

BR8816890 LITHIUM PHOTOIONIZATION CROSS-SECTION AND
INIS-BR--1004 DYNAMIC POLARIZABILITY USING SQUARE-
INTEGRABLE BASIS SETS AND CORRELATED
WAVE FUNCTIONS

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ABSTRACT

The photoionization cross-section and dynamic polarizability for lithium atom are calculated using a discrete basis set to represent both the bound and the continuum states of the atom, to construct an approximation to the dynamic polarizability. From the imaginary part of the complex dynamic polarizability one extracts the photoionization cross-section and from its real part the dynamic polarizability. The results are in good agreement with the experiments and other more elaborate calculations.

INTRODUCTION

A large number of important phenomena depend, for their understanding, on the knowledge of photoionization cross-sections and dynamic polarizabilities [1-6]. Because of that the calculation of these properties has become an important problem in theoretical chemistry. The main difficulty in determining these properties resides in the need for the continuum functions.

In the method to be discussed below, we avoid the continuum functions, using a discrete basis set (L^2) to represent both the bound and the continuum states of the system. Another advantage of the method is that it also avoids the need for explicit inclusion of asymptotic boundary conditions. This method has been used to calculate photoionization cross-sections for He ($2^1S, 2^3S$), H^- [7], He (1^1S) and H_2 [8].

METHOD

The dynamic polarizability is given by
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$$\alpha(\omega) = \int_0^{\infty} [(df/d\epsilon)/(\epsilon^2 - \omega^2)] d\epsilon \quad (1)$$

with

$$df/d\epsilon = \sum_{n \neq 0}^{\infty} f_{on} \delta(\omega_{on} - \epsilon) + g(\epsilon) \quad (2)$$

ω_{on} , f_{on} and $g(\epsilon)$ being the transition frequencies and the bound and continuum oscillator strengths, respectively. Extending this definition to complex frequencies leads to

$$\alpha(z) = \int_0^{\infty} [(df/d\epsilon)/(\epsilon^2 - z^2)] d\epsilon \quad (3)$$

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 $\epsilon_1 \leq \text{Re}(z) < \infty$, where ϵ_1 is the first ionization threshold of the system. Since the cross-section can be written as (ref. [9])

$$\sigma(\omega) = (2\pi^2/c)g(\omega) \quad (4)$$

and since

$$\alpha(\omega + i\eta) = \sum_{n \neq 0} \frac{f_{on}}{\omega_{on}^2 - \omega^2} + P \int_{\epsilon_1}^{\infty} \frac{g(\epsilon) d\epsilon}{\epsilon^2 - \omega^2} + i \frac{\pi g(\omega)}{2\omega}$$

as $\eta \rightarrow 0$, we obtain the relationships

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

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

To use eqs. (5-6), $\alpha(z)$ is first approximated by a finite sum

$$\alpha(z) = \sum_{n \neq 0} \bar{f}_{on} / (\bar{\omega}_{on}^2 - z^2) \quad (7)$$

where \bar{f}_{on} and $\bar{\omega}_{on}$ stand for the approximate oscillator strengths and transition frequencies obtained from a discrete basis-set calculation. Using eq. (7) we calculate $\alpha(z)$ at a number of points in the complex plane. 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 to $\alpha(w)$. The imaginary part of $\alpha(z)$ on the real axis thereby provides the cross-section by eq. (5). Having the representation for $\alpha(z)$, we can evaluate $\sigma(w)$ and $\alpha(w)$ at a very large number of points with little effort.

As discussed in detail in refs. [7,8], the basis set is chosen as to generate a discrete distribution of oscillator strengths capable of reproducing the moments (sum-rules) of the continuous distribution of oscillator strengths. Once this is achieved one can say that the finite sum in eq. (7) furnishes a good representation for $\alpha(z)$.

One crucial point is the process of calculating the cross-section is the analytical continuation procedure, as discussed in ref. [7]. Padé type II approximants were used in all the calculations, to perform the analytical continuation.

COMPUTATIONAL DETAILS AND RESULTS

All calculations were carried out using Huzinaga gaussian basis sets [10], augmented with diffuse s and p basis whose orbital exponents have been chosen as a geometrical factor, β , times the previous exponent

$$\phi, \beta\phi, \beta^2\phi, \dots$$

Tight p functions of boron atom were also included to provide the right orbital size to describe angular correlations.

The ground state of lithium atom was described by the five term MCSCF [11] wave function

$$f(^2S) = c_1 |\phi_{1\bar{s}}^2 \phi_{2s}| + c_2 |\phi_{2\bar{s}}^2 \phi_{2s}| + c_3 (|\phi_{2\bar{p}_x}^2 \phi_{2s}| + |\phi_{2\bar{p}_y}^2 \phi_{2s}| + |\phi_{2\bar{p}_z}^2 \phi_{2s}|) \quad (8)$$

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.

