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Polarization and Exchange Effects in Slow-Electron Scattering from Lithium and Sodium*

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Total elastic-scattering cross sections have been calculated for low-energy electrons incident on lithium and sodium. The effects of target distortion by the electric field of the incident particle and electron exchange between incident and bound electrons have been included through the "adiabatic exchange" approximation. In this method, the effect of the distortion induced in the target atom is computed through a polarization potential which is obtained by the method of polarized orbitals. The phase shifts and the total elastic-scattering cross sections are obtained through the solution of a set of integrodifferential equations. The calculated polarization potential agrees asymptotically with experimental determinations of the dipole polarizability of Li and Na, and the total elastic-scattering cross sections agree well with recent measurements over the entire experimental range. Results for both alkalis exhibit a small resonance at the experimental peak around 1 V and a second peak at lower energies outside the present experimental range.

I. INTRODUCTION

In treating the problem of low-energy elastic scattering of electrons by an atomic system, there are two major effects which complicate the problem a great deal. These are the exchange interactions between the incident electron and the atomic electrons, and the distortion of the atomic system by the electric field of the incident charged particle. In the case of the alkali atoms, both of these effects are particularly important, since the valence electron is very loosely bound. Earlier calculations for the alkali atoms[1–3] have shown the extreme sensitivity of the calculated cross sections to the accuracy of the polarization potential in the total scattering interaction and to the exchange effects.[3] In this paper, the problem of low-energy elastic scattering of electrons by atomic lithium and sodium is treated in the energy range from 0.003 to 25.0 eV. The effects of exchange and target distortion have been calculated here through the use of the adiabatic exchange approximation wherein the target atom is distorted by the static field of the incoming electron. The polarization potential is calculated by a method of polarized orbitals similar to that used by Temkin[4,5] and Callaway,[6] and electron exchange between the incident and the valence electron is included through explicit use of the adiabatic-exchange approximation which leads to a set of integrodifferential equations for the free-electron wave functions.[3–5]

II. POLARIZATION POTENTIAL

In this section, the distortion of an atomic system by a slow incident electron and the resulting polarization potential is developed from the application of first-order perturbation theory to Hartree-Fock electron orbitals. We note that analogous perturbation calculations on Hartree and Hartree-Fock systems have been carried out heretofore in order to determine atomic dipole polarizabilities (Sternheimer[7]); core polarization due to valence electrons in alkali atoms (Callaway[6]); and the polarization potential for electron scattering (Temkin[4]).

We consider the first-order perturbation by a free electron of an atomic system whose unperturbed Hartree-Fock (HF) self-consistent-field wave functions have been determined. Under the influence of the perturbation, the HF one-electron orbitals and the HF energy depend on the coordinates of the free electron. The perturbed orbitals Ψ_i of the HF determinant for the atomic system then satisfy the following equation (in rydberg units) which depends on the free-electron coordinate r_f [4,6]:

$$\left[-\nabla_1^2+V(\mathbf{r}_1,\mathbf{r}_f)-A(\mathbf{r}_1,\mathbf{r}_f)+\frac{2}{r_{1f}}\right]\Psi_i(\mathbf{r}_1,\mathbf{r}_f)=\epsilon_i(\mathbf{r}_f)\Psi_i(\mathbf{r}_1,\mathbf{r}_f)\,, \qquad (1)$$

where

$$V(\mathbf{r}_1,\mathbf{r}_f)=-\frac{2Z}{r_1}+\sum_j\int|\Psi_j(\mathbf{r}_2,\mathbf{r}_f)|^2\frac{2}{r_{12}}d\mathbf{r}_2 \qquad (2)$$

and

$$A(\mathbf{r}_1,\mathbf{r}_f)g(\mathbf{r}_1,\mathbf{r}_f)=\sum_j\left(\int\Psi_j^*(\mathbf{r}_2,\mathbf{r}_f)g(\mathbf{r}_2,\mathbf{r}_f)\frac{2}{r_{12}}d\mathbf{r}_2\right)\Psi_j(\mathbf{r}_1,\mathbf{r}_f)\,. \qquad (3)$$

In these equations, $\mathbf{r}_1$, $\mathbf{r}_2$ are the coordinates of bound electrons and $\mathbf{r}_f$ is that of the free electron. In order to simplify the above equations for the perturbed HF orbitals, we write $\Psi_i(\mathbf{r}_1,\mathbf{r}_f)$ in the form

$$\Psi_i(\mathbf{r}_1,\mathbf{r}_f)=\Phi_i(\mathbf{r}_1)+\chi_i(\mathbf{r}_1,\mathbf{r}_f)\,, \qquad (4)$$

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[2] W. R. Garrett and R. A. Mann, Bull. Am. Phys. Soc. **10**, 128 (1964).

[3] P. M. Stone and J. R. Reitz, Phys. Rev. **131**, 2101 (1963).

[4] A. Temkin, Phys. Rev. **107**, 1004 (1957).

[5] A. Temkin and J. C. Lamkin, Phys. Rev. **121**, 788 (1961).

[6] J. Callaway, Phys. Rev. **106**, 868 (1957).

[7] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954); **115**, 1198 (1959).

where $\Phi_i(\mathbf{r}_1)$ is the unperturbed HF orbital which satisfies

$$[-\nabla_1^2+V(\mathbf{r}_1)-A(\mathbf{r}_1)]\Phi_i(\mathbf{r}_1)=\epsilon_i^0\Phi_i(\mathbf{r}_1) \tag{5}$$

with

$$V(\mathbf{r}_1)=-\frac{2Z}{r_1}+\sum_j\int|\Phi_j(\mathbf{r}_2)|^2\frac{2}{r_{12}}d\mathbf{r}_2 \tag{6}$$

and

$$A(\mathbf{r}_1)g(\mathbf{r}_1)=\sum_j\left[\int\Phi_j(\mathbf{r}_2)g(\mathbf{r}_2)\frac{2}{r_{12}}d\mathbf{r}_2\right]\Phi_j(\mathbf{r}_1). \tag{7}$$

Our objective is to determine the first order perturbations χ_i of the single-electron orbitals Ψ_i of the Hartree-Fock determinant for the bound atomic system. In this calculation, the term $2/r_{1f}$ is treated as a perturbation on the atomic system, and the perturbations χ_i are determined from first-order perturbation theory.[4,6,7] The integrodifferential equations for the first-order perturbation $\chi_i(\mathbf{r}_1,\mathbf{r}_f)$ of the HF orbitals may be determined from Eq. (1). These have been written down explicitly by Callaway[6] but are too complicated to solve in any reasonable time. However, if all the perturbed Coulomb and exchange integrals are dropped from the equations for the first-order perturbation of the HF orbitals, the resulting differential equations are more tractable. The effect of omitting these integrals is discussed by Callaway[6] and is shown to be reasonably small.

