

Polarization Potentials for Low-Energy Scattering: e^+ -H and e^- -Li

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Polarization-potential calculations are given for positron scattering by hydrogen and for electron scattering by lithium. The potentials are obtained in the adiabatic approximation by a simple variational calculation of the energy of the disturbed atom. This approach is more general than perturbation theory and is valid even for the large interactions typical of the alkali elements. The $l=0$ phase shifts are calculated for positron-hydrogen scattering with differing numbers of excited states included in the coupling. First, only the $2p$ state is considered, next, all p states, and finally all p states plus the $2s$ state. Phase shifts and cross sections of five partial waves ($l=0$ to $l=4$) are calculated for the lithium problem when the interaction of the first excited state ($2p$) is considered. This accounts for all of the experimentally observed polarizability. Comparison with close-coupling results in both cases shows the present method to be of similar accuracy when coupling with the same excited states is included. The adiabatic approximation, inherent in the polarization potential, is therefore not a serious limitation and the method can be used with confidence for more complex atoms.

I. INTRODUCTION

SCATTERING by an atomic system can be reduced to an essentially exact one-electron problem by use of the optical-model potential.¹ In practice, this potential is intractable and approximations to it are necessary. "Coupled equations" procedures, such as the strong-coupling approximation, are often used for hydrogen.² They require solving a set of coupled differential equations (integrodifferential equations when exchange is included) and have been shown³ to be the first approximation to a modified set of optical-potential equations.

A second procedure that is frequently used is the adiabatic approximation to the optical potential.^{1,4} The result is a polarization potential, and it is usually determined by perturbation theory. However, when considering heavy atoms or scattering from excited states, perturbation theory may not be valid. This is because coupling to the other atomic states may be large and the interaction is not a small perturbation whose higher order terms can be neglected. Such was the situation in cesium⁴ and is found here to be the situation in lithium.

An adiabatic approximation can still be employed even though the interaction is large. The essence of adiabatic theory is that the target atom establishes new wave functions for each position of the scattered particle. If perturbation theory is invalid, some other procedure must be used to determine the wave functions. Of course, a large interaction is accompanied by large particle acceleration and eventually the particle moves so fast that atomic wave functions cannot be established. In such cases, adiabatic theory breaks down.

The purpose of the present paper is to show that

adiabatic theory does not break down as easily as might be expected and that polarization potential methods are of comparable accuracy to coupled equations methods. The greater simplicity—especially when many atomic states are closely coupled—and comparable accuracy suggest their use for heavy-atom scattering.

Two elastic-scattering calculations are performed: the scattering of positrons from hydrogen⁵ and electrons from lithium. The positron problem is an excellent theoretical test of an approximation because symmetry of the wave function is not required (no exchange). Moreover, the polarization forces are opposed to the nuclear force and are consequently of much greater importance than in the electron-hydrogen problem. Scattering from lithium is a simple example of heavy-atom scattering. Coupling to only one state represents nearly all the polarizability, and it is too large to be treated by perturbation theory. In both problems, coupled equations calculations are available for comparison.

The polarization potential is determined here in the same way as was previously done for cesium.⁴ This is a procedure where the atomic wave function is assumed to be of the form given by perturbation theory. The coefficient giving the coupling of higher states is chosen, however, by minimizing the energy of the atom. This procedure is valid when the interaction is large and reduces to the perturbation theory result when the interaction is small (e.g., at large scattering distances). The cesium calculation gave reasonable agreement with the scattered experimental results but there were no coupled equations or variational results to compare with. Consequently, little could be said of the generality of the method.

Section II discusses the positron problem and Sec. III discusses the lithium calculation. Section IV is a short statement of conclusions.

II. POSITRON-HYDROGEN SCATTERING

Many calculations have been performed for this process but there is still no satisfactory treatment short

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¹ M. H. Mittleman and K. M. Watson, *Phys. Rev.* **113**, 198 (1959). Also B. A. Lippmann, M. H. Mittleman, and K. M. Watson, *Phys. Rev.* **116**, 920 (1959).

² P. G. Burke and H. M. Schey, *Phys. Rev.* **126**, 147 (1962).

³ M. H. Mittleman and R. Pu, *Phys. Rev.* **126**, 370 (1962).

⁴ P. M. Stone and J. R. Reitz, *Phys. Rev.* **131**, 2101 (1963).

⁵ P. M. Stone, *Bull. Am. Phys. Soc.* **10**, 186 (1965).

of the extensive variational calculations.⁶ The reason for this seems to be that the attractive polarization force opposes the repulsive force of the shielded nucleus. As a result, the total interaction is sensitive to the polarization, and it must be accurately determined.

It is clear that without polarization the phase shift will be negative (repulsion) and can become positive only when polarization or some other attractive interaction is included. The elaborate variational calculation of Schwartz⁶ shows that the phase shifts are indeed positive at low energies (<0.36 Ry).

A series of calculations by Cody, Lawson, Massey, and Smith⁷ have included polarization by means of the Temkin-Lamkin⁸ polarization potential (often referred to as the polarized orbital or P.O. method). Cody *et al.*, have also redone calculations neglecting polarization entirely (just the mean static interaction⁹), and have done a coupled-equations calculation using the $1s$, $2s$, and $2p$ states. They have also considered positronium formation (virtual) both with and without the Temkin-Lamkin polarization. Their paper compares phase shifts with the variational calculations⁶ and gives a rather complete summary of earlier work on scattering-length calculations. Additional works that should be emphasized are the calculations of Rotenberg,¹⁰ using an expansion of the total wave function in Sturmian functions, and the nonadiabatic s -wave scattering calculations of Temkin.¹¹ Both of these give phase shifts larger than the variational results of Schwartz, though as many as 50 variational parameters had been used. The calculation of Cody *et al.*,⁷ that includes positronium formation and polarization also gives phase shifts greater than those of Schwartz.

All that can be said conclusively of positron-hydrogen scattering from the earlier work is that polarization is the most important addition to the static approximation and that without it the phase shifts remain negative at low energies. Virtual positronium formation is of next importance. The actual phase shifts are probably close to the variational values of Schwartz.

It is clear from the above discussion that positron-hydrogen scattering serves as an ideal test of a polarization potential. By comparison, the electron-scattering problem is very poor because polarization is in that case a small effect.

