

Photoionization of lithium

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The photoionization of lithium from threshold to 50 eV above threshold is calculated via the method of polarized orbitals. The method is applied in as orthodox a manner as possible; this means that total wave functions are constructed as by Temkin and Lamkin using only the static dipole part of the perturbation of core electrons by the outer part of the external electron. According to other previously given prescriptions, both initial (bound) and final (continuum) wave functions are so polarized, only the length form of the matrix is calculated, and bilinear terms from the polarization contributions are retained (although their effect in this calculation is small). The results themselves are essentially identical to those of a recent diagrammatic calculation of Chang and Poe (in the region below 5 eV where they have calculated), and as such they differ in certain significant components from exchange adiabatic and extended polarization results of Matese and LaBahn (although their over-all result is similar). Discussion of these points is included. The s - and p -wave e -Li⁺ phase shifts, which are derived as by-products of this calculation, are also presented and compared to other phase-shift calculations.

I. INTRODUCTION

In addition to its importance in space physics, photoionization is a significant probe of electron interaction with atomic systems. For, in the final state, the appropriate wave function is just that of electron scattering from the residual ion; thus, one learns about this scattering continuum from it, and in particular one can compare different methods for calculating it. Our interest here is in the method of polarized orbitals^{1,2} and especially in those aspects which make the method particularly suitable for photoionization calculations.

The method of polarized orbitals, as we have stressed in a recent review article,³ is not intended as a brute-force technique to yield in principle arbitrary precision. Rather, by putting the essential physics in the ansatz for the wave function, one can improve the scattering, we maintain, to better than first order over the simple exchange approximation. This derives in the first instance from the requirement of antisymmetrizing the total wave function, a condition which then carries additional information beyond what the polarized increment would otherwise be expected to contain. Additionally one has, in the case of photoionization of a many-electron atomic target, the possibility of similarly improving the accuracy of the Hartree-Fock initial state of the target system by including the polarization of the core electrons by the outer electron (in the case of an alkali), which in turn modifies the valence orbital in a completely analogous fashion to what goes into the final- (scattering) state wave function. Thus, in the computation of the photoionization matrix element, one can expect a similar improvement in accuracy coming from the bilinear cross terms as that

which one gets from the exchange polarization terms in the scattering calculation for the phase shifts.

Some of these ideas have been included in polarized-orbital-like photoionization calculations by LaBahn and collaborators.^{4,5} Unfortunately, the general philosophy toward the polarized orbital in these and other calculations is quite different from our own. For example, the potentially important bilinear term is simply dropped under the rubric that polarization effects are first order and that anything beyond that is inconsistent.

In view of the fact that diagrammatic calculations of lithium photoionization have been carried out,⁶ in particular a very recent one by Chang and Poe,⁷ which we consider reasonably definitive, one is afforded an opportunity to compare these different polarization calculations.

II. THEORY AND CALCULATION

The photoionization cross section (in units of a_0^2 ; Rydberg units are used throughout) is given by the well-known formula

$$\sigma_L = 4\pi\alpha_f k(I + k^2) \left| \langle \Psi_f | \sum_{j=1}^3 z_j | \Psi_i \rangle \right|^2. \quad (2.1)$$

In (2.1) α_f is the fine-structure constant, k^2 is the energy of the outgoing electron, and I is the binding energy of that electron. Thus the incident-photon energy is given by

$$\omega = I + k^2. \quad (2.2)$$

As long as we are calculating the integrated (i.e., total) cross section, as we shall exclusively do in this paper, then Ψ_f can be taken as an ordinary scattering wave function of the electron incident in the z (photon) direction, so that the matrix ele-

ment contains no reference to the direction of the ionized electron. In addition, as long as one partial wave is required, no special provision need be taken to account for the fact that Ψ_f should be a solution with ingoing radial-wave boundary conditions.

That photoionization cross sections should only be calculated in the length form, when using polarized-orbital functions, is a central item in our view of the method³; it follows from the fact that the wave functions (for a three-electron system of total angular momentum l)

$$\Psi_i = \mathcal{Q}\{U_i(1)[\Phi_0(2, 3) + \Phi^{(\text{pol})}(1; 2, 3)]\} \quad (2.3a)$$

are such as to emphasize (through $\Phi^{(\text{pol})}$) the static polarization of the core electrons, 2 and 3, by the outer electron, labeled 1 in (2.3a). Therefore, a transition operator which also emphasizes this outer region of configuration space is clearly to be preferred, and this is quite obviously the length form.

