

Photoionization cross sections and dynamic polarizabilities for the lithium atom and positive ion using L^2 basis sets and correlated wave functions

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The photoionization cross sections and dynamic polarizabilities for the lithium atom and its positive ion are calculated using a discrete basis set to represent both the bound and the continuum states of these systems. Using this discrete-basis-set representation, we construct an approximation to the complex dynamic polarizability from which both the photoionization cross section and the frequency-dependent polarizability are extracted. The calculated results agree well with previous theoretical calculations but differ with experimental results, in the case of the neutral atom. The reason for the discrepancy observed among all the theoretical results and the experiments, in the case of the lithium atom, can be established in terms of the sum-rule criterion. When examined under this criterion, the experimental values furnish a total oscillator strength to the continuum states that exceeds the limit imposed by the oscillator strength sum rule $S(0)$, suggesting that the experiments should be in error.

I. INTRODUCTION

In order to understand large number of important phenomena, it is necessary to study photoionization cross sections and dynamic polarizabilities.¹⁻⁶ Therefore the calculation of those properties has become an important problem.

From the theoretical point of view, the main difficulty in determining those properties resides in the need for the continuum wave functions. To circumvent this problem some methods have been proposed in the literature⁷⁻¹³ that avoid the continuum wave functions by using a discrete basis set (L^2) to represent both the bound and the continuum states of the system. As a consequence these methods also avoid the need for explicit inclusion of asymptotic boundary conditions. A further advantage of using L^2 basis sets to represent the continuum states is that the complete methods commonly employed for calculating bound states can be immediately transferred to processes involving continuum states.

The alkali-metal atoms, Li and Na, provide an excellent test for the method discussed briefly below, mainly because none of the previous calculated cross sections, for the neutral species, agree with the available experimental results. For those relatively simple systems reliable wave functions can be constructed from which the effects of electronic correlation and orbital relaxation on the calculated properties can be well described. In the present paper we examine the lithium atom and its positive ion. The sodium atom will be the subject of a future publication.

II. METHOD

The method has been described in detail in Refs. 10 and 14 and only a brief description will be presented here.

The dynamic polarizability is given by

$$\alpha(\omega) = \int_0^\infty \left[\left(\frac{df}{d\varepsilon} \right) / (\varepsilon^2 - \omega^2) \right] d\varepsilon, \quad (1)$$

with

$$\frac{df}{d\varepsilon} = \sum_{n \neq 0} f_{0n} \delta(\omega_{0n} - \varepsilon) + g(\varepsilon), \quad (2)$$

ω_{0n} , f_{0n} , and $g(\varepsilon)$ being the transition frequencies and the oscillator strengths for the bound and continuum transitions, respectively. Extending this definition to complex frequencies leads to

$$\alpha(z) = \int_0^\infty \left[\left(\frac{df}{d\varepsilon} \right) / (\varepsilon^2 - z^2) \right] d\varepsilon. \quad (3)$$

The complex polarizability $\alpha(z)$ is analytical throughout the complex plane except for an infinite number of poles along the real axis and a branch cut in the photoionization interval $\varepsilon_I \leq \text{Re}(z) < \infty$, where ε_I is the first ionization threshold of the system. Since the cross section can be written as¹⁵

$$\sigma(\omega) = \left(\frac{2\pi^2}{c} \right) g(\omega) \quad (4)$$

and since

$$\alpha(\omega + i\eta) = \sum_{n \neq 0} \frac{f_{0n}}{\omega_{0n}^2 - \omega^2} + \text{P} \int_{\varepsilon_I}^\infty \frac{g(\varepsilon)}{\varepsilon^2 - \omega^2} d\varepsilon + \frac{i\pi g(\omega)}{2\omega},$$

as $\eta \rightarrow 0$, we obtain

$$\sigma(\omega) = \lim_{\eta \rightarrow 0} \left(\frac{4\pi\omega}{c} \right) \text{Im}[\alpha(\omega + i\eta)] \quad (5)$$

and

$$\alpha(\omega) = \lim_{\eta \rightarrow 0} \text{Re}[\alpha(\omega + i\eta)] . \quad (6)$$

