equation) and  $\bar{f}_l$  by

$$\Omega_l \bar{f}_l(R) = \chi_{nl}(R). \quad (62)$$

Straightforward operation on the right-hand side of Eq. (60) by  $\Omega_l$  yields

$$\Omega_l f_l^\pm(R) = \mp \gamma_l^\pm(k) \chi_{nl}(R). \quad (63a)$$

Since  $|n0\rangle$  represents the ground state,  $C_{n0}=1$  and Eqs. (55) and (57) taken together yield

$$\Omega_l f_l^\pm(R) = \mp g_{nl^\pm}(k) \chi_{nl}(R), \quad (63b)$$

when it is remembered that only the  $n'=n$  term is retained in the expansion. A comparison of Eqs. (63a) and (63b) readily demonstrates that

$$\gamma_l^\pm = g_{nl^\pm}. \quad (64)$$

After substituting Eqs. (60) and (64) into Eq. (58), one obtains

$$\gamma_0^\pm = \bar{h}_0 / (1 \pm \bar{h}_0) \quad (65)$$

and

$$\gamma_1^\pm = \bar{h}_1 \mp \gamma_0^\pm \bar{h}_1, \quad (66)$$

where

$$\bar{h}_l = \langle \chi_{n0} | H_x | C_{nl} \bar{f}_0 \rangle \quad (67)$$

and

$$\bar{h}_l = \langle \chi_{n0} | H_x | C_{nl} \bar{f}_l \rangle. \quad (68)$$

The asymptotic solution to Eqs. (61) and (62) can be written

$$\bar{f}_l = \bar{a}_l \sin(kR - l\pi/2 + \bar{\delta}_l) \quad (69)$$

and

$$\bar{f}_l = \bar{a}_l \sin(kR - l\pi/2 + \bar{\delta}_l). \quad (70)$$

Since, in the asymptotic region, Eq. (62) has the same form as Eq. (61), the partial wave shifts  $\bar{\delta}_l$  and  $\tilde{\delta}_l$  can be obtained in the usual manner.<sup>21</sup> Recombining the solutions Eqs. (69) and (70) by means of Eq. (60), the partial wave shifts with exchange  $\delta_l^\pm$  are found to be given by

$$\tan \delta_l^\pm = (\bar{a}_l \sin \bar{\delta}_l \mp \bar{a}_l \gamma_l^\pm \sin \tilde{\delta}_l) / (\bar{a}_l \cos \bar{\delta}_l \mp \bar{a}_l \gamma_l^\pm \cos \tilde{\delta}_l). \quad (71)$$

The solutions of the uncoupled phase-shift equations, (61) and (62), are effected and the integrals represented by Eqs. (67) and (68) evaluated. Then, the coupling constants given by Eqs. (65) and (66) can be obtained. These, in turn, permit determination of the exchange phase shifts. It can be seen that the relative amplitude  $\bar{a}_l/\bar{a}_l$  of the two asymptotic solutions  $\bar{f}_l$  and  $\tilde{f}_l$  is needed in addition to the phase shifts  $\bar{\delta}_l$  and  $\tilde{\delta}_l$ . It is important to note that Eq. (71) requires the proper phase for  $\bar{\delta}_l$  and  $\tilde{\delta}_l$  (quadrants one through four) not just the principle value as usually obtained from machine calculations.

The partial cross sections (in units of  $\pi a_0^2$ ) can be obtained from

$$\sigma_l = (4/k^2)(2l+1) \sin^2 \delta_l, \quad (72)$$

where the nonexchange values are obtained using  $\bar{\delta}_l$  and the exchange values ( $\sigma_l^\pm$ ) are obtained using  $\delta_l^\pm$ . In the latter case allowance must be made for the relative statistical spin weights:

$$\sigma_l = (\sigma_l^+ + 3\sigma_l^-)/4. \quad (73)$$

The total cross section, in either case, is given by

$$\sigma = \sum_{l=0}^{\infty} \sigma_l. \quad (74)$$

## B. Numerical Algorithm for Solution

The numerical solution of a problem is frequently considered anticlimactic and given relatively superficial consideration. However, it is indeed possible that non-trivial errors can be made in this area as well as in the analytic derivations. In the present case, numerical analyses were made to insure the validity of the numerical results. These analyses were found useful in preventing truncation error from blanketing the true solution and in precluding instabilities in the solution algorithm.