The presence of the unperturbed exchange integrals $A(r_1)$ which are retained in the equations for the perturbed Hartree-Fock orbitals still leave the equations in a very complicated form. However, these terms can be replaced very conveniently and with reasonable accuracy by an average exchange potential by the method given by Slater.[8] In the simplest form of Slater's method, the exchange term of Eq. (7) is replaced by the function

$$A_s(r_1)g(r_1)=6\left[\frac{3}{8\pi}\sum_j\Phi_j^*(\mathbf{r}_1)\Phi_j(\mathbf{r}_1)\right]^{1/3}g(r_1). \tag{8}$$

The summation in this expression is carried over all occupied orbitals of both spins. With this substitution and with the omission of the perturbation terms in the Coulomb and exchange integrals, the resulting equation for the perturbation χ_i of a HF orbital becomes

$$[-\nabla_i^2+V(\mathbf{r}_1)-A_s(\mathbf{r}_1)-\epsilon_i^0]\chi_i(\mathbf{r}_1,\mathbf{r}_f)$$
$$=\left[\int|\Phi_i(\mathbf{r}_1)|^2\frac{2}{r_{1f}}d\mathbf{r}_1-\frac{2}{r_{1f}}\right]\Phi_i(\mathbf{r}_1). \tag{9}$$

In this equation, we expand the perturbation term $2/r_{1f}$ which appears in the two terms on the right-hand side by the multipole expansion

$$\begin{aligned}\frac{2}{r_{1f}}&=\frac{2}{r_1}+\frac{2r_f}{r_1^2}\cos\theta+\frac{2r_f^2}{2r_1^3}(3\cos^2\theta-1)+\cdots\quad(r_1>r_f),\\ \frac{2}{r_{1f}}&=\frac{2}{r_f}+\frac{2r_1}{r_f^2}\cos\theta+\frac{2r_1^2}{2r_f^3}(3\cos^2\theta-1)+\cdots\quad(r_f>r_1),\end{aligned} \tag{10}$$

where θ is the angle between r_1 and r_f. Substituting (10) into the two terms in the brackets on the right of (9), we note that all but the spherically symmetric term in the integral will vanish. Dropping the quadrupole and higher order terms, the bracket expression then becomes

$$\left[\int|\phi_i(\mathbf{r}_1)|^2\frac{2r_<}{r_>^2}d\mathbf{r}_1-\frac{2}{r_<}-\frac{2r_<}{r_>^2}\cos\theta\right],$$

where $r_<$ is the lesser and $r_>$ the greater of r_1, r_f. We note that for large values of r_1 the first and second terms in this expression will cancel each other, leaving only the dipole term $2r_</r_>^2\cos\theta$. Also noting that for smaller values of r_1 the spherically symmetric term of the potential will be small as compared to the Coulomb term, we make the dipole approximation and retain only the dipole term in the bracketed expression.

To obtain the first-order perturbation of each of the atomic electron orbitals Φ_i, we thus have the following pair of differential equations to solve:

$$[-\nabla_1^2+V(r_1)-A_s(r_1)-\epsilon_1^0]\chi_i(\mathbf{r}_1,\mathbf{r}_f)$$
$$=-\frac{2r_1}{r_f^2}\cos\theta\Phi_i(\mathbf{r}_1),\quad\text{for}\quad r_f>r_1; \tag{11a}$$

$$[-\nabla_1^2+V(r_1)-A_s(r_1)-\epsilon_1^0]\chi_i(\mathbf{r}_1,\mathbf{r}_f)$$
$$=-\frac{2r_f}{r_1^2}\cos\theta\Phi_i(\mathbf{r}_1),\quad\text{for}\quad r_1>r_f. \tag{11b}$$

These equations must be solved in the "inner" region where $r_f<r_1$ and in the "outer" region where $r_f>r_1$ and the solutions matched at the boundary $r_f=r_1$.

With the solutions for the perturbations χ_i of the Hartree-Fock orbitals, the dipole polarization potential is then determined from the expression[6,9]

$$V_p(r_f)=\sum_j\int\Phi_j^*(\mathbf{r}_1)\frac{2r_<}{r_>^2}\cos\theta\chi_j(\mathbf{r}_1,\mathbf{r}_f)d\mathbf{r}_1, \tag{12}$$

where the sum extends over all occupied orbitals Φ_j.

The reduction of Eqs. (11) into radial equations and (12) into integrals over radial coordinates is accomplished easily by expansion of the functions Φ_i and χ_i

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[8] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. II, p. 14.

[9] L. C. Allen, Quarterly Progress Report, Massachusetts Institute of Technology, 1955 (unpublished).

in the form

$$\Phi_i(\mathbf{r}_1)=[P_{nl}(r_1)/r_1]Y_l^m(\theta,\phi) \tag{13}$$

and

$$\chi_i(\mathbf{r}_1,\mathbf{r}_f)=\sum_{l',m'}[U_{nl\to l'}(r_1,r_f)/r_1]\times C_{nl\to l'}{}^{m\to m'}Y_{l'}{}^{m'}(\theta,\phi). \tag{14}$$

With these substitutions, the differential equations (9) separate into the radial equations

$$\left[\frac{d^2}{dr_1^2}-\frac{l'(l'+1)}{r_1^2}-V(r_1)+A_s(r_1)+\epsilon_1{}^0\right]U_{nl\to l'}(r_1,r_f)=\frac{2r_1}{r_f^2}P_{nl}(r_1),\quad r_f>r_1, \tag{15a}$$

$$\left[\frac{d^2}{dr_1^2}-\frac{l'(l'+1)}{r_1^2}-V(r_1)+A_s(r_1)+\epsilon_1{}^0\right]U_{nl\to l'}(r_1,r_f)=\frac{2r_f}{r_1^2}P_{nl}(r_1),\quad r_1>r_f, \tag{15b}$$

which must be solved and matched at the boundary $r_1=r_f$. The constants $C_{nl\to l'}{}^{m\to m'}$ in Eq. (14) are determined from the Clebsch-Gordan coefficients which occur from the angular integrals. These are tabulated by Sternheimer and are zero unless $l'=l\pm1$, where only the upper sign holds for $l=0$. With the solutions to (15), the polarization potential becomes

$$V_p(r_f)=\sum_{nll'}V_{nl\to l'}(r_f),$$

where

$$V_{nl\to l'}(r_f)=K_{nl\to l'}\left[\frac{2}{r_f^2}\int_0^{r_f}P_{nl}(r_1)r_1U_{nl\to l'}(r_1,r_f)dr_1+r_f\int_{r_f}^{\infty}P_{nl}(r_1)U_{nl\to l'}(r_1,r_f)r_1^{-2}dr_1\right]. \tag{16}$$

The constants $K_{nl\to l'}$ are numbers which depend on l' and on the number of electrons in an *nl* shell and have been given by Sternheimer. In the limit as $r_f\to\infty$, the polarization potential calculated here should approach $-\alpha/r^4$, where α is the dipole polarizability, thus providing a convenient check on the accuracy of the solutions V_p.