The Temkin-Lamkin⁸ polarization potential includes the contribution of all p states of hydrogen (including the continuum) in a perturbation-theory calculation of part of the interaction potential. The part included is the long range or "inside" part of the dipole term in the expansion of the inverse of the electron-electron distance

(or electron-positron distance in this case). It becomes correct only at large scattering distances. It nevertheless represents an important improvement over previous treatments of polarization because it successfully includes all excited states. The restrictions to perturbation theory are not important for hydrogen but limit the usefulness of the method for the alkalis.

The calculations here⁵ neglect positronium formation and compare the results with the corresponding calculations of Cody *et al.*⁷ A series of calculations is performed that attempts to include more and more of the contribution of excited states. The numerical results clearly show that the accuracy is comparable to other methods (coupled equations, Temkin-Lamkin polarization potential) that include contributions from the corresponding number of excited states.

A. Equations Including the $2p$ State

The equations have been introduced previously⁴ and will only be outlined here. Atomic units are used; i.e., energy in Ry (13.6 eV) and length in Bohr radii. The approximation arises by taking the two-particle wave function as (neglect positronium formation)

$$\psi(\mathbf{r}_1\mathbf{r}_2) = [\psi_0(\mathbf{r}_1) + \beta(r_2)\psi_1(\mathbf{r}_1)]F(\mathbf{r}_2), \quad (1)$$

where \mathbf{r}_1 is the coordinate of the atomic electron and \mathbf{r}_2 is the positron coordinate. The scattered positron function $F(\mathbf{r}_2)$ is to be determined. The term in brackets is the wave function of the atomic electron when the positron is a distance r_2 away. When $r_2 = \infty$, β becomes zero and the atom is in the unperturbed ground state ψ_0 . Only the $2p$ excited state ψ_1 is used to describe the change in the wave function as the positron approaches. It is well established that such an approximation will include 65.8% of the long-range polarization.

The procedure is adiabatic in that it is assumed that an altered atomic wave function is established for each position of the scattered particle. It is not required, however, that the change in the atomic wave function be small. It turns out that the change is small in hydrogen and perturbation theory could be used to calculate $\beta(r_2)$.

The procedure that is followed here is to choose $\beta(r_2)$ so that the energy E_A of the atom is a minimum. Thus, the requirement is that

$$\partial E_A / \partial \beta = 0, \quad (2)$$

where

$$E_A = \frac{\langle \psi_0 + \beta\psi_1 | H_A + V | \psi_0 + \beta\psi_1 \rangle}{\langle \psi_0 + \beta\psi_1 | \psi_0 + \beta\psi_1 \rangle}. \quad (3)$$

The Hamiltonian for the atom is H_A and the interaction of the atomic electron with the positron is $V(r_1, r_2)$. Matrix elements are over the electron coordinate r_1 . The coefficient β chosen by (2) for positron scattering is given by

$$\beta = \frac{V_{01}}{1 - \beta^2 E_1 - E_0 + V_{00} - V_{11}}, \quad (4)$$

⁶ C. Schwartz, Phys. Rev. **124**, 1468 (1961).

⁷ W. J. Cody, J. Lawson, H. Massey, and K. Smith, Proc. Roy. Soc. (London) **278**, 479 (1964).

⁸ A. Temkin, Phys. Rev. **116**, 358 (1959); A. Temkin and J. C. Lamkin, Phys. Rev. **121**, 788 (1961).

⁹ K. Smith and P. G. Burke, Phys. Rev. **123**, 174 (1961); L. Spruch and L. Rosenberg, Phys. Rev. **117**, 143 (1960).

¹⁰ M. Rotenberg, Ann. Phys. (N. Y.) **19**, 262 (1962).

¹¹ A. Temkin, Proc. Phys. Soc. (London) **80**, 1277 (1962).

where

$$V_{ij}(r_2) = \langle \psi_i | V(\mathbf{r}_1 \mathbf{r}_2) | \psi_j \rangle \quad (5)$$

and

$$V(\mathbf{r}_1 \mathbf{r}_2) = -2/r_2 + 2/|\mathbf{r}_1 - \mathbf{r}_2|. \quad (6)$$

The neglect of angular dependence in $V_{ij}(r_2)$ is the mathematical statement of the adiabatic approximation. E_1 and E_0 are the binding energies of the 0 and 1 states. The interaction energy of the positron with the unperturbed ground-state atom is $-V_{00}$ and is positive at all distances. Similarly, $-V_{11}$ is the interaction energy when the atom is in the $2p$ state. At large positron distances, V_{00} and V_{11} are negligible and β^2 is small. Expression (4) then gives

$$\beta \rightarrow V_{01}/(E_1 - E_0) = \frac{4}{3}V_{01}, \quad (7)$$

which is precisely the perturbation-theory result. The expression in (7) could be used at all distances with no significant loss of accuracy because β is always small. However, for alkali scattering, the value of β given by (7) becomes greater than one at small distances and perturbation theory is no longer valid. In such cases, the expression (4) must be used.

The equation for the scattered particle is obtained by using (1) in the two-particle Schrödinger equation.

$$[H_A(r_1) + \nabla_2^2 + V(r_1 r_2) + E]\psi(\mathbf{r}_1 \mathbf{r}_2) = 0, \quad (8)$$

where the Laplacian operator ∇_2^2 operates on \mathbf{r}_2 . If this equation is premultiplied by ψ_0^* and integrated over \mathbf{r}_1 , the equation for $F(r)$ is (use r instead of r_2 now)

$$[\nabla^2 + E - E_0 + V_{00} + V_p]F(r) = 0, \quad (9)$$

with the polarization potential V_p given by

$$V_p(r) = \beta(r)V_{01}(r). \quad (10)$$

V_p is positive at all distances and V_{00} is negative. Equation (9) is solved by the usual procedure of expansion in partial waves (Legendre expansion of angular coordinates). Only the zero-order partial waves ($l=0$) contribute significantly for hydrogen.