The numerical solution of the differential equations (61) and (62) was effected numerically using a fourth-order form of the second-sum procedure.<sup>28</sup> From considerations of truncation error, the initial increment in the integration was chosen to be  $\Delta R = 0.002$ . The adequacy of this choice will be demonstrated subsequently. Again from truncation error considerations, the increment was doubled when the initial accuracy could be maintained with the larger interval. Doubling

was effected as long as the condition

$$\Delta R < (60/11)^{1/2} k^{-1} \quad (75)$$

was always satisfied. This limiting interval size was obtained from a stability analysis (as in Ref. 29) of the numerical algorithm. For interpolation purposes, curves were spline fit,<sup>30</sup> and Simpson's formula was used to evaluate the integrals involved in Eqs. (67) and (68).

It was attempted to integrate the differential equations out to a point at which the principle value of the phase shift (multiplies of  $\pi$  subtracted out) no longer changed by more than one part in 1000. However, near resonances, where the phase shifts tended toward multiples of  $\pi$ , truncation error precluded convergence to this criterion but did permit convergence to within 0.001 rad, approximately. The calculations were run in the IBM 7090, and for an absolute cutoff the integration was stopped when the potential was some small fraction of the incident energy:  $|V/k^2| = 10^{-5}$  (or sometimes  $10^{-6}$ ). For  $k = 0.01$ , this corresponded to  $R \approx 750$ , while for  $k = 1$  this corresponded to  $R \approx 75$ .

On the other hand, Robinson<sup>10</sup> integrates out to  $R = 100$ , Stone and Reitz<sup>17</sup> integrate out to  $R = 92$ , while Garrett and Mann<sup>11</sup> integrate out to  $|V/k^2| = 10^{-3}$ . From the nature of the problem, the use of some small value of  $|V/k^2|$  to terminate the integration seems preferable to use of a large value of  $R$ . Furthermore, a study of intermediate results indicates that while the present convergence criterion may be unduly strict, a value of  $|V/k^2| = 10^{-3}$  frequently leads to errors in the partial cross sections of the order of 50%, especially in the general vicinity of resonances (in the immediate vicinity of the resonance, the errors were much greater). It seemed that the maximum value of  $|V/k^2|$  that should be used as an integration limit is  $10^{-4}$ .

As previously mentioned, the initial increment was chosen to be  $\Delta R = 0.002$ . Stone and Reitz<sup>17</sup> used  $\Delta R = 0.02$ . In order to ascertain the adequacy of the estimated starting increment, various values were tried, and the results are given in Table IV. It can be seen that the results for  $\Delta R = 0.0002$  corroborate the present results ( $\Delta R = 0.002$ ). The results for  $\Delta R = 0.02$  differ significantly and, hence, corresponding errors may be suspect in the calculations of Stone and Reitz.<sup>17</sup>

TABLE IV. Effect of various starting increments on phase shifts. [No exchange,  $\alpha_\infty = 51.3 \text{ \AA}^3$ —see Eq. (47) ff.]

$k$	$\Delta R$	$\delta_0$	$\delta_1$	$\delta_2$	$\delta_3$
0.1	0.02	-0.1352	-0.2729	0.1902	0.0355
	0.002	-0.1731	-0.2088	0.1902	0.0357
	0.0002	-0.1732	-0.2088	0.1902	0.0356
0.2	0.02	-0.8613	-0.8503	-0.3493	0.1584
	0.002	-0.9025	-0.7689	-0.3490	0.1585
	0.0002	-0.9027	-0.7690	-0.3499	0.1585

<sup>28</sup> R. W. Hamming, J. Assoc. Comp. Mach. 6, 37 (1959).

<sup>30</sup> J. L. Walsh, J. H. Ahberg, E. N. Nilson, J. Math. Mech. 11, 225 (1962).

