PHYSICAL REVIEW A VOLUME 23, NUMBER 6 JUNE 1981

Saddle-point technique for autoionizing states of the lithium atom. I. $^2P^o$ resonances in the elastic scattering region

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(Received 29 October 1980)

A total of eleven autoionizing ^2P resonances has been observed by Ederer *et al.* in the lithium absorption spectrum below the $2\,^3S$ Li$^+$ threshold. In this work, all eleven states have been calculated using a saddle-point technique. The results of this calculation agree with those of experiment. For the highest-eight resonances, the present results are higher by an average of 0.010 eV. The errors of the lowest-three resonances are slightly larger. A perturber which is presented in the observed spectrum is positively identified. The full effect of this perturber is studied with the concept of dynamic coupling. The oscillator strength and the various radial expectation values of these states are also calculated.

I. INTRODUCTION

The absorption spectrum of the autoionizing states of Li atom was accurately measured ten years ago.[1] However, the understanding and interpretation of these results is far from settled. The reason for this is twofold. First of all, there are six possible series which may converge towards the four different series limit, namely, the $2^{1\,3}S$ and $2^{1\,3}P$ states of Li$^+$. These six series may or may not couple together strongly. Secondly, there is a lack of a thorough and accurate theoretical calculation carried out for these autoionizing states. Many other experimental observations of the Li$\,^2P$ states have been reported. For example, by Cantu *et al.*[2] using the flash-pyrolysis technique, by Pegg *et al.*[3] using projectile-electron spectroscopy, and by Ziem *et al.*[4] using H$^+$ and He$^+$ bombardment. Most experimental results are reported with very small uncertainties. All of these results are in very good agreement with each other.

Theoretically, the situation is more obscure. Although the results of Weiss[5] appeared to agree with that of the lowest-five states observed, the method he used is very approximate in nature, and not suitable for making accurate predictions. A better method was developed by Temkin and collaborators,[6] but the application of this method[7] has been limited to the lowest few resonance leaving the main question unanswered. That is, in the elastic scattering region a perturber is observed in the optical spectrum of Ederer *et al.*[1] and Cantu *et al.*[2] No attempts have been made to explain the nature of this perturber. Energywise the theoretical result of Wakid *et al.*[8] appears to be very impressive, but their work differs substantially with Refs. 1 and 2 on the classification of resonance. For example, the $[(1s2s)^3S, 4p]$ and $[(1s2s)^3S, 5p]$ states in these two references are classified in Ref. 8 as the $[(1s2s)^1S, 3p]$ and $[(1s2s)^3S, 4p]$ states, respectively. With the lack of the rigorous upper-bound property in calculating the energy of these autoionizing states, the apparent closeness of the energy to that of the experiment can no longer be used as the only criterion in evaluating the theoretical results. Cooper *et al.*[9] also made a close-coupling calculation for the ^2P resonances, but their calculations are limited to the resonances above the $2\,^3S\,$Li$^+$ threshold. A simple model potential method is carried out by Barden *et al.*,[10] only the lowest resonance is investigated in this reference.

Recently, a saddle-point method was developed.[11] The application of this method in the He and He$^-$ systems shows that the method is not only effective in calculating resonances in the elastic scattering region but also in the inelastic as well as multipuly excited energy regions.[12,13] In this work a detailed calculation will be carried out for the eleven resonances observed below the $2\,^3S$ threshold to further demonstrate the utility of this saddle-point technique. In Sec. II, the saddle-point method will be outlined. Section III gives the results of this calculation before dynamic coupling is considered. Section IV gives the results of oscillator strengths and moments of these states. Section V discusses the concept of dynamic coupling and the results obtained from this coupling. Comparison of the theoretical results and those of experiments is given in Sec. VI.

II. SADDLE-POINT METHOD

The problem with calculating autoionizing states is the fact that although they comprise a discrete spectrum of the Hamiltonian, they lie in the continuum and coupled to the continuum via Coulomb interaction. In many cases the coupling to this continuum is very weak and the autoionizing width will in turn be narrow. In these instances, the continuum contributes very little to the energy of the resonance as well as to other characteristics such as its optical transition probability to lower states. Hence many properties of this system can be accurately studied if the discrete energy and wave function of the resonance can be obtained.