The potentials and atomic wave functions that enter in (4), (9), and (10) can be written down explicitly. In atomic units they are

$$\begin{aligned} \psi_0 &= (\sqrt{\pi})^{-1} e^{-r}, \quad 1s \text{ state} \\ \psi_1 &= 4\sqrt{(2\pi)^{-1}} \cos\theta r e^{-r/2}, \quad 2p, m=0 \text{ state} \\ V_{00} &= -2(1+1/r)e^{-2r}, \\ V_{01} &= \frac{\sqrt{2}}{3} \left[\frac{256}{81} \frac{1}{r^2} - \left(\frac{256}{81} \frac{1}{r^2} + \frac{128}{27} \frac{1}{r} + \frac{32}{9} + \frac{4}{3} \right) e^{-(3/2)r} \right], \\ V_{11} &= \frac{24}{r^3} - \left(\frac{24}{r^3} + \frac{24}{r^2} + \frac{14}{r} + \frac{11}{2} + \frac{3}{2} + \frac{1}{4} \right) e^{-r}. \end{aligned} \quad (11)$$

At large distances the polarization potential becomes

$$V_p = \frac{4}{3}V_{01}^2 = 2.96/r^4. \quad (13)$$

The polarizability here is 2.96 and is 65.8% of the value obtained (4.5) when all p states are included.

B. All p States

The approximation (1) for the two-particle wave function can be extended in a manner analogous to the "polarized orbital" method of Temkin⁸ to include contributions of all p states. The form is

$$\psi(\mathbf{r}_1 \mathbf{r}_2) = [\psi_0(\mathbf{r}_1) + \beta(r_2)\varphi(\mathbf{r}_1)]F(r_2), \quad (14)$$

with

$$\varphi(\mathbf{r}) = r(1 + \frac{1}{2}r)\cos\theta\psi_0(\mathbf{r}). \quad (15)$$

This $\varphi(r_1)$ has the r_1 dependence that perturbation theory gives⁸ for the correction to the wave function when the summation is performed over all $l=1$ states for hydrogen. To agree further with perturbation theory, $\beta(r_2)$ must become r_2^{-2} at large values of r_2 .

The method of evaluation of β follows as before and the same scattering equation (9) results. The polarization potential is

$$V_p(r) = \beta(r)V_{0p}(r), \quad (16)$$

with $\beta(r)$ determined by

$$\frac{\beta}{2 - (43/4)\beta^2} = \frac{V_{0p}}{9 + (43/4)V_{00} - 2V_{pp}}. \quad (17)$$

The potentials here are

$$\begin{aligned} V_{0p}(r) &= \langle \psi_0 | V(\mathbf{r}_1 \mathbf{r}) | \varphi \rangle \\ &= \frac{1}{r^2} - \left(\frac{1}{r^2} + \frac{9}{r} + 9 + 5r + r^2 \right) e^{-2r}, \quad (18) \\ V_{pp}(r) &= \langle \varphi | V(\mathbf{r}_1 \mathbf{r}) | \varphi \rangle \\ &= 48/r^3 - (48/r^3 + 96/r^2 + 106.75/r + 71.25 \\ &\quad + 45r + 18r^2 + \frac{1}{2}r^3 + \frac{1}{2}r^4) e^{-2r}. \quad (19) \end{aligned}$$

At large r , V_{00} and V_{pp} become negligible and the polarization potential becomes

$$\begin{aligned} \beta &\rightarrow (2/9)V_{0p} = 1/r^2, \\ V_p &\rightarrow (2/9)|V_{0p}|^2 = \frac{2}{9}1/r^4. \quad (20) \end{aligned}$$

This method includes all the long-range polarization.

C. All p States and the $2s$ State

The p states do not contribute to polarization at small radii so that the polarization potential in the two cases above is zero at the origin. The s states give the polarization potential a finite value and this subsection estimates the contribution by adding the first excited s state to the p states already considered. The small radius behavior of V_p is not expected to be significant because the static potential [V_{00} in (9)] becomes large and dominates.

The total wave function is taken as

$$\psi(\mathbf{r}_1 \mathbf{r}_2) = [\psi_0(\mathbf{r}_1) + \beta(r_2)\varphi(\mathbf{r}_1) + \alpha(r_2)\psi_2(\mathbf{r}_1)]F(r_2), \quad (21)$$

where ψ_2 is the $2s$ state. The coefficient α is chosen in the same way as has been discussed for β . However, a further simplification is introduced: α is calculated as if β were zero, and β is calculated as if α were zero.

Clearly, the same β as in the previous subsection is obtained—Eq. (17)—and α is given by

$$\frac{\alpha}{1-\alpha^2} = \frac{V_{02}}{E_2 - E_0 + V_{00} - V_{22}}. \quad (22)$$

The polarization potential is then

$$V_p = \beta V_{0p} + \alpha V_{02}. \quad (23)$$

The new potentials are

$$\begin{aligned} V_{02} &= \langle \psi_0 | V(\mathbf{r}_1 \mathbf{r}) | \psi_2 \rangle \\ &= (32/81)^{1/2} (r + \frac{2}{3}) e^{-(3/2)r}, \end{aligned} \quad (24)$$

$$\begin{aligned} V_{22} &= \langle \psi_2 | V(\mathbf{r}_1 \mathbf{r}) | \psi_2 \rangle \\ &= -\frac{1}{2} r^{-1} (r^3 + 2r^2 + 6r + 8) e^{-r}. \end{aligned} \quad (25)$$

It would be more correct to solve for α and β simultaneously, i.e., to minimize the energy of the atom when the p states and $2s$ state are included together in the interaction. However, the $2s$ -state correction is important at small distances ($< a_0$) while the p -state corrections are important at larger radii. It is then not a severe simplification to calculate the correction separately.

D. Results and Discussion

The zero-order positron-hydrogen phase shifts have been calculated for each of the polarization potentials discussed above. Summarizing, these are

$$\begin{aligned} V_{p1} &= \beta_1 V_{01}, & 2p \text{ state} \\ V_{p2} &= \beta_2 V_{0p}, & \text{all } p \text{ states} \\ V_{p3} &= V_{p2} + \alpha V_{02}, & \text{all } p \text{ states plus } 2s \text{ state.} \end{aligned}$$

These potentials are shown in Fig. 1 with the static potential V_{00} and the Temkin-Lamkin⁸ or “polarized orbital” (P.O.) potential for p states ($l=1$). The P.O. potential and V_{p2} are nearly the same at large radii and become identical at infinity. This is because both include the p states in the same way at large radii. At small distances, the P.O. potential is larger, and then both become zero at zero radius. V_{p3} is greater than V_{p2} at small distances because of the $2s$ -state contribution. They are identical beyond $3a_0$. The differences of the potential at small radii are not of major importance because V_{00} dominates the interaction.