<sup>21</sup> S. Herrick, Math. Tables Aides Comp. 34, 61 (1951).

TABLE V. Partial and total elastic-scattering cross sections without exchange (in units of  $\pi a_0^2$ ,  $\alpha_\infty = 51.3 \text{ \AA}^3$ ).

$k$ (Ry) <sup>1/2</sup>	$\sigma_0$	$\sigma_1$	$\sigma_2$	$\sigma_3$	$\sigma_4$	$\sigma_5$	$\sigma_6$	$\sigma_7$	$\sigma_8$	$\sigma_9$	$\sigma_{10}$	$\sigma$
0.01	1517.6	4.26	0.042	0.0003								1521.9
0.02	731.1	7.77	0.86	0.015								739.7
0.04	146.0	2.31	3.76	0.56	0.024	0.001						152.6
0.06	17.00	2.30	10.17	1.20	0.33	0.12						31.12
0.065	7.40	5.48	12.88	1.47	0.39	0.14						27.75
0.07	2.24	9.85	16.13	1.64	0.45	0.16						30.47
0.08	0.33	21.99	25.48	2.18	0.55	0.21						50.74
0.09	4.88	36.98	41.51	2.86	0.74	0.26						87.23
0.10	12.37	53.34	71.49	3.57	0.88	0.32						142.0
0.12	29.27	85.32	300.5	5.28	1.32	0.47						422.1
0.13	36.98	99.33	732.5	6.28	1.54	0.54						877.2
0.14	43.78	111.7	1011.1	7.42	1.80	0.62						1176.5
0.15	49.39	121.9	538.7	8.70	2.08	0.72						721.5
0.16	53.91	130.3	269.7	10.11	2.38	0.82						467.2
0.17	57.32	136.8	158.2	11.68	2.70	0.93						367.6
0.2	61.98	146.6	58.47	17.44	3.82	1.29						289.6
0.25	56.72	140.3	26.29	31.25	6.24	2.06	0.85	0.41				264.1
0.3	44.32	120.4	17.40	50.66	9.45	3.02	1.24	0.59				247.1
0.35	31.17	96.83	13.46	72.63	13.49	4.22	1.71	0.81				234.3
0.45	11.81	55.17	9.93	97.04	23.37	7.31	2.91	1.36				208.9
0.6	0.91	18.06	8.22	76.73	34.89	12.87	5.32	2.48				159.5
1.0	2.44	0.33	7.41	15.59	26.16	17.60	10.52	6.00	3.42	2.00	1.21	92.68
2.0	0.20	2.90	4.98	5.03	8.85	6.87	5.74	4.75	3.79	2.98	2.32	46.09

### C. Results of Scattering Calculations

#### a. No Exchange

The results of the nonexchange scattering calculations are shown in Fig. 4. The curve labeled  $\alpha_\infty = 60.3 \text{ \AA}^3$  represents the results obtained by using the polarization potential previously computed and the curve labeled  $\alpha_\infty = 0$  represents the results obtained by ignoring this term. Since the present calculation of the atomic polarizability of cesium is about 15% too high, and since the polarizability represents the proportionality constant in the asymptotic region [see Eq. (32)], it was felt that some modification of the polarization potential was appropriate and that a 15% reduction of the whole polarization-potential distribution was the least artificial way to effect this modification in the absence of other information. Thus, from Eq. (47), using  $P = 0.85$ , a modified polarization potential was obtained for which  $\alpha_\infty = 51.3 \text{ \AA}^3$  corresponding to the experimental data (see Table I).

The polarization potential corresponding to  $\alpha_\infty = 51.3 \text{ \AA}^3$  was used in subsequent calculations. The corresponding total scattering cross section is also given in Fig. 4. These calculations were obtained using  $l = 0-3$  components at  $k = 0.01$ , but including angular momentum components up to  $l = 10$  at  $k = 1.0$ . The various partial cross sections are given in Table V.