To make use of Eqs. (5.6), $\alpha(z)$ is first approximated by a finite sum

$$\alpha(z) = \frac{\tilde{f}_{0n}}{\tilde{\omega}_{0n}^2 - z^2} , \quad (7)$$

where \tilde{f}_{0n} and $\tilde{\omega}_{0n}$ stand for the approximated oscillator strengths and transition frequencies obtained from a discrete-basis-set calculation. From Eq. (7) we calculate $\alpha(z)$ at a number of different points in the complex plane. The values of $\alpha(z)$ at these points are fitted by a Padé approximant, providing a representation of $\alpha(z)$ in the complex plane. Using this representation we calculate $\alpha(z)$ on the real axis where it equals $\alpha(\omega)$. The imaginary part of $\alpha(z)$, on the real axis, thereby provides the cross section through Eq. (5). Having the representation for $\alpha(z)$, we can evaluate $\sigma(\omega)$ and $\alpha(\omega)$ at a very large number of points with very little effort.

The uncertainty in choosing the basis set concerns which continuum functions to include. We cannot optimize the basis set as we do for bound-state calculations. Instead, we want an expansion leading to a good description of (at least) the region of the continuum spectra most involved in the process. As shown in Ref. 14 a basis-set criterion can be established once we recognize that $\alpha(z)$ is a Stieltjes series¹⁶ and therefore can be written as

$$\alpha(z) = \sum_{k=0}^{\infty} b_k (-z)^k , \quad (8)$$

with b_k being the moments of a given distribution, $\phi(u)$,

$$b_k = \int_0^{\infty} u^k d\phi(u) . \quad (9)$$

It can be shown that the moments b_k are the moments of the distribution of oscillator strengths and that they are equal to

$$b_k = \sum_{n \neq 0} \frac{f_{0n}}{\omega_{0n}^k} + \int_{\epsilon_I}^{\infty} \frac{g(\epsilon)d\epsilon}{\omega^k} . \quad (10)$$

From Eq. (10) we identify the moments of the distribution of oscillators strengths with the ‘‘sum rules’’ and from this equality we obtain the desired criterion: the basis set is to be chosen so as to generate a discrete distribution of oscillator strengths capable of reproducing the moments (sum rules) of the complete distribution of oscillator strengths. Once this is achieved, and knowing from the theory of moments¹⁷ that a given distribution can be reconstructed once its moments are known, we can say that the finite sum [Eq. (7)] furnishes a good representation of $\alpha(z)$.

The crucial point in the process of calculating the cross sections is the analytical continuation procedure. Once more, the fact that $\alpha(z)$ is a Stieltjes series provides a clue on how to proceed. For this type of series a sequence of $[N + J/N]$ Padé approximants (with $J \geq -1$) will converge, as N goes to infinity, to the function $\alpha(z)$ in the cut.¹⁶ Of course, we hope to achieve convergence with

small values of N . Convergence of the Padé sequence is also an indication of the quality of the discrete representation [Eq. (7)] to $\alpha(z)$. Padé type-II approximants were used in all the calculations.

III. COMPUTATIONAL DETAILS

The ground state of the lithium atom was described by the five-term multiconfiguration (MC) self-consistent-field (SCF) wave function:

$$\Psi(^2S) = c_1 |\phi_{1\bar{s}}^2 \phi_{2s} + c_2 |\phi_{2\bar{s}}^2 \phi_{2s} | + c_3 (|\phi_{2\bar{p}_x}^2 \phi_{2s} | + |\phi_{2\bar{p}_y}^2 \phi_{2s} | + |\phi_{2\bar{p}_z}^2 \phi_{2s} |) , \quad (11)$$

where $\phi_{1\bar{s}}$, $\phi_{2\bar{s}}$, $\phi_{2\bar{p}_x}$, $\phi_{2\bar{p}_y}$, and $\phi_{2\bar{p}_z}$ represent the five natural orbitals used to describe the $1s^2$ lithium pair. A similar wave function, omitting the ϕ_{2s} orbital in the Slater determinants, was used to describe the Li^+ species:

$$\Psi(^1S) = c_1 |\phi_{1\bar{s}}^2 + c_2 |\phi_{2\bar{s}}^2 | + c_3 (|\phi_{2\bar{p}_x}^2 | + |\phi_{2\bar{p}_y}^2 | + |\phi_{2\bar{p}_z}^2 |) . \quad (12)$$