The other item which makes polarized orbitals particularly suitable to photoionization, and this was appreciated by LaBahn and collaborators,^{4,5} is the fact that the method can be used to calculate an initial- (bound) state wave function as well as the final- (scattering) state function,^{3,4} for which, of course, the method was originally devised.¹ Thus, the ansatz (2.3a) is to be used for both states. The symbol \mathcal{Q} in (2.3a) is the antisymmetrizer, which, assuming Φ_0 and $\Phi^{(\text{pol})}$ are antisymmetric in their (last) two arguments, reduces to the sum

$$\mathcal{Q} \equiv (3N)^{-1/2}[(1; 2, 3) + (2; 3, 1) + (3; 2, 1)] \quad (2.3b)$$

The factor $3^{-1/2}$ is necessary for quadratic normalizability, assuming each term is normalized to unity for the bound state; the factor $N^{-1/2}$ includes the effect of the cross terms in the quadratic normalization. The $3^{-1/2}$ factor is also necessary for the over-all normalization of the continuum function, in addition to the appropriate normalization

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2(Z-2)}{r} + 4\left(\xi + \frac{1}{r}\right)e^{-2\xi r + k^2} \right] u_i(r) + rT_4 = 2\frac{\alpha(\xi r)}{(\xi r)^4} u_i(r) - r(T_5 + T_6), \quad (2.10a)$$

where T_4 , T_5 , and T_6 are given in the Appendix A, and the function $\alpha(x)$ is the Callaway-Temkin form of cutoff^{2,3}:

$$\alpha(x) = 4.5[1 - e^{-2x}(1 + 2x + 2x^2 + \frac{4}{3}x^3 + \frac{2}{3}x^4 + \frac{4}{27}x^5)]. \quad (2.10b)$$

The polarizability of the Li^+ is $2\alpha(\infty)/\xi^4$, which turns out to be 0.17 from (2.9b) and (2.10b). This is to be compared with the value 0.191 used by

of U_i as the partial-wave component of a plane wave at infinity. (See below for further details of the continuum normalization.) Including spin factors, U_i in (2.3a) is

$$U_i(1) = \frac{u_i(r_1)}{r_1} Y_{i0}(\Omega_1) \chi_{1/2}(1).$$

In the orthodox form of polarized orbitals, radial equations are derived from the projection³

$$\int Y_{i0}^*(\Omega_1) \chi_{1/2}^*(1) \Phi_0^*(2, 3) (H - E) \Psi_i d\mathbf{r}_1^{-1} = 0. \quad (2.4)$$

Integrations in (2.4) include spin variables; in addition to the doublet spin function $\chi_{1/2}$ in (2.4), we shall need the singlet spin function χ_0 associated with the ground state and its polarized parts:

$$\Phi_0(2, 3) = \varphi_0(\mathbf{r}_2, \mathbf{r}_3) \chi_0(2, 3) \quad (2.5)$$

$$\begin{aligned} \Phi^{(\text{pol})}(1; 2, 3) = & [\phi^{(\text{pol})}(\mathbf{r}_1, \mathbf{r}_2) v_0(r_3) \\ & + \phi^{(\text{pol})}(\mathbf{r}_1, \mathbf{r}_3) v_0(r_2)] \chi_0(2, 3), \end{aligned} \quad (2.6)$$

where

$$\phi^{(\text{pol})}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\epsilon(r_1, r_2)}{r_1^2} e^{-\xi r_2(\frac{1}{2}\xi r_2^2 + r_2)} \frac{\cos \theta_{12}}{(\pi \xi)^{1/2}}, \quad (2.7)$$

$$\varphi_0(\mathbf{r}_2, \mathbf{r}_3) = v_0(2) v_0(3), \quad (2.8)$$

$$v_0(r) = (\xi^3/\pi)^{1/2} e^{-\xi r}, \quad (2.9a)$$

and $\epsilon(r_1, r_2)$ in (2.7) is a step function.² Equation (2.8) implies that we have used a separable form of core wave function, and Eqs. (2.8) and (2.9) say that we have used the simplest Slater form for these orbitals. Within these approximations the screening parameter which minimizes the ground-state energy is related to the nuclear charge Z by

$$\xi = Z - \frac{5}{16}. \quad (2.9b)$$

The radial equations coming from (2.4) can be worked out straightforwardly. We write them in the general form [letting $r_1 = r$ in (2.3)]

Matese and LaBahn⁴ (also McDowell, cf. Ref. 11) which comes from using the FCHF orbital.

For the case of electron-helium scattering ($Z=2$) these equations agree, although they are written somewhat differently, with those derived by Duxler *et al.*¹² (with the Slater orbital replaced by the FCHF orbital there), but the form for general Z , (2.10a), given here may be useful for many other applications.