From the results presented in Fig. 4, it is apparent that the scattering cross sections are extremely sensitive to the perturbation potential. While the  $\alpha_\infty = 0$  curve is not, of course, expected to be very realistic, the difference between the  $\alpha_\infty = 60.3 \text{ \AA}^3$  and  $\alpha_\infty = 51.3 \text{ \AA}^3$  curves illustrates the sensitivity of the results to even minor modifications in the polarization term. Figure 5 presents

a comparison of the present nonexchange cross sections (for  $\alpha_\infty = 51.3 \text{ \AA}^3$ ) with other theoretical calculations.<sup>10,11,17</sup> As indicated in Fig. 2 and previously discussed, the polarization potentials used by Robinson<sup>10</sup> and Garrett and Mann<sup>11</sup> are sufficiently inaccurate that any similarity between their results and the present ones would be largely coincidental. On the other hand, the polarization potential used by Stone and Reitz<sup>17</sup> is

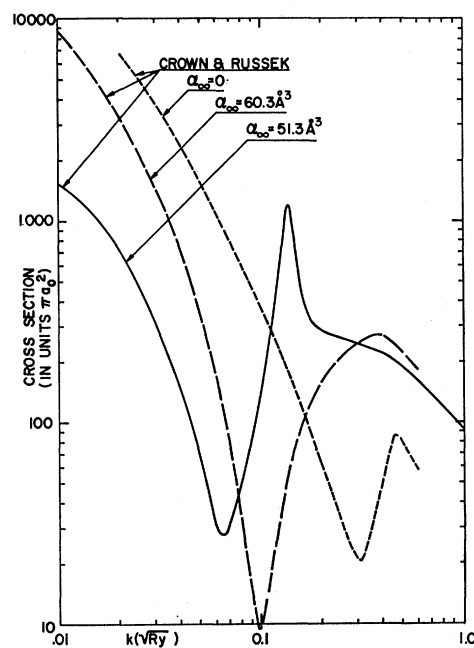


FIG. 4. Nonexchange elastic-scattering cross section corresponding to various polarizabilities.

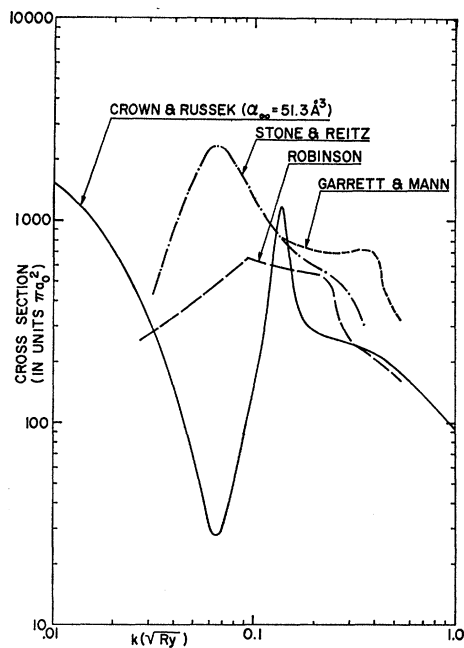


FIG. 5. Comparison of various calculations of nonexchange elastic-scattering cross sections.

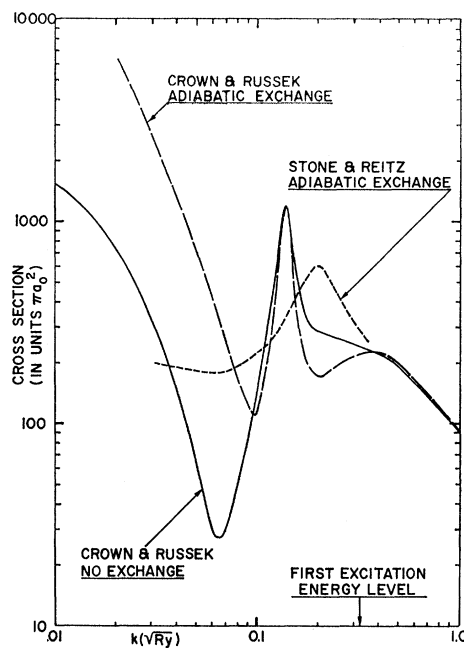


FIG. 6. Comparison of calculations of elastic-scattering cross sections with exchange with that without exchange.

similar in form to the present one; however, it corresponds to a value of  $\alpha_\infty = 66.5 \text{ \AA}^3$ . Thus, again no agreement in results is to be expected except at the higher energies where the effect of polarization is less.