As an approximation to the n^2P continuum states of the lithium atom, we solved for the wave functions:

$$\Psi_n(^2P) = \mathcal{A}(\phi_{1\bar{s}}^2 \phi_{n\bar{p}_x}) , \quad (13)$$

and similarly, for the continuum states of Li^+ ,

$$\Psi_n(^1P) = \mathcal{A}(\phi_{1\bar{s}} \phi_{n\bar{p}_x}) . \quad (14)$$

The shape of the $\phi_{1\bar{s}}$ orbital for the Li^+ was found to be almost identical to the $\phi_{1\bar{s}}$ of the neutral atom, indicating that relaxation effects are negligible. The coefficients c_i of the multiconfigurational wave functions (11) and (12) are shown in Table I.

The final wave functions were obtained from configuration-interaction (CI) calculations. For the ground state of the lithium atom we allowed all the possible excitations (single, double, and triple) among the natural orbitals, while for the continuum states we allowed single and double excitations in the space of the natural orbitals plus one electron in one of the np_x orbitals representing the continuum. Similarly, for the Li^+ system, the ground-state CI wave function includes all single + double excited configurations constructed from the natural orbitals, while for the continuum states we allowed single excitations in the space of the natural orbitals plus one electron in the continuum np_x orbitals. These CI wave functions were then used to evaluate the

TABLE I. Coefficients of the multiconfigurational wave functions for Li [Eq. (11)] and Li^+ [Eq. (12)].

c_i	Li	Li^+
1	0.998 575	0.998 483
2	-0.034 040	-0.036 683
3	-0.023 731	-0.023 703

TABLE II. Dependence of the spectra of the lithium atom upon basis set. f_{0n} is the dipole length oscillator strength and w_{0n} the transition energy (eV).

n	[10s/11p; $\beta=1/1.5$]		[10s/10p; $\beta=1/1.75$]		[10s/9p; $\beta=1.5$] _{opt} ^a	
	f_{0n}	w_{0n}	f_{0n}	w_{0n}	f_{0n}	w_{0n}
1	0.7856	1.873	0.7911	1.881	0.7897	1.876
2	0.0042	3.827	0.0036	3.830	0.0038	3.827
3	0.0049	4.507	0.0036	4.508	0.0036	4.507
4	0.0042	4.859	0.0023	4.821	0.0037	4.858
5	0.0078	5.324	0.0038	5.067	0.0079	5.320
6	0.0159	6.178	0.0115	5.649	0.0157	6.197
7	0.0313	7.810	0.0289	7.103	0.0356	7.904
8	0.0492	11.182	0.0504	10.293	0.0765	13.061
9	0.0670	19.694	0.0701	18.646	0.0727	35.554
10	0.0449	49.836	0.0460	49.012		
11	0.0005	146.941				

^a[]_{opt} derives from a basis set optimized for the P state of lithium (see text).

transition frequencies and oscillator strengths for the various $n^2P \leftarrow 2S$ and $n^1P \leftarrow 1S$ transitions for the Li and Li^+ , respectively. The spectra were used to compute the sum rules and the approximated representations for $\alpha(z)$ [Eq. (7)].

Most of the calculations have been carried out using the Huzinga [9s/6s] expansion¹⁸ of the 1s orbital of the lithium atom plus the (5p) expansion of the 2p orbitals of the boron atom. Another set of calculations has been performed using a (5p) expansion of the 2p orbital for the 2P state of the lithium atom.¹⁹ To these basis sets we added diffuse s and p basis functions to represent the continuum states. The last basis set has been designated []_{opt} (Table II).

It is important in this type of study to have a systematic way of varying both the number of basis functions and the range of exponents of the basis sets. We accomplished that by considering each member of the diffuse s

and p basis sets to have orbital exponents as

$$\xi, \beta\xi, \beta^2\xi, \dots,$$

that is, each orbital exponent being the geometrical factor β times the preceding exponent. Different geometrical factors β_p were used, with the exponents of the p diffuse functions covering approximately the range 0.02–0.004, in order to verify the influence of the basis set on the final results. The β_s factor was taken^{10,14} equal to 1/1.5

In Table II we show the spectra, obtained for the lithium atom, resulting from three different basis sets covering the same range of exponents. It is clear from the examination of the Table II that the spectra are very similar and should therefore produce comparable sum rules. Table III shows that this is indeed the case but also that all the spectra satisfy the sum-rule criterion. This same behavior has been observed for the case of the Li^+ sys-

TABLE III. Sum rules dependence on the basis sets used for the lithium atom. Sum rules are computed in the dipole length approximation.