The zero-order phase shifts ($l=0$) are shown in Fig. 2 and listed in Table I. The calculation that includes all p states gives phase shifts very close to the P.O. results. The addition of the $2s$ state is seen to have only a small effect. Similarly, the calculation using the $2p$ state differs only slightly from the $1s$ - $2s$ - $2p$ coupled-equations calculations of Cody, Lawson, Massey, and Smith.⁷ The slopes of the curves at $k=0$ come from scattering-length calculations. All the values are below the variational results of Schwartz.⁶

The numerical work was done in the same manner as previously reported.⁴ Power series expansions were used

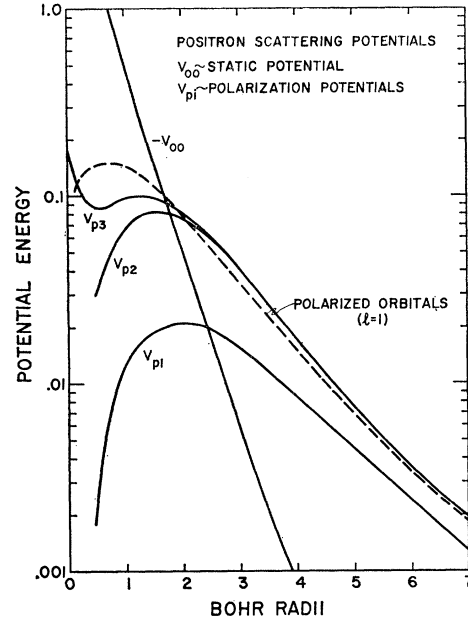


Fig. 1. Positron-hydrogen potentials. V_{00} is the static potential and repels the positron. The three polarization potentials correspond to coupling with the $2p$ state (V_{p1}), coupling with all p states (V_{p2}), and coupling with all p states plus the $2s$ state (V_{p3}). The polarized orbital potential of Temkin and Lamkin (Ref. 8), that couples to all p states, is also shown.

to start the solutions and the integration was carried forward by the Numerov procedure. At $20a_0$ the solution was matched to a linear combination of spherical Bessel functions and the phase shifts determined from the coefficients. A mesh spacing of $0.1a_0$ was used from 0 to $5a_0$ and a spacing of $0.2a_0$ was used thereafter. Numerical checks were made by using a mesh twice as fine and by integrating to $30a_0$ in some cases. No significant changes in phase shifts were obtained. An over-all check was obtained by comparing static calculations ($V_p=0$) with the literature. The numerical results are estimated to give phase shifts accurate to better than 0.001 radian.

It is possible to divide (1) by $[1+\beta^2(r_2)]^{1/2}$ so that the disturbed atomic wave function is normalized to unity. Numerical tests in the cesium calculation⁴ have shown that the results are not sensitive to the normalization. In the present case there is no exchange and it

TABLE I. Positron-hydrogen zero-order ($l=0$) phase shifts in radians compared with other calculations. k is in $\text{Ry}^{1/2}$. The $k=0$ values are scattering lengths.

k	$2p$	All p	All p + $2s$	$1s$ - $2s$ - $2p^a$	Schwartz ^b	Polarized ^a orbitals
0	-0.3	-1.239	-1.276	0.0	-2.10	-1.276
0.1	0.006	0.095	0.102	-0.0054	0.151	0.0803
0.2	-0.024	0.105	0.111	-0.0426	0.188	0.0853
0.3	-0.072	0.073	0.078	-0.0931	0.168	0.0528
0.4	-0.125	0.021	0.031	-0.1472	0.120	0.0048
0.5	-0.178	-0.037	-0.027	-0.1990	0.062	-0.0476
0.6	-0.227	-0.095	-0.082	-0.2461	0.007	-0.0989
0.7	-0.270	-0.149	-0.135	...	-0.054	-0.1467
0.8	...	-0.199

^a Reference 7.
^b Reference 6.

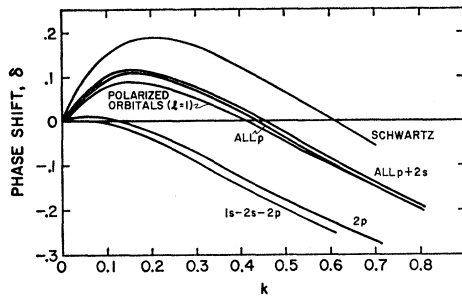


FIG. 2. Zero-order phase shifts in radians for positron-hydrogen scattering. k^2 is in rydbergs. The $2p$, all p , and all p plus $2s$ curves are the present calculations with the indicated coupling. The $1s$ - $2s$ - $2p$ curve is a coupled equations calculation (Ref. 7) and the polarized orbital curve uses the Temkin-Lamkin (Refs. 7, 8) potential for p states ($l=1$). The variational results of Schwartz (Ref. 6) are shown to indicate the values that are probably nearly correct. The curves indicate that the number of excited p states included in the coupling is more important than the computational model.

becomes clear that the lack of normalization is completely unimportant. With normalization the function determined by the wave equation (9) would be $F(r)/[1+\beta^2(r)]^{1/2}$ instead of $F(r)$. Since β becomes negligible at large distances, the phase shifts calculated with and without normalization are insignificantly different. For instance, at $20a_0$, where the phase shifts have been calculated, β_2 is only 2.5×10^{-3} .

Figure 2 shows clearly that the results are primarily dependent on the number of states included in the calculation. By including more states—particularly s states—the phase shifts will approach the values of Schwartz.¹² The main point here is that the polarization potential method gives phase shifts equivalent to the more involved coupled equations method. The “extra” assumption of adiabatic interaction that is inherent in polarization potentials does not appear to be a serious limitation. This suggests that these simpler procedures can be used with confidence for scattering by heavy, many-electron atoms.

III. ELECTRON-LITHIUM SCATTERING

It is well established^{4,13,14} that polarization is important for scattering by alkalis. Moreover, it must be treated carefully because the results are sensitive to both the magnitude and shape of the potential. Vinkalns, Karule, and Obedkov¹⁵ have reported a calculation of scattering by lithium using a polarization potential obtained from coupling with the first excited p state ($2p$) by perturbation theory. The wave function was taken spatially symmetric and then antisymmetric

¹³ R. J. Drachman, Phys. Rev. **138**, A1582 (1965). This reference has included all hydrogen states in a perturbation-theory calculation and finds that the phase shifts greatly exceed those of Schwartz!

¹⁴ A. Salmona and M. J. Seaton, Proc. Phys. Soc. (London) **77**, 617 (1961).