In the photoionization application the equation

for $l=0$ will describe the 2s orbital of the valence electron of Li, in which case the energy k^2 in (2.10a) goes into an eigenvalue

$$k^2 = -I,$$

where I is the binding energy of the 2s electron in this approximation.

Before discussing the actual results, we point out that the usual orthogonality condition between bound and continuum solutions does not hold for s waves. This is because an exchange term contains the energy explicitly (cf. T_4 of Appendix A). Therefore the relationship between bound and continuum solutions becomes

$$\begin{aligned} \int_0^\infty u_b(r)u_a(r)dr \\ = 4\pi \int_0^\infty u_b(x)xv_0(x)dx \int_0^\infty u_a(y)yv_0(y)dy. \end{aligned} \quad (2.11)$$

This relationship is derived in Appendix B. It holds for s-wave solutions where u_a and u_b are continuum and bound solutions, respectively, of the s-wave equation. It also is restricted to the exchange and exchange-adiabatic approximations, where the potentials are effectively Hermitian. For the full polarized-orbital approximation a more complicated relation can be derived and is given in Appendix B also. Equation (2.11) was used as a check of the numerical integration of (2.10a) in the appropriate approximations and was found to hold to about 0.5% in the worst case.

Table I compares binding energies in various approximations. They are arranged in pairs in increasing order of sophistication. Exchange corresponds to using only the left-hand side of (2.10a) whereas fixed-core Hartree-Fock (FCHF) corresponds to the same approximation with a Hartree-Fock wave function for the Li^+ core. The difference in these results is very small, indicating (but not proving) that a simple closed shell should be adequate for this part of the wave function. In the next category one adds to the static polarizability of the core in the form of the first term on the right-hand side of (2.10a) in exchange-adiabatic approximation; AED corresponds to the same approximation but with the $2\alpha/r^4$ potential replaced by the Bethe-Reeh dipole⁸ part of the static potential. This corresponds to including the dipole part of static interaction (in second-order perturbation theory) for all distances of the static electron from the core electrons. The fact that the binding energy is too large in this approximation is not a surprising consequence of the unphysical nature of the static model for positions of the perturbing electron inside the core electrons. Finally, one adds

nonadiabatic and/or exchange-polarization terms. The former is done in the manner of Callaway *et al.*,⁹ which is essentially a perturbation-theoretic inclusion of nonadiabaticity. We have recently made a comparison of these two methods for excited states of helium¹⁰ and concluded that for triplet states, where the electrons are kept apart by spatial exchange, the extended polarization approximation can actually improve things, but where such spatial exclusion is not implied, as in the present case, the polarized-orbital approximation does better, as is clear from Table I.

We now return to the calculation of the photoionization matrix element. The continuum function in (2.1) is assumed to be normalized as (the partial-wave component of) a plane wave, but in addition one desires the flux of scattered electrons to be constant for all points in configuration space, not only at infinity. Therefore one renormalizes $u_1(r)$, the p-wave orbital which solves (2.10a) for each positive energy k^2 , to $u_k(r)$:

$$u_k(r) = u_1(r)/[1 + 2F(r)]^{1/2}, \quad (2.12)$$

where

$$F(r_1) = \int [\phi^{(\text{pol})}(1, 2)]^2 d\vec{r}_2. \quad (2.13a)$$

Substituting (2.7) into the right-hand side of (2.13a) one can perform the integral to find

$$\begin{aligned} F(r) = \frac{43}{8\xi^2} \frac{1}{x^4} [1 - e^{-2x}(1 + 2x + 2x^2 + \frac{4}{3}x^3 + \frac{2}{3}x^4 \\ + \frac{28}{129}x^5 + \frac{4}{129}x^6)], \end{aligned} \quad (2.13b)$$

where again $x = \zeta r$. This form of normalization is the same as used by Matese and LaBahn⁴ except that their F is the appropriate one to their form of $\phi^{(\text{pol})}$.

The calculation of the photoionization matrix element in (2.1) is broken down into three parts.

TABLE I. Binding energy of the 2s orbital of the Li ground state in various approximations.

Approximation	Binding energy (Ry)
Exchange ^a	0.3931
Fixed core HF ^b	0.3936
Adiabatic exchange dipole (AED) ^c	0.4001
Exchange adiabatic ^a	0.3979
Extended polarization ^c	0.3935
Polarized orbital ^a	0.3972
Experiment ^d	0.3963

^a This calculation.

^b Value quoted in Ref. 4.

^c Matese and LaBahn, Ref. 4.

^d B. Edlen and K. Linden, Phys. Rev. **75**, 890(L) (1949).