In 1961 Fano[14] formulated his well-known theory of configuration interaction which explicitly examines the effect of the interaction of the discrete spectrum with the continuum. However, the method of obtaining such discrete spectrums is not explicitly spelled out in this reference. One way to obtain such a spectrum explicitly is the method of Feshbach projection operators.[15] In this formulism, the discrete spectrum of the system is associated with the eigenvalues of the QHQ operator where Q is the closed-channel projection operator. However, in this theory the projection operators Q and P, which is the open-channel projection operator are not uniquely defined for any system. They are only uniquely defined in the asymptotic sense.[16]

Another fundamental handicap with the projection-operator approach is the fact that for systems with three or more electrons the idempotant property of the P and Q operator can not be satisfied due to the Pauli antisymmetry principle and the electron correlation. To circumvent this problem, a quasi-projection-operator method was developed by relaxing the idempotent condition.[6] For many systems this gives rise to a number of predictable spurious singularities. This method is in close analogy to the QHQ approximation, utilizing the target states in constructing the Q operator. However, in real calculations one can only use a highly approximate expression for these states[7] because the computation effort will be drastically increased if a better target-state wave function is to be used. A poorer target state always results in a lower resonant energy.

Recently, a method has been developed by taking a different approach.[11] It is well known that the existence of the closed-channel resonances is due to the excitation of the core electrons. In some instances, the resonant configuration is complicated due to degeneracy but the simple feature that a particular core electron or electrons have been excited thus leaving a well-defined vacancy in the inner shell is easily visualized. Therefore if one can build such a vacancy into the wave function, the closed-channel resonances should come out naturally as the discrete spectrum of the Hamiltonian. Such a wave function can be given by

$$\Psi = A[1 - |\phi_0(\vec{r}_j)\rangle\langle\phi_0(\vec{r}_j)|\,]\psi(\vec{r}_1, \vec{r}_2 \cdots \vec{r}_j, \cdots \vec{r}_n)\,. \quad (1)$$

Here we are assuming the $\phi_0(\vec{r})$ is the wave function of the vacancy orbital, of which electron j has the same symmetry, and is therefore the only particle that may fill the vacancy.

The problem is now reduced to finding a way to properly determine the orbital wave function ϕ_0. In Ref. 11, a theorem is proved which shows that if one parameterizes ϕ_0 and ψ, the discrete resonant spectrum of the Hamiltonian can be obtained by maximizing the parameters in ϕ_0 and minimizing the parameters in ψ in the Ritz-Raleigh variation method:

$$\delta\langle H\rangle = \delta\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = 0\,. \quad (2)$$

In this way, the energy, the wave function of the resonant state, and the vacancy orbital are obtained in this variation process. In applying this technique to two electron systems,[12] it is found that highly accurate results can be obtained by assuming the vacancy to be hydrogenic. In fact, in an attempt to improve the vacancy orbital by making it more flexible does not change the result of Ref. 12 appreciably. This seems to suggest that unlike the structure of the particle orbitals, the structure of the vacancy is relatively simple. This further lends incentive to this saddle-point technique.

In applying this method to the Li ^2P resonances of interest, the nonrelativistic Schrödinger equation is

$$\left[-\sum_{i=1}^{3}\left(\frac{1}{2}\nabla_i^2 + \frac{3}{r_i}\right) + \sum_{i<j}^{3}\frac{1}{r_{ij}}\right]\Psi = E\Psi\,. \quad (3)$$