¹⁵ W. R. Garrett and R. A. Mann, Phys. Rev. **135**, A580 (1964).

¹⁶ I. Zh. Vinkalns, E. M. Karule, and V. D. Obedkov, Opt. i Spektroskopiya **17**, 197 (1964) [Eng. transl.: Opt. Spectry. (USSR) **17**, 105 (1964)].

so as to include the effects of exchange. Exchange with core electrons and polarization of the core were neglected.

A coupled equations calculation has also been reported¹⁶ that uses the $2s$ and $2p$ states. The cross sections were calculated in the 2.0- to 3.0-eV range and give elastic scattering results below the polarization potential values by 15 to 40%. Moreover, the partial cross sections differ considerably.

The lithium polarization calculation is redone here with the atomic orbitals determined by minimizing the energy of the atom rather than by using perturbation theory. This is necessary because the interaction is large and higher order terms in the perturbation expansion are not negligible. The formulation is analogous to the treatment in Sec. IIB above. Exchange is also included. The results agree much better with the coupled equations results than do the perturbation calculations of Vinkalns *et al.*, but all the cross sections are below experiment.¹⁷

The effect of polarization and exchange interactions with the core is expected to be small because of the large binding energies of core electrons relative to the valence electrons. In fact, the self-consistent-field (SCF) calculations of Ivanova and Ivanova¹⁸ have shown that the core wave functions are hardly affected by such interactions. This helps justify the neglect of interactions with core electrons in the present calculations.

The lithium wave functions used are the same as used by Vinkalns *et al.* These are analytic SCF results of Clementi, Roothaan, and Yoshimine¹⁹ for P_{1s} and P_{2s} orbitals and the analytical function of Gailitis²⁰ for the $2p$ orbital:

$$P_{2p}(r) = 0.22805r^2e^{-0.5227r}, \quad (26)$$

where $P(r)/r$ is the radial part of the wave function. The orbitals agree well with the SCF values of the Ivanovas.¹⁸

A. Equations

The scattering equations follow from the development previously reported for cesium.⁴ In that case, a one-electron potential and the associated wave functions were available for the valence electron. The present calculation uses SCF orbitals for the core and valence electrons, and the formulation of the static potential is therefore slightly different. The atomic ground-state wave function is written as

$$\psi_0(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3) = u_{1s}(\mathbf{r}_2)u_{1s}(\mathbf{r}_3)u_{2s}(\mathbf{r}_1), \quad (27)$$

¹⁸ E. M. Karule and R. K. Peterkop, Opt. i Spektroskopiya **16**, 958 (1964) [Eng. transl.: Opt. Spectry. (USSR) **16**, 519 (1964)].

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

¹⁸ A. V. Ivanova and A. N. Ivanova, Opt. i Spektroskopiya **16**, 917 (1964). [English transl.: Opt. Spectry. (USSR) **16**, 499 (1964)].

¹⁹ E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).

²⁰ Quoted in Ref. 16.

where \mathbf{r}_1 is the coordinate of the valence electron and $\mathbf{r}_2, \mathbf{r}_3$ are the core electron coordinates. For brevity, the core electron functions are written as $\psi_c(r_c)$ so that

$$\psi_0 = u_c(\mathbf{r}_c)u_{2s}(\mathbf{r}_1). \quad (28)$$

The first excited state is accordingly

$$\psi_1 = u_c u_{2p}(\mathbf{r}_1), \quad (29)$$

and clearly indicates that it is the valence electron that is in the excited state.

The wave function, including valence-electron exchange, for the system of ground-state atom plus scattered electron is written as

$$\psi(\mathbf{r}_c \mathbf{r}_1 \mathbf{r}_2) = \{\psi_0(\mathbf{r}_c \mathbf{r}_1) + \beta(r_2)\psi_1(\mathbf{r}_c \mathbf{r}_1)\}F(r_2) \pm \psi_0(\mathbf{r}_c \mathbf{r}_2)F(r_1). \quad (30)$$

The coordinate \mathbf{r}_2 now refers to the scattered electron, consistent with the notation in Sec. II. The upper sign describes the singlet state and the lower sign describes the triplet state.

The wave function (30) does not quite have the proper symmetry because the unaltered atomic wave function is used in the \pm term. Exchange has thus been introduced as if the atom were not polarized, while polarization is included as if exchange did not take place. This is done for simplicity of calculation and because it should not introduce significant error. If the full symmetry were included (see Appendix), the wave equation for the l th partial wave of $F(r)$ would be coupled to the $l+1$ and $l-1$ partial waves,²¹ and considerable complexity would be introduced into the numerical solutions. The error involved in the omission is small because the polarization to the wave function is small at distances below $3a_0$ where exchange is most important. Numerical estimates⁴ suggest that the error in calculated phase shifts is less than 10%.

The scattering-electron wave equation resulting from the use of (30) is

$$\{\nabla^2 + E - E_0 - V_{00} - V_p\}F(r) = \mp \langle u_{2s} | k_0^2 - E_0 - (2/|\mathbf{r}_1 - \mathbf{r}|) | F \rangle u_{2s}(r), \quad (31)$$

where the matrix element is an integration over the valence electron coordinate \mathbf{r}_1 (integration over \mathbf{r}_c already done). The potentials V_{00} and V_p are of the same form as in the positron case, but use the atomic wave functions (28) and (29). These are [$P(r)/r$ is the radial part of $u(r)$]

$$V_{ij}(r_2) = \langle \psi_i | -2/r_2 + (2/|\mathbf{r}_1 - \mathbf{r}_2|) | \psi_j \rangle, \\ V_{00}(r_2) = -\frac{2Z}{r_2} + \frac{4}{r_2} \int_0^{r_2} P_{1s}^2 dr + 4 \int_{r_2}^{\infty} \frac{1}{r} P_{1s}^2 dr \\ + \frac{2}{r_2} \int_0^{r_2} P_{2s}^2 dr + 2 \int_{r_2}^{\infty} \frac{1}{r} P_{2s}^2 dr, \quad (32)$$

²¹ There appears to be confusion on this point as both Vinkal *et al.* (Ref. 15) and J. C. Crown and A. Russek, *Phys. Rev.* **138**, A669 (1965), use incorrect exchange terms.

$$V_p(r_2) = \beta(r_2)V_{01}(r_2),$$

$$V_{01}(r_2) = \frac{2}{\sqrt{3}} \frac{1}{r_2^2} \int_0^{r_2} P_{2s} P_{2p} r dr \\ + \frac{2}{\sqrt{3}} \int_{r_2}^{\infty} P_{2s} P_{2p} \frac{1}{r^2} dr, \quad (33)$$

$$\frac{\beta}{1-\beta^2} = \frac{-V_{01}}{E_1 - E_0 + V_{11} - V_{00}}. \quad (34)$$

The function $\beta(r)$ is always negative so that the polarization contribution in (31) is positive, just as it was in the positron case; i.e., polarization always causes attraction of the particle. The static potential enters with different sign in the electron and positron cases, representing an attractive force and a repulsive force, respectively.