If we call the dipole length operator L ,

$$L \equiv \sum_{i=1}^3 z_i ,$$

then we can write the matrix element

$$M_0 = \frac{1}{3\sqrt{N}} \langle \mathcal{G}\{U_k(1)\Phi_0(2, 3)\} | L | \mathcal{G}\{U_b(1)\Phi_0(2, 3)\} \rangle , \quad (2.15)$$

$$M_1 = \frac{1}{3\sqrt{N}} \langle \mathcal{G}\{U_k(1)\Phi^{(\text{pol})}(1; 2, 3)\} | L | \mathcal{G}\{U_b(1)\Phi_0(2, 3)\} \rangle + \frac{1}{3\sqrt{N}} \langle \mathcal{G}\{U_k(1)\Phi_0(2, 3)\} | L | \mathcal{G}\{U_b(1)\Phi^{(\text{pol})}(1; 2, 3)\} \rangle \quad (2.16a)$$

$$= \frac{2}{3\sqrt{N}} \langle \mathcal{G}\{U_k(1)\Phi^{(\text{pol})}(1; 2, 3)\} | L | \mathcal{G}\{U_b(1)\Phi_0(2, 3)\} \rangle , \quad (2.16b)$$

$$M_2 = \frac{1}{3\sqrt{N}} \langle \mathcal{G}\{U_k(1)\Phi^{(\text{pol})}(1; 2, 3)\} | L | \mathcal{G}\{U_b(1)\Phi^{(\text{pol})}(1; 2, 3)\} \rangle . \quad (2.17)$$

In the above U_k and U_b are the full correctly normalized (as discussed above) polarized orbitals for the continuum and bound states, respectively. If the radial functions are derived from a lesser approximation, such as the exchange approximation, then the difference between using the polarized-orbital or the lesser approximation constitutes implicitly higher-order corrections, the most important of which is

$$\Delta M_0^{(\text{pol orb})} = M_0^{(\text{pol orb})} - M_0^{(\text{exch})} \quad (2.18a)$$

or

$$\Delta M_0^{(\text{ex ad})} = M_0^{(\text{ex ad})} - M_0^{(\text{exch})} . \quad (2.18b)$$

The reason for dividing M into components is that essentially the same components have been separately calculated in Refs. 4 and 7; thus an effective comparison can be made. This comparison is given in Table II. The salient points of that table are the following: exchange (exch.), extended polarization (EP), and diagrammatic (diag.) results should be the same for M_0 ; differences in our results from the other two reflect the differences in our core wave functions (closed shell vs fixed-core HF). In principle EP and diagrammatic (diag.) results should be identical; we do not understand why they are not, but the differences are very small, so that for practical purposes we can consider them identical. First-order results (M_1) are perhaps the most significant; whereas polarized-orbital and diagrammatic results are very similar, the extended polarization calculation shows a markedly different energy dependence, changing sign at $k=0.5$. This dissimilarity was noted by Chang and Poe⁷ and we similarly have no explanation for it.

The ΔM_0 results reflect in our own case strictly the difference in the form of the outer orbital in

$$M = \langle \Psi_f | L_i | \Psi_i \rangle \quad (2.14a)$$

as the sum of three terms

$$M = M_0 + M_1 + M_2 , \quad (2.14b)$$

where

the initial and final wave functions in the various approximations. They therefore can be obtained by subtracting the appropriate columns under M_0 . Although the magnitudes can vary significantly in the different approximations, the k dependence in all cases is similar.

The quantity M_2 only occurs in the polarized-orbital approximation. Although its magnitude here is quite small, we have no reason to think that this will generally be the case. (We shall discuss this again in the conclusion of this paper.) It should also be pointed out that what we mean by the exchange-adiabatic approximation to the final matrix element M would be the ex. ad. column of M_0 , whereas AED results include the AED contributions from M_1 in addition to M_0 . The final matrix elements M are compared in the last columns of Table II. Here the most perplexing feature of the various results is the fact that EP and AED approach each other as k increases, whereas one would expect exactly the opposite behavior since EP contains nonadiabatic (i.e., velocity dependent) effects whereas AED does not. (We are indebted to Dr. Poe for this observation.) On the other hand, the agreement of polarized-orbital and diagrammatic results is noteworthy. Given the differences in the various components, this virtual identity might be considered coincidental and no doubt the agreement to almost four significant figures is. In a less exact sense, however, we believe that the similarity reflects the fact that each method is consistent within itself, but there is not a one-to-one correspondence of component parts. For example, M_1 is considered a short-range correlation term by Poe and Chang,⁷ whereas in our own case it definitely contains long-range effects. From this point of view one would then expect greater agreement in the sum than in

