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Photoionization of Lithium by the Method of Polarized Orbitals*

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The method of polarized orbitals is used to calculate the photoionization cross section of lithium for photon energies from threshold to 15 eV. Initial-state corrections are obtained by representing the lithium atom as a perturbed Li^+ core plus an electron in the 2*s* state. Final-state corrections are similarly obtained by including perturbations of the Li^+ core by the continuum electron. Results are obtained using the length and velocity forms of the matrix elements, and are in good agreement with one another as well as with existing calculations using many-body perturbation theory. The theoretical results compare favorably with experimental data near threshold, but disagree slightly for higher energies.

I. INTRODUCTION

The method of polarized orbitals, which takes into account the effect of target polarization by an external charge, has been extensively applied to the problem of the scattering of low-energy charged particles by an isolated atom.[1-6] Callaway *et al.*[7] have extended the analysis and have demonstrated that the ordinary polarization potential which is induced by the scattering particle should be modified by an additional term, which they call the distortion potential. These techniques have been applied to obtain phase shifts for electron and positron scattering on one- and two-electron atoms.[7]

Application of the polarized orbital method to the problem of photoionization has to date been made for only a few systems; He, C^-, N^-, and O^-. Bell and Kingston[8] have calculated photoionization cross sections near threshold for helium using the Bates formalism[9] in both the length and velocity approximations. The results are in good agreement with one another and with the experimental data.

Photodetachment cross sections using the method of polarized orbitals have been performed for O^- by Garrett and Jackson[5] and for O^-, C^-, and N^- by Henry.[6] In general, the dipole-velocity results are in good agreement with experiment but are substantially larger than the dipole-length results.

The essential feature of these calculations is that the effect of target polarization on the process is included *only* by taking into account its influence on the continuum electron. In forming the matrix elements, all bound states are represented by either undistorted Hartree-Fock or variational wave functions. This is equivalent to neglecting first-order final-state corrections, but including second-order effects. Further, any perturbation corrections to the initial state are neglected.

In addition to these investigations, several other photoionization and photodetachment calculations have been performed using a semiempirical potential which takes into account target polarization.[10-13] The essence of these calculations is similar to the method of polarized orbitals as used by others (Refs. 5, 6, and 8).

Chang and McDowell[14] have shown, explicitly, the relative sizes of the various initial- and final-state corrections in a many-body perturbation-theory (MBPT) approach to the problem of photoionization of lithium. Their results indicate that in the dipole-length approximation, the second-order final-state correction does indeed dominate. However, in the dipole-velocity approximation, first-order initial-state and first-order final-state corrections are comparable in magnitude to second-order final-state corrections.

This implies that discrepancies between calculated photoionization cross sections using the length and velocity approximations, which take into account only the corrections to the continuum wave function, may be due to the neglect of first-order effects. These first-order effects can be included, in part, by extending the core wave function to include perturbed orbitals in the matrix elements.

In Sec. II, we discuss various ways that the initial and final states can be represented in the polarized orbital method. Section III includes the formalism for computing photoionization cross sections in the dipole-length and dipole-velocity approximations. A comparison with the MBPT approach of Chang and McDowell[14] is made in Sec. IV. Results are given in Sec. V, and conclusions are presented in Sec. VI.

II. REPRESENTATION OF INITIAL AND FINAL STATES

The form we take for the initial- and final-state wave functions (Li and $Li^+ + e$) is given by the ansatz

$$\Psi(1,2,3) = 3^{-1/2} \sum [u(1)u(2) + \omega(1,3)u(2) + u(1)\omega(2,3)]\phi(3)S(1,2,3) \ , \quad (1)$$

where u is the unperturbed Li^+ $1s$ orbital, $\omega(\vec{r}, \vec{R})$ is the perturbed $1s$ orbital at the point $\vec{r}$ due to a stationary point charge located at $\vec{R}$, ϕ is the $2s$ orbital for the initial state or the continuum wave function for the final state, and S is the spin function

$$S(1,2,3) = 2^{-1/2}(\alpha_1\beta_2 - \alpha_2\beta_1)\alpha_3 \ , \quad (2)$$

where α, β are the one-electron spin-up and spin-down functions, respectively. The summation is over cyclic permutations of the indices.

