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Modification of the method of polarized orbitals for electron–alkali-metal scattering: Application to *e*-Li

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The method of polarized orbitals is modified to treat low-energy scattering of electrons from highly polarizable systems, specifically alkali-metal atoms. The modification is carried out in the particular context of the *e*-Li system, but the procedure is general; it consists of modifying the polarized orbital, so that when used in the otherwise orthodox form of the method, it gives (i) the correct electron affinity of the negative ion (in this case Li$^-$), (ii) the proper (i.e., Levinson-Swan) number of nodes of the associated zero-energy scattering orbital, and (iii) the correct polarizability. A procedure is devised whereby the scattering length can be calculated from the (known) electron affinity without solving the bound-state equation. Using this procedure we adduce a ^1S scattering length of $8.69a_0$. (The ^3S scattering length is $-9.22a_0$.) The above modifications can also be carried out in the (lesser) exchange adiabatic approximation. However, they lead to qualitatively incorrect ^3S phase shifts. The modified polarized-orbital phase shifts are qualitatively similar to close-coupling and elaborate variational calculations. Quantitative differences from the latter calculations, however, remain; they are manifested most noticeably in the very-low-energy total and differential spin-flip cross sections.

I. INTRODUCTION

The scattering of electrons from alkali atoms is of obvious importance in many applications, however, the particular challenge of this problem is a theoretical one stemming from the very large polarizabilities of the alkali targets. In principle the close-coupling approach is well suited to this problem, because as is well known the lowest excited state provides the bulk of the long-range polarizability. Indeed close-coupling calculations[1–4] are among the best presently available in such cases. Nevertheless the question of the importance of the shorter-range correlations and the extent to which close coupling can include them still remains, and it is compounded by the well-known fact that any multistate method like close coupling is necessarily a long and involved one and is not well suited to whole sequences of calculations which may be necessary for the purpose of space or plasma physics.

For these reasons we have considered the electron-alkali scattering problem from the point of view of polarized orbitals.[5,6] In fact, such attempts are not new.[7] Most recently and most completely, Bui and Stauffer[8] have attempted to follow the orthodox polarized orbital methodology most closely,[6] but when carefully analyzed (and our calculation when similarly performed qualitatively supports their results), it must be concluded that those results are unsatisfactory; hence the method is unreliable for highly polarizable targets. We shall therefore attempt to modify the method of polarized orbitals to apply to electron scattering from highly polarizable targets in the specific context of *e*-Li scattering problem.

Starting first from the unmodified equations whose derivations and results are given in Sec. II, we are led to a modification which necessarily restores the main elements of a correct solution, Sec. III. The essential part of the modification concerns the manner in which the polarized orbital, $P_{2s\rightarrow p}(r)$ in this case, is constructed. Given the modification, the new results in the form of phase shifts and cross sections are seen to be very satisfactory, and they are given in some detail and compared with other good results where possible.

An alternative method of constructing the polarized orbital has been given by Stone,[9] when used in the otherwise conventional polarized orbital methodology by Vo Ky Lan,[10] this too gave satisfactory results. In Sec. IV we shall contrast and discuss Stone's method with the present modification. In that section we shall also give some concluding remarks.

II. UNMODIFIED POLARIZED ORBITAL CALCULATION

Specializing immediately to *e*-Li scattering, we start with a Slater determinantal approximation for the ground, $^2S(1s^22s)$, state of Li

$$\Phi_\chi^{(0)}(123) = (1/\sqrt{3!})\det[\varphi_{1s}(1)\alpha(1)\varphi_{1s}(2)\times\beta(2)\varphi_{2s}(3)\chi(3)]\,. \qquad (2.1)$$

The function χ represents the spin which can be "up" ($\chi=\alpha$) or "down" ($\chi=\beta$). To include polarization via the method of polarized orbitals,[5] we augment each orbital in an approximate form as it would be perturbed by a scattering electron at a point r_4

$$\varphi_{ns}^{(i)} \rightarrow \varphi_{ns}(i) + \varphi_{ns\rightarrow p}(i;4)\,, \tag{2.2}$$

where

$$\varphi_{ns}(i) = [P_{ns}(r_i)/r_i]\, y_{00}(\Omega_i)\,, \tag{2.3}$$

$$\varphi_{ns}(i;4) = -\frac{\epsilon(r_4, r_i)}{r_4^2}\,\frac{P_{ns\rightarrow p}(r_i)}{r_i}\,\frac{\cos\theta_{i4}}{\sqrt{4\pi}}\,, \tag{2.4}$$

and ϵ is a step function

$$\epsilon(x,y) = \begin{cases} 1, & x > y\,, \\ 0, & x < y\,. \end{cases}$$

With the replacement indicated in (2.2) the unpolarized ground state goes into polarized function (we shall neglect throughout the polarization of the tightly bound P_{1s} orbitals)

$$\Psi_\chi(123;4) = \Phi_\chi^{(0)}(123) + \Phi_\chi^{(\mathrm{pol})}(123;4)\,, \tag{2.5}$$

where

$$\Phi_\chi^{(\mathrm{pol.})}(123;4) = (1/\sqrt{3!}\,)\det[\varphi_{1s}(1)\alpha(1)\varphi_{1s}(2)\beta(2) \times \varphi_{2s\rightarrow p}(3;4)\chi(3)]\,. \tag{2.6}$$

A total scattering wave function, unsymmetrized with respect to electron 4, but of good total spin S, is then

$$\Psi^{\pm}(123;4) = [F(r_4)/\sqrt{2!}\,][\Psi_\alpha(123;4)\beta(4) \pm \Psi_\beta(123;4)\alpha(4)]\,. \tag{2.7}$$

In (2.7) the superscript + (−) refers to triplet, $S=1$ (singlet, $S=0$) spin state. Note the difference from e-H where (+) is usually associated with singlet and (−) with triplet scattering. Finally a totally antisymmetric scattering wave function can be formed by cyclic permutation (since $\Psi^{\pm}$ is antisymmetric in its first three indices)

$$\Psi_A^{\pm} = (1/\sqrt{4})[\Psi^{\pm}(123;4) - \Psi^{\pm}(234;1) + \Psi^{\pm}(341;2) - \Psi^{\pm}(412;3)]\,. \tag{2.8}$$

In (2.7) $F(\vec{r})$ is a scattering wave function, which one conveniently decomposes in partial wave form

$$F(\vec{r}) = \sum_l \frac{u_l(r)}{r}\, y_{l0}(\Omega)\,. \tag{2.9}$$

Uncoupled equations for the scattered orbitals, $u_l(r)$, can be derived from whose asymptotic forms the phase shifts η_l can be derived in the well-known way

$$\lim_{r\rightarrow\infty} u_l(r) = A\sin(kr - \tfrac{1}{2}l\pi + \eta_l)\,. \tag{2.10}$$

(We here suppress the ± superscripts on F, u_l, and η_l.)