TABLE II. Comparison of dipole length matrix-element components.

k Approx.	Zeroth-order matrix-element component M_0			EP ML ^a	diag. CP ^b	pol. orb. this calc.	M_1	
	exch.	ex. ad. this calc.	pol. orb.				EP ML ^a	diag. EP ^b
0.1	3.411	3.853	3.859	3.588	3.653	0.060	0.0729	0.0771
0.2	2.412	2.520	2.693	2.530	2.566	0.041	0.0387	0.0527
0.3	1.914	1.990	2.106	2.001	2.020	0.031	0.0105	0.0408
0.4	1.547	1.601	1.681	1.605	1.619	0.025	0.0	0.0328
0.5	1.242	1.281	1.336	1.248	1.288	0.020	-0.0244	0.0269
0.6	0.985	1.015	1.052	1.011	1.015	0.016	-0.0298	0.0222
Photoionization cross section of Li in the polarized-orbital approximation								
k^2 (eV)	0.136	0.544	1.225	1.667	2.177	3.401	3.980	4.898
ω (eV)	5.540	5.948	6.629	7.071	7.581	8.805	9.384	10.302
$\sigma_{\text{photo ion}}^{(\text{pol orb})} (10^{-18} \text{ cm}^2)$	1.601	1.672	1.709	1.697	1.660	1.521	1.427	1.324

^a Matese and LaBahn, Ref. 4.^b Chang and Poe, Ref. 7.

the parts.

In the lower part of Table II we give the numerical values of the photoionization cross section (cf. Fig. 1) vs the outgoing-electron energy k^2 and the appropriate photon energy from Eq. (2.2), for the polarized orbital approximation.

Next we compare phase shifts obtained as a by-product of the continuum calculation corresponding to e -Li⁺ scattering. In the matrix element only the p -wave scattering solutions are required; however we have also calculated s -wave scattering solutions in order to check Eq. (2.11) as discussed above.

In Table III we give the phase shifts (all relative

to pure Coulomb phases, of course) in various approximations and calculations. McDowell¹¹ has used almost the same approximation as the AED approximation of Matese and LaBahn; the differences are that he includes both dipole and quadrupole parts of the Bethe-Reeh polarization potential (for s waves) and he uses an open-shell form for the Li⁺ ground state. The differences from Matese and LaBahn are seen to be small and the ground-state wave functions are presumably mainly responsible for what difference there is. Both those results are in turn similar to our own exchange-adiabatic results, but here the differences are mainly due to the greater attractiveness of the

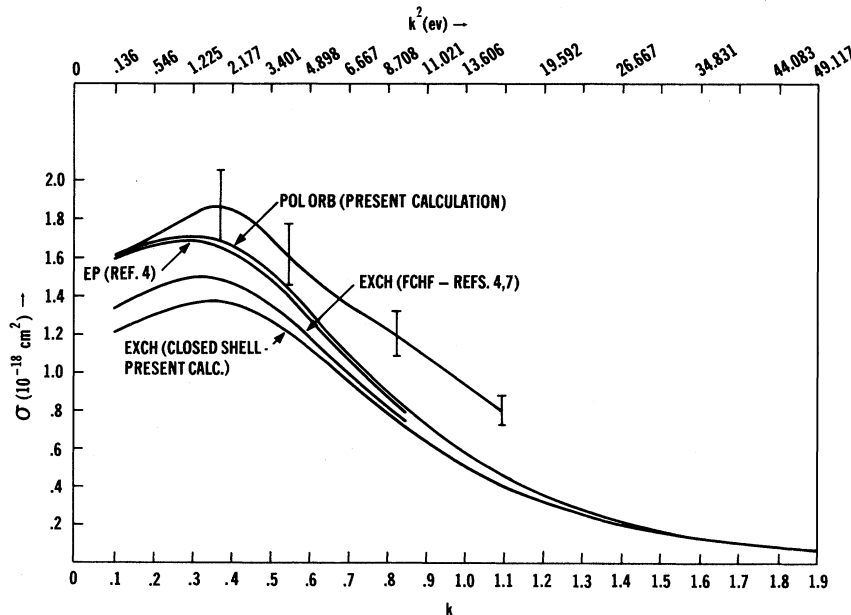


FIG. 1. Photoionization of Li in various approximations. The two exchange calculations reflect differences in the Li⁺-target-state wave function. The present polarized-orbital result is identical to the diagrammatic results of Chang and Poe, Ref. 7, up to the maximum energy of their calculation ($k=0.6 \Rightarrow k^2=4.9$ eV). The abscissa is given as a function of momentum (and energy) of the outgoing electron. To get the incident-photon energy one must add the appropriate binding energy from Table I, which will be different for each approximation. The experimental results which are the ones with the error bars attached are from Hudson and Carter, Ref. 17.