Basis sets	$S(-4)$	$S(-3)$	$S(-2)$	$S(-1)$	$S(0)$
[10s/11p; $\beta=1/1.5$]	35 030	2416	167.531	11.868	1.005
[10s/10p; $\beta=1/1.75$]	34 675	2401	167.245	11.952	1.011
[10s/9p; $\beta=1/1.5$] _{opt}	34 985	2416	167.877	11.970	1.009
Other results	35 038 ^a	2385 ^a	163.9 ^a	12.14 ^b	
			164.3 ^c	11.53 ^c	
			163.7 ^d		
			164.0 ^e		
Bounds			164.0±3.4 ^f	≤ 12.8±0.6 ^g	1 ^h

^aReference 43.

^bReference 44.

^cReference 45.

^dReference 46.

^eReference 47.

^fReference 42.

^g $S(-1) \leq \sqrt{S(0)S(-2)}$.

^hOnly excitations from the 2s orbital have been considered.

TABLE IV. Largest basis set used with $\beta = \beta = 1/1.5$. Exponents above the solid line are contracted together. Exponents below the dotted lines are considered as diffuse functions (and depend on the choice of β).

<i>S</i> exponents	<i>P</i> exponents
921.1710	11.3413
138.7300	2.4360
31.9415	0.6836
9.3432	0.2134
-----	0.0701
3.1579	-----
0.4446	0.0467
1.1568	0.0208
0.4446	0.0092
0.0766	0.0138
-----	0.0092
0.0286	0.0062
0.0191	0.0041
0.0127	
0.0085	
0.0057	

tem. Consequently one expects that similar results of cross sections and dynamic polarizabilities will arise from calculations using any of those basis sets. This is exactly what has been observed but for the purpose of future discussion we select the results obtained with the $[10s/10p, \beta=1.5]$ basis set shown in Table IV because it produces the smoothest spectrum covering a larger range of the continuum spectra. For the same reasons we choose the $[10s/10p, \beta=1/1.75]$ basis set in the discussion of the Li^+ system. Table V shows the sum rules obtained with these basis sets.

The quality of the wave functions describing the ground states of lithium and lithium ions [Eqs. (11) and (12)], and also the ones describing the first discrete excited states, can be assessed from calculations of properties like ionization potentials, transition energies, and intensities. Table VI shows our results compared to some more elaborate calculations. From Table VI it is clear that the wave functions used, although structurally simple, are quite accurate for the present purposes.

IV. RESULTS AND DISCUSSION

A. Lithium atom

The first theoretical predictions about the lithium photoionization cross section has been made as early as 1929, by Hargreaves²⁰ and Trumphy.²¹ Much later, experiments conducted by Tunsted²² confirmed those predictions that the cross sections should exhibit a maximum value of about 2.4 Mb at a photon energy very close to the photoionization threshold (2200 Å). On the other hand, more elaborate calculations, performed by Stewart²³ and also by Burgess and Seaton,²⁴ indicated a much lower maximum value (1.16–1.4 Mb) at a higher photon energy (1800 Å). The experimental results of Tunsted have been corrected^{25(a)} and extended to the vacuum uv region^{25(b)} by Marr, using new data for the vapor pressure of the atomic lithium. Marr's experimental results showed a much better agreement with the calculations of Stewart²³ and Burgess and Seaton,²⁴ although the experimental maximum cross section still remained somewhat larger than the theoretical predictions. The latest experimental results were obtained by Hudson and Carter,²⁶ and covered the region from 600 to 2300 Å. These authors obtained a maximum cross section of 1.86 Mb at a photon energy of 7.34 eV and these results are the ones used in literature as the standard for comparison purposes.