The scattering equations for $u_l(r)$ are derived by projecting on the unperturbed ground state[6] ($dr^{(4)}$ means integration over all coordinates *except* the radial distance r_4)

$$\int [\Phi_\alpha^{(0)}(123)\beta(4) \pm \Phi_\beta^{(0)}(123)\alpha(4)]^* \times y_{l0}^*(\Omega_4)(H-E)\Psi_A^{\pm}\, dr^{(4)} = 0\,, \tag{2.11a}$$

where H is the total Hamiltonian

$$H = -\sum_{i=1}^{4}\left(\nabla_i^2 + \frac{2Z}{r_i}\right) + \sum \sum_{i>j=1}^{4} \frac{2}{r_{ij}}\,. \tag{2.11b}$$

That one uses the unperturbed ground state $\Phi^{(0)}$ in this projection is a very important aspect of the method of polarized orbitals,[6] and we have discussed it at length elsewhere.[11] The result of the projection is an integro-differential equation for the scattered orbitals u_l (in rydberg units)

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k^2\right) u_l(r) = [V(r) + V_p(r) - W^{\pm}(r)]u_l(r)\,. \tag{2.11c}$$

In principle the direct, polarization, exchange-polarization potentials, $V(r)$, $V_p(r)$, $-W^{(\pm)}(r)$, respectively, should be identical to those given by Bui and Stauffer[8] (cf. the Appendix of their paper). In fact, our equations exhibit some differences which we are unable to establish as being typographical on their part or not. Specifically we find (Z = charge on the nucleus → $Z=3$ in this application)

$$V(r) = 4\Gamma_0(1s,1s;r) + 2\Gamma_0(2s,2s,r) - 2Z/r\,, \tag{2.12}$$

$$V_p(r) = -\frac{2}{3r^4}\int_0^r P_{2s}(x)\, x P_{2s\rightarrow p}(x)\, dx\,, \tag{2.13}$$

$$W^{\pm}u_l = 2(W_{\mathrm{ex}}^{\pm}u_l + W_{\mathrm{ep}}^{\pm}u_l)\,, \tag{2.14}$$

where

$$W_{\mathrm{ex}}^{\pm}u_l = \frac{1}{2l+1}[P_{1s}(r)\Gamma_l(1s,kl;r) \pm P_{2s}(r)\Gamma_l(2s,kl;r)] + \tfrac{1}{2}\delta_{l0}\Big(P_{1s}(r)\int_0^\infty dx\, P_{1s}(x)[\epsilon_{1s} - k^2 + 2\Gamma_0(2s,2s;x)]u_l(x) \mp 2P_{1s}(r)\int_0^\infty dx\, P_{2s}(x)\Gamma_0(1s,2s;x)u_l(x) \pm (\epsilon_{2s} - k^2)P_{2s}(r)\int_0^\infty dx\, P_{2s}(x)u_l(x)\Big)\,, \tag{2.15}$$

and $W^{\pm}_{\text{ep}}u_l$ is written in three parts

$$W^{\pm}_{\text{ep}}u_l=[\delta_{l0}W^{(0)}_{\text{ep}}\pm\delta_{l1}W^{(1)}_{\text{ep}}\pm\tilde{W}^{(l)}_{\text{ep}}]u_l\,, \tag{2.16}$$

with

$$W^{(0)}_{\text{ep}}u_l=P_{1s}(r)\left(\frac{1}{2}\int_0^\infty P_{1s}(x)V_p(x)u_l(x)\,dx\mp\int_0^\infty P_{2s}(x)\overline{V}_p(x)u_l(x)\,dx\right), \tag{2.17a}$$

$$\overline{V}_p(x)=-\frac{1}{3x^4}\int_0^x P_{1s}(y)yP_{2s\to p}(y)\,dy\,,$$

$$\begin{aligned}W^{(1)}_{\text{ep}}u_l={}&-\frac{1}{6}\left(P_{2s\to p}(r)\frac{d}{dr}\frac{P_{2s}(r)u_l(r)}{r^2}+\frac{2P_{2s}(r)u_l(r)}{r^2}\frac{d}{dr}P_{2s\to p}(r)\right)\\&+\frac{1}{6}\left(\frac{d^2}{dr^2}-\frac{2}{r^2}+k^2+\frac{2Z}{r}-4\Gamma_0(1s,1s;r)\right)P_{2s\to p}(r)\int_r^\infty dx\frac{P_{2s}(x)u_l(x)}{x^2}\\&+\frac{1}{9}P_{1s}(r)\int_0^\infty dx\frac{P_{2s}(x)u_l(x)}{x^2}\int_0^x dyP_{1s}(y)g_1(y,r)P_{2s\to p}(y)+\tfrac{1}{3}P_{2s\to p}(r)\Gamma_0(1s,2s;r)\int_r^\infty dx\frac{P_{1s}(x)u_l(x)}{x^2}\\&\mp\frac{1}{9}P_{1s}(r)\int_0^\infty dx\frac{P_{1s}(x)u_l(x)}{x^2}\int_0^x dyP_{2s}(y)g_1(y,r)P_{2s\to p}(y)\,,\end{aligned} \tag{2.17b}$$

$$\tilde{W}^{(l)}_{\text{ep}}u_l=-\frac{P_{2s\to p}(r)}{2l+1}\left(\frac{l+1}{2l+3}r^{l+1}\int_r^\infty dx\frac{P_{2s}(x)u_l(x)}{x^{l+4}}+\frac{l}{2l-1}r^{l-1}\int_r^\infty dx\frac{P_{2s}(x)u_l(x)}{x^{l+2}}\right). \tag{2.17c}$$

To complete the specification of quantities appearing in the foregoing equations, we have

$$\Gamma_\lambda(nl,n'l';r)\equiv\int_0^\infty P_{nl}(x)g_\lambda(x,r)P_{n'l'}(x)\,dx\,, \tag{2.18}$$

where

$$g_\lambda(x,y)\equiv\begin{cases}x^\lambda/y^{\lambda+1}\,, & x<y\,,\\ y^\lambda/x^{\lambda+1}\,, & x>y\,,\end{cases} \tag{2.19}$$

The indices $n'l'$ in (2.18) can also refer to the scattered orbital $kl\equiv u_l(r)$.

For P_{1s}, P_{2s} we take as the frozen core Hartree-Fock (HF) orbitals of Cohen and Kelly[12] satisfying

$$\left(\frac{d^2}{dr^2}+\frac{2Z}{r}-2\Gamma_0(1s,1s;r)\right)P_{1s}(r)=-\epsilon_{1s}P_{1s}(r)\,, \tag{2.20a}$$

$$\left(\frac{d^2}{dr^2}+\frac{2Z}{r}-4\Gamma_0(1s,1s;r)\right)P_{2s}(r)+2\Gamma_0(1s,2s;r)P_{1s}(r)=-\epsilon_{2s}P_{2s}(r)\,. \tag{2.20b}$$

Our own solutions of those equations yield eigenvalues $\epsilon_{1s}=-5.584\,729$ Ry, $\epsilon_{2s}=-0.392\,616$ Ry corresponding to a total Li energy

$$\begin{aligned}E_0&=2\epsilon_{1s}+\epsilon_{2s}-2\int_0^\infty P^2_{1s}(x)\Gamma_0(1s,1s,x)\,dx\\&=-14.865\,447\text{ Ry}\end{aligned}$$

compared to the experimental value[12] $E_0=-14.956\,138$ Ry.

The equation for the polarized orbital $P_{2s\to p}$ is obtained by projecting with the adiabatic Hamiltonian H_{ad} acting on the adiabatically perturbed target function, ψ_χ of Eq. (2.5), on the $(1s)^2$ Li$^+$ core function, $\Phi_{(1s)^2}(12)$:

$$\langle\Phi_{(1s)^2}(12)\alpha(3)|\,H_{\text{ad}}-E_0|\,\Psi_\alpha(123;4)\rangle=0\,, \tag{2.21}$$

where

$$H=H_{\text{ad}}-\nabla^2_4\,. \tag{2.22}$$

Drooping second-order terms gives

$$\left(\frac{d^2}{dr^2}-\frac{2}{r^2}+\epsilon_{2s}+\frac{2Z}{r}-4\Gamma_0(1s,1s;r)\right)P_{2s\to p}(r)+\tfrac{2}{3}P_{1s}(r)\Gamma_1(1s,2s\to p;r)=-2rP_{2s}(r)\,. \tag{2.23}$$

This procedure is a somewhat more elaborate version of the original prescription of Sternheimer[13] for obtaining the polarized orbital $P_{nl\to l'}$. Specifically (2.23) contains a Γ_1 term coming from the fact that Ψ_α in (2.21) is completely antisymmetric in (123). It is not clear in the case of alkali scattering how important that term is, however we have retained it to give the closest correspondence with Bui and Stauffer.[8] [Equation (2.23) agrees with their equation (4) in $\lim r\to\infty$.] On the other hand, our numerical solution does