The sensitivity of the scattering to the polarization potential may be explained by comparing the centrifugal term  $l(l+1)/R^2$  and the scattering potential  $V(R)$  in Eq. (55) (see Fig. 1). This scattering potential corresponds to an attractive scattering center, while the

centrifugal term corresponds to a repulsion. Thus, these two terms tend to counteract each other. The scattering potential has been decomposed into various components, which, in the present analysis, includes only the core potential and the monopole and dipole perturbation potentials. The core potential  $S(R)$  is considered quite accurate at small radii and becomes of increasingly uncertain accuracy at larger radii. However, at large radii the core potential is relatively unimportant.

TABLE VI. Partial and total elastic-scattering cross sections with adiabatic exchange (in units  $\pi a_0^2$ ,  $\alpha_\infty = 51.3 \text{ \AA}^3$ ).

$k$ ( $Ry$ ) <sup>1/2</sup>	Singlet		Triplet		$\sigma_0$	$\sigma_1$	$\sigma$
	$\sigma_0^+$	$\sigma_1^+$	$\sigma_0^-$	$\sigma_1^-$			
0.01	1576.5	3.09	37225.6	6.04	28313.29	5.30	28318.6
0.02	760.47	4.06	8687.75	18.49	6705.93	14.88	6721.67
0.04	153.77	2.28	1690.15	41.95	1306.06	32.03	1342.43
0.06	18.88	0.63	512.95	42.63	389.43	32.13	433.38
0.065	8.59	0.22	374.16	39.04	282.77	29.34	326.98
0.07	2.86	0.050	282.97	34.85	212.94	26.15	257.47
0.08	0.16	0.16	159.95	24.78	120.01	18.62	167.05
0.09	4.21	1.20	87.49	15.06	66.60	11.59	123.56
0.10	11.43	3.47	44.58	7.20	36.30	6.27	118.84
0.12	28.11	12.06	6.98	0.055	12.26	3.06	322.85
0.13	35.79	18.21	0.18	0.98	9.09	5.29	755.23
0.14	42.58	25.28	0.66	4.39	11.14	9.61	1041.73
0.15	48.29	33.16	3.45	9.85	14.68	15.67	580.58
0.16	52.90	41.36	7.52	16.74	18.89	22.90	324.81
0.17	56.40	49.64	12.13	24.59	23.22	30.86	227.61
0.2	61.34	72.69	25.84	49.75	34.71	55.49	171.22
0.25	50.47	96.83	38.64	81.60	43.10	85.40	195.60
0.3	44.30	100.81	39.03	92.65	40.35	94.69	217.40
0.35	31.24	90.92	32.50	87.48	32.18	88.34	226.84
0.45	11.90	57.99	16.18	58.85	15.11	58.63	215.66
0.6	0.93	20.95	2.51	24.41	2.11	23.54	166.16
1.0	2.42	1.35	1.71	0.34	1.89	0.59	92.39

Similar considerations probably apply to the monopole term  $Q_0(R)$ . The dipole term  $Q_1(R)$  is negligible at small radii and asymptotically correct at large radii. Higher order multipole terms, neglected herein, would contribute to the over-all scattering potential mainly in the middle range. All components of the scattering potential decrease more rapidly than the centrifugal term as the radius becomes increasingly large. Thus, it is in the middle range where an error in  $V(R)$  is most probable, and it is in this range wherein the centrifugal term and  $V(R)$  tend to cancel each other. Thus, a slight change in  $V(R)$  can change the sum  $V(R)+l(l+1)/R^2$  from attractive to repulsive or vice versa, and it is not surprising that small changes in the polarization potential yield significantly different scattering results. It also points out the region in which further effort should be applied to obtain more accurate results.