In LS coupling the trial function Ψ is expanded in terms of a basis set whose angular component is given by

$$Y^{l_3, LM}_{l_1 l_2; L_{12}}(\hat{r}_1, \hat{r}_2, \hat{r}_3) = \sum_{\substack{m_1 m_2 \\ m_3 \mu}} Y^{m_1}_{l_1}(\hat{r}_1) Y^{m_2}_{l_2}(\hat{r}_2) Y^{m_3}_{l_3}(\hat{r}_3) \times\langle l_1 l_2 m_1 m_2 | L_{12}\mu\rangle \times\langle L_{12} l_3 \mu m_3 | LM\rangle\,, \quad (4)$$

and the spin part is given by

$$\chi(1,2,3) = (\alpha(1)\beta(2) \mp \alpha(2)\beta(1))\alpha(3) - (1\mp 1)\alpha(1)\alpha(2)\beta(3)\,. \quad (5)$$

Here the Clebsch-Gordan coefficients and spin functions α, β are defined in the usual manner.[17] The $\mp$ are chosen so that the total wave function satisfies the Pauli antisymmetry principle. $L=1$ for ^2P states. The radial part is given by

$$\phi_{mnk}(r_1, r_2, r_3) = r_1^m r_2^n r_3^k e^{-(\alpha_i r_1 + \beta_i r_2 + \gamma_i r_3)}\,, \quad (6)$$

where α_i, β_i, γ_i are the nonlinear parameters associated with a particular angular- and spin-component basis element. Combining these, the basis functions become

$$\psi^{l_1 l_2 L_{12} l_3}_{mnk}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \phi_{mnk}(r_1, r_2, r_3) Y^{l_3, LM}_{l_1 l_2; L_{12}}(\hat{r}_1, \hat{r}_2, \hat{r}_3) \times \chi(1,2,3) \qquad (7)$$

For the closed-channel resonances of interest, the vacancy within the system is usually the 1s orbital. In some cases the 2s orbital also needs to be built in. These orbitals are taken to be

$$\phi_{n0} = N R_{n0}(r) Y^0_0(\theta, \phi) , \qquad (8)$$

where

$$R_{n0}(r) = e^{-qr/n} L^1_n\left(\frac{2qr}{n}\right) \qquad (9)$$

and L^1_n is the associated Laguerre polynomial.[18] q is the parameter to be optimized and N is the normalization constant for ϕ_{n0}. The total wave function becomes

$$\Psi = A \sum C^{l_1 l_2 L_{12} l_3}_{mnk} (1 - P) \psi^{l_1 l_2 L_{12} l_3}_{mnk}(\vec{r}_1, \vec{r}_2, \vec{r}_3) , \qquad (10)$$

where the C's are the linear parameters and P is the projection operator constructed from ϕ_{n0}. The parameters and the energy are then determined from Eq. (2). For ease of discussion, we will use the notation $[(l_1, l_2)^k L_{12}, l_3]$ to represent a particular angular and spin partial wave. Here $l_1 l_2$ forms a two-electron core of spin multiplicity k and angular momentum L_{12}. This L_{12} again couples with the angular momentum of the third electron to give the ^2P state of interest.

III. COMPUTATIONAL ASPECTS AND RESULTS

A. $[(2s2p)^3P, 1s]^2P$ and $[(2s2p)^1P, 1s]^2P$

The lowest ^2P resonance observed by Ederer *et al.*[1] is 58.910 eV above the ground state of lithium. In atomic units, this corresponds to an energy of −5.312 97 a.u.[19] It is classified in Ref. 1 as a $[(2s2p)^3P, 1s]^2P$ resonance. This classification is probably appropriate. In a $[(s,p)^3P, s]$, one partial wave, ten linear parameter calculation we obtain an energy of −5.293 34 a.u. Here the nonlinear parameters are $\alpha_1 = 1.02$, $\beta_1 = 0.95$, and $\gamma_1 = 2.85$. In this calculation, a vacancy is built into the first s electronic coordinate. The q value in the vacancy orbital is chosen to be the optimized value 2.46 for this state. However, if this wave function is further expanded by increasing the linear parameters and by including the partial waves such as $[(p,d)^3P, s]$ and $[(d,f)^3P, s]$, etc., we found the convergence is slow and the result is still away from the experimental position. This is because for this low-lying state, the correlation effects of all three electrons is strong and the configurations are complex. Realizing this situation, we recalculate the energy with partial waves which simulate $[(1s2s)^1S, 2p]$, $[(1s2p)^1P, 2s]$, $[(1s2p)^3P, 2s]$, $[(1s2s)^3S, 2p]$, $[(1s2p)^3P, 3d]$, and $[(1s2p)^1P, 3d]$ configurations. The final result −5.312 184 a.u. is obtained with 13 partial waves and 104 linear parameters. This result is given in Table I. In this table, the partial waves are given with the associated nonlinear parameters in the radial functions. These parameters are optimized in-