III. SCATTERING EQUATION

As mentioned in Sec. I, both target distortion and electron exchange are extremely important in electron scattering by the alkali atoms and must be dealt with accordingly in the scattering equation. On the other hand, if one wishes to obtain cross sections over a fairly wide energy range as in the present investigation, the scattering equation must be written in a reasonably tractable form, since many partial waves are required in the calculation. In order to achieve these objectives, the scattering equation is written as essentially a two-electron equation for the free electron and the single valence electron in the field of the perturbed core orbitals with exchange between the incident and valence electrons included explicitly. Exchange with core electrons is accounted for implicitly through the exchange term $A_s(r)$ of Eq. (7), and core polarization is included directly through $V_{p_c}(r)$, which is the polarization of the core electrons. The Schrödinger equation may then be written in the form

$$\left[\nabla_1^2+\nabla_2^2+E-V(r_1)-V(r_2)+A_s(r_1)+A_s(r_2)+V_{p_c}(r_1)+V_{p_c}(r_2)-\frac{2}{r_{12}}\right]\Psi(\mathbf{r}_1,\mathbf{r}_2)=0, \tag{17}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are position vectors for the two electrons, and the terms $V(r)$, $A_s(r)$ are given by Eqs. (6) and (8). $V_{p_c}(r)$ is the polarization potential for the core electron calculated by the method of Sec. II.

With this scattering equation, the adiabatic exchange model is again utilized to express the wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ for the free and the bound electron. In this approximation, Ψ is written in the form

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\Psi'(\mathbf{r}_1,\mathbf{r}_2)F(\mathbf{r}_2)\pm\Psi_0(\mathbf{r}_2)F(\mathbf{r}_1), \tag{18}$$

where Ψ_0 is the ground-state wave function for the valence electron, Ψ' is the perturbed ground-state function which is perturbed adiabatically by the free electron whose wave function is F, and the perturbation term is $2/r_{12}$.

The plus sign in (16) refers to the symmetric (singlet) state of the two electrons, and the minus sign to the antisymmetric (triplet) state. In the adiabatic exchange approximation adopted here, the symmetry of the wave function Ψ is partially destroyed, since the unperturbed bound state function Ψ_0 appears in the second term of (18) rather than the first-order perturbed function Ψ'. The omission of the first-order perturbed term in the exchange wave function means that the function $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ is not completely antisymmetric except in the limit of large r_2 where the perturbation becomes zero. This approximation is consistent with the perturbation calculation of HF functions in Sec. II and should have an equally small effect on the accuracy of the scattering equation.[3,10]

The perturbed ground-state function Ψ' is written, as in Sec. II, in the form

$$\Psi'(\mathbf{r}_1,\mathbf{r}_2)=\Psi_0(\mathbf{r}_1)+\chi(\mathbf{r}_1,\mathbf{r}_2), \tag{19}$$

and the perturbation χ is determined from Eq. (9).

Equation (18), with Ψ' written as in (19), may be substituted into Eq. (17) in order to obtain an equation for the free-electron function F. With this substitution,

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[10] R. W. LaBahn and J. Callaway, Phys. Rev. **135**, A1539 (1964).

Eq. (17) may be multiplied on the left by $\Psi_0^*(\mathbf{r}_1)$ and the result integrated over $\mathbf{r}_1$. With the use of Eqs. (5), (9), and (12), the Schrödinger equation becomes

$$[\nabla_2^2+k_0^2-V_0(r_2)+A_s(r_2)+V_{p_c}(r_2)+V_{p_v}(r_2)]F(\mathbf{r}_2)$$
$$=\mp\int d\tau_1\Psi_0^*(\mathbf{r}_1)\left(k_0^2-E_0-\frac{2}{r_{12}}\right)F(\mathbf{r}_1)\Psi_0(\mathbf{r}_2)\,, \quad (20)$$

where the upper and lower signs refer to the singlet and triplet states, respectively. Here the term $k_0^2=E-E_0$ is the kinetic energy of the free electron and E_0 is the ground-state energy of the bound electron. $V_0(r_2)$ is defined as

$$V_0(r_2)=\left\langle\Psi_0\left|\frac{2}{r_{12}}+V(r_2)\right|\Psi_0\right\rangle,$$

which is the screened Hartree-Fock potential for the neutral atom. The term $V_{p_v}(r_2)$ is the polarization potential due to the perturbed valence electron and is given by

$$V_{p_v}(r_2)=\int\Psi_0^*(\mathbf{r}_1)\left|\frac{2}{r_{12}}\right|\chi(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1,$$

which is, in the dipole approximation, just that of Eq. (12), where χ is to be determined from Eq. (11). Thus the sum of the two terms $V_{p_c}+V_{p_v}$ is the polarization potential for the core plus the valence electron and is just the polarization potential of Eq. (12) for the complete atom. This will be denoted by V_p.

By the use of a partial wave expansion of the free-electron wave function $F(r)$, Eq. (20) can be reduced to a radial equation for each partial wave f_l. Thus we write

$$F(\mathbf{r}_2)=\sum_l r^{-1}f_l(r)Pl(\cos\theta_2)\,. \quad (21)$$

With this expansion, the equation for the partial wave f_l becomes

$$\frac{d^2}{dr^2}f_l+\left[k_0^2-V_0+A_s+V_p-\frac{l(l+1)}{r^2}\right]f_l$$
$$=\pm U_0\left[(E_0-k^2)\delta_{l0}\int_0^\infty f_0U_0dr+\left\{\frac{1}{2l+1}\right\}\right.$$
$$\times\left\{\int_0^\infty r^lf_lU_0r^{-(l+1)}dr+r^{-(l+1)}\int_0^r f_lu_0r^ldr\right.$$
$$\left.\left.-r^l\int_0^r f_l\phi_0r^{-(l+1)}dr\right\}\right], \quad (22)$$

where $u_0=r^{-1}\Psi_0$ is the radial part of the normalized ground-state wave function for the valence electron.

The integrodifferential equation (22) may be solved in a noniterative fashion by a procedure used by Marriott,[11] or in an iterative self-consistent calculation as was used in the present work.