Various procedures were investigated for determining the one-electron orbitals. Hartree-Fock theory was used to determine the unperturbed Li^+ core orbital u. The continuum state ϕ_k was obtained in three different approximations; (i) the fixed core Hartree-Fock method (FCHF),[14] (ii) the adiabatic-exchange-dipole method (AED),[1,2] (iii) the extended polarization potential method (EP).[7] The $2s$ orbital of the initial state ϕ_{2s} was also determined using these three approximations.[15]

We now give a brief discussion of the AED and EP methods as applied to the problem of obtaining ϕ_{2s} and ϕ_k. In either case, the relevant Schrödinger equation is of the form

$$[h_0(i) + \mathcal{V}(i) - \epsilon]\,\phi(i) = 0 \ , \quad (3)$$

where $h_0(i) = -\nabla_i^2 - (2Z/r_i)$

$$+ 2\langle u(j)|\,(r_{ij})^{-1}(2 - P_{ij})|\,u(j)\rangle \ , \quad (4)$$

and $P_{ij} f(i,j) = f(j,i)$.

In the AED method, $\mathcal{V}$ is taken as the Bethe dipole-polarization potential,[2] which is asymptotic to $-0.191/r^4$. In the EP method, $\mathcal{V}$ is given by the sum of a polarization potential V_P and a distortion potential V_D.[7] The explicit form of $\mathcal{V}$ for the AED and EP methods is shown in Fig. 1.

Equation (3) then represents a scattering equation for $\phi = \phi_k$ and an eigenvalue problem for $\phi = \phi_{2s}$. Table I lists the eigenvalues obtained, as well as the experimental ionization energy. The results given are for the case of nonorthogonality between ϕ_{2s} and u.[15] Imposing orthogonality changes the energies by about 1 part in 4000 with a similar small change in the wave function. However, the wave functions ϕ_{2s}, obtained using $\mathcal{V}_{EP}$ and $\mathcal{V}_{AED}$ do differ noticeably (the wave function obtained using the AED method differs from that obtained using the FCHF method by 1–3% in the region of importance, whereas the EP $2s$ function differs from the FCHF function by less than 1%).

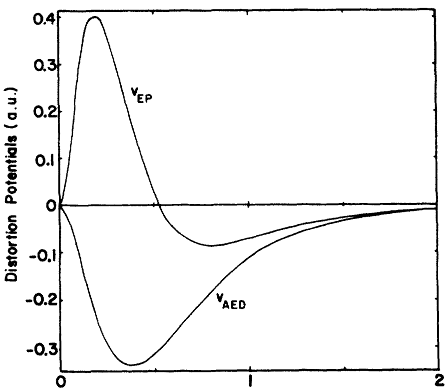

FIG. 1. Distortion potentials $\mathcal{V}_{AED}$ and $\mathcal{V}_{EP}$.

The non-Coulomb p-wave phase shifts [η_1 of Eq. (9)] as obtained from the asymptotic form of the continuum-state solutions of Eq. (3) are given in Table II. The three columns of data refer to calculations with the FCHF ($\mathcal{V} = 0$), AED ($\mathcal{V} = \mathcal{V}_{AED}$), and EP ($\mathcal{V} = \mathcal{V}_{EP}$) approximations used in this work. The FCHF and AED phase shifts are in good agreement with the corresponding calculations of McDowell.[16]

The ansatz [Eq. (1)] is not properly normalized. The error introduced by ignoring the initial-state normalization factor $\langle \Psi_i | \Psi_i \rangle$ is negligibly small.[14] The final state is properly normalized if we replace

$$\phi_k(3) \rightarrow \phi_k(3)/\left[1 + 2\int \omega^2(1,3)\,dx_1\right]^{1/2} \quad (5)$$

in Eq. (1). This was done in the calculations.