As an approximation for the n^2P continuum states, we solved for the wave functions

$$\psi(^2P) = A[\phi_{1\bar{s}}^2 \phi_{np_x}]$$

where $\phi_{1\bar{s}}$ is the doubly occupied $1s$ orbital of lithium. The shape of the $\phi_{1\bar{s}}$ for Li^+ was found to be very similar to $\phi_{1\bar{s}}$ indicating that relaxation effects could be negligible. The final wave functions were obtained from CI calculations. For

the ground state we allowed all possible excitations (S+D+T) among the natural orbitals, while for the continuum states we allowed (S+D) in the natural orbital space plus one electron in the P orbitals representing the continuum. The CI wave functions [12] were used to evaluate oscillator strengths and transition frequencies for various $^2P+^2S$ transitions, which, in turn, were used to compute sum-rules.

Table I shows the spectrum used to compute the complex dynamic polarizability and table II presents the sum-rules. Figure I shows the photoionization cross-section compared with the experimental results [13] and Fig. II shows the results of other theoretical calculations [14]. Figure III shows the dynamic polarizability. It is interesting to notice that while the agreement among the theoretical results is good, none of them reproduce the maximum value of the experimental cross-section (1.85Mb). On the other hand the experimental sum of oscillator strengths for the discrete transitions is 0.77 [17], leaving 0.23 for all the other transitions before the $1s \rightarrow 2p$ channel is open. Working backwards from the expression for the cross-section one finds that, for the maximum experimental value to be achieved it would be necessary to concentrate all the oscillator strength left for the continuum transitions on that particular energy corresponding to the maximum value of the cross-section. The curve should be very sharp at that point and should fall down much faster than it is experimentally or theoretically observed.

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Table I
Transition energies (eV) and oscillator strenghts

A		B		C	
f_{on}	w_{on}	f_{on}	w_{on}	f_{on}	w_{on}
0.785	1.873	0.786	1.873	0.786	1.873
0.004	3.827	0.004	3.827	0.004	3.827
0.006	4.572	0.006	4.572	0.007	4.514
0.015	5.428	0.015	5.427	0.016	5.874
0.032	7.094	0.032	7.094	0.031	7.525
0.054	10.526	0.054	10.526	0.051	10.922
0.069	19.126	0.069	19.127	0.067	19.470
0.047	49.387	0.047	49.386	0.045	49.657

Table II.
Sum-Rules

K =	-2	-1	0	1	2
A	167.6	11.94	1.015	0.227	0.232
B	167.6	11.94	1.013	0.226	0.225
C	167.6	11.95	1.015	0.226	0.225
exp	164.0*		1.000		

*See ref. 18

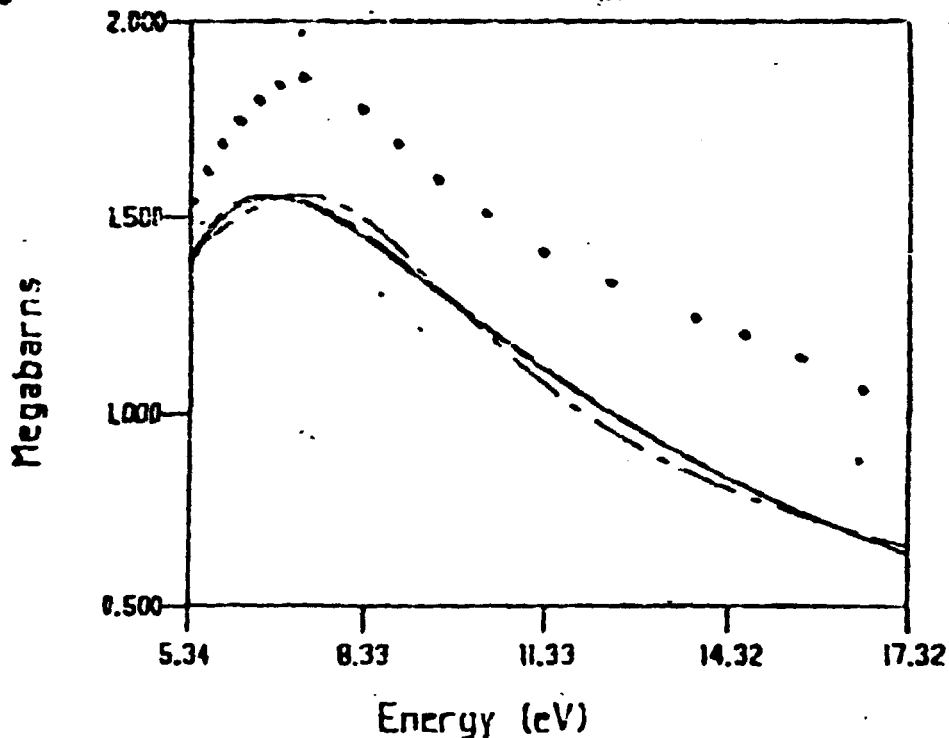


FIGURE 1

Photoionization Cross-sections; σ , experimental result (13); _____, present result, basis set using 10p for the p virtual orbitals and 10s10p for the 2S fund. state; _____, 11p for the p and 10s10p for the 2S state; _____, 10p for the p and 10s5p for 2S state