The lithium potentials are shown in Fig. 3. Also shown is the perturbation theory (P.T.) potential obtained when

$$\beta_{P.T.} = -V_{01}/(E_1 - E_0). \quad (35)$$

Figure 4 compares the β 's, and it is evident that perturbation theory is invalid ($|\beta| \gtrsim 1$) over a large region of space. When the denominator of the right side of (34)

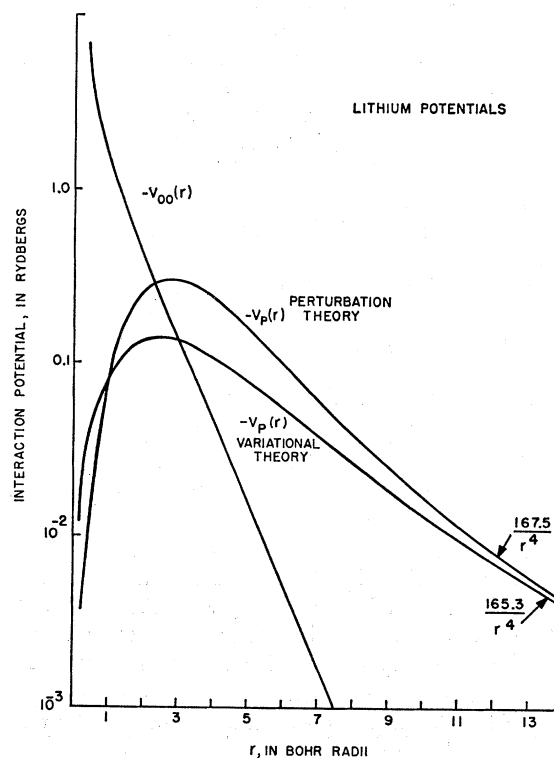


Fig. 3. Electron-lithium potentials. The static potential V_{00} attracts the electron. The polarization potentials are also attractive and include coupling to the $2p$ state. The variational theory curve results from Eq. (34) and the perturbation curve results from Eq. (35). The polarizability constants in the asymptotic form indicated on the curves were calculated at $r = 25a_0$.

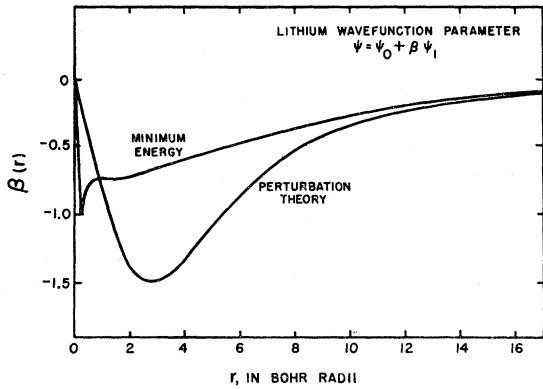


FIG. 4. The parameter β that gives the $2p$ -state correction to the ground-state lithium wave function when the scattered electron is at r . Perturbation theory [Eq. (35)] gives values larger than one in magnitude at small radii and is invalid. (Higher order terms are not negligible.) The minimum energy (or variational theory) curve is from Eq. (34).

is zero, the value of β is -1 . Figure 4 shows that this occurs at a radius of $0.25a_0$.

The long-range behavior of the polarization potential is

$$V_p \rightarrow -\alpha/r^4.$$

Evaluation of this potential from (33) and (34) at $r=25a_0$ gives $\alpha=165.3a_0^3$. This compares with the experimental value²² of 149 ± 14 and is in close agreement with other calculations that use similar wave functions²³ ($\alpha=169$). It also agrees with the calculation of Sternheimer²⁴ ($\alpha=168$) that obtains the correction to the ground-state wave function directly from the differential equation for the perturbation.

B. Results and Discussion

The scattered electron wave function $F(r)$ has been expanded in Legendre polynomials in the usual way and the resulting partial wave equations⁴ solved numerically. The phase shifts are given in Table II. Five partial waves ($l=0$ to $l=4$) have been calculated for each energy though not all are shown. Phase shifts for higher values of l have also been calculated but are so small that they are not presented. Their contribution to the cross section is less than 3%.

The cross sections are shown in Fig. 5 along with other calculations and with experimental results. Also shown are the present calculations using perturbation theory [Eq. (35)] to obtain the potential. The difference between perturbation theory results and variational theory results is seen to be considerable. In particular, the variational theory agrees much better with the $2s$ - $2p$ coupled equations calculations.¹⁶ This is true of the partial waves as well as the total cross section.

The polarization-exchange calculation of Vinkalns

TABLE II. Lithium phase shifts and cross sections from the variational potential. The last column is the total cross section (plotted in Fig. 5) obtained by summing Q_l over partial waves. The next to last column is the summation of the partial waves listed. The difference is the effect of partial waves not included in the table.

k^2 (eV)	l	δ_l^+ (rad)	δ_l^- (rad)	Q_l (πa_0^2)	ΣQ_l (πa_0^2)	Q (πa_0^2)
0.02	0	5.965	6.406	96.84		
	1	0.044	3.153	4.69		
0.05	0	5.750	6.3355	72.60		
	1	0.111	3.140	10.06		
0.10	0	5.51	6.22	68.03		
	1	0.198	3.087	19.44		
0.15	0	5.34	6.12	67.33		
	1	0.262	3.03	28.96		
0.20	0	5.195	6.026	66.54		
	1	0.310	2.968	37.08		
0.30	0	4.98	5.87	63.74		
	1	0.37	2.86	48.89		
0.40	0	4.81	5.75	60.33		
	1	0.402	2.77	55.99		
0.50	0	4.67	5.64	56.76		
	1	0.418	2.69	60.21		
1.0	0	4.212	5.227	41.38		
	1	0.430	2.398	63.26		
1.5	0	3.94	4.94	30.44		
	1	0.439	2.21	57.87		
2.0	0	3.752	4.712	22.62		
	1	0.475	2.064	51.76		
2.5	0	3.619	4.536	16.94		
	1	0.536	1.945	46.36		
3.0	0	3.507	4.376	12.73		
	1	0.612	1.867	41.84		
	2	0.406	0.779	37.07		
	3	0.245	0.294	9.96		
	4	0.139	0.146	3.36		
					104.96	104.96

et al.,¹⁵ is identical in principle to the perturbation-theory calculations done here. The difference in results shown in Fig. 5 is because of the different exchange terms that have been used. Vinkalns *et al.*, have added an additional term on the right side of (31) that is presumably meant to arise from the use of full symmetry in the total wave function (3). However, it is shown in the Appendix that their additional term is incorrect.