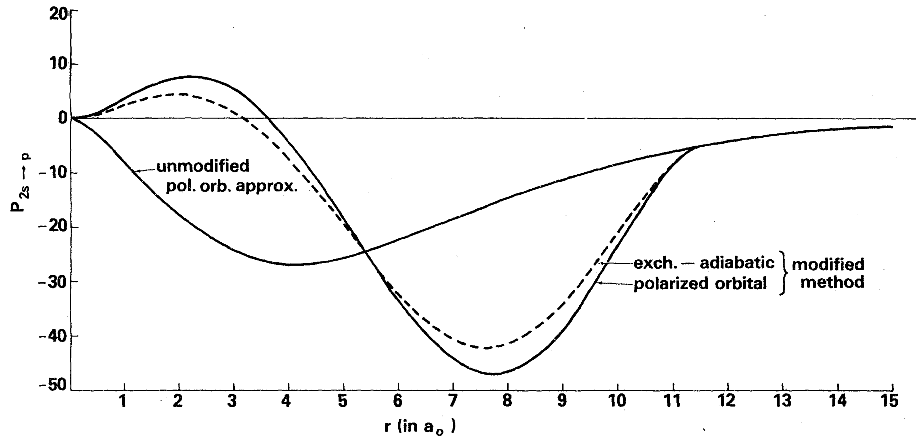

FIG. 1. Polarized orbital in unmodified ($P_{2s\to p}$) and modified ($\bar{P}_{2s\to p}$) approximations.

not completely agree with theirs. Ours is given in Fig. 1 (together with some modified $P_{2s\to p}$ functions which we shall discuss below), leading to a polarizability $\alpha(\infty)=169a_0^3$ derived from

$$\alpha(r)=\frac{2}{3}\int_0^r P_{2s}(x)\,xP_{2s\to p}(x)\,dx \tag{2.24}$$

to be contrasted with Bui and Stauffer's value of $\alpha=149.2a_0^3$. Furthermore, the adiabatic polarization potential (Fig. 2)

$$V_p(r)=-\alpha(r)/r^4 \tag{2.25}$$

is significantly different from theirs mainly in that ours changes sign and becomes repulsive for $r\leq 1$. The necessity for a change in sign is obvious from (2.24), because $P_{2s\to p}$ from Fig. 1 is nodeless, whereas P_{2s} as always has a node. The appearance of a repulsive part to polarization potential would appear to be in contradiction to the adiabatic hypothesis, however it must be remembered that the polarized orbital procedure[6,11] does make modifications in the adiabatic hypothesis. In particular, because of the presence of the step function $\epsilon(r_1,r_2)$, a part

$$\left(-\tfrac{2}{3}r^{-4}\int_r^\infty P_{2s}(x)\,xP_{2s\to p}(x)\,dx\right)$$

of the polarization potential that would otherwise occur in $V_p(r)$ is removed. If one included that piece, one would achieve a negative definite potential, but so deep as to be quantitatively useless. Various polarization potentials are given in Fig. 2.

As to the comparison of our scattering equations with those after Bui and Stauffer,[8] we will not go into detail on this: the differences are of the form of the inversion of couple of ± signs and the interchange of the functions P_{2s} and P_{1s} in some places. Our equations can be checked by letting $P_{1s}\to 0$ and $P_{2s}\to 2(Z^3)^{1/2}re^{-Zr}$. In that case our equations reduce to the polarized orbital equations for general Z of the one-electron target as deduced by Sloan.[14]

The effect of the variations in the unmodified polarized orbital equations in the respective calculations do not seem to be large. Before considering them, we briefly discuss the numerical solution of the scattering equations. As is usual the integro-differential scattering equation was

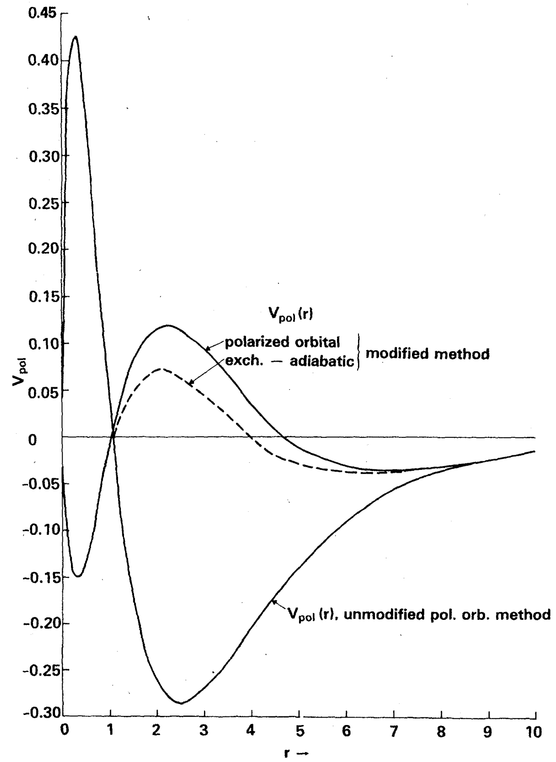

FIG. 2. Adiabatic polarization potential (V_{pol}) using the various polarized orbitals (Fig. 1). Note the huge difference in the modified vs the unmodified potentials for $r\lesssim 5$.

decomposed into a set of inhomogeneous ordinary differential equations.[15] However, this set does not have a unique solution in the full polarized orbital (and also exchange) approximation. We therefore have augmented these equations by imposing the condition that the s-wave scattering function $u(r)$ be orthogonal to P_{1s} in the singlet case and P_{1s} as well as P_{2s} in the triplet case. The justification for these conditions is that $1s^2$ and $1s^2 2s$ represent closed shells in the singlet, triplet cases, respectively, so that the incoming electron is excluded from them. In the Appendix we show that this procedure does not compromise the physical validity of the resultant solutions. (However, we remind the reader we consider that the imposition of orthogonality for nonclosed shells suspect.[11]) The numerical procedure for integrating the differential equations was a Nordsieck predictor-corrector method, with a variable mesh size.

The s- and p-wave phase shifts of the unmodified approximation are given in Table I. The s-wave functions have two nodes at $k^2=0$, thus phase shifts approach 2π radians in accord with the Swan-Levinson "theorem".[16] But the absolute phase shifts[17] are quantitatively too large (cf. Table III) particularly in the ^3S case. This stems from the fact that the polarization function is much too deep at intermediate r $(1<r<4)$, cf. Fig. 2. That, rather than the repulsive core, dominates, because at the smaller r the scattered orbitals $u_l(r)$ are themselves small so that the effect, which is proportional to $[\alpha(r)/r^4]u_l(r)$, is minimized where $\alpha(r)$ is repulsive.

The effect on the p waves of this over attractiveness is much more pronounced. Here we see both singlet and triplet absolute phase shifts approach π radians, whereas correctly neither should approach π (cf. Table III).[18] The completely unacceptable behavior of the p waves, in addition to the quantitative deficiencies of the s waves, makes it clear that a modification of the polarized orbital method is required.

TABLE I. Unmodified polarized orbital phase shifts.[a]

k^2 (Ry)	^3S	^1S	^3P	^1P
0.0	(−11.49)[b]	(−9.48)[b]	π	π
0.001	6.437	6.395	3.139	3.174
0.01	6.169	6.124	2.901	3.355
0.02	5.936	5.910	2.703	3.414
0.04	5.611	5.629	2.442	3.380
0.06	5.374	5.437	2.266	3.295
0.08	5.186	5.291	2.134	3.204
0.10	5.030	5.172	2.027	3.116
0.12	4.897	5.071	1.939	3.033

[a] Phase shifts are in radians in all tables.

[b] Quantities in parentheses are scattering lengths (in a_0) in all tables.