TABLE II. (Continued)

ex. ad. this calc.	pol. orb. this calc.	ΔM_0		diag. CP ^b	M_2		M		AED
		AED	EP		pol. orb. this calc.	pol. orb. this calc.	diag. CP ^b	EP	
		ML ^a							ML ^a
0.442	0.448	0.0821	0.3138	0.1819	-0.006	3.912	3.9122	3.974	3.743
0.118	0.281	0.0439	0.1871	0.1105	-0.004	2.729	2.7292	2.756	2.613
0.076	0.192	0.0296	0.1247	0.0747	-0.004	2.134	2.1355	2.136	2.041
0.054	0.134	0.0228	0.0868	0.0542	-0.003	1.703	1.7061	1.692	1.628
0.039	0.124	0.0220	0.0620	0.416	-0.003	1.353	1.3566	1.286	1.246
0.030	0.067	0.0186	0.0440	0.0326	-0.002	1.065	1.0704	1.025	0.9998
Photoionization cross section of Li in the polarized-orbital approximation									
6.667	8.708	11.021	13.606	19.592	26.667	34.831	44.083	49.117	
12.071	14.112	16.425	19.010	24.996	32.171	40.235	49.487	54.521	
1.110	0.905	0.724	0.574	0.355	0.219	0.136	0.087	0.069	

Bethe-Reeh dipole potential compared to our own dipole form. A recent calculation of p -wave phase shifts by Stewart¹³ using a time-dependent Hartree-Fock formalism yields results (given in graphical form) similar to our exchange-adiabatic results. They are therefore also similar to extended polarization results discussed in the next paragraph.

With regard to the polarized-orbital-vs.-extended-polarization results, it should be noted that the nature of the latter will always be to reduce AED phase shifts, by virtue of the repulsive non-adiabatic potential, whereas the exchange-polarization terms, which are the distinguishing feature of the polarized-orbital approximation, do not act in one set way in changing polarized-orbital results

from exchange approximate ones.

Finally in Fig. 1 we graph the photoionization cross sections in some of the various (length) calculations. Of those calculations *not* given in Fig. 1, we mention one due to Norcross,¹⁴ who computed a matrix element from continuum and bound ($2s$) orbitals in a Thomas-Fermi plus polarization potential field with parameters adjusted to fit the bound-state energies of Li. His results are between our exchange-adiabatic and polarized-orbital results. A very similar physical idea but in a somewhat more elaborate mathematical setting, has also been used by Caves and Dalgarno¹⁵ with very similar results. Stewart¹³ also obtains similar results. The results of the diagrammatic cal-

TABLE III. Phase shifts (relative to pure Coulomb phase) for e -Li⁺ scattering.

approx. k /author	exch. present	$l=0$			$l=1$			pol. orb. present	EP ML ^b
		AED McD ^a	ex. ad. present	pol. orb. present	exch. present	ML ^b	ex. ad. present	AED McD ^a	
0.1	1.2378		1.2621	1.2564	0.0977	0.1107	0.1443	0.1677	0.1470
0.2	1.2348	1.258	1.2593	1.2535	0.0997	0.1128	0.1465	0.173	0.1489
0.3	1.2300	1.255	1.2546	1.2488	0.1029	0.1162	0.1501	0.177	0.1522
0.4	1.2233	1.248	1.2481	1.2422	0.1073	0.1207	0.1549	0.182	0.1566
0.5	1.2149	1.241	1.2398	1.2338	0.1127	0.1263	0.1607	0.189	0.1619
0.6	1.2047	1.230	1.2297	1.2235	0.1189	0.1326	0.1674	0.195	0.1680
0.7	1.1928	1.221	1.2178	1.2116	0.1256	0.1395	0.1746	0.202	0.1744
0.8	1.1793	1.209	1.2043	1.1979	0.1327	0.1467	0.1821	0.210	0.1810
0.9	1.1641	1.194	1.1893	1.1828	0.1400		0.1896	0.217	0.2154
1.0	1.1476	1.178	1.1729	1.1662	0.1474		0.1971	0.224	0.2226
1.2					0.1616		0.2113		0.2353
1.4					0.1746		0.2236		0.2454
1.6					0.1859		0.2338		0.2527
1.8					0.1953		0.2419		0.2575
1.9					0.1993		0.2451		0.2591