### b. Adiabatic Exchange

The results of the adiabatic exchange calculations are compared with the nonexchange results in Fig. 6. The exchange cross sections are significantly different from the nonexchange cross sections at low energies below about the first excitation level ( $k=0.322$ ), but essen-

TABLE VII. Scattering length.

$k$	$a_0^+$ (singlet)	$a_0^-$ (triplet)
0.01	-20.26	-366.3
0.02	-14.34	-128.7
0.04	-6.40	-36.12
0.06	-2.19	-15.43

tially reduce to the nonexchange results above this point. The concurrence of the two curves at the peak located at  $k=0.14$  is due to the dominance of the  $l=2$  contribution which was unaffected by exchange to the order of the dipole approximation used herein.

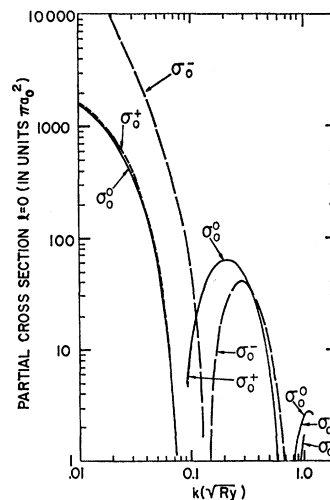
It is of interest to consider the relative influence of the singlet and triplet components. These are tabulated in Table VI and plotted in Figs. 7 and 8 for  $l=0$  and  $l=1$ , respectively. It is apparent that a great amount of structure is present in these partial cross sections at the low energies considered. Consider the scattering length, defined by

$$a = \lim_{k \rightarrow 0} [\tan \delta(k)/k] \quad (76)$$

for the  $l=0$  component. The scattering length evaluated at various values of  $k$  is given in Table VII. It can be seen that while the triplet term seems to dominate the singlet term at low energies, even  $k=0.01$  is not sufficiently low to be considered the limit of "zero energy."

The first resonances of the singlet and triplet partial cross sections (shown in Figs. 7 and 8) are slightly displaced and this shift is similar for both the  $l=0$  and

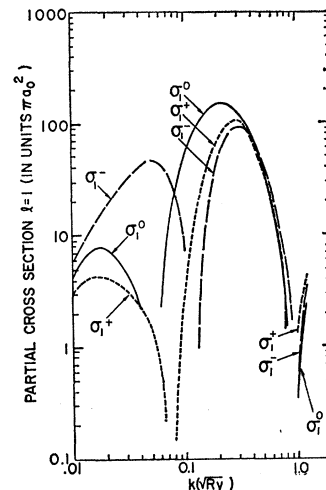
Fig. 7. Components of exchange cross sections:  $l=0$ .



$l=1$  components. Consequently, at the lowest energies indicated, the triplet scattering components dominate the singlet. As the energy increases, a range is entered in which singlet scattering dominates. At still higher energies, the relative contribution of the singlet and triplet contributions is less important since the  $l \geq 2$  components dominate.

The present exchange cross sections are compared in Fig. 6 with the results of exchange calculations of Stone and Reitz.<sup>17</sup> At low energies, there is no particular agreement between the two, although as the energy approaches the first excitation level their results approach the present ones. Aside from questions concerning the numerical accuracy of their solution and the fact that their polarizability ( $\alpha_\infty = 66.5 \text{ \AA}^3$ ) is greater than the experimental value ( $\alpha_\infty \approx 51.3 \text{ \AA}^3$ ), Stone and Reitz<sup>17</sup> approximate the symmetrization of the wave function when including the effect of exchange in their calculations as previously mentioned. Thus, the present results are considered more reliable.

Fig. 8. Components of exchange cross sections:  $l=1$ .