III. MODIFIED POLARIZED ORBITAL AND RESULTS

We have seen that the main effect of the unmodified polarized orbital is to give an overly attractive polarization potential and a consequent exaggeration of the phase shifts. To some extent this represents a break down of the adiabatic hypothesis. however the mathematical framework of polarized orbitals, *particularly when one consistently includes exchange*, goes beyond the adiabatic hypothesis.[5,6,11] Thus, we are led to ask if we can simply modify the polarized orbital, $P_{2s\rightarrow p}(r)$, in order to achieve the desired changes. In order to judge the effect of such an alteration, we have found it incisive to focus on the electron affinity of the negative ion and the satisfaction of the Levinson-Swan "theorem."[16] The latter states that the zero-energy phase shift of the partial wave of a given symmetry is

$$\lim_{k\to 0} \eta = (n+m)\pi\,. \tag{3.1}$$

In (3.1) η is the phase shift (with its symmetry indices, l and spin, suppressed), n is the number of additional bound states (with its given quantum numbers) of the negative ion, and m is the number of filled orbital shells of the target which the incoming electron can thus *not* occupy. In this case of Li the $(1s)^2$ shell is filled for both singlet and triplet s-wave electron; in the former case there is also one bound state of the negative ion, and in the latter the $2s$ shell is also forbidden (since a triplet wave function cannot have both spins identical implying their spatial parts must be different). Thus, for ^1S we have $n=1=m$, whereas in ^3S $n=0, m=2$, thus in both s-wave cases we have

$$\lim_{k\to 0} \eta_0 = 2\pi\,. \tag{3.2}$$

For all other partial waves,

$$\lim_{k\to 0} \eta_{l>0} = 0\,. \tag{3.3}$$

(We have seen in the unmodified calculation that $\lim \eta_1 = \pi$ as $k\rightarrow 0$).

The other succinct piece of information that we shall use in the electron affinity of Li$^-$(^1S); the

Weiss' value[19] is

$$\epsilon = 0.616 \text{ eV} = 0.045 \text{ Ry}. \tag{3.4}$$

In order to find a consistent and sufficiently accurate (^1S) scattering length we use the relationship[20]

$$a^{-1} = \epsilon^{1/2} - \epsilon \int_0^\infty [H_b^2(r) - G_b^2(r)]\, dr. \tag{3.5}$$

$H_b(r)$ is the exponential function having the same asymptotic form as the bound $2s$ orbital $G_b(r)$ of Li$^-$. In our calculation $G_b(r)$ would correspond to a bound solution of our polarized orbital equation (2.4c). In practice we found it very difficult to find G_b directly, therefore we have developed the following iterative procedure, which is expected to be quite accurate, and should be useful elsewhere as well.

Since

$$\lim_{r\to\infty} G_b(r) = H_b(r) = -e^{-\kappa r}, \tag{3.6}$$

where

$$\kappa = \sqrt{\epsilon}, \tag{3.7}$$

then knowing κ is small, we can well assume that

$$G_b(r) \cong u_0(r), \quad r < r_c. \tag{3.8}$$

That is, $G_b(r)$ is essentially the same as the zero-energy solution of the scattering equation, $u_0(r)$, for small values of r (less than some r_c, defined below). That is so because the potentials in Eq. (2.4c) are much larger than the energy term ϵ in (2.4c), the more so the smaller the value of ϵ. The point is, however, that we can readily solve for the zero-energy solution $u_0(r)$. The value of r_c is chosen as that value of r at which $u_0(r)$ merges into the asymptotic solution $H_b(r)$:

$$\left(\frac{u_0'(r)}{u_0(r)} = \frac{H_b'(r)}{H_b(r)}\right)_{r=r_c}. \tag{3.9}$$

The procedure is illustrated in Fig. 3. The resultant $G_b(r)$ is thus

$$G_b(r) = \begin{cases} Nu_0(r), & r < r_c, \\ H_b(r), & r > r_c, \end{cases} \tag{3.10}$$

where N is a normalization constant such that

$$Nu_0(r_c) = H_b(r_c). \tag{3.11}$$

Of course even to solve for $u_0(r)$ we need to know our modified polarized orbital $\overline{P}_{2s\to p}(r)$, which we do not know to begin with. We do know that any satisfactory $\overline{P}_{2s\to p}$ will have to approach the adiabatic $P_{2s\to p}$ for large enough r:

$$\overline{P}_{2s\to p}(r) = P_{2s\to p}(r), \quad r > r_b. \tag{3.12a}$$

A smooth joining is assured by demanding

$$[\overline{P}'_{2s\to p}(r)/\overline{P}_{2s\to p}(r) = P'_{2s\to p}(r)/P_{2s\to p}(r)]_{r=r_b} \tag{3.12b}$$

In (3.12), $P_{2s\to p}$ is the solution of the unperturbed static equation (2.23) which we have given in Fig. 1. We also require that our ultimate $\overline{P}_{2s\to p}(r)$ should give the correct polarizability

$$\alpha = \frac{2}{3}\int_0^\infty P_{2s}(r)\, r\, \overline{P}_{2s\to p}(r)\, dr = 164 a_0^3. \tag{3.13}$$

(This experimental value[21] rather than the calculated value $169a_0^3$ is used at this point.)

These conditions allow us to establish an iteration procedure which proceeds thus:

A first guess $a^{(0)}$ for the scattering length a is made

$$a^{(0)} = \epsilon^{-1/2}.$$

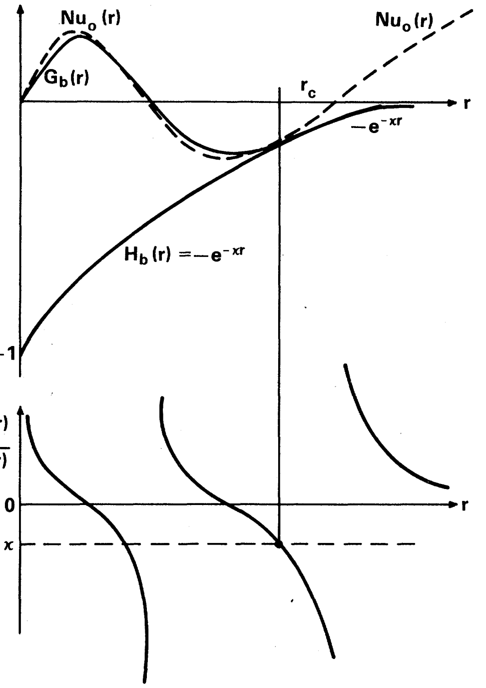

FIG. 3. Curves illustrating the bound function $G_b(r)$ (solid curve), zero-energy scattering function $Nu_0(r)$ (dashed curve) and the asymptotic bound-state function $H_b(r)$. In the bottom half of the graph the logarithmic derivative of $u_0(r)$ is plotted and the value of r_c is where (after the first node) it intersects $-\kappa$ which is the logarithmic derivative of $H_b(r)$. The approximation to the desired $G_b(r)$ is $Nu_0(r)$ for $r \leq r_c$ and $H_b(r)$ for $r > r_c$ as given in Eq. (3.10).

A first guess $\bar{P}^{(0)}_{2s\to p}$ is generated of the form

$$\bar{P}^{(0)}_{2s\to p}(r) = \begin{cases} \sum_{n=2}^{5} C_n^{(0)} r^n & r<r_b\,, \\ P_{2s\to p}(r) & r>r_b\,, \end{cases} \tag{3.14}$$

such that conditions (3.12) and (3.13) are satisfied. (A reasonable value of $r_b \cong 11$ was chosen; at the end of the iteration procedure r_b was varied to make sure final results were insensitive to it.) Specifically the coefficients $C_n^{(0)}$ had one degree of flexibility left such that $u_0^{(0)}(r)$ (with the correct number of nodes) did indeed correspond to a scattering length $a^{(0)}$,

$$\lim_{r\to\infty} u_c^{(0)}(r) = r/a^{(0)} - 1\,.$$

From this, a zeroth-order bound orbital $G_b^{(0)}$ could be generated from (3.10),

$$G_b^{(0)} = \begin{cases} N u_c^{(0)}(r)\,, & r<r_c^{(0)}\,, \\ H_b(r)\,, & r>r_c^{(0)}\,. \end{cases} \tag{3.15}$$

From $G_b^{(0)}$ we can form a new iteration for the scattering length $a^{(1)}$; from (3.5),

$$(a^{(1)})^{-1} = \epsilon^{1/2} - \epsilon \int_0^\infty [H_b^2(r) - (G_b^{(0)}(r))^2]\,dr \tag{3.16}$$

And now this whole process can be repeated until convergence of both a and $\bar{P}_{2s\to p}$ is obtained. Table II contains the convergence for a. The converged $\bar{P}_{2s\to p}$ is given in Fig. 1, and the resultant polarization potential in Fig. 2.