IV. APPLICATION TO Li AND Na

A. Calculated Polarization Potential

In the calculation of the polarization potential, the unperturbed wave functions for the atomic system were taken as the Hartree-Fock-Slater (HFS) wave functions obtained from a slightly modified program originally written by Herman and Skillmann.[12] The output of the program furnished the functions $V(r)$, $A_s(r)$, ϵ_1^0, and $P_{nl}(r)$ in Eqs. (15), which could then be solved for the perturbations $U_{nl\to l'}$ of a given orbital whose radial function is P_{nl}. For a given value of r_f, Eqs. (15) were integrated by the Numerov process for inhomogeneous equations as described by Hartree,[13] over the same r_1 mesh as that of the HFS program which furnished the unperturbed functions. The integration in the inner region was started by noting, as did Sternheimer,[6] that for $r_1\sim 0$ the inhomogeneous term on the right-hand side of (11) is negligible as compared to the potential terms on the left. The solution may thus be started by a series expansion[13] near the origin and continued by numerical integration. With this procedure there is an arbitrary constant in the starting values, this being the value of $(U_{nl\to l'}/r^{l'+1})_0$. For the inhomogeneous set of equations (11), this parameter in the starting conditions must be determined in order to satisfy the boundary conditions; that the solutions to (15a) and (15b) and their derivatives match at $r_1=r_f$ and that the solution be exponentially decreasing at infinity. The value of $(U_{nl\to l'}/r^{l'+1})_0$ was varied automatically in the coded program until two values were found which enclosed the correct one. The choice was then narrowed by successive solutions until an accuracy of five to six significant figures in the starting value was achieved. The calculations were performed on a Univac 1107 computer at the University of Alabama Research Institute.

In the present calculation, the total polarization potential was taken to be that contributed by electrons in the two outermost shells of the alkali atom. For Li, both the core and valence electrons are in s states. In Sternheimer's notation, these undergo $s\to p$ perturbations, and the radial equations must be solved for the perturbation $U_{1,0\to1}$ and $U_{2,0\to1}$. In the case of Na, the 2s and 3s electrons experience $s\to p$ excitations similar to Li. However, for the 2p electrons, two modes of excitation $2p\to d$ and $2p\to s$ are possible, and the perturbation $U_{2,1\to2}$ and $U_{2,1\to0}$ are required.

The solutions to the pair of differential equations (15) for the perturbations $U_{nl\to l'}(r,r_f)$ exhibit a be-

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[11] R. Marriott, Proc. Phys. Soc. (London) **72**, 121 (1958).

[12] F. Herman and S. Skillmann, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1960).

[13] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

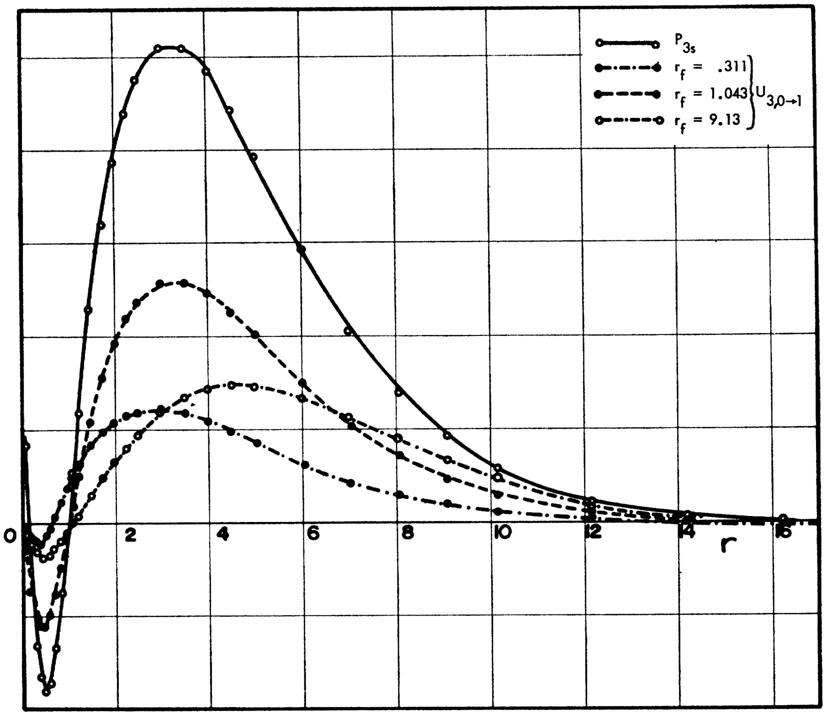

FIG. 1. Unperturbed $3s$ radial function of Na and the $3s\to p$ perturbation $U_{3,0\to1}(r,r_f)$ for three values of the free-electron coordinate r_f.

havior very similar to the simpler solutions obtained by Sternheimer. Thus the nodes of the radial function $U_{nl\to l'}$ correspond in number to the orbital next higher in energy than nl having l' angular momentum. Also the contributions $ns\to p$ and $np\to s$ are opposite in sign as found in Sternheimer's calculations and tend to cancel each other in their contribution to V_p. (Sternheimer supports this behavior with a reasonable physical and mathematical argument.) The solutions to Eqs. (11) are, of course, more complicated than those of Sternheimer, since his equations correspond to those only in the asymptotic region of r_f where only one of Eqs. (11) hold. As the free electron moves in toward the nucleus, the pair of equations must be solved for each value of r_f. In the actual solution, the equations were solved over a 441-point mesh on r_1 and for 110 values of r_f. As one would expect from physical arguments, the amplitude, and to some extent the shape of the perturbation $U_{nl\to l'}(r,r_f)$ of an nl orbital, depends on the position r_f of the free electron. The perturbation is small for large r_f, largest when $r_f\sim r_0$, where r_0 is the position of the largest maximum of the unperturbed function, and small again for $r_f\sim 0$. This is clearly shown in Fig. 1, where the unperturbed radial function $P_{3s}(r)$ for sodium and the perturbation $U_{3,0\to1}(r,r_f)$ for three values of r_f are shown.

We have so far considered the core polarization as being due only to the electric field of the incident electron. However, since the valence electron is strongly polarized by the field of the incident particle, there is an induced field acting on the core due to the polarized valence electron orbital.[14] This field tends to induce a moment of opposite sign in the core orbitals, thus decreasing the effective polarization of the core. An estimate of the size of this effect can be obtained by calculating the electric field at the nucleus $\Delta E_{\mathrm{val}}(0)$ due to the perturbation of the valence-electron wave functions. The z component of this field is given by[14]

$$\Delta E_{\mathrm{val},z}(0,r_f)=e\int_0^\infty \rho_{\mathrm{ind}}r^{-2}\cos\theta dv\,, \qquad (23)$$

where ρ_{ind} is the electron density induced by the field $-e/r_f^2$ of the charge $-e$ at $z=r_f$. For the valence electron in an s state, this becomes

$$\Delta E_{\mathrm{val},z}(0,r_f)=e\frac{4}{3}\int_0^\infty P_{n0}(r)U_{n,0\to1}(r,r_f)r^{-2}dr\,. \qquad (24)$$

If the valence electron were completely external, the total field acting on a core electron would be the sum of that due to the free electron and that given by the induced field of Eq. (24). However, since the valence electron penetrates the core, the effective field due to the valence electron is reduced from this value. But more important for our purposes is the fact that in the scattering problem the perturbing electron also penetrates the atomic system. Thus the induced field [Eq. (24)] is a function of r_f, and since the core polarization potential only becomes appreciable for small values of

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[14] R. M. Sternheimer, Phys. Rev. **127**, 1220 (1962).