*c. Comparison with Experimental Results*

Up to this point, attention has been centered on the elastic-scattering cross section given by

$$\sigma = \int \frac{d\sigma}{d\Omega}, \quad (77)$$

which leads to components given by Eqs. (72) and (74). However, experimentally one usually measures the momentum-transfer cross section given by

$$\sigma_M = \int (1 - \cos\theta) \frac{d\sigma}{d\Omega}. \quad (78)$$

This momentum-transfer cross section has been put in the following form by Kramers<sup>31</sup>:

$$\sigma_M = \frac{4}{k^2} \sum_{l=0}^{\infty} (l+1) \sin^2(\delta_{l+1} - \delta_l). \quad (79)$$

The momentum-transfer cross section has been calculated and is presented in Fig. 9 together with the elastic scattering cross section for comparison. At low energies, there is little difference between  $\sigma$  and  $\sigma_M$ , although at higher energies the difference becomes appreciable. While in the present calculations the

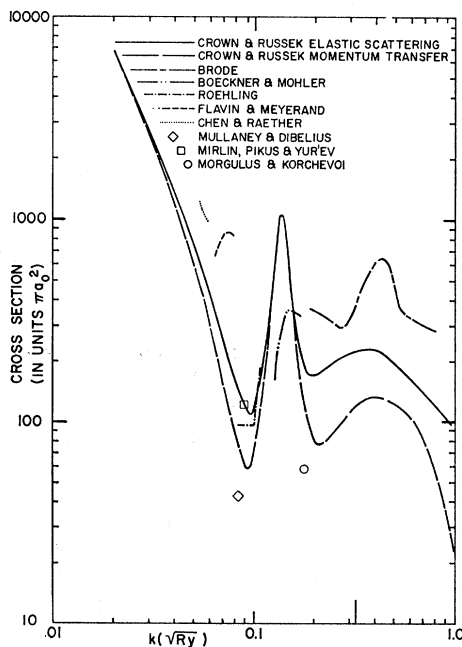


FIG. 9. Elastic and momentum cross sections (with exchange) and comparison with experimental results.

<sup>31</sup> L. Waldmann, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. XII, p. 459.

momentum-transfer cross section was found to be always less than the elastic-scattering cross section, Stone and Reitz,<sup>17</sup> on the other hand, find a small region in which the inverse holds. Such a result implies more back scattering than forward scattering and is surprising, if true.

Figure 9 also shows a comparison of the theoretical calculations with experimental results. Of the experimental data, only Brode's<sup>32</sup> involve monoenergetic electrons; the others<sup>33-39</sup> involve electrons with a velocity spectrum, presumably Maxwellian. While the various data do not yield a unique scattering curve, they do seem to confirm the existence of resonance in the approximate energy range where theoretically predicted. The degree to which the experimental data are not consistent with each other is a measure of experimental error incurred either in obtaining the data or in interpreting it to obtain the scattering cross sections. The present calculations are in rough agreement with the data within this experimental error, except for Brode's data, which seems high.

## V. CONCLUSIONS

The degree of inconsistency in the experimental scattering data is sufficient to preclude an evaluation of any but grossly inappropriate theoretical models. Thus, only the difference between the theoretically calculated polarizability ( $61 \text{ \AA}^3$ ) and that measured experimentally ( $\approx 52 \text{ \AA}^3$ ) is of help in determining the shortcomings of the theoretical model. Here, the need is for more accurate wave functions.

The present theoretical model predicts the location of resonances with reasonable certainty and the scattering cross section with fair accuracy. More accurate theoretical calculations could be obtained by going beyond the dipole approximation used herein or by using a nonadiabatic theory. On the other hand, it is believed that one's understanding of scattering processes will be more enhanced by an investigation of improved theoretical techniques for reducing data, so that from various experimental setups a unique scattering curve can be obtained.

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<sup>34</sup> D. Roehling, Symposium on Thermionic Power Conversion, Colorado Springs, May 1962 (unpublished report); *Advan. Energy Conversion* **3**, 69 (1963).

<sup>35</sup> R. K. Flavin and R. G. Meyerand, Jr., Proceedings of the IEEE Thermionic Converter Specialist Conference, Gatlinburg, Tennessee, 1963 (unpublished).

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<sup>39</sup> N. D. Morgulis and Yu. P. Korchevoi, *Zh. Techn. Fiz.* **32**, 900 (1962) [English transl.: *Soviet Phys.—Tech. Phys.* **7**, 655 (1962)].