It is interesting to note from Table II that the iteration procedure converges very rapidly, but that the converged value of a is quite different from the zeroth-order iterate $a^{(0)}$. That the final scattering length is larger than $a^{(0)}$ seems virtually assured from (3.5). For since $H_b(r)$ is finite at the origin, whereas $G_b(r)$ is zero; it is clear that the integrand and hence the integral will almost certainly be positive, with the net effect that $a^{(i)} > a^{(i-1)}$. Table II confirms a monotonically increasing convergence pattern and in particular that $a > a^{(0)}$. The whole effect is similar to what happens in H^- wherein the zeroth-order (^1S) iterate of $a^{(0)} = (0.0555)^{-1/2} = 4.24$ increases, when account is in effect taken of the second term[22] in (3.5), to $a \cong 6.$[22] The error in the H^- is such[22] that we feel we can assert that our final e-Li scattering length (Table II) is correct to within 10%.

TABLE II. Iterative results for (modified) polarized orbital and exchange adiabatic (^1S) scattering lengths.

	Polarized orbital		Exchange adiabatic	
Iteration	a	r_c	a	r_c
0	4.70	7.1	4.70	7.15
1	8.90	9.0	8.01	8.95
2	8.62	9.3	8.57	9.30
3	8.68	9.35	8.64	9.35
4	8.69	9.35	8.64	9.35

Under the circumstance, we find it very difficult to understand how the (^1S) scattering length of other calculations[2,4] (cf. Table III), being less not only than a but even $a^{(0)}$, can be correct. Or to put it another way, we do not believe that the previous scattering lengths are consistent with the electron affinity of Li$^-$.

The same iterative procedure can also be carried through in the exchange adiabatic approximation. The results for the scattering length (Table II) and $\bar{P}_{2s\to p}(r)$ (Fig. 1) are of necessity similar to the results of the similarly modified polarized orbital procedure. In formulating the exchange adiabatic equation we have, for consistency, added a Lagrange multiplier term to impose the same kind of orthogonality constraints on the solutions that we *had* to impose in the polarized orbital equation. (The constraints, Appendix A, are necessary even in the modified polarized orbital, but not in the exchange adiabatic approximation. They are also necessary in the exchange approximation.)

In either of the approximations once the appropriate $\bar{P}_{2s\to p}$ has been determined, there are no free parameters. That means the equations in all other symmetries are fixed. Table III contains the resultant S-wave phase shifts; Table IV contains P-wave results. In both cases the results are compared to close-coupling[3,4] and elaborate variational results of Sinfailam and Nesbet.[23] In Table III we give very low-energy ^3S close-coupling phase shift of Norcross[4] which correct the original ^3S phase shifts of Burke and Taylor.[3]

The salient features are the following: the ^1S phase shifts conform to the results of Table II. The larger scattering length corresponds to less attraction, and Table III shows that the phase shifts are correspondingly smaller than the ones to which we compare. For the reason as the scattering length result, we find it equally difficult to believe that the polarized orbital results should not be the most accurate here also. The ^3S phase shifts on the other hand are quite close to one another. Here we see one of the main advantages of the polarized orbital technique, whereby between exchange-polarization and direct polarization one does not obtain a uniform effect in all phase shifts relative to unpolarized (say exchange approximation) results. Note, however, that the exchange approximate results are qualitatively

TABLE III. Modified polarized orbital and comparison S-wave shifts.

			^3S					^1S		
k^2 (Ry)	exch.	ex. ad. [a]	pol. orb. [a]	c.c. [b]	var. [c]	exch.	ex. ad. [a]	pol. orb. [a]	c.c. [b]	var. [c]
0	(5.48)	(+3.21)	(−9.22)	(−7.12)		(17.01)	(8.64)	(8.69)	(3.65)	
10^{-5}	6.266	9.403	6.309	6.304		6.229	6.246	6.253	6.272	
10^{-4}	6.228	9.356	6.354	6.336		6.114	6.165	6.183	6.239	
5×10^{-4}	6.161	9.269	6.391	6.356		5.909	6.020	6.042	6.158	
10^{-3}	6.110	9.199	6.391	6.348		5.763	5.912	5.931	6.086	
0.0025	6.010	9.049	6.346		6.300	5.495	5.701	5.710	5.973	5.940
0.01	5.741	8.584	6.101		6.049	4.922	5.164	5.151		5.510
0.02	5.524	8.189	5.862	5.826		4.572	4.788	4.759	5.192	
0.0225	5.479	8.109	5.812		5.778	4.508	4.718	4.685		5.138
0.04	5.229	7.648	5.525	5.511	5.495	4.184	4.359	4.300	4.797	4.793
0.06	5.016	7.247	5.279	5.284		3.992	4.090	4.008	4.542	
0.0625	4.992	7.204	5.251		5.234	3.917	4.063	3.976		4.532
0.08	4.845	6.922	5.081			3.765	3.898	3.793		
0.09	4.771	6.778	4.996		5.003	3.692	3.820	3.704		4.306
0.10	4.702	6.644	4.918			3.627	3.750	3.626		
0.12	4.579	6.399	4.777			3.515	3.632	3.492		
0.1225	4.565	6.371	4.761		4.768	3.503	3.619	3.477		4.139

[a] Polarized orbital and exchange adiabatic calculation each uses its appropriately modified $P_{2s\rightarrow p}$, see text.

[b] S results for $k^2 \leq 0.06$ are from Norcross, Ref. 4. Remaining close coupling results from Burke and Taylor, Ref. 3. All close-coupling scattering lengths from Norcross also. The scattering lengths from Karule's c.c. calculation (Ref. 1) are $-5.66a_0$ and $3.65a_0$ for ^3S, ^1S, respectively.

[c] Sinfailam and Nesbet, Ref. 22.

not bad, whereas the exchange adiabatic in the ^3S case approach (as $k^2 \rightarrow 0$) the wrong multiple of π. (By construction, the ^1S in the exchange adiabatic approximation is necessarily good.) This is the most vivid case we have showing the unreliability of the exchange adiabatic approximation for highly polarizable targets and we would advise extreme caution in using it. The other half of the conclusion from this comparison is that the *simple exchange approximation is a more uniformly reliable approximation for highly polarizable targets than the exchange adiabatic approximation.*

This is confirmed also in the ^3P phase shifts (Table IV), where the exchange results show the shape resonance which is known to be the dominant feature of the P-wave scattering. The polarized orbital ^3P phase shifts are seen to be

TABLE IV. Modified polarized orbital and comparison P-wave phase shifts. [a]

			^3P					^1P		
k^2 (Ry)	exch.	ex. ad.	pol. orb.	c.c.	var.	exch.	ex. ad.	pol. orb.	c.c.	var.
10^{-5}	4.1×10^{-6}	4.8×10^{-5}	1.5×10^{-4}	(0.0192) [b]		-8.0×10^{-7}	2.1×10^{-5}	1.4×10^{-4}	(4.0×10^{-4}) [b]	
10^{-4}	1.3×10^{-4}	0.0015	0.004	(0.0724)		-2.5×10^{-5}	6.5×10^{-4}	0.0031	(0.0032)	
5×10^{-4}	1.5×10^{-3}	0.0175	0.023	(0.209)		-2.8×10^{-4}	0.007	0.0166	(0.0163)	
10^{-3}	4.2×10^{-3}	0.0515	0.051	(0.346)		-7.1×10^{-4}	0.0190	0.0328	(0.028)	
0.0025	0.017	0.230	0.159		0.307	−0.003	0.0641	0.0787		0.058
0.01	0.158	1.571	0.956		1.952	−0.022	0.240	0.240		0.189
0.02	0.509	1.849	1.457	2.107		−0.053	0.334	0.332	0.262	
0.0225	0.612	1.856	1.501		2.162	−0.061	0.346	0.342		0.239
0.04	1.162	1.806	1.588	2.017	1.981	−0.118	0.353	0.346	0.293	0.272
0.06	1.375	1.714	1.566	1.911	1.876	−0.175	0.307	0.296	0.292	
0.0625	1.386	1.702	1.560			−0.182	0.299	0.287		0.276
0.08	1.422	1.631	1.528	1.820		−0.222	0.248	0.233	0.304	
0.09	1.423	1.594	1.510		1.787	−0.241	0.219	0.204		0.301
0.10	1.418	1.560	1.493	1.743		−0.258	0.192	0.175	0.360	
0.12	1.396	1.500	1.463	1.678		−0.285	0.142	0.122	0.530	
0.1225	1.393	1.493	1.460		1.660	−0.287	0.136	0.116		0.515

[a] Footnotes a, b, and c from Table III apply here also except that all close-coupling results are from Ref. 3.