In the last 20 years several theoretical calculations, using various techniques, have appeared in the literature. They all predict the position of the maximum cross section very close to the photon energy value obtained by Hudson and Carter.²⁶ On the other hand, all the calculations disagree with the experiments on the maximum value of the cross section. Matase and La Bahan,²⁷ using the method of polarized orbitals, obtained a value of 1.48 Mb for σ_{max} ; Chang and Poe,²⁸ using the many-body perturbation theory (MBPT) approach, obtained 1.68 Mb; Amusia *et al.*,²⁹ using the random-phase approximation with exchange (RPAE), obtained 1.6 Mb and, more recently, Serrão³⁰ obtained a maximum cross section of 1.72 Mb. Besides that the theoretical photoionization curves fall off faster than the experimental curve of Hudson and Carter.²⁶

TABLE V. Sum rules with selected basis sets. Sum rules are computed in the dipole length approximation.

Basis sets	<i>S</i> (−4)	<i>S</i> (−3)	<i>S</i> (−2)	<i>S</i> (−1)	<i>S</i> (0)
Lithium atom					
$[10s/10p; \beta=1/1.5]$	35 030	2413	167.254	11.874	1.001
Lithium ion					
$[10s/10p; \beta=1/1.75]$	0.0253	0.0674	0.188	0.572	1.989
Bounds					
Li			164.0±3.4	≤ 12.8±0.6	1
Li ⁺			0.195 ^a	≤ 0.624 ^b	2

^aReference 41.

^bSee footnote (g) on Table III.

TABLE VI. Ground-state energy, first ionization potential, transition energy, and intensity for the first discrete dipole allowed transition for lithium and lithium ion. Ground-state energies (GSE) are in hartrees, ionization potentials (IP), and transition energies (w_{0n}) are in eV, and f_{0n} is in the dipole length approximation.

Calculation	GSE	IP	w_{0n}	f_{0n}
Lithium atom ^a				
HF	-7.423 964	5.104		
MCSCF	-7.462 950	5.308		
MCSCF+CI	-7.464 106	5.338	1.873	0.7856
James and Coolidge ^b	-7.476 08			
Weiss ^c	-7.477 10			0.753
Expt.		5.392 ^d	1.848 ^e	0.753 ^e
Lithium Ion ^f				
HF	-7.2364			
MCSCF	-7.267 881			
MCSCF+CI	-7.267 881	75.383	63.658	0.4537
Sabeli and Hinze ^g	-7.279 91			
Weiss	-7.2781			
Expt.		75.619 ^d	62.254 ^h	

^a $\beta=1/1.5$. w_{0n} and f_{0n} for the $2s \rightarrow 2p$ transition.

^bReference 48.

^cReference 49.

^dReference 50.

^eReference 31.

^f $\beta=1/1.75$. w_{0n} and f_{0n} for the $1s \rightarrow 2p$ transition.

^gReference 51.

^hReference 41.

of Hudson and Carter.²⁶

The fact that calculations using different techniques exhibit a fair agreement among themselves but consistently give rise to lower cross sections than experimentally observed motivated us not only to reexamine the problem from the theoretical point of view but also to examine the experimental results in the light of the sum-rule criterion.

Using the method described in Sec. II and the wave functions from Sec. III, we computed photoionization cross section and dynamic polarizabilities.

Figure 1 shows the results of three distinct analytical continuations^{10,14} compared to the experimental results of Hudson and Carter.²⁶ The figure clearly indicates the convergence of the present calculations, but also, in agreement with the previous calculations, a lower value for σ_{\max} and a faster falloff for the photoionization cross section when compared to the experiments.

At this point it would be appropriate to test the accuracy of the experimental results. Using the sum-rule criterion and the experimental values of the oscillator strength for the $2s \rightarrow np$ discrete transitions, one can calculate how much intensity is left to the continuum transitions, $2s \rightarrow kp$. Since the integrated photoionization cross section is proportional to the sum of the oscillator strengths for the transitions to the continuum, one could try to extract this number from the experimental curve and compare it to its value as predicted by the sum rule $S(0)$.

Using Eq. (4) and expressing the photoionization cross section in Mb and the energy in eV we obtain

$$df_{2s \rightarrow kp} = 9.10728 \times 10^{-3} \sigma(\epsilon) d\epsilon. \quad (15)$$

From the experimental results of Hudson and Carter,²⁶ an analytical expression for $\sigma(\epsilon)$ was derived in the form of a polynomial in $(\epsilon - \epsilon_I)$ times a decreasing exponential in order to assure the correct asymptotic behavior:

$$\sigma(\epsilon) = \sum_{n=1}^N c_n (\epsilon - \epsilon_I)^n e^{-\alpha(\epsilon - \epsilon_I)}, \quad (16)$$

where ϵ_I is the first ionization threshold and c_n and α are adjustable parameters. The best fitting was achieved with