The theoretical values are considerably below experiment¹⁷ and some effort has been made to understand this. It becomes clear that agreement can be obtained throughout the energy region when the contribution of

²² G. E. Chamberlain and J. C. Zorn, Phys. Rev. **129**, 677 (1963).

²³ D. Parkinson, Proc. Phys. Soc. (London) **A75**, 169 (1960).

²⁴ R. M. Sternheimer, Phys. Rev. **127**, 1220 (1962).

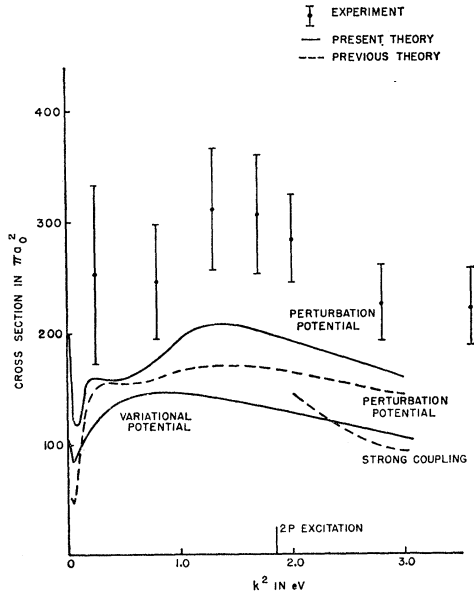


FIG. 5. Lithium cross sections including exchange. All the calculations are below experiment (Ref. 17) and the variational potential values are below the perturbation theory results. The perturbation-potential calculation of Ref. 15 differs from the present perturbation-theory curve because of the different exchange terms used. The variational potential gives the best agreement with the $2s$ - $2p$ strong coupling calculation of Ref. 16.

$l=3$ partial waves is considerably increased. Evaluation of the addition to the polarization potential resulting from coupling with the $3s$ state (P_{3s} from Ref. 18) and from the $3d$ state (P_{3d} from hydrogen) shows their contributions to be too small at radii where $l=3$ scattering is important ($\approx 10a_0$). The contribution of all s and d states together may, however, be significant. Polarization of the core electrons alters the potential only at small radii ($\lesssim 2a_0$) and detailed calculations show that it changes the cross sections by less than 7% (mostly $l=0$ waves affected). Coupling with higher p states is not expected to help significantly because the first p state includes nearly all the theoretical long-range polarizability. Moreover, the polarizability is already greater than experiment so that perhaps the long-range potential should really be lowered. This would decrease the $l=3$ contribution even further.

The effect of the neglected exchange terms has not been accurately evaluated and may contribute to $l=3$ scattering. They are smaller than the exchange terms that are included but may not be negligible. It would be desirable to have further experimental verification.

As in the case of positron scattering, it is clear that adiabatic polarization potentials give numerical results in good agreement with coupled equations calculations when the same excited states are considered.

The numerical work was done in the same manner as previously described⁵ and discussed in Sec. II above. Mesh spacing starting at $0.05a_0$ and increasing in two steps to $0.20a_0$ are generally used. The integrations with exchange are done to $25a_0$ and continued without

exchange to $65a_0$. The phase shifts are determined at that point. The integrity of the computer code has been established by comparing electron-hydrogen results with the literature and by comparing lithium perturbation theory results without exchange with the values given by Vinkalns *et al.*¹⁵ Essentially exact agreement was obtained in all cases. Calculations using smaller mesh sizes ($0.02a_0$ increasing to $0.08a_0$) and integrations to larger distances ($90a_0$) at 0.2, 1.0, and 2.0 eV give phase shifts that differ from Table II by less than 0.001 radian.

IV. CONCLUSIONS

The two elastic-scattering calculations performed here indicate that, with proper use, the adiabatic approximation is not a serious limitation. More important is the effect of coupling to states that are usually not included and the proper treatment of exchange. It has been emphasized that perturbation theory is not always valid for calculating distorted atomic wave functions and that a simple variational calculation can be used instead.

The contribution of many states is handled more easily in polarization calculations than in coupled-equations methods. The polarization potential is then suitable for use in studies of low-energy scattering from heavy atoms or from excited states, where coupling to many levels is important.

APPENDIX

The use of a fully antisymmetric wave function with distorted atomic orbitals leads to scattering equations where the partial waves are coupled in the exchange terms. As there has been some confusion²¹ as to the proper terms, they are derived here.

The fully symmetric version of (30) considering only the valence electron is

$$\psi(\mathbf{r}_1\mathbf{r}_2) = [\psi_0(\mathbf{r}_1) + \beta(r_2)\psi_1(\mathbf{r}_1)]F(\mathbf{r}_2) \pm [\psi_0(\mathbf{r}_2) + \beta(r_1)\psi_1(\mathbf{r}_2)]F(\mathbf{r}_1). \quad (\text{A1})$$

This form leads directly to (31) with a second term on the right side

$$\begin{aligned} & \{\nabla^2 + k_0^2 - V_{00} - V_p\}F(\mathbf{r}_2) \\ &= \pm \langle \psi_0 | \left[\frac{2}{|\mathbf{r}_1 - \mathbf{r}_2|} + E_0 - k_0^2 \right] F \rangle \psi_0(\mathbf{r}_2) \\ & \pm \langle \psi_0 | \left[\frac{2}{|\mathbf{r}_1 - \mathbf{r}_2|} + E_1 - k_0^2 \right] \beta F \rangle \psi_1(\mathbf{r}_2), \quad (\text{A2}) \end{aligned}$$

where the matrix elements are integrations over the atomic electron coordinates \mathbf{r}_1 .