In the succeeding discussions, we refer to calculations using FCHF wave functions and neglecting the perturbed orbitals in Eq. (1) as zeroth-order calculations. Then, constructing matrix elements using initial and final states of the form Eq. (1), with the one-electron wave functions obtained from the FCHF method, will be referred to as the first-order corrections. Second-order corrections can be obtained by using the continuum states and

TABLE I. Calculated $2s$ binding energies and experimental ionization energy for lithium.

Approximation	ϵ
FCHF	-0.39362
AED	-0.40008
EP	-0.39349
Experiment (I_{2s})	0.39632

TABLE II. Non-Coulomb p-wave phase shifts for electron scattering from Li^+ in the fixed-core Hartree-Fock (FCHF), adiabatic-exchange dipole (AED), and extended-polarization potential (EP) approximations (in rad).

k	FCHF	AED	EP
0.0	0.1100	0.1670	0.1463
0.05	0.1102	0.1672	0.1465
0.10	0.1107	0.1677	0.1470
0.15	0.1116	0.1687	0.1478
0.20	0.1128	0.1700	0.1489
0.25	0.1143	0.1717	0.1504
0.30	0.1162	0.1738	0.1522
0.35	0.1183	0.1762	0.1543
0.40	0.1207	0.1789	0.1566
0.45	0.1234	0.1818	0.1592
0.50	0.1263	0.1851	0.1619
0.55	0.1294	0.1885	0.1649
0.60	0.1326	0.1921	0.1680
0.65	0.1360	0.1958	0.1711
0.70	0.1395	0.1996	0.1744
0.75	0.1430	0.2034	0.1777
0.80	0.1467	0.2073	0.1810
0.85	0.1503	0.2111	0.1843

$2s$ orbitals of the AED or EP methods.

III. THEORY

The formalism necessary to obtain photoionization cross sections is well known.[17] In the dipole approximation, the electron ejected from the ground state of the lithium atom is in a p-wave state, and the cross sections in the length and velocity forms are

$$\sigma_L = \tfrac{4}{3}\pi\alpha a_0^2 (I+\epsilon) \sum |\vec{\mathrm{M}}_{fi}^{(L)}|^2 , \tag{6}$$

$$\sigma_V = \tfrac{4}{3}\pi\alpha a_0^2 \cdot [4/(I+\epsilon)] \sum |\vec{\mathrm{M}}_{fi}^{(V)}|^2 , \tag{7}$$

where I is the first ionization potential in lithium, $\epsilon = k^2/2m$ is the energy of the ejected electron,

$$\vec{\mathrm{M}}_{fi}^{(L,V)} = \int \Psi_f^*(1,2,3) \sum_j \vec{\mathrm{O}}_j^{(L,V)} \Psi_i(1,2,3)\, d\tau , \tag{8}$$

and $\vec{\mathrm{O}}^{(L)} = \vec{\mathrm{r}}, \vec{\mathrm{O}}^{(V)} = \vec{\nabla}$. The summation is over final-state orbital-projection quantum numbers.

The matrix elements are evaluated after inserting $\phi = \phi_{2s}$ into Eq. (1) for Ψ_i, and $\phi = \phi_k$ into Eq. (1) for Ψ_f using Eq. (5). The continuum state is normalized to

$$\phi_k = r^{-1} R_k(r) Y_{1m}(\hat{r}) , \tag{9}$$

$$R_k(r) \xrightarrow[r\to\infty]{} k^{-1/2} \sin(kr - \tfrac{1}{2}\pi + \eta_1 + \sigma_1 + k^{-1}\ln 2kr) .$$

In the above formulas, $\frac{4}{3}\pi\alpha a_0^2 = 8.56\times 10^{-19}\,\mathrm{cm}^2$, and the remaining quantities are taken in the system of atomic units $\hbar = 1$, $e^2 = 1/m = 2$. η_1 is the non-Coulomb phase shift, and $\sigma_1 = \arg\Gamma(2 + i/k)$.