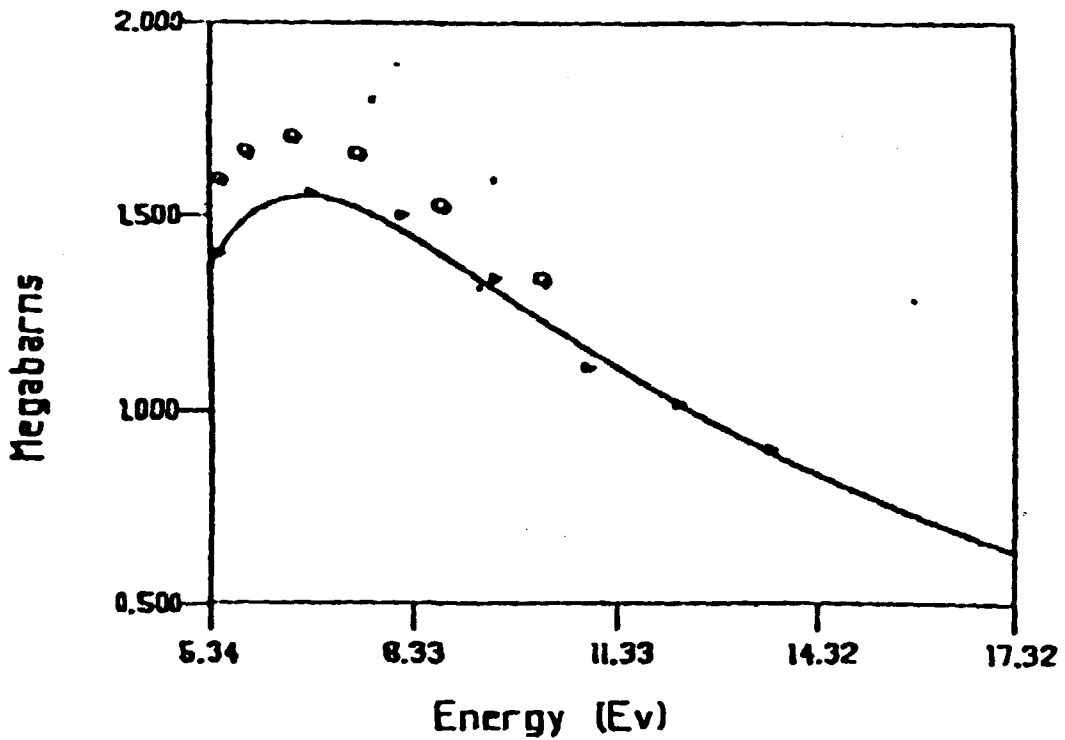


FIGURE II - Photoionization Cross-sections; solid line, this work (10p for p and 10s10p for 2S state); Δ , Amusia et al (14); \square , +, Chang and Poe in the dipole L and V formulations.

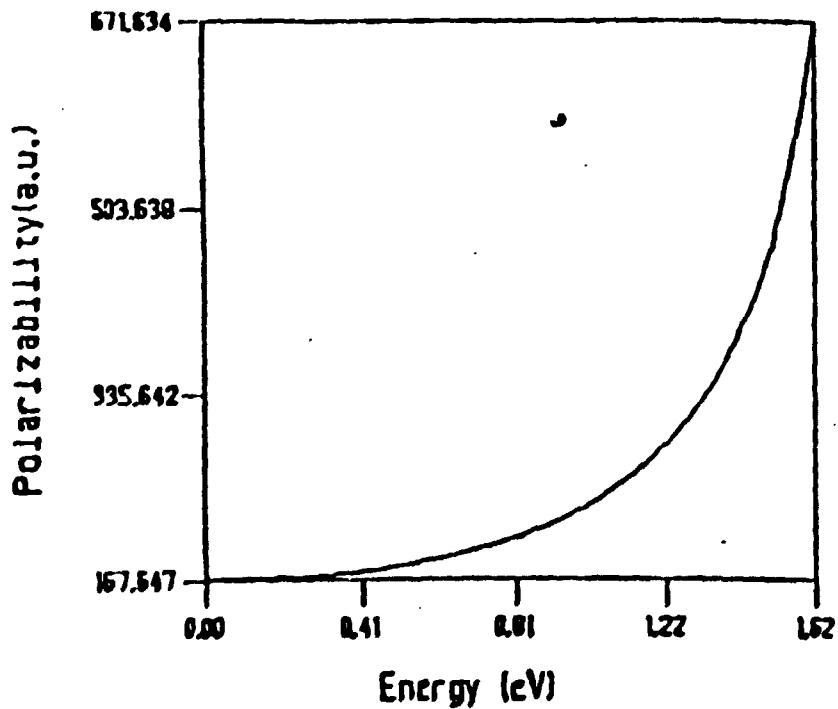


FIGURE III - Dynamic Polarizability, up to the threshold of the first excited state. (All the basis sets give very similar results).