The difficulty is in the evaluation of the second exchange term when $F(\mathbf{r})$ is expanded in Legendre polynomials,

$$F(\mathbf{r}) = \sum_m P_m(z) (f_m(r)/r). \quad (\text{A3})$$

The second exchange term is not present when the

$\psi_1(\mathbf{r}_2)$ term in Eq. (A1) is neglected. The expansion of $2/|\mathbf{r}_1-\mathbf{r}_2|$ is

$$\frac{2}{|\mathbf{r}_1-\mathbf{r}_2|} = 2 \sum_l \frac{r_{<}^l}{r_{>}^{l+1}} P_l(z_1) P_l(z_2) + \text{terms that become zero on } \varphi_1 \text{ integration.} \quad (\text{A4})$$

In this expression $r_{<}$ and $r_{>}$ are, respectively, the smaller and larger of r_1 and r_2 . As the φ_1 integration can be done immediately, the extra terms in Eq. (A4) need not be exhibited.

An important point is that $P_l(z_2)$ has been set equal to one in the evaluation of V_p because the z axis is taken as the nuclear to scattered-electron direction. This is the mathematical statement of the adiabatic approximation for the polarization of the atom. But neither $P_l(z_1)$ nor $P_l(z_2)$ of Eq. (A4) can be set equal to one in the exchange term. A proper description of exchange requires that the angular dependence of both particles be included. Essentially, polarization can be treated in the adiabatic approximation but not exchange.

The angular dependence of an s state for ψ_0 and a

p state for ψ_1 is obtained by using

$$\begin{aligned} \psi_0(\mathbf{r}_1) &= (4\pi)^{-1/2} \varphi_0(r_1)/r_1 \\ \psi_1(\mathbf{r}_1) &= (3/4\pi)^{1/2} P_1(z_1)(\varphi_1(r_1)/r_1). \end{aligned} \quad (\text{A5})$$

With Eqs. (A3), (A4), and (A5) the exchange terms of Eq. (A2) are (after integration over φ_1 and θ_1)

$$\begin{aligned} &\pm \varphi_0(r_2) \sum_m \frac{P_m(z_2)}{r_2} \int dr_1 \varphi_0 f_m \\ &\quad \times \left\{ (E_0 - k_0^2) \delta_{m,0} + \frac{2}{2m+1} \frac{r_{<}^m}{r_{>}^{m+1}} \right\} \\ &\pm \sqrt{3} \varphi_1(\mathbf{r}_2) P_1(z_2) \sum_m \frac{P_m(z_2)}{r_2} \int dr_1 \beta \varphi_0 f_m \\ &\quad \times \left\{ (E_1 - k_0^2) \delta_{m,0} + \frac{2}{2m+1} \frac{r_{<}^m}{r_{>}^{m+1}} \right\}. \end{aligned} \quad (\text{A6})$$

An equation for the l th partial wave is obtained by multiplying by $P_l(z_2)$ and integrating over z_2 . If the equation is also multiplied by $r_2(l+\frac{1}{2})$, the terms in Eq. (A6) become finally

$$\begin{aligned} &\pm \varphi_0(r_2) \left\{ (E_0 - k_0^2) \delta_{l,0} \int dr_1 \varphi_0 f_l + \frac{2}{2l+1} \int dr_1 \varphi_0 f_l \frac{r_{<}^l}{r_{>}^{l+1}} \right\} \pm \sqrt{3} \varphi_1(r_2) \left\{ (E_1 - k_0^2) \delta_{l,1} \int dr_1 \beta \varphi_0 f_0 \right. \\ &\quad \left. + \frac{2l}{(2l-1)^2} \int dr_1 \beta \varphi_0 f_{l-1} \frac{r_{<}^{l-1}}{r_{>}^l} + \frac{2l+2}{(2l+3)^2} \int dr_1 \beta \varphi_0 f_{l+1} \frac{r_{<}^{l+1}}{r_{>}^{l+2}} \right\}. \end{aligned} \quad (\text{A7})$$

The set of terms multiplied by $\varphi_1(r_2)$ are not included in the calculations reported here and earlier⁴ and are generally absent when the wave function has the form of (30) rather than (A1). It is clear that the last terms couple the partial wave equations to neighboring equations. The fully coupled set can be closed by substituting the spherical Bessel function for f_{l+1} at sufficiently high l .

The second set of terms are generally less important because β is small and because $\varphi_1(r_2)$ is small at small radii. At larger radii where $\varphi_1(r_2)$ becomes important, polarization is the largest effect and the exchange terms do not contribute significantly to the scattering.

Note added in proof. The coupling in (A7) can be avoided by allowing β to have angular dependence. Thus if

$$\beta(\mathbf{r}_2) = \beta(r_2) Y_{1m}(\Omega_2) \quad (\text{A8})$$

is used along with $\psi_{1m}(r_1)$ and a summation over $m = -1, 0, +1$ performed, the coupling will not occur. The terms multiplied by $\varphi_0(r_2)$ in (A7) are unchanged

while the terms multiplied by $\varphi_1(r_2)$ become

$$\begin{aligned} &\pm \frac{\varphi_1(r_2)}{(4\pi)^{3/2}} \left[(E_1 - k_0^2) \delta_{l,1} \int dr_1 \beta \varphi_0 f_1 \right. \\ &\quad \left. + \left(\frac{6}{2l+1} \right) \left(\frac{l}{2l-1} \right) \int dr_1 \beta \varphi_0 f_l \frac{r_{<}^{l-1}}{r_{>}^l} \right. \\ &\quad \left. + \left(\frac{6}{2l+1} \right) \left(\frac{l+1}{2l+3} \right) \int dr_1 \beta \varphi_0 f_l \frac{r_{<}^{l+1}}{r_{>}^{l+2}} \right]. \end{aligned} \quad (\text{A9})$$

Either (A9) or (A7) can be used although (A9) is clearly simpler. (A9) was not formulated in time to be included in the lithium calculations.

W. R. Garrett [Phys. Rev. **140**, A705 (1965)] has recently published a Li calculation (also Na) that is very similar to the present work in the treatment of the valence electron. In addition, he includes polarization of the core and uses the Slater approximation to allow for exchange with core electrons. His large cross sections (above experiment) seem to follow from the core-exchange term and from the use of somewhat different atomic wave functions.