TABLE I. Energies and wave functions of the $[(2s2p)^3P, 1s]^2P$ and $[(2s2p)^1P, 1s]^2P$ states of the lithium atom (in a.u.). In this table, α, β, γ are the nonlinear parameters and N is the number of linear parameters for each angular partial wave. $-\Delta E$ is the binding energy contributed by including the corresponding angular partial wave. q is the parameter in the vacancy orbital.

		$[(2s2p)^3P, 1s]^2P$, $q = 2.46$			$[(2s, 2p)^1P, 1s]^2P$, $q = 2.52$		
	Angular wave	α, β, γ	N	$-\Delta E$	α, β, γ	N	$-\Delta E$
1	$[(s,s)^1S, p]$	3.0, 1.36, 0.75	10	5.249 518	3.0, 1.26, 0.65	20	5.099 817
2	$[(s,p)^1P, s]$	3.0, 0.86, 0.85	20	0.050 390	3.0, 1.16, 0.85	10	0.102 955
3	$[(s,p)^3P, s]$	3.0, 1.36, 0.65	10	0.002 608	3.0, 1.46, 0.60	20	0.016 107
4	$[(s,s)^3S, p]$	3.0, 1.01, 0.70	10	0.000 229	3.0, 1.11, 0.75	10	0.006 190
5	$[(s,p)^3P, d]$	3.0, 1.46, 0.85	10	0.005 045	3.0, 1.46, 0.85	10	0.020 776
6	$[(s,p)^1P, d]$	3.0, 1.36, 0.95	10	0.001 562	3.0, 1.26, 0.85	10	0.008 280
7	$[(p,d)^1P, s]$	3.0, 2.66, 0.55	10	0.001 265	1.0, 1.4, 3.0	4	0.000 081
8	$[(d,f)^1P, s]$	3.0, 3.70, 0.75	4	0.000 137	0.9, 1.8, 3.0	4	0.000 806
9	$[(p,p)^1S, p]$	3.0, 2.86, 0.75	4	0.000 803	3.0, 2.66, 0.75	4	0.000 722
10	$[(p,p)^3S, p]$	2.9, 2.26, 0.75	4	0.000 453	2.9, 1.86, 0.65	4	0.000 431
11	$[(p,d)^3P, s]$	3.0, 3.06, 0.95	4	0.000 072	3.0, 2.26, 0.85	4	0.000 607
12	$[(d,d)^1S, p]$	4.2, 4.1, 0.75	4	0.000 072			
13	$[(d,d)^3S, p]$	3.4, 2.5, 0.75	4	0.000 027			
14	$[(p,d)^1P, d]$				2.90, 2.0, 1.05	4	0.000 038
15	$[(p,d)^3P, d]$				3.05, 1.80, 1.05	4	0.000 056
Total			104	5.312 185		108	5.256 864

dividually in the presence of most of the other partial waves in the total wave function. To a certain extent the value of the optimized nonlinear parameter represents the principal quantum number of the electron orbital. For example, for the first six partial waves $\alpha = 3.0$ clearly suggest that this electron is in the $1s$ state. On the other hand, functions of the seventh and eighth partial waves seem to improve the core states of the second partial wave. The ninth and twelfth partial waves are to improve the states of the first partial wave, etc. In calculating the energy of the autoionizing three-electron system, there are many ways the angular momentum of the three electrons may couple to give the desired symmetry. In actual calculations, we always find that the most effective terms are those which improve a relevant core state. In Table I, N is the linear parameter used in each partial wave and $-\Delta E$ is the contribution to the binding energy obtained by including the corresponding partial wave. Here one must realize that this energy contribution is sensitively dependent on the order in which a partial wave is included in the wave function, especially when the partial waves are not orthogonal. Nevertheless, it does give a reliable measure as to the importance of the partial wave to the total wave function. In this calculation, the $1s$ vacancy is built into the first three partial waves. The $1s$ vacancy in the fourth partial wave is taken care of by the Pauli exclusion principle.