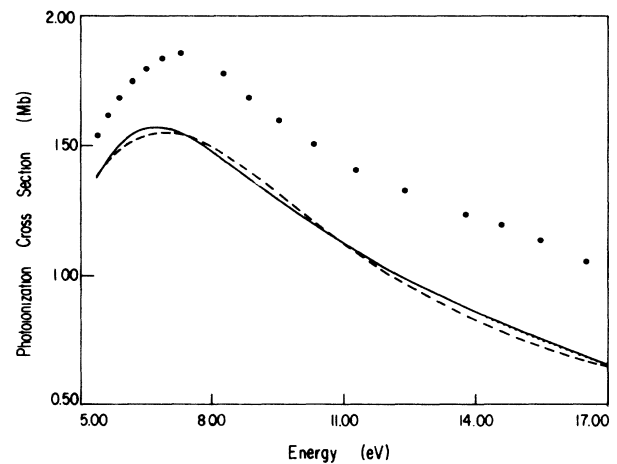


FIG. 1. The dependence of the calculated Li photoionization cross section on different analytical continuations: (—) Padé [4/5]; (· · · ·) Padé [3/4]; (---) Padé [2/3]. The dots represent experimental points (Ref. 26).

$\alpha=0.185$, $n=5$, and the resulting cross section is shown in Fig. 2. Equations (15) and (16) furnished an integrated oscillator strength equal to 0.2667. From the $S(0)$ sum rule the total oscillator strength for the transitions from the $2s$ electron to all the allowed bound and continuum states must be equal to 1. Since the contribution to $S(0)$ from the discrete transitions, known experimentally,³¹ is equal to 0.7685, the total integrated oscillator strength for the transitions to the continuum states, $g(\epsilon)$, must have a maximum value of 0.2315, which is lower than the value extracted from the Hudson and Carter²⁶ experiments. Also, a value of $g(\epsilon)$ higher than the limit imposed by $S(0)$ is obtained from the Hudson and Carter²⁶ data even if we stop the integration at the last experimental point. It is interesting to notice that even if we considered a single sharp transition, at the energy corresponding to the maximum value of the cross section, and carrying all the oscillator strength available to the continuum states, we should not get a cross section as large as the maximum cross section obtained by Hudson and Carter.²⁶ Therefore the sum-rule criterion indicates that the experiments should be in error and that the maximum value of the cross section should be lower than the one determined experimentally.

For the experiments to satisfy the sum-rule criterion, we renormalized the Hudson and Carter²⁶ results such that their integrated oscillator strength was given by the value of $g(\epsilon)$ above. Figure 3 shows the results of the present calculations compared to other theoretical results and the renormalized experimental data. A much better agreement is now observed, although the experimental curve still exhibits a slower falloff.

The presence of lithium dimer in the experimental beam, as recognized by Hudson and Carter,²⁶ is most certainly the reason for the discrepancies observed between the experiment and all the theoretical results. Preliminary calculations³² indicate a quite large (~ 5 Mb) photoionization cross section for the lithium dimer at a threshold energy practically equal to the one for the atomic case. Based on these preliminary data the presence of 10% of the dimer in the experiment should suffice to ex-

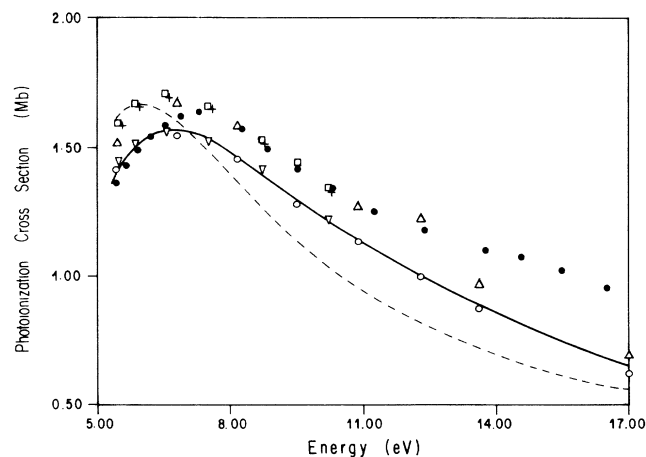


FIG. 3. Comparison of theoretical and experimental photoionization cross sections for lithium atom. Present results in dipole length form (solid line) and dipole velocity form (dashed line). Experimental points (●) are the renormalized results of Hudson and Carter (Ref. 26); (○) Ref. 29; (□) Ref. 28; (△) Ref. 30; (+) Ref. 28; (▽) Ref. 27.