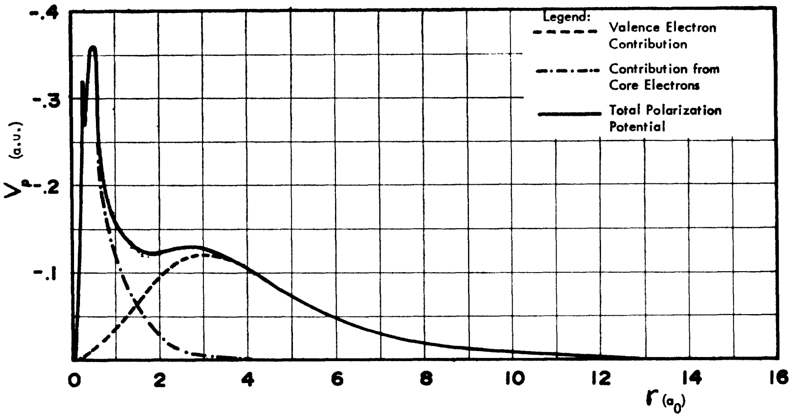

FIG. 2. Polarization potential for Na showing the contribution from the core electrons V_{p_c} and from the valence electron V_{p_v} together with their sum V_p.

r_f, it is necessary to calculate the induced field of the valence electron for several values of r_f in order to estimate the size of this effect on the core polarization as compared to the direct field of the penetrating electron. This has been done by evaluating Eq. (24) for several values of r_f. The results for Na are shown in Table I.

We note that the induced field of the valence electron first increases as r_f decreases from infinity, reaches a maximum for $r_f \sim r_0$ (see Fig. 1), and then decreases rapidly for smaller values of r_f, approaching zero at $r_f = 0$. This can easily be seen from Fig. 1 where the amplitude of the perturbation of the valence electron is seen to first increase and then decrease as r_f gets smaller.

In order to estimate the effect of this interaction on the calculated polarization potential, we show separately in Fig. 2 the polarization potential from the valence electron and from the core electrons as calculated from Eq. (16). Then note that for values of r greater than $\sim 2a_0$, where the induced field of the valence electron is appreciable, the polarization potential due to the core electrons (whether due to the direct terms from the incident particle or from the induced field of the valence electron) is essentially negligible as compared to the large valence electron contribution. Furthermore, for small values of r_f where the core polarization potential becomes appreciable, the induced field due to the valence electron becomes small as compared to the perturbing field of the incident electron [down by a factor of six from its maximum (Table I)] and thus can reasonably be neglected in the calculation of V_{p_c}, since this is the only region where V_{p_c} is important. Thus, in the present treatment, the core and valence contributions to V_p are calculated independently and added (Fig. 2), neglecting the induced effects of one upon the other. The core contribution is almost entirely due to the $2p \rightarrow d$ excitation, since the $2p \rightarrow s$ and $2s \rightarrow p$ contributions canceled each other almost exactly.

TABLE I. Electric field at the nucleus due to perturbed valence electron of Na as a function of r_f.

$r_f(a_0)$	0.211	0.597	3.017	6.075
$\Delta E_{\mathrm{val},z}(0,r_f)$	0.0169	0.0372	0.0949	0.0501

As a check on the accuracy of the calculations, one can compare the asymptotic value of the calculated dipole polarization potential with the value which one knows should result, namely, $V_p(r_f) \sim \alpha/r^4$ for $r \rightarrow \infty$, where α is the dipole polarizability whose value is available from experiment. Thus, in Table II, we give the calculated value of α from the present calculation which is obtained from the equation $\alpha = V_p(r)r_f^4$ at $r_f = 25a_0$. The results are converted to Å^3 in Table II and compared with experimental values[15] and with other calculations.[14] The agreement with experiment is very good.

B. Solutions to the Scattering Equation

The solutions of the scattering equation (22) for all partial waves f_l having $l \leq 7$ were obtained by an iterative self-consistent method of solution. In this technique, the integration was started by expanding f_l in a power series near the origin and continued by Numerov's method.[13] In addition, the required starting values for the integrals on the right-hand side of (22) were obtained by first solving (22) with the right-hand side set equal to zero (no-exchange approximation). The resulting wave functions were then used in the integrals for the next iteration.

Having started the iteration, the entire integro-differential equation was iterated through a self-

TABLE II. Dipole polarizabilities from asymptotic value of V_p in present calculation and from experiment[a] (Å^3).

	Li	Na
Present	22.2	23.9
Measured	20–23	20–25
Sternheimer[b]	24.9	22.9

[a] Reference 15. [b] Reference 14.

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[15] A. Dalgarno, Advan. Phys. 11, 281 (1962).

TABLE III. Singlet and triplet phase shifts for Li.