[b] Results in parentheses are digitized interpolation results from Fig. 3 of Ref. 3.

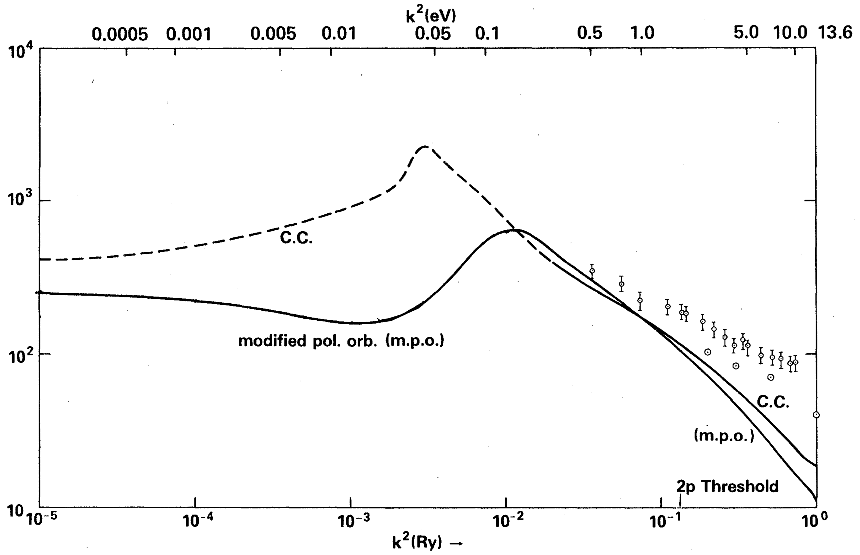

FIG. 4. Elastic cross section in (modified) polarized orbital and close-coupling approximations. Experimental points are total cross-section measurements (Ref. 25). Above 0.136 Ry they therefore include inelastic contributions; cf. text for discussion. The c.c. curve, where dashed, was calculated from digitized interpolation of graphical phase shift from Ref. 3 and may not be accurate. Cf. footnote b of Table IV.

quantitatively smaller than the comparison results in Table IV, and they peak at a somewhat larger energy with a value closer to $\frac{1}{2}\pi$. This difference in the respective ^3P-wave phase shifts is the major factor accounting for lower polarized orbital scattering cross section below the maximum and the higher cross section above it compared to the close-coupling results[3] (Fig. 4). The larger values correspond to the lower side of the presently measured[25] range and they therefore qualitatively support the somewhat larger experimental value[25] than those predicted by close coupling. A good measurement at the lowest energies should clearly distinguish these various calculations.

The various partial waves, including higher partial waves, at a coarser mesh in energy are given in Table V. In general the $l \geqslant 2$ phase shifts follow the α/r^4 polarization formula[24]

$$\eta_l = \pi\alpha k^2/(2l-1)(2l+1)(2l+3) \qquad (3.17)$$

to increasingly larger values of k^2 as l increases. The value of k^2 where (3.17) ceases to hold can be judged from Table V by noting where singlet and triplet phase shifts (for each l) begin to differ significantly from each other.

In Fig. 4 one also sees increasing deviation from experiment[25] above the inelastic threshold at 1.4 eV. This is mostly due to omission of the excitation of $^1S(1s^22p)$ first excited state. If one takes the $2s$-$2p$ cross sections of Williams *et al.*[26] and adds it to their elastic cross section, then that sum is indeed close to Bederson and Miller.[25] How-

TABLE V. Collected (modified) polarized orbital phase shifts.

k^2 (Ry)	^3S	^3P	^3D	^3F	^3G	^3H	^1S	^1P	^1D	^1F	^1G	^1H
0.01	6.095	0.956	0.046	8.8×10^{-3}	$1.4\ \times10^{-4}$	1.6×10^{-4}	5.148	0.240	0.046	0.009	$1.4\ \times10^{-4}$	1.6×10^{-4}
0.02	5.859	1.457	0.101	0.031	9.87×10^{-3}	0.0025	4.755	0.332	0.102	0.031	9.88×10^{-3}	0.0025
0.04	5.522	1.588	0.194	0.065	0.028	0.014	4.298	0.346	0.201	0.065	0.028	0.013
0.06	5.278	1.566	0.262	0.100	0.044	0.022	4.006	0.296	0.274	0.101	0.044	0.022
0.08	5.081	1.528	0.308	0.131	0.060	0.031	3.793	0.233	0.324	0.133	0.060	0.031
0.10	4.918	1.493	0.337	0.159	0.075	0.039	3.626	0.175	0.351	0.163	0.075	0.039
0.12	4.777	1.463	0.353	0.182	0.090	0.047	3.492	0.122	0.364	0.189	0.090	0.048
0.20	4.360	1.381	0.365	0.239	0.141	0.080	3.137	−0.020	0.332	0.253	0.144	0.080
0.30	4.018	1.319	0.355	0.253	0.180	0.115	2.904	−0.063	0.244	0.266	0.188	0.117
0.40	3.779	1.274	0.352	0.243	0.196	0.140	2.778	−0.004	0.168	0.243	0.207	0.144
0.50	3.599	1.239	0.357	0.229	0.197	0.155	2.704	0.102	0.113	0.212	0.207	0.161
0.60	3.455	1.211	0.365	0.216	0.191	0.162	2.660	0.217	0.077	0.181	0.198	0.169
0.70	3.340	1.186	0.373	0.206	0.183	0.163	2.630	0.318	0.056	0.155	0.185	0.171
0.80	3.237	1.164	0.382	0.200	0.174	0.161	2.608	0.401	0.046	0.133	0.170	0.168
0.90	3.151	1.145	0.390	0.195	0.166	0.156	2.590	0.467	0.044	0.116	0.156	0.162
1.0	3.075	1.127	0.397	0.193	0.158	0.151	2.573	0.519	0.049	0.102	0.143	0.155

ever Williams *et al.*[26] specify a rather large error bar (32%) in their experiment. Thus, if we add their $2s$-$2p$ cross section to our elastic result we obtain a total cross section about 20% lower than the presently measured one.[25]

That deviation is in general accord with Walters'[27] claim that the measured total e-Li cross section is too large. However, we believe the present calculations and experiments are not sufficiently definitive to substantiate that assertion. (This remark is intended in the low-energy range just beyond the $2p$ threshold; we do not wish to comment on the higher-energy range which was the main concern of the Walters paper.[27])

Some differential cross sections are given in Fig. 5; although experimental angular results[26] are more complete at higher energies, we believe our calculation is more reliable below the inelastic threshold. We therefore have also plotted in Fig. 5 the angular distribution at the presently unmeasured energy of 1.36 eV.