plain the larger values of cross section obtained by Hudson and Carter.²⁶

Several calculations of the dynamic polarizability of the lithium atom have been published,³³⁻³⁶ the most sophisticated one by Muszynka *et al.*,³⁶ who used an 85-term, explicitly correlated, variational wave function. Figure 4 shows our results for the dynamic polarizability, in the normal dispersion region, compared to the Muszynka *et al.* calculations.³⁶ The excellent agreement between the two calculations is another indication of the good quality of the discrete representation [Eq. (7)] to $\alpha(z)$

B. Lithium positive ion

The cross section for the photoionization of the K shell of the neutral atom has been measured by Baker and Tombouljian³⁷ and more recently by Mehlman, Cooper,

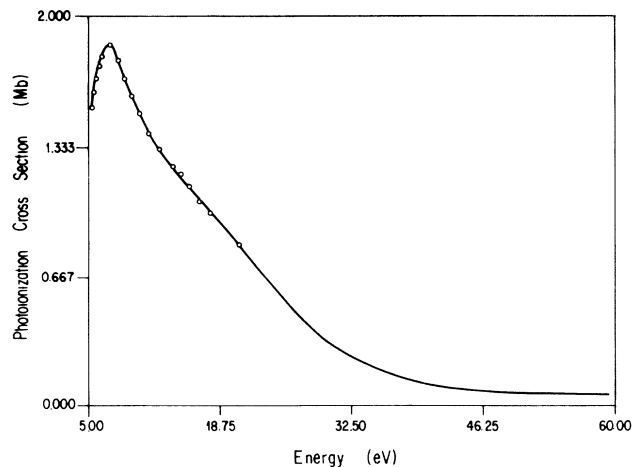


FIG. 2. The best fitting (see text) of the experimental (Ref. 26) photoionization cross section of lithium atom.

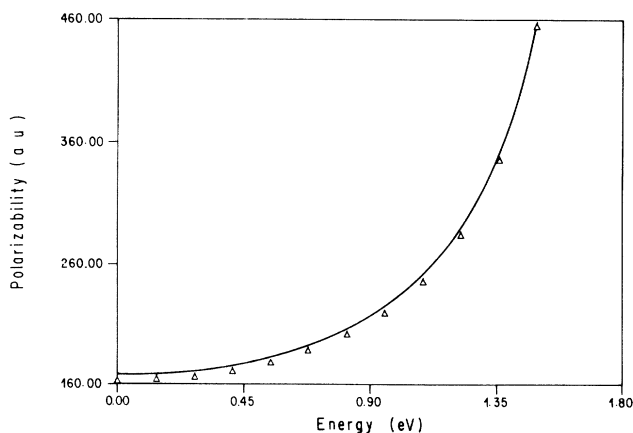


FIG. 4. Theoretical dynamic polarizabilities: solid line, present results; (△) Ref. 36.

and Soloman.³⁸ Although these results refer to the neutral species, they are usually compared to the theoretical calculations on the positive ion, following the suggestion by Bell and Kingston³⁹ that due to the large difference in the binding energy of the 1s electron relative to the 2s electron, the inner-shell photoionization cross section should not be perturbed by the presence of the 2s electron.

The first theoretical calculation of the photoionization cross section for the positive lithium ion was carried out by Bell and Kingston.³⁹ Their results showed qualitative agreement with the available experiments³⁷ but predicted a higher value of σ_{\max} and a much larger ionization threshold than observed experimentally.³⁷ Bell and Kingston attributed the large discrepancy to the fact that Baker and Tomboulian have used a film of metallic lithium to perform the experiments. The strong absorption (1.5 Mb), observed by Baker and Tomboulian at energies below the 1s ionization threshold of the lithium vapor was pointed out by Bell and Kingston as an indication of the effect of the state of aggregation of the lithium on the photoionization cross section. Thus the proper comparison should be made between the theoretical calculations and experiments performed with lithium vapor.