^a McDowell, Ref. 11.^b Matese and LaBahn, Ref. 4.

culation of Chang and McDowell,⁶ with corrections as stated in Ref. 4, are similar to the AED results of Matese and LaBahn.⁴

In the figure the two exchange-approximate results reflect differences in the Li^+ ground-state approximation used in each. The remaining curves compare extended polarization to the present polarized-orbital results. The latter as we have indicated are identical to Chang and Poe⁷ within the accuracy of the drawing up to $k^2 = 4.9$ eV, which is the maximum energy of their calculation. Our own calculation has been taken to 50 eV, which is just below the resonant region. The latter has been measured by a heat-pipe technique¹⁶ using a vacuum-ultraviolet source of photons. The vacuum-ultraviolet source plus newly developing laser techniques should soon be able to cover the whole nonresonant domain. Present experiments^{17, 18} cover a lower energy region. Although they are consistent with polarized-orbital and diagrammatic results at the lowest energies, one notes, as has been noted by others¹⁵ (and for the case of sodium also¹⁹), that deviations develop at higher energies. On the other hand, differences between exchange and polarized-orbital (and presumably most other) calculations tend to disappear at the higher energies. Thus we find it difficult to believe that the error resides primarily in the calculations. This lends renewed motivation for new experiments and particularly to a definitive solu-

tion of the problem of removing or distinguishing the contribution of molecular components and other possible contaminants in the metal vapor or photon beam. (We are indebted to Dr. D. Ederer for discussions on this point.)

III. CONCLUSIONS

To conclude, we feel that the agreement with diagrammatic results of Chang and Poe⁷ constitutes the best argument for the validity of the polarized-orbital method for photoionization calculations in the form we have suggested. Since this method of calculation differs significantly in detail from LaBahn and collaborators,^{4, 5} we again reiterate¹⁰ the necessity for skepticism regarding their negative conclusions about polarized orbitals on the basis of their Na and K photoionization calculations,⁵ pending a similar recalculation as has been done here for Li. (The argument here concerns the low-energy behavior, which will be much more sensitive to precise methodology than the high-energy behavior discussed in the previous paragraph.)

APPENDIX A

We give here T_4 , T_5 , and T_6 appearing in Eq. (2.10). The quantities ξ and Z are the same as defined in the text; cf. Eq. (2.9b).

$$T_4 = -4\xi^3 e^{-\xi r} \left\{ \delta_{10} \left[\left(3\xi^2 + E + \frac{2(Z-\xi)}{r} + 2\xi(Z-\xi) - \frac{2}{r} [1 - e^{-2\xi r}(\xi r + 1)] \right) I_{(1)}^\xi \right. \right. \\ \left. \left. + 2(Z-\xi-2)I_{(0)}^\xi + 2\xi I_{(1)}^\xi + 2I_{(0)}^{3\xi} - \frac{2}{r} U(1, \xi) + 2U(0, \xi) \right] \right. \\ \left. - \frac{2}{(2l+1)}(1-\delta_{10}) \left[\int_0^r dx e^{-\xi x} u_l(x) \left(\frac{x^{l+1}}{r^{l+1}} - \frac{r^l}{x^l} \right) + r^l I_{(-1)}^\xi \right] \right\}, \quad (\text{A1})$$

$$T_5 = -\frac{4}{\xi} e^{-\xi r} \left(\delta_{10} \int_0^\infty dx \frac{u(x)}{x^3} \alpha(\xi x) \right. \\ \left. + \delta_{11} \frac{r}{3} \left\{ \frac{\alpha(\xi r)}{r^3} I_{(-1)}^\xi - \frac{2}{3} \xi^5 \left[I_{(1)}^{3\xi} + \frac{3}{\xi} I_{(0)}^{3\xi} + \frac{3}{2\xi^2} I_{(-1)}^{3\xi} - e^{-2\xi r} \left(r^2 + \frac{3}{\xi} r + \frac{3}{2\xi^2} \right) I_{(-1)}^\xi \right] \right\} \right), \quad (\text{A2})$$