For the second lowest resonance, the experimental energy appears at 60.396 eV or $-5.258\,359$ a.u. This state is classified as a $[(2s2p)^1P, 1s]^2P$ resonance in Ref. 1. In our calculation, if a 10-term $[(s,p)^1P, s]$ wave function is used, the lowest energy is -5.2146 a.u. If another 10-term $[(p,d)^1P, s]$ partial wave is included in the wave function to improve the core state, the energy becomes -5.2454 a.u. The q value in the vacancy is optimized to be 2.52. Rigorously speaking, since this is the second $^2P^o$ autoionizing state, it should correspond to the second lowest root. To account for this, a 10-term $[(s,p)^3P, s]$ function is also included. In this case, the second lowest root of the secular equation becomes $-5.246\,95$ a.u. This seems to suggest that the classification of Ref. 1 is probably appropriate. However, the energy obtained by expanding the wave function along this line of approach does not converge to the experimental value quickly. With this in mind a wave function of the character of the lowest state with 13 partial waves and 108 linear parameter was used to obtain an energy of $-5.256\,864$ a.u. for this state. These results are given in Table I. Compared with the experimental result, there is a difference of 0.001 495 a.u. or 0.0407 eV. This is still very disappointing in view of the size of the wave function and the partial waves used. As it turns out, this is the worst result among the 11 resonances investigated. Notice that in this table, the seventh and eigth partial waves are used primarily to represent a better $[(2s2p)^1P, 1s]^2P$ state. The contribution of the seventh partial wave is small because of the presence of fifth and sixth partial waves.

B. $[(1s2s)^3S, np]^2P$, $n = 3$ to 6

In calculating the higher roots of the secular equation, the situation becomes much simpler in that it becomes apparent which angular partial wave contributes more to the energy. Many partial waves which make a substantial contribution in the two lower states are no longer important. This allows us to use more terms in the main partial waves and to be more selective in using these terms. For example, in calculating the contribution from the first partial wave for the $n = 3$ state, we first compute the energy E, from a 60-term wave function. The 60 linear parameters are then determined. After examining the absolute value of the coefficients of the normalized basis functions, the wave function is reordered according to the coefficients in descending order. The contribution of each term to the energy is then examined. If the term contribution is too small, it will be dropped. The final resulting energy after excluding 20 terms is then compared with E to see whether the 40 selected terms give an energy sufficiently close to E. All this can be done with an efficient computer code.

It is fairly easy to decide the classification of the higher states. For example, for the $[(1s2s)^3S, 3p]^2P$ calculation, using a single partial wave $[(s,s)^3S, p]$ and nonlinear parameters: $\alpha = 3.095$, $\beta = 0.895$, and $\gamma = 0.585$, the second lowest root of the secular equation becomes $-5.175\,508$ a.u. Since the lowest state of this configuration is $1s2s2p$, the second one must be $1s2s3p$ or $1s2p3s$. Judging from the coupling of the spin and the nonlinear parameters, one must conclude that it is a $[(1s2s)^3S, 3p]^2P$ resonance. Interestingly, if a seven term $[(s,p)^3P, d]$ wave function is added, the second root becomes $-5.179\,105$ a.u., but if a $[(s,p)^3P, s]$ partial wave is included, this root immediately becomes the third lowest. This is expected because this partial wave together with the first partial waves allows $[(2s2p)^3P, 1s]^2P$ and $[(2s2p)^1P, 1s]^2P$ to be formed. The final result $-5.183\,387$ a.u. is obtained by using an 8 partial wave, 93 linear-parameter wave function. This result is given in Table II. Also included in this table is the

TABLE II. Energy and wave function of the $[(1s2s)^3S, 3p]^2P$ states of lithium atom (in a.u.), $q=2.48$.