E (Ry)	δ_0^+	δ_1^+	δ_2^+	δ_3^+	δ_4^+	δ_5^+	δ_6^+	δ_0^-	δ_1^-	δ_2^-	δ_3^-	δ_4^-	δ_5^-	δ_6^-
0.00025	9.2756	6.2738	3.1426	0.000				9.3549	6.2850	3.1426	0.000			
0.0050	9.2055	6.2548	3.1437	0.000				9.3140	6.2857	3.1438	0.000			
0.00075	9.1501	6.2327	3.1446	0.000				9.2796	6.2832	3.1450	0.000			
0.0010	9.1023	6.2058	3.1452	0.001				9.2486	6.2787	3.1461	0.001			
0.0015	9.022	6.157	3.147	0.002				9.195	6.267	3.149	0.002			
0.0020	8.954	6.111	3.148	0.003				9.148	6.253	3.152	0.003			
0.0025	8.894	6.067	3.149	0.004				9.105	6.236	3.155	0.004			
0.0030	8.840	6.026	3.149	0.006	0.002			9.066	6.219	3.158	0.005	0.002		
0.0040	8.745	5.952	3.148	0.006	0.003			8.995	6.184	3.164	0.006	0.003		
0.0050	8.662	5.886	3.147	0.008	0.003			8.932	6.148	3.170	0.008	0.003		
0.0060	8.588	5.827	3.145	0.010	0.004			8.875	6.111	3.177	0.010	0.004		
0.075	8.490	5.748	3.142	0.013	0.005			8.798	6.058	3.188	0.013	0.005		
0.010	8.355	5.636	3.135	0.017	0.007			8.684	5.975	3.209	0.018	0.007		
0.020	7.955	5.321	3.109	0.049	0.016	0.008		8.345	5.704	3.300	0.049	0.016	0.008	
0.030	7.683	5.113	3.089	0.100	0.027	0.012	0.007	8.095	5.499	3.380	0.101	0.027	0.012	0.007
0.050	7.313	4.853	3.065	0.270	0.064	0.025	0.013	7.733	5.223	3.448	0.282	0.063	0.025	0.013
0.065	7.101	4.732	3.043	0.451	0.102	0.038	0.018	7.523	5.053	3.458	0.486	0.103	0.038	0.018
0.075	6.984	4.642	3.027	0.590	0.133	0.048	0.022	7.393	4.963	3.451	0.650	0.134	0.048	0.022
0.085	6.879	4.562	3.011	0.734	0.167	0.061	0.027	7.293	4.873	3.436	0.827	0.168	0.061	0.027
0.100	6.741	4.462	2.989	0.922	0.223	0.081	0.036	7.148	4.763	3.402	1.060	0.224	0.081	0.036
0.125	6.546	4.302	2.946	1.210	0.325	0.121	0.054	6.939	4.622	3.346	1.410	0.329	0.122	0.054
0.150	6.383	4.182	2.902	1.410	0.419	0.167	0.075	6.763	4.482	3.285	1.640	0.426	0.167	0.075
0.250	5.909	3.821	2.746	1.662	0.776	0.353	0.174	6.241	4.064	3.061	1.902	0.805	0.356	0.174
0.500	5.243	3.328	2.461	1.812	1.200	0.710	0.419	5.482	3.490	2.676	1.982	1.270	0.726	0.422
0.750	4.837	3.047	2.270	1.767	1.323	0.896	0.592	5.025	3.117	2.431	1.919	1.398	0.924	0.600
1.000	4.511	2.857	2.127	1.727	1.357	0.993	0.704	4.704	2.950	2.254	1.838	1.428	1.028	0.718

consistent-field procedure. For this, the integrals on the right-hand side were compared at some large value of r ($r=30$, at which point the integrands vanish to a good approximation because of the bound orbitals) with the value from the preceding iteration. If the value of the integrals from one iteration differed by more than 0.1% from that of the preceding solution, then the process was repeated until this criterion was satisfied.

For values of $l>7$, it was found that the exchange terms of Eq. (22) were completely negligible; therefore the solutions f_l were found by simply solving the homogeneous equation obtained by setting the right side of (22) equal to zero.

TABLE IV. Singlet and triplet phase shifts for Na.

E (Ry)	δ_0^+	δ_1^+	δ_2^+	δ_3^+	δ_4^+	δ_5^+	δ_6^+	δ_0^-	δ_1^-	δ_2^-	δ_3^-	δ_4^-	δ_5^-	δ_6^-
0.00025	12.4297	6.3070	3.1430					12.5002	9.4183	3.1430	0.000			
0.00050	12.3625	6.3460	3.1444	0.000				12.4587	9.4017	3.1445	0.000			
0.00075	12.3090	6.3995	3.1450	0.000				12.4237	9.3814	3.1459	0.000			
0.0010	12.2609	6.4740	3.1451	0.000				12.3912	9.3528	3.1454	0.0003			
0.0015	12.183	6.680	3.147	0.001				12.336	9.307	3.148	0.001			
0.0020	12.116	6.960	3.149	0.002				12.288	9.262	3.152	0.002			
0.0025	12.060	7.283	3.152	0.003				12.240	9.219	3.156	0.003			
0.0030	12.006	7.573	3.153	0.004	0.000			12.206	9.177	3.159	0.004	0.000		
0.0040	11.913	7.765	3.156	0.006	0.002			12.133	9.100	3.167	0.006	0.002		
0.0050	11.832	8.113	3.157	0.008	0.003			12.069	9.031	3.175	0.008	0.003		
0.0060	11.759	8.193	3.158	0.010	0.004			12.010	8.968	3.183	0.011	0.004		
0.0075	11.663	8.035	3.158	0.014	0.006			11.931	8.883	3.198	0.014	0.006		
0.010	11.526	8.025	3.157	0.021	0.009			11.814	8.762	3.224	0.021	0.009		
0.020	11.126	7.845	3.150	0.057	0.018	0.009		11.466	8.415	3.348	0.057	0.018	0.009	
0.030	10.855	7.753	3.144	0.121	0.031	0.014	0.008	11.216	8.185	3.461	0.124	0.031	0.014	0.008
0.050	10.475	7.473	3.133	0.345	0.075	0.028	0.014	10.835	7.885	3.554	0.370	0.075	0.028	0.014
0.065	10.259	7.313	3.116	0.583	0.123	0.043	0.020	10.615	7.743	3.567	0.654	0.124	0.043	0.020
0.075	10.137	7.221	3.101	0.760	0.161	0.056	0.025	10.495	7.633	3.559	0.874	0.162	0.056	0.025
0.085	10.028	7.139	3.086	0.935	0.204	0.071	0.031	10.382	7.543	3.538	1.100	0.205	0.071	0.031
0.100	9.886	7.029	3.065	1.140	0.273	0.097	0.042	10.231	7.413	3.507	1.350	0.276	0.097	0.042
0.125	9.683	6.871	3.022	1.420	0.397	0.146	0.064	10.016	7.232	3.445	1.610	0.403	0.147	0.064
0.150	9.512	6.738	2.979	1.590	0.567	0.201	0.089	9.833	7.079	3.382	1.712	0.519	0.202	0.090
0.250	9.016	6.349	2.833	1.752	0.986	0.420	0.208	9.292	6.626	3.159	2.002	0.939	0.424	0.209
0.500	8.305	5.790	2.597	1.842	1.270	0.797	0.483	8.506	5.975	2.811	2.012	1.360	0.819	0.488
0.750	7.840	5.453	2.464	1.792	1.370	0.969	0.662	8.028	5.588	2.617	1.928	1.451	1.003	0.673
1.000	7.568	5.212	2.383	1.761	1.380	1.049	0.766	7.683	5.316	2.497	1.843	1.456	1.088	0.783

TABLE V. Phase shifts for higher l values Li and Na $\delta_l^+ \sim \delta_l^- = \delta_l$.