and

$$T_6 = \frac{4\xi}{3} \delta_{11} \left\{ f(r) \left(2Z\xi I_{(-1)}^\xi + 2(Z-\xi-1)I_{(-2)}^\xi + 2\xi I_{(-1)}^{3\xi} + 2I_{(-2)}^{3\xi} + E I_{(-1)}^\xi \right. \right. \\ \left. \left. - \int_0^r dx \frac{u_l(x)}{x^2} e^{-\xi x} [2Z\xi x + 2(Z-\xi-1) + 2e^{-2\xi x}(\xi x + 1) + E x] \right) \right. \\ \left. - f(r) \frac{e^{-\xi r}}{r} \frac{d}{dr} u_l(r) + e^{-2\xi r} \left(\frac{3}{2} \xi^2 r^2 + \frac{1}{2} \xi r - 3 \right) \frac{u_l(r)}{r} \right. \\ \left. + e^{-\xi r} \left[2(Z-\xi-1) + 2(Z-2\xi-1)r + \frac{1}{2} \xi^3 r^2 + 2f(r) e^{-\xi r} \left(\xi + \frac{1}{r} \right) \left(I_{(-1)}^\xi - \int_0^r dx \frac{u_l(x)}{x} e^{-\xi x} \right) \right] \right. \\ \left. - \frac{8\xi}{(2l+1)} f(r) \left[\left(\frac{l+1}{2l+3} \right) r^{l+1} \int_r^\infty dx \frac{u_l(x)}{x^{l+3}} e^{-\xi x} + \frac{l r^{l-1}}{(2l-1)} \int_r^\infty dx \frac{u_l(x)}{x^{l+1}} e^{-\xi x} \right] \right\}, \quad (\text{A3})$$

where

$$I_{(n)}^a = \int_0^\infty dx u_i(x) x^n e^{-ax}, \quad (\text{A4})$$

$$U(n, a) = \int_0^r dx u_i(x) x^n e^{-ax}, \quad (\text{A5})$$

$$f(r) = e^{-\xi r} \left(\frac{1}{2} \xi r^2 + r \right), \quad (\text{A6})$$

and

$$E = -2\xi^2 + k^2. \quad (\text{A7})$$

APPENDIX B

In the exchange and exchange-adiabatic approximations, the scattering equations for u_k and u_b in the s wave are given by

$$\left(\frac{d^2}{dr^2} + k^2 + v(r) \right) u_k(r) + r T_4(u_k) = 0, \quad (\text{B1})$$

$$\left(\frac{d^2}{dr^2} - I + v(r) \right) u_b(r) + r T_4(u_b) = 0, \quad (\text{B2})$$

where $v(r)$ is the appropriate local potential for each approximation, and $T_4(u) = T_4$ from (A1). Multiplying (B1) by u_b and (B2) by u_k , subtracting and integrating, we get

$$\begin{aligned} & \int_0^\infty \left(u_b(r) \frac{d^2}{dr^2} u_k(r) - u_k(r) \frac{d^2}{dr^2} u_b(r) \right) dr \\ & + (k^2 + I) \int_0^\infty u_b(r) u_k(r) dr \\ & + \int_0^\infty dr [u_b(r) r T_4(u_k) - u_k(r) r T_4(u_b)] = 0. \end{aligned}$$

The first integral above becomes

$$\left(u_b(r) \frac{d}{dr} u_k(r) - u_k(r) \frac{d}{dr} u_b(r) \right) \Big|_0^\infty$$

and vanishes at the end points.

Using the definitions (2.9a) and (A4), we find that the remaining terms can be written

$$\begin{aligned} & \int_0^\infty u_b(r) u_k(r) dr \\ & = 4\pi \int_0^\infty dx u_b(x) x v_0(x) \int_0^\infty dy u_k(y) y v_0(y). \quad (\text{B3}) \end{aligned}$$

For the polarized-orbital approximation, there are additional terms on the right-hand sides of (B1) and (B2) giving an augmentation to the right-hand side of (B3):

$$\begin{aligned} & \int_0^\infty u_b(r) u_k(r) dr \\ & = 4\pi \int_0^\infty dx u_b(x) x v_0(x) \int_0^\infty dy u_k(y) y v_0(y) \\ & + \frac{4}{\xi} J_1 + \frac{8}{3} \xi J_2, \quad (\text{B4}) \end{aligned}$$

where

$$\begin{aligned} J_1 &= \int_0^\infty dx u_b(x) x e^{-\xi x} \int_0^\infty dy u_k(y) \frac{\alpha(\xi y)}{y^3} \\ & - \int_0^\infty dx u_k(x) x e^{-\xi x} \int_0^\infty dy u_b(y) \frac{\alpha(\xi y)}{y^3}, \quad (\text{B5}) \end{aligned}$$

$$\begin{aligned} J_2 &= \int_0^\infty dx f(x) u_b(x) x \int_x^\infty dy \frac{u_k(y)}{y^3} e^{-\xi y} \\ & - \int_0^\infty dx f(x) u_k(x) x \int_x^\infty dy u_b(y) \frac{e^{-\xi y}}{y^3}, \quad (\text{B6}) \end{aligned}$$

and $f(r)$ is given by (A6).

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