Angular wave		α, β, γ	N^a	$-\Delta E$	$\lvert\psi_i\rvert^{2\,b}$
1	$[(s,s)^3S,p]$	3.095, 0.895, 0.585	40/60	5.175 508	0.915
2	$[(s,p)^3P,d]$	2.84, 0.96, 0.71	7/10	0.003 597	0.104(−1)
3	$[(s,p)^3P,s]$	2.64, 1.18, 0.585	22/30	0.002 871	0.381(−1)
4	$[(p,p)^3S,p]$	3.03, 1.88, 0.41	7/10	0.001 057	0.179(−3)
5	$[(s,p)^1P,d]$	2.44, 0.96, 1.06	5/10	0.000 111	0.205(−3)
6	$[(p,d)^3P,s]$	3.14, 1.78, 0.585	5/8	0.000 104	0.175(−4)
7	$[(s,d)^3D,f]$	3.00, 1.5, 1.5	2/6	0.000 080	0.532(−4)
8	$[(d,d)^3S,p]$	3.53, 3.08, 0.41	5/8	0.000 060	0.541(−5)
Total			93	5.183 387	

[a] $N=x/y$ implies that x terms are chosen from a y-term angular wave function.

[b] $\lvert\psi_i\rvert^2$ is the contribution of the ith angular partial wave to the normalization in the 93-term–8-partial-wave normalized wave function. $(-x)$ indicates 10^{-x} is to be multiplied. For other notations see Table I.

contribution of each partial wave to the normalization of the 93-term wave function. This gives a clear picture of the composition of the complex wave function. However, one should realize that some partial waves are not exactly orthogonal to each other. For example the first and third partial waves have an overlap of 0.0360, the second and sixth have an overlap of −0.000 009, hence conclusions drawn from this column must be taken with some caution. Nevertheless, it clearly illustrates the essential composition of this resonance state. The experimental position of this state is 62.419 eV or −5.184 01 a.u., compared with this, the present result is too high by 0.000 62 a.u. or 0.017 eV.

From calculating the energies and wave functions of the higher members of the ^2P resonances, a clear convergence pattern emerges. That is, the importance of the partial waves other than the $[(s, s)^3S,p]$ becomes less, both in number, and in contribution to the energy. For example, in Table III where $[(1s2p)^3S, np]^2P$ state with $n=4$ to 6 are tabulated, only six partial waves were needed in the calculation. Furthermore, the contribution of the second, third, and fifth partial waves became smaller both for energy and normalization as n increases. The presence of the second and third partial waves is to provide coupling of the form $[(1s2p)^3P, nd]$ and $[(1s2p)^3P, ns]$. It is interesting to note that the optimized nonlinear parameter γ in the first partial wave decreases rapidly as n increases, but the γ of second and third partial waves remains stable. Notice that the presence of the fourth and sixth partial waves is to provide a better core state for the first partial wave. Therefore the contribution of these two partial waves to the energy and normalization of the wave function are remarkably stable. Notice also that the fourth partial wave contributes significantly to the energy but its contribution to normalization is very small. The presence of the fifth partial wave is to provide a better core for the third partial wave. The results for $[(1s2s)^3S, 4p]$ and $[(1s2s)^3S, 5p]$ agree excellently with experiment. The agreement in $[(1s2s)^3S, 6p]^2P$ is somewhat worse. The reason for this discrepancy and a method to improve this situation will be discussed in Sec. V. It is worthwhile to point out that the two-electron cores in the six partial waves in this table all couple as triplets. This will be true also for the states from $n=7$ to 10 as well.

C. $[(1s2s)^3S,np]$ for $n=7$ to 10

For these resonant states, a large number of nodes are present in the wave function. To account for these nodes and the correlation effect we need a variational wave function with a large number of linear parameters, especially for the $[(s, s)^3S,p]$ partial wave. However, due to limitations on computation time, numerical accuracies, the occurrence of overflow and underflow in the IBM 370 computer we are using, we are limiting the number of linear parameters to 110 or less. Because of this, the term selection in the first partial wave is only used for the $n=7$ state, while for the $n=8$ to 10 states the first partial wave is fixed at 68 terms each. The results of this calculation are given in Table IV. In this table, the optimized q changes slowly from 2.48 for $n=7$ to $q=2.50$ for $n=10$. It should be noted that from $q=2.46$ to 2.52 the change in energy because of variation of q is very small.