Even more sensitive to the phase shifts is the spin-flip cross section. Specifically the amplitude for converting the target (or the scattered electron) from spin "down" to spin "up" (sometimes called spin exchange cross section) is[28]

$$f_{\text{spin-flip}}(\theta)=\tfrac{1}{2}[f^{(-)}(\theta)-f^{(+)}(\theta)]\,. \tag{3.18}$$

The ratio of the associated cross section to the full elastic cross section

$$\sigma_{\text{el}}(\theta)=\tfrac{3}{4}|f^{(+)}(\theta)|^2+\tfrac{1}{4}|f^{(-)}(\theta)|^2$$

is given by

$$R(\theta)=\tfrac{1}{4}|f^{(-)}(\theta)-f^{(+)}(\theta)|^2/\sigma_{\text{el}}(\theta)\,.$$

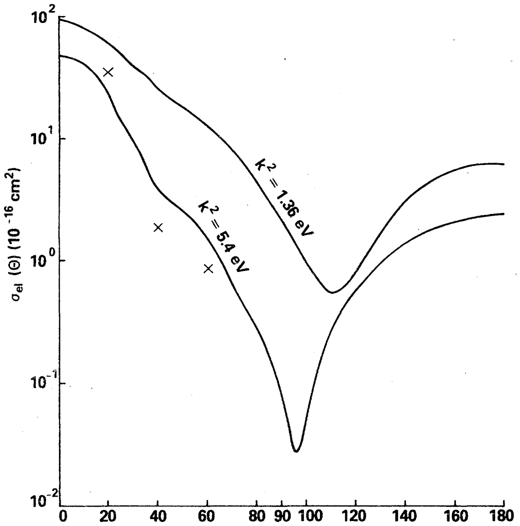

FIG. 5. Elastic differential cross section in (modified) polarized orbital approximation. Experimental points at 5.4 eV are those of Williams, *et al.* (Ref. 26).

Results are plotted in Figs. 6 and 7. In Fig. 6 the ratio is compared to measurement of Bederson and Miller[25] and close coupling result of Burke and Taylor[3] (where to their $l=0$ plus $l=1$ close-coupling phase shifts we have added our higher partial phase shifts). The differences between the calculated results is quite evident, but the errors in the experimental results which are in qualitative accord with both calculations, do not allow a definitive comparison. In Fig. 7 we have given our own (polarized orbital) results at two lower energies which can provide useful tests for a future experiment.

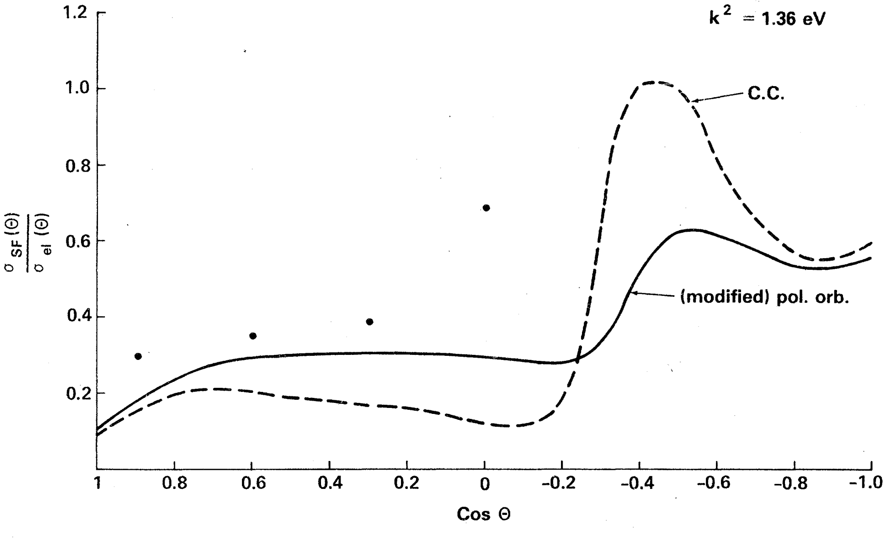

FIG. 6. Differential spin-flip cross section at $k^2 = 1.36$ eV. Experimental points, from Bederson and Miller (Ref. 25) do not contain error estimates.

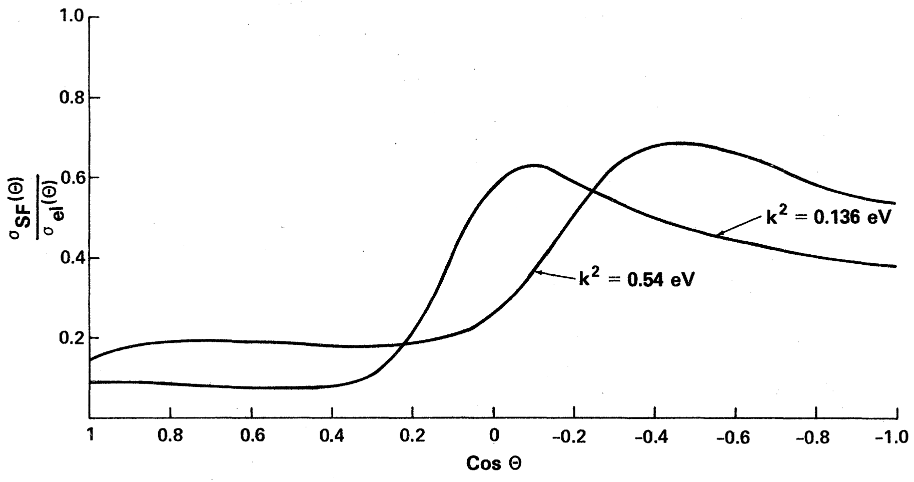

FIG. 7. (Modified) polarized orbital differential spin-flip cross sections at two lower energies.

IV. DISCUSSION

We believe that our modification of the polarized orbital method to treat electron-alkali scattering is a reasonable one. One further test of the procedure is that it should reduce to the unmodified method when the polarizability of the target becomes moderate. This in turn means that in the general case the $\overline{P}_{nl\to l'}$ are satisfactorily given by the unmodified, essentially Sternheimer,[13] form of $P_{nl\to l'}$ and that latter will lead to a good polarizability, a good electron affinity, and the satisfaction of the Levinson-Swan "theorem." In the canonical case of the e-H system it is well known that the unmodified polarized orbital $P_{1s\to p}$ used in the traditional polarized orbital method[6] passes all three tests.[11]

The modification contains another—although more subtle—advantage, which to some extent corrects for the necessarily inexact target wave function. Namely since we have fit to the experimental or equivalently highly accurate theoretical Li^- electron affinity,[19] neither of which knows anything about the approximate target wave function, our modified $\overline{P}_{2s\to p}$ must contain a part which corrects for the approximate target state function which must be used in the polarized orbital (or any other scattering) formalism. It may be thought that this correlation only applies to the ^1S results, however we would again argue that since the polarized orbital procedure puts this information into a wave function[5,6] (and not into an effective potential), with all the benefits accruing from correctly antisymmetrizing the wave function,[11] that the correction should be operative for other partial waves symmetries as well. We therefore believe that this set of modified polarized orbital shifts are overall the most accurate e-Li phase shifts presently available.

One shortcoming of the modification is that it is not *ab initio,* i.e., one must know values of the electron affinity and the polarizability to make it work, and even with these modifications the modified polarized orbital $P_{nl\to l'}$ is not uniquely defined. In contrast to this it is interesting to observe that Vo Ky Lan[10] has obtained satisfactory phase shifts using Stone's form[9] of polarized orbital in an otherwise conventional polarized orbital calculation. (Vo Ky Lan calls this the *POM* III variant.[10]) In Stone's form the polarized orbital that replaces $P_{2s\to p}(i,4)$ of (2.2) is

$$\begin{aligned}\varphi_{2s\to p} &\to \varphi_{\text{Stone}}(i,4)\\ &= \beta(r_4)[P_{2p}(r_i)/r_i]\cos\theta_{i4}\,. \end{aligned}\tag{4.1}$$

The fact that P_{2p} replaces $P_{2s\to p}$ in (2.4) is a simple outgrowth of the fact that for alkalis most of the polarizability does derive from the lowest p orbital in the expansion of $P_{2s\to p}$. More important is the dependence of β on the incident coordinate r_4, specifically the fact that in Stone's method $\beta(r)$ is determined *ab initio* by minimizing the adiabatic energy of the Li atom for each (stationary) position r_4 of the incident electron. The ansatz for the adiabatic wave function is Ψ_X (123; 4) of (2.5) with the replacement of $\phi_{2s\to p}$ by ϕ. The graphical result for β is given in Stone's paper and we repeat it here (Fig. 8) together with a β coming from our polarized orbital treatment, which is obtained from equating the right-hand side of (4.1) and (2.4) (with $P_{2s\to p}$ replaced by $\overline{P}_{2s\to p}$)

$$\beta_{p0}(r_4,r_i) = -\frac{\epsilon(r_4,r_i)}{\sqrt{4\pi}\,r_4^2}\,\frac{\overline{P}_{2s\to p}(r_i)}{P_{2p}(r_i)} \tag{4.2}$$