The matrix element can be readily reduced. Keeping terms linear in ω, we obtain

$$\begin{aligned}\vec{\mathrm{M}}_{fi} = {} & \int d\vec{\mathrm{R}}\, \phi_k^*(\vec{\mathrm{R}}) \vec{\mathrm{O}}(\vec{\mathrm{R}}) [\phi_{2s}(\vec{\mathrm{R}}) - \lambda u(\vec{\mathrm{R}})] + \int\int d\vec{\mathrm{R}}\, d\vec{\mathrm{r}}\, \phi_k^*(\vec{\mathrm{R}}) \{ 2\omega^*(\vec{\mathrm{r}};\vec{\mathrm{R}}) \phi_{2s}(\vec{\mathrm{R}}) \vec{\mathrm{O}}(\vec{\mathrm{r}}) u(\vec{\mathrm{r}}) + 2u^*(\vec{\mathrm{r}}) \phi_{2s}(\vec{\mathrm{R}}) \\ & \times \vec{\mathrm{O}}(\vec{\mathrm{r}}) \omega(\vec{\mathrm{r}},\vec{\mathrm{R}}) - \omega^*(\vec{\mathrm{r}};\vec{\mathrm{R}}) [\vec{\mathrm{O}}(\vec{\mathrm{R}}) + \vec{\mathrm{O}}(\vec{\mathrm{r}})] \phi_{2s}(\vec{\mathrm{r}}) u(\vec{\mathrm{R}}) - u^*(\vec{\mathrm{r}}) [\vec{\mathrm{O}}(\vec{\mathrm{R}}) + \vec{\mathrm{O}}(\vec{\mathrm{r}})] \phi_{2s}(\vec{\mathrm{r}}) \omega(\vec{\mathrm{R}},\vec{\mathrm{r}}) \} ,\end{aligned} \tag{10}$$

where $\lambda = \langle u | \phi_{2s} \rangle$.

The interpretation of the various terms in $\vec{\mathrm{M}}_{fi}$ is as follows: The first integrand contains the zeroth-order effect as well as the effect of nonorthogonality between the $2s$ orbital and the $1s$ orbital. If the continuum state and the $2s$ orbital are obtained from the AED or EP methods, it also contains second-order direct interactions in the final and initial states. The second and third terms contain first-order direct effects in the final and initial states, respectively, while the fourth and fifth terms are interpretable as first-order exchange effects in the final and initial states, respectively. We make a small error by neglecting terms containing products of λ and ω. Section IV contains a justification of these comments.

IV. COMPARISON WITH MBPT

The direct terms of the matrix element [Eq. (10)] are readily derived from MBPT. We illustrate the procedure by discussing the first-order direct final-state term:

$$2\int\int d\vec{R}\,d\vec{r}\,\phi_k^*(\vec{R})\omega^*(\vec{r};\vec{R})\phi_{2s}(\vec{R})\vec{O}(\vec{r})u(\vec{r})\ . \qquad (11)$$

The perturbed orbital ω can be expressed in first order as

$$\omega^*(\vec{r};\vec{R}) = \sum_{j\neq 1s} \frac{u_j^*(\vec{r})}{\epsilon_{1s}-\epsilon_j}\int d\vec{r}\,'\,u^*(\vec{r}\,')v(\vec{r}\,',\vec{R})u_j(\vec{r}\,')\ . \qquad (12)$$

Then Eq. (11) becomes

$$2\sum_{j\neq 1s}\int d\vec{r}\,u_j^*(\vec{r})\vec{O}(\vec{r})u(\vec{r})\int\int d\vec{R}\,d\vec{r}\,' \times\frac{u^*(\vec{r}\,')\phi_k^*(\vec{R})v(\vec{r}\,',\vec{R})u_j(\vec{r}\,')\phi_{2s}(\vec{R})}{\epsilon_{1s}-\epsilon_j}\ . \qquad (11')$$

Equation (11′) differs from the corresponding matrix element of Chang and McDowell[14] only in the form of the energy denominator. The correct denominator should be $\epsilon_{1s}-\epsilon_{2s}+k^2-\epsilon_j$, which differs only slightly from $\epsilon_{1s}-\epsilon_j$ for energies of interest. The diagram corresponding to this first-order final-state effect is shown in Fig. 2.