Amusia *et al.*,²⁹ using the RPAE approach, calculated the photoionization cross section for the positive ion and obtained excellent agreement with the results of Bell and Kingston.³⁹ The agreement between the two theoretical calculations gives strong support to the observations of Bell and Kingston about the influence of the state of aggregation of lithium on the value of the cross section.

Further evidence in favor of Bell and Kingston's interpretation has been provided by the experiments of Mehlman, Cooper, and Soloman³⁸ and the recent calculation of Daskan and Ghosh.⁴⁰ Mehlman, Cooper, and Soloman³⁸ measured absolute photoionization cross section for the *K* shell of the lithium vapor and found very good

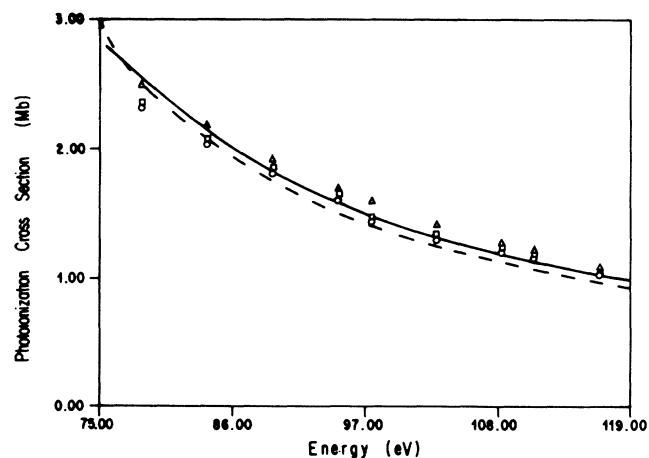


FIG. 5. Comparison of theoretical and experimental photoionization cross sections for Li^+ . Present results in dipole length form (solid line) and dipole velocity form (dashed line). Experimental points (\square) of Mehlman, Cooper, and Soloman (Ref. 38); (\triangle) Ref. 39; (\circ) Ref. 40.

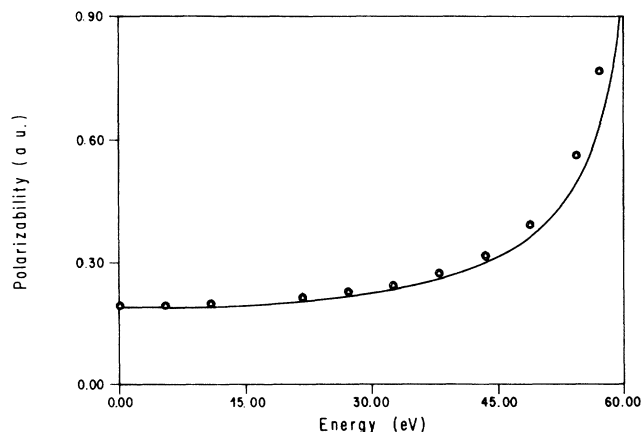


FIG. 6. Theoretical dynamic polarizabilities. Solid line, present results; (\circ) and (\triangle), results by Chung (Ref. 41).

agreement with the previous theoretical calculations^{29,39} and also with the recent theoretical results of Daskan and Ghosh.⁴⁰

Figure 5 shows our results obtained with two different analytical continuations compared to the experiments of Mehlman, Cooper, and Soloman and other theoretical calculation. As in the case of the neutral atom, our calculation exhibits excellent convergence and also very good agreement with the available theoretical and the vapor phase experimental results.

The dynamic polarizability is shown in Fig. 6 together with the results of a much more sophisticated treatment by Chung,⁴¹ who used a 52-term Hylleraas-type wave function in a variational-perturbation calculation. Once more, the excellent agreement between the two results is a good indication of the validity of the discretization procedure implied in Eq. (7).

V. CONCLUSIONS

The results obtained allow us to conclude that a discrete-basis-set expansion can be effectively used to represent the continuum wave functions. This "discretization" of the continuum, together with techniques of analytical continuation, can be efficiently used to calculate cross sections for photoionization once an adequate basis set is chosen.

Besides that, the sum rules can be used not only as a criterion to select the basis sets representing the continuum states but also as a method to assess the quality of the experimental results. As applied to the neutral lithium atom, the sum-rule criterion strongly suggests that the experiments should be reviewed.

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