	Li									Na								
E	δ_7	δ_8	δ_9	δ_{10}	δ_{11}	δ_{12}	δ_{13}	δ_{14}	δ_{15}	δ_7	δ_8	δ_9	δ_{10}	δ_{11}	δ_{12}	δ_{13}	δ_{14}	δ_{15}
0.050	0.008									0.008								
0.065	0.011	0.007								0.012	0.008							
0.075	0.013	0.008								0.014	0.009							
0.085	0.015	0.009								0.016	0.010							
0.100	0.019	0.012								0.021	0.013							
0.125	0.028	0.016	0.010							0.031	0.018	0.011						
0.150	0.038	0.021	0.013							0.045	0.025	0.015						
0.250	0.095	0.054	0.032							0.114	0.064	0.037						
0.500	0.256	0.159	0.103	0.066						0.301	0.188	0.123	0.080					
0.750	0.392	0.263	0.178	0.123	0.086	0.061	0.044	0.032		0.448	0.306	0.209	0.146	0.101	0.072	0.052	0.038	
1.000	0.496	0.349	0.247	0.176	0.128	0.092	0.069	0.051	0.038	0.556	0.396	0.286	0.206	0.152	0.110	0.081	0.062	0.044

The phase shifts δ_l^+ and δ_l^- were obtained directly from the solutions to Eq. (22) by integrating the equation out to a distance which was large enough that all terms in the differential equation were negligible as compared to k^2 ($<10^{-4}$). The phase shifts were obtained by comparison with the spherical Bessel functions. The distance at which this criterion is satisfied depends, of course, on the value of k^2. For the smallest values of k this distance was chosen as large as $500a_0$, and for the highest values of k it was as small as $35a_0$. The proper multiple of π to be added to the phase was obtained directly by a node count on the solutions f_l and on the corresponding Bessel functions j_l. The result was available directly from the additional number of nodes in the function f_l.

In Tables III and IV are listed the phase shifts for singlet and triplet scattering for several energies,[16] and in Table V are the phase shifts for higher values where the triplet and singlet partial waves were indistinguishable.

V. TOTAL ELASTIC-SCATTERING CROSS SECTIONS

With the phase shifts δ_l^+ and δ_l^- determined, the total elastic-scattering cross section for the singlet or triplet may be determined (in units of πa_0^2) from the expression

$$\sigma^{\pm} = \left(\frac{4}{k^2}\right) \sum_l (2l+1) \sin^2\delta_l^{\pm},$$

where the (+) refers to the singlet and the (−) to the triplet states of the system. The total cross section is then

$$\sigma = \tfrac{1}{4}\sigma^+ + \tfrac{3}{4}\sigma^-.$$

TABLE VI. Scattering lengths for Li and Na.

Li		Na	
A^+	A^-	A^+	A^-
7.554	2.088	6.511	1.634

In Figs. 3 and 4, the total elastic-scattering cross sections for Li and Na are shown compared to the experimental results of Perel, Englander, and Bederson[17] and of Brode.[18] [The results are plotted as a function of (volts)$^{1/2}$ in order to show the low-energy values more clearly.] The agreement with experimental values over the range of the experiments is quite good. In particular, we note the double resonance exhibited by the total cross section, one at about $\frac{1}{4}$ V and another smaller peak at about 1.5 V, which corresponds exactly in energy to the experimental peak in this region. Unfortunately, no experimental cross sections are available for Na and Li in the very low-energy region as in the case of Cs; thus the second peak in the calculated cross section cannot be checked against experiment at present. The calculated cross sections are about 5–15% higher than the experimental values of Perel *et al.*; however, their results were normalized to those of Brode at 2 eV; thus the absolute values of the experimental curve may be in error by this amount, particularly since Brode[18] states that his values below 4 eV are uncertain to ±15%.

We note in Figs. 3 and 4 that the calculated cross sections for both Li and Na decrease to relatively small values at very low energies. The values at zero energy were determined by calculating the scattering lengths $A^{\pm}$ for singlet and triplet states from the modified effective-range theory expansion[19]

$$\tan\delta_0^{\pm} = -A^{\pm}k - (\pi\alpha/3)k^2 - (4\alpha A^{\pm}/3)k^2 \ln(1.23\alpha^{1/2}k) + \cdots,$$

where $A^{\pm}$ is the scattering length. The values of A were obtained from the phase shifts at $k = [0.00025\ (\text{Ry})]^{1/2}$ and are shown in Table VI. It is worthwhile to compare the scattering lengths of Table VI with those calculated for electron-hydrogen scattering by various methods. In the case of hydrogen the singlet scattering length is $A^+ \cong 6a_0$ and the triplet $A^- \cong 2a_0$ (Rosenberg, Spruch,

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[16] A more complete list of phase shifts is available through W. R. Garrett, University of Alabama Research Institute Report No. 19, 1965 (unpublished).

[17] J. Perel, P. Englander, and B. Bederson, Phys. Rev. **128**, 1148 (1962).

[18] R. B. Brode, Phys. Rev. 34, 673 (1929).

[19] T. F. O'Malley, L. Rosenberg, and L. Spruch, Phys. Rev. **125**, 1300 (1962).

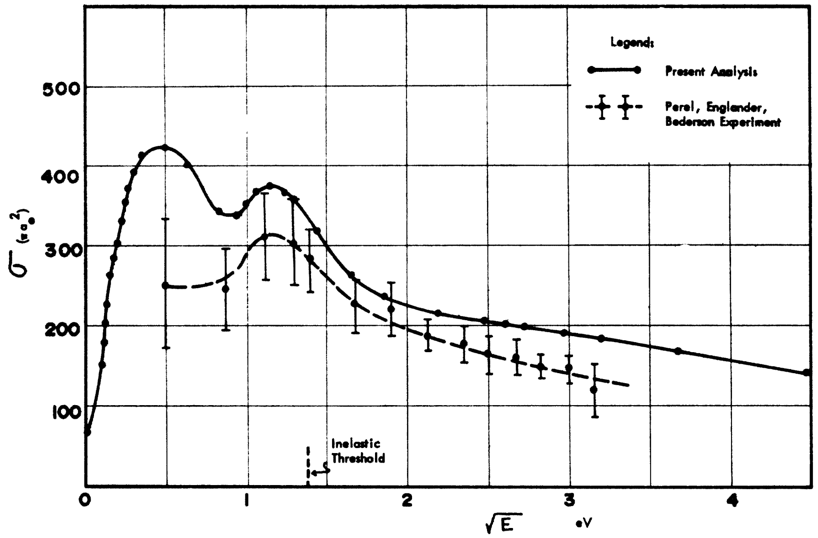

FIG. 3. Total elastic-scattering cross sections for Li. Experimental values are those of Perel, Englander, and Bederson.

and O'Malley[20] give upper bounds of $6.23a_0$ and $1.91a_0$, respectively, for A^+ and A^-; other calculations agree well with these results.[21]) We note from the results of Table VI that both the singlet and triplet scattering lengths of Li and Na are very little different from those of hydrogen. This is significant for two reasons. First, though the alkali atoms are much more complicated than hydrogen, they retain hydrogen-like characteristics and polarization and exchange effects are similarly important as in the hydrogen atom. Second, and perhaps more important for comparison purposes, is the fact that the negative ions of Li and Na are estimated to have approximately the same binding energy as that of the hydrogen atom (roughly 0.7–0.8 eV).[22] Thus, heuristically one would predict that the singlet and triplet scattering lengths for these alkalis should resemble those for hydrogen, which is true in the present calculation.