However, we emphasize that in the present calculation we do not use Eq. (12) to evaluate the perturbed orbital but instead we compute ω using an approximation to Hartree-Fock perturbation theory in analogy to earlier electron-helium scattering calculations.[18] In this calculation, an available parameter is adjusted to yield the experimental dipole polarizability ($0.191a_0^3$). The implications of this procedure will be discussed in Sec. V.

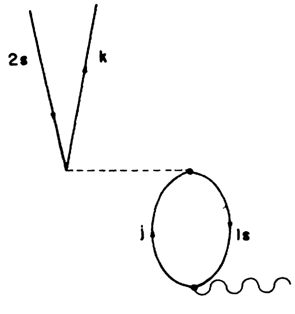

FIG. 2. First-order direct final-state diagram from MBPT.

The first-order direct initial-state correction can similarly be shown to agree with the MBPT result. Further, Callaway[19] has demonstrated that second-order direct corrections to the continuum wave function and the 2s orbital as obtained in the AED or EP methods can be obtained from MBPT using certain reasonable approximations.

Finally, we note that our exchange terms cannot be directly related to the exchange terms of MBPT. In particular, first-order corrections in MBPT only include contributions from p-wave intermediate states, whereas our exchange terms involve both s- and p-wave components of ω. However, even though the s-wave component of ω should not arise in the perturbed matrix elements, we include it in this calculation for consistency. The problem with the exchange interactions appears to be intrinsic to the polarized orbital method.

V. RESULTS

The perturbed orbital ω is decomposed into partial waves. Angular integrations in Eq. (10) are then readily performed after which only the monopole and dipole components of ω remain. If the radial parts of ϕ_{2s} and ϕ_k are obtained from the FCHF method, then Eq. (10) yields the photoionization matrix element, corrected to first order. The separate contributions from the zeroth-order matrix elements as well as the first-order initial- and final-state corrections are listed in Table III for both the length and velocity approximations.

Our zeroth-order matrix elements agree with the results of Chang and McDowell[14] to within 0.5% for all energies considered. Our first-order corrections, however, differ in several respects from the results of MBPT.[14] First, our initial-state correction in the length approximation, although small, is of opposite sign to the MBPT result. This results from the anomalous first-order exchange contribution from the monopole component of ω as mentioned in Sec. IV. In addition, both initial- and final-state first-order corrections in the velocity form decrease in magnitude with increasing energy, contrary to the conclusions of Chang and McDowell. Somewhat better agreement with the MBPT first-order corrections are obtained in all cases if the contributions from the monopole component of ω are neglected.

Photoionization cross sections in the length and velocity approximations, corrected to first-order, are shown in Fig. 3. The results of Chang and McDowell, also correct to first order, are given for comparison. The length and velocity cross sections are seen to be in better agreement with one another when first-order corrections are included.

We have considered two different potentials in obtaining second-order corrections. Both $\mathcal{V}_{\mathrm{AED}}$

TABLE III. Zeroth-order matrix elements and first-order corrections in the length (L) and velocity (V) forms for initial (i) and final (f) states.

k	$L0$	$L1_i$	$L1_f$	$V0$	$V1_i$	$V1_f$
0.00	1.960	−0.014	0.018	−0.3640	0.0767	−0.0937
0.05	1.962	−0.014	0.018	−0.3667	0.0765	−0.0935
0.10	1.966	−0.014	0.018	−0.3746	0.0758	−0.0931
0.15	1.968	−0.014	0.018	−0.3867	0.0748	−0.0924
0.20	1.961	−0.014	0.017	−0.4017	0.0733	−0.0913
0.25	1.939	−0.015	0.017	−0.4180	0.0716	−0.0901
0.30	1.898	−0.015	0.016	−0.4343	0.0694	−0.0885
0.35	1.837	−0.015	0.016	−0.4495	0.0670	−0.0869
0.40	1.758	−0.015	0.015	−0.4626	0.0644	−0.0851
0.45	1.666	−0.016	0.014	−0.4731	0.0616	−0.0833
0.50	1.566	−0.016	0.013	−0.4808	0.0587	−0.0814
0.55	1.462	−0.016	0.013	−0.4858	0.0556	−0.0795
0.60	1.357	−0.016	0.012	−0.4881	0.0523	−0.0774
0.65	1.253	−0.016	0.011	−0.4879	0.0491	−0.0755
0.70	1.150	−0.016	0.010	−0.4855	0.0458	−0.0735
0.75	1.053	−0.015	0.009	−0.4813	0.0425	−0.0718
0.80	0.963	−0.015	0.008	−0.4755	0.0391	−0.0699
0.85	0.879	−0.015	0.008	−0.4684	0.0358	−0.0681