The result, Eq. (4.2), is a function of r_i as well as r_4. In Fig. 8 we show β_{p0} at two values of r_i compared to Stone's. One value $r_i = 3.05$ is where

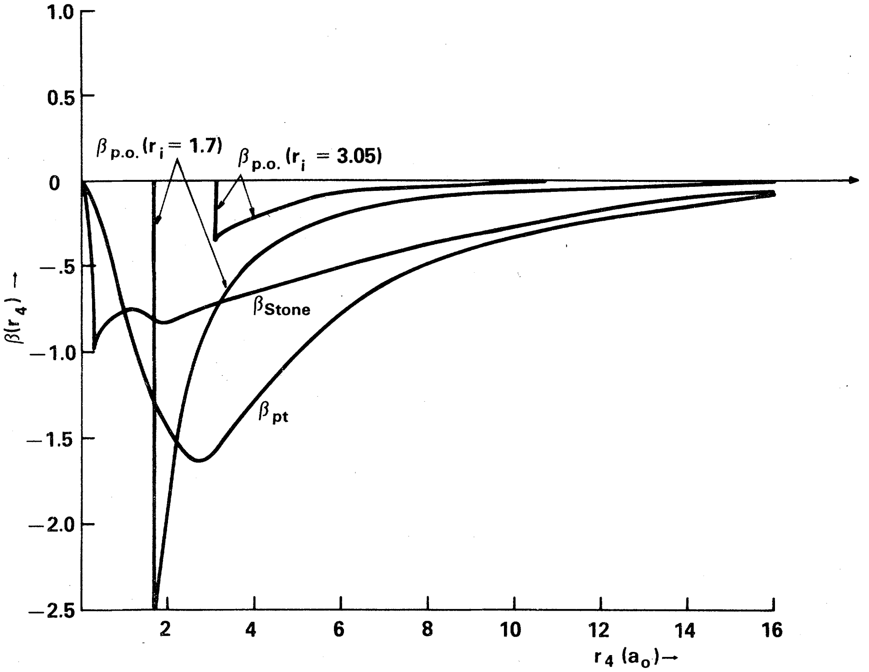

FIG. 8. $\beta(r_4)$ in various approximation (cf. text). Note the effective β_{po} [Eq. (4.1)] depends on the value of r_i and has a discontinuity there; it is shown for two values of r_i. Stone's (adiabatic variational) β_{Stone} has a cusp plus a minimum and is roughly similar to β_{po} for a value of r_i near this minimum.

the unperturbed $P_{2s}(r_i)$ has its second maximum; the second, $r_i = 1.7$ is a mean between the first and second maxima of $P_{2s}(r_i)$. The figures demonstrate both the differences and the similarities as compared to Stone's β. Note specifically that the latter has a cusp, compared to β_{p0} which has a discontinuity; the perturbation theoretic $\beta_{pt}(r_4)$ (also shown in the figure and taken from Stone's paper[9]) is completely smooth as a function of r_4.

To the extent that one can draw general conclusions from this circumstance, it would appear that it *may not* be the adiabatic hypothesis which is at fault in constructing the polarized orbital wave function for electron-alkali scattering, but rather the use of first-order perturbation theory to approximate the adiabatic result (rather than Stone's formulation which is variational and does not depend on perturbation theory). If this is true, it is significant, because Stone's method does constitute an *ab initio* prescription. However, we believe one will require direct comparison of the phase shifts themselves, and comparison of both methods when applied to other alkalis and highly polarizable targets before one can be sure that that is the case. Nevertheless, we emphasize again the agreement of our qualitative conclusions with those of Vo Ky Lan.[10]

To conclude we mention that since we have derived a total (polarized orbital) wave function, it can also be used for photodetachment (of Li⁻)[29] and distorted wave calculations of electron impact excitation of Li, particularly of the resonance transition (2s - 2p). Both calculations are in progress.

APPENDIX

It can be shown that $u = P_{1s}(r)$ is an "integral" solution in singlet and triplet states in exchange and polarized orbital approximations.

Let $u_{l=0} = P_{1s}$ in Eq. (2.11c), we get

$$\begin{aligned}\left(\frac{d^2}{dr^2}+k^2\right)P_{1s} &= [\,4\Gamma_0(1s,1s;r)+2\Gamma_0(2s,2s;r)-2Z/r+V_p\,]P_{1s}(r)\\ &\quad-\Big[2P_{1s}\Gamma_0(1s,1s;r)\pm 2P_{2s}\Gamma_0(2s,1s;r)\\ &\quad+P_{1s}\Big(\epsilon_{1s}-k^2+2\int_0^\infty P_{1s}(x)\Gamma_0(2s,2s;x)P_{1s}(x)\,dx\mp 2\int_0^\infty P_{2s}(x)\Gamma_0(1s,2s;x)P_{1s}(x)\,dx\\ &\quad+\int_0^\infty P_{1s}(x)V_p(x)P_{1s}(x)dx\mp 2\int_0^\infty P_{2s}(x)\overline{V}_p(x)P_{1s}(x)dx\Big)\Big]\pm\tfrac{2}{3}rP_{2s\to p}(r)\int_r^\infty\frac{P_{1s}(x)P_{2s}(x)}{x^4}\,dx\,. \end{aligned} \tag{A1}$$

Multiply on the left by $P_{1s}(r)$ and integrate to get

$$\int_0^\infty P_{1s}\left(\frac{d^2}{dr^2}+k^2\right)P_{1s}\,dr$$

$$=\int_0^\infty P_{1s}(r)[2\Gamma_0(1s,1s;r)-2Z/r-\epsilon_{1s}+k^2]\,dr$$

or

$$\int_0^\infty dr\,P_{1s}\left(\frac{d^2}{dr^2}+\frac{2Z}{r}-2\Gamma_0(1s,1s;r)+\epsilon_{1s}\right)P_{1s}=0\,. \tag{A2}$$

In the derivations of the above equation we use the fact that P_{1s} is orthogonal to P_{2s} in the frozen-core approximation. Equation (A2) is the same equation as Eq. (2.20a), thus (A2) is indeed zero. That is what we mean by an "integral" solution.

It can be shown that $u=P_{2s}(r)$ is an "integral" solution in exchange and polarized orbital approximation for triplet state only. Let $u_{l=0}=P_{2s}(r)$ in Eq. (2.11c), multiply on the left by P_{2s} and integrate. We get

$$\int_0^\infty dr\,P_{2s}(r)\left[\left(\frac{d^2}{dr^2}+\frac{2Z}{r}-4\Gamma_0(1s,1s;r\pm\epsilon_{2s}\right)P_{2s}(r)+2\Gamma_0(1s,2s;r)P_{1s}(r)\right]$$

$$=2(1\mp1)\left(\int_0^\infty dr\,P_{2s}(r)[\Gamma_0(2s,2s;r)+V_p/2]P_{2s}(r)\right)\,. \tag{A3}$$

We see that only in the triplet state (upper sign), the above equation reduces Eq. (2.20b), the equation satisfied by P_{2s}.

In conclusion then, it would appear that the apparent lack of determinacy of the original equations stems from the fact shown above that $P_{1s}(r)$ [and $P_{2s}(r)$] are "integral" solutions of the appropriate scattering equations. Therefore, the orthogonality conditions serve to make the solutions unique for all r, and they should not affect the phase shifts significantly (modulo π), since the added function $P_{1s}(r)$ and $P_{2s}(r)$ vanish at infinity.

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$$v_l(r_4)=\int\varphi_0\Psi_A^{(l)}\,dr^{(4)}$$

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