The present results for zero energy differ quite drastically from those of other calculations for alkali atoms. The results of Vinkalns, Karule, and Obedkov[23] for Li are $A^+=-4.8$ and $A^-=-10.4$, and those of Salmona and Seaton[24] for Na are $A^+=9$ and $A^-=-12$. Both these results are very much different from those for hydrogen and from the present results, being exactly opposite in relative magnitude and yielding much larger values of σ for $E=0$. The present results also differ greatly from those for Cs by Crown and Russek,[25] $A^+=-20$ and $A^-=360a_0$ which yield very large cross sections at zero energy. Though no experimental data is available for comparison at very low energies, the present results seem more reasonable from the above argument. Also the results at higher energies are much better in the present calculation than in any of the previous alkali atom calculations, which lends some support to the present low-energy results.

VI. CONCLUSIONS

From the results obtained in the present calculations, it seems that the method of polarized orbitals and the adiabatic exchange approximation is capable of describing low-energy electron scattering from more complicated atomic systems, these being represented by HF-type wave functions. In the calculation of the polarization potential for the alkali atoms, the approximation used in earlier calculations,[4,6,10] that only the outer region of the perturbation equations be included, seems to be inadequate. Since the valence electron is very weakly bound, the wave function of the valence orbital has an appreciable amplitude over a rather large distance, and the inclusion of the inner and outer regions in the equations for the perturbed radial functions gives a strong dependence of the amplitude and the shape of the perturbation $U_{nl\to l'}$ on the free-electron position. With the strong dependence of the scattering cross sections on the shape of the polarization potential in the region near the atomic radius, this behavior should not be ignored in the calculation of V_p.

There are two points which should be mentioned in comparing the present interaction potential for electron-alkali atom scattering with other calculations on the same problem. The first, which was pointed out by Temkin,[4] is that the perturbed orbitals χ_i contain, at least partially, the effects of both the continuum and configuration interactions. The perturbed wave function contains terms of higher angular asymmetry than the original function and corresponds roughly to a per-

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[20] L. Rosenberg, L. Spruch, and T. O'Malley, Phys. Rev. **119**, 164 (1960).

[21] See A. Temkin and J. C. Lamkin, Phys. Rev. **121**, 788 (1961).

[22] See Review of L. M. Branscomb, *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), pp. 100–138.

[23] I. Z. Vinkalns, E. M. Karule, and V. D. Obedkov, Opt. i Spektroskopiya **17**, 197 (1964) [English transl.: Opt. Spectry. (USSR) **17**, 105 (1964)].

[24] A. Salmona and M. J. Seaton, Proc. Phys. Soc. (London) **A77**, 619 (1961).

[25] J. C. Crown and A. Russek, Phys. Rev. **138**, A669 (1965).

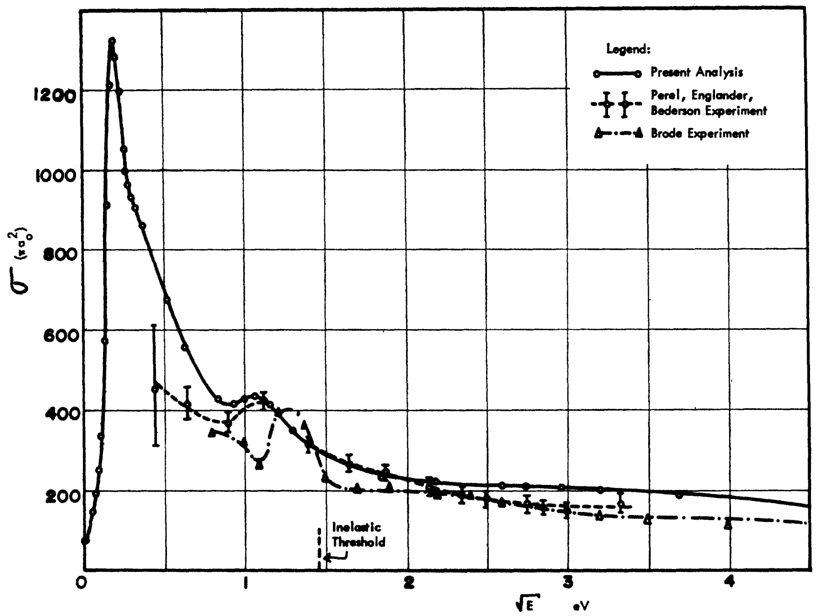

FIG. 4. Total elastic-scattering cross sections for Na. Experimental values are those of Perel, Englander, and Bederson, and of Brode.

turbation of some closely lying configuration. Furthermore, the radial dependence, which arrives from the solution of an inhomogeneous set of equations, reflects the effects of all higher states even of the states of the continuum.[4] The methods employed in other calculations for the alkalis include the contributions from only a limited number of higher states to the polarization potential, usually only one[5,23] or at most two or three[24,25] excited states. This has been shown to be adequate for very large r_f where the results may be compared to that yielded by the dipole polarizability,[24] but for values of r_f comparable to the atomic radius where the perturbation is considerably stronger this approximation may be inadmissible.

Another significant difference in this comparison is the treatment of the core electrons. Here, both the effects of core polarization and exchange are included, at least approximately; core polarization by direct calculation and exchange in the core through the use of the Slater exchange approximation for the exchange potential in Eq. (17). Sample calculations for Na, neglecting these effects, indicate that both contributions are important for some values of E. The method of Bauer and Browne[26] yields a convenient approximation to both effects, though adjustable parameters are involved in the calculation. Their calculated cross sections for Li are well below experimental values in the region just below the first excitation threshold.

In the present treatment, the Slater approximation for the exchange terms in the Hartree-Fock equations was utilized in calculating the bound state as well as the free wave functions. There are, of course, more accurate wave functions available for Li and Na, but the magnitude of the problem begins to be unmanagable in the complete HF perturbation calculation. The HFS wave functions are, in fact, very close approximations to the HF solutions; since exchange polarization terms are neglected in the polarization-potential calculations, it seems that little would be gained by using more exact HF ground-state wave functions in the equations derived here. In fact, the present investigation indicates that a useful criterion for a "good" set of bound-state wave functions, in a low-energy scattering problem where the polarization potential is so important, is that set which gives a good value of the polarizability in the polarization-potential calculation. The HFS wave functions used here satisfy this requirement very well.

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[26] E. Bauer and H. N. Browne, *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 16.