and v_{EP} have the same asymptotic behavior $-0.191/r^4$ at large distances, but differ markedly in their short-range behavior. Figure 1 illustrates the repulsive core of v_{EP}. The wave functions ϕ_{2s} and ϕ_k were obtained using the potentials v_{AED} and v_{EP} as discussed in Sec. III, and therefore contain second-order direct interactions. Second-order exchange contributions are presumed to be small.

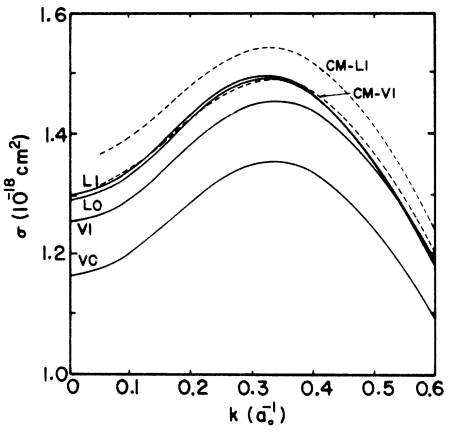

FIG. 3. Photoionization cross sections of lithium. $L0$ and $V0$ are the Hartree-Fock calculations in the length and velocity forms, respectively. $L1$ and $V1$ include first-order corrections as computed in this work, and CM-$L1$, CM-$V1$ indicates the first-order results of Chang and McDowell (Ref. 14).

In Table IV, we give the second-order corrections to the matrix element which are obtained by taking the difference between

$$\int d\vec{R}\,\phi_k^*(\vec{R})\vec{O}(\vec{R})[\phi_{2s}(\vec{R})-\lambda u(\vec{R})]\ ,$$

and $$\int d\vec{R}\,\phi_k^{(0)*}(\vec{R})\vec{O}(\vec{R})\phi_{2s}^{(0)}(\vec{R})\ ,$$

where $\phi^{(0)}$ signifies the FCHF wave function. The entries in Table IV are separated according to whether the initial or final state was corrected and according to whether $v=v_{\mathrm{AED}}$ or $v=v_{\mathrm{EP}}$.

We observe that second-order final-state corrections are substantial, being roughly 50–100% larger in the AED method than in the EP method. However, we note that second-order initial-state corrections effectively cancel second-order final-state corrections in the AED method, whereas no such cancellation occurs in the EP method. The large differences in second-order initial-state effects in the AED and EP methods are due to the distinctive short-range behaviors of v_{AED} and v_{EP}. Small changes in the AED $2s$ wave function (1–3%) give rise to large second-order initial-state effects. The repulsive core of the EP potential partially compensates for the attractive tail and leads to a $2s$ wave function which differs only slightly from the FCHF $2s$ orbital.

Chang and McDowell approximate the second-order MBPT diagrams and obtain corrections in a manner essentially equivalent to the AED method. There are small differences in that they use the calculated value of $0.174a_0^3$ for the polarizability

TABLE IV. Zeroth-order matrix elements and second-order corrections obtained using $\mathcal{V}_{\mathrm{AED}}$ and $\mathcal{V}_{\mathrm{EP}}$ in the length (L) and velocity (V) forms for initial (i) and final (f) states.

k	$L0$	$L2_i$(AED)	$L2_i$(EP)	$L2_f$(AED)	$L2_f$(EP)	$V0$	$V2_i$(AED)	$V2_i$(EP)	$V2_f$(AED)	$V2_f$(EP)
0.00	1.960	−0.255	−0.016	0.308	0.198	−0.3640	0.0410	−0.0063	−0.0458	−0.0256
0.05	1.962	−0.254	−0.017	0.303	0.195	−0.3667	0.0409	−0.0063	−0.0454	−0.0253
0.10	1.966	−0.246	−0.017	0.293	0.188	−0.3746	0.0401	−0.0064	−0.0446	−0.0248
0.15	1.968	−0.236	−0.018	0.277	0.177	−0.3867	0.0391	−0.0065	−0.0432	−0.0238
0.20	1.961	−0.221	−0.018	0.256	0.163	−0.4017	0.0375	−0.0066	−0.0412	−0.0224
0.25	1.939	−0.202	−0.017	0.233	0.148	−0.4180	0.0355	−0.0070	−0.0390	−0.0210
0.30	1.898	−0.181	−0.014	0.209	0.132	−0.4343	0.0334	−0.0072	−0.0365	−0.0192
0.35	1.827	−0.158	−0.010	0.184	0.116	−0.4495	0.0310	−0.0075	−0.0339	−0.0174
0.40	1.758	−0.135	−0.006	0.161	0.101	−0.4626	0.0284	−0.0078	−0.0311	−0.0155
0.45	1.666	−0.113	−0.001	0.139	0.087	−0.4731	0.0257	−0.0082	−0.0283	−0.0137
0.50	1.566	−0.093	0.002	0.120	0.074	−0.4808	0.0231	−0.0084	−0.0256	−0.0117
0.55	1.462	−0.077	0.005	0.102	0.063	−0.4858	0.0208	−0.0087	−0.0228	−0.0100
0.60	1.357	−0.062	0.006	0.087	0.053	−0.4881	0.0185	−0.0087	−0.0203	−0.0083
0.65	1.253	−0.050	0.008	0.074	0.044	−0.4879	0.0164	−0.0088	−0.0178	−0.0067
0.70	1.150	−0.039	0.010	0.062	0.037	−0.4855	0.0144	−0.0088	−0.0155	−0.0052
0.75	1.053	−0.030	0.010	0.052	0.030	−0.4813	0.0127	−0.0087	−0.0132	−0.0038
0.80	0.963	−0.023	0.011	0.044	0.026	−0.4755	0.0112	−0.0085	−0.0111	−0.0025
0.85	0.879	−0.018	0.011	0.037	0.021	−0.4684	0.0098	−0.0084	−0.0092	−0.0013

of Li$^+$ and neglect the nonorthogonality of ϕ_{2s} and u. Their second-order initial-state corrections contained a numerical error which has subsequently been corrected.[20] These corrected results along with their second-order final-state corrections are in good agreement with our corresponding AED calculations.

Total photoionization cross sections as calculated using the AED and EP methods in the length and velocity approximation[21] are given in Fig. 4 and are compared with the experimental results of Hudson and Carter[22] and the corrected[20] MBPT calculations of Chang and McDowell.[14] The experimental data are quoted as accurate to within ±10%. The agreement between the length and velocity cross sections is better than 5% in both the AED and EP methods. We note that the AED calculations are lower than the EP calculations and lie outside the experimental error for all energies considered.

The EP cross sections, however, are in good agreement with experimental data near threshold. As energy increases the calculated cross sections all decrease more rapidly than the experimental data.

VI. CONCLUSIONS

The purpose of the present investigation is twofold. We have demonstrated that the polarized orbital method can readily be extended in photoionization calculations to give first-order corrections to the cross section. However, the first-

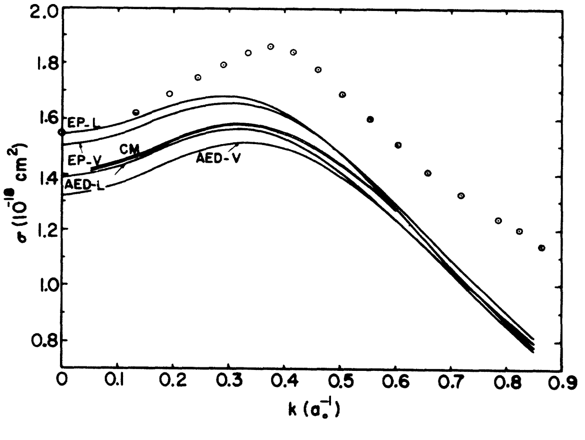

FIG. 4. Photoionization cross sections of lithium, corrected to second order. L and V indicate the length and velocity forms of the matrix elements. The distortion potentials used were AED (adiabatic-exchange dipole) and EP (extended polarization potential). Experimental results of Hudson and Carter (Ref. 22) are given by the circles. The region indicated CM represents the extent of the length and velocity MBPT results of Chang and McDowell (Refs. 14 and 20).

order exchange corrections, although small, are not properly treated in the polarized orbital method. We have further shown that the neglect of first-order corrections may, in part, explain discrepancies in calculated photoionization cross sections using the dipole-length and dipole-velocity approximations.

In addition, we have shown that the extended polarization potential method, which takes into account nonadiabatic effects, gives cross sections which are in better agreement with experimental data than calculations using the AED method.

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[1] A. Temkin, Phys. Rev. 107, 1004 (1957); 116, 358 (1959); A. Temkin and J. C. Lamkin, *ibid.* 121, 788 (1961).

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

[3] P. M. Stone, Phys. Rev. 141, 137 (1966).

[4] R. J. Drachman, Phys. Rev. 138, A1582 (1965); 144, 25 (1966); 173, 190 (1968).

[5] W. R. Garrett and H. T. Jackson, Phys. Rev. 153, 28 (1967).

[6] R. J. W. Henry, Phys. Rev. 162, 56 (1967); 172, 99 (1968).

[7] J. Callaway, R. W. LaBahn, R. T. Pu, and W. M. Duxler, Phys. Rev. 168, 12 (1968).

[8] K. L. Bell and A. E. Kingston, Proc. Phys. Soc. (London) 90, 31 (1967).

[9] D. R. Bates, Monthly Notices Roy. Astron. Soc. 106, 432 (1946).

[10] M. M. Klein and K. A. Brueckner, Phys. Rev. 111, 115 (1958).

[11] J. W. Cooper and J. B. Martin, Phys. Rev. 126, 1482 (1962).

[12] V. P. Myerscough and M. R. C. McDowell, Monthly Notices Roy. Astron. Soc. 128, 288 (1964).

[13] A. H. Boyd, Planet Space Sci. (GB) 12, 729 (1964).

[14] E. S. Chang and M. R. C. McDowell, Phys. Rev. 176, 126 (1968).

[15] The orthogonality between ϕ_{2s} and u in the AED and EP approximations was examined. In standard perturbation-theory calculations there is no requirement that the second-order perturbed state be orthogonal to the core wave functions. Thus, we have not enforced orthogonality in the calculations reported here. In a subsidiary set of calculations, orthogonality between ϕ_{2s} and u was imposed by the use of Lagrange multipliers [cf. R. W. LaBahn, Phys. Letters 26A, 326 (1968)]. The differences in cross sections and energies with and without imposing orthogonality are relatively small and unimportant.

[16] M. R. C. McDowell, Phys. Rev. 175, 189 (1968).

[17] H. A. Bethe and E. F. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms (Academic Press Inc., New York, 1957), p. 295 ff.

[17] R. W. LaBahn and J. Callaway, Phys. Rev. 147, 28 (1966).

[19] J. Callaway, Phys. Letters 29A, 126 (1969).

[20] E. S. Chang (private communication).

[21] For the sake of computing final photoionization cross sections, we have used the AED and EP forms for the continuum (ϕ_k) and bound (ϕ_{2s}) states throughout rather than using the FCHF ($\phi^{(0)}$) wave functions in the first-order matrix elements in Eq. (10). This results in some third-order corrections being included through these perturbed matrix elements. However, their contribution to the final cross sections is essentially negligible.

[22] R. D. Hudson and V. I. Carter, J. Opt. Soc. Am. 57, 651 (1967).