In this table, the result of the $[(1s2s)^3S, 10p]^2P$ resonance is −5.115 954 a.u., higher than the ex-

TABLE III. Energies and wave functions of the $[(1s2s)^3S,np]^2P$ states of the lithium atom for $n=4$ to 6, $q=2.48$. For notations see Tables I and II.

		1	2	3	4	5	6	
		$[(s,s)^3S,p]$	$[(s,p)^3P,d]$	$[(s,p)^3P,s]$	$[(p,p)^3S,p]$	$[(p,d)^3P,s]$	$[(d,d)^3S,p]$	
Angular wave	α,β,γ	3.09, 0.945, 0.42	3.0, 0.94, 0.58	3.03, 0.97, 0.57	2.76, 2.2, 0.30	3.14, 1.96, 0.57	2.75, 2.80, 0.28	Total
$[(1s2s)^3S,4p]$	N	51/64	4/17	13/20	8/12	3/9	4/8	83
	$-\Delta E$	5.145 546	0.000 678	0.001 624	0.001 146	0.000 046	0.000 059	5.149 100
	$\lvert\psi_i\rvert^2$	0.958	0.298(−2)	0.217(−1)	0.195(−3)	0.749(−5)	0.573(−5)	
	α,β,γ	3.08, 0.95, 0.33	3.00, 0.93, 0.59	3.04, 0.96, 0.59	2.43, 1.9, 0.22	3.10, 1.96, 0.55	2.81, 3.34, 0.23	
$[(1s2s)^2S,5p]$	N	57/64	4/11	15/20	8/16	2/9	4/7	90
	$-\Delta E$	5.131 921	0.000 245	0.000 937	0.001 142	0.000 028	0.000 061	5.134 334
	$\lvert\psi_i\rvert^2$	0.971	0.139(−2)	0.156(−1)	0.197(−3)	0.477(−5)	0.521(−5)	
	α,β,γ	3.00, 0.95, 0.26	3.00, 0.81, 0.60	2.96, 0.91, 0.70	2.5, 1.7, 0.18	2.96, 1.86, 0.70	2.9, 3.1, 0.18	
$[(1s2s)^3S,6p]$	N	57/84	5/9	7/13	10/15	3/12	4/10	86
	$-\Delta E$	5.124 703	0.000 124	0.000 618	0.001 156	0.000 021	0.000 062	5.126 683
	$\lvert\psi_i\rvert^2$	0.978	0.732(−3)	0.129(−1)	0.192(−3)	0.363(−5)	0.546(−5)	

TABLE IV. Energies and wave functions for the $[(1s2s)^3S,np]^2P$ states of the lithium atom for $n=7$ to 10 (in a.u.). For notations see Tables I and II.

		1	2	3	4	5	
		$[(s,s)^3S,p]$	$[(s,p)^3P,s]$	$[(p,p)^3S,p]$	$[(s,p)^3P,d]$	$[(d,d)^3S,p]$	
Angular wave	α,β,γ	3.00, 0.99, 0.215	2.96, 0.80, 0.82	2.4, 1.8, 0.143	3.0, 0.75, 0.75	2.4, 2.6, 0.143	Total
$[(1s2s)^3S,7p]$	N	69/93	12/18	11/18	8/10	5/6	105
$q=2.48$	$-\Delta E$	5.120 421	0.000 550	0.001 151	0.000 068	0.000 054	5.122 244
	$\lvert\psi_i\rvert^2$	0.975	0.170(−1)	0.196(−3)	0.400(−3)	0.579(−5)	
	α,β,γ	3.05, 1.01, 0.15	2.96, 0.91, 0.85	2.4, 2.0, 0.135	3.0, 1.05, 0.75	2.88, 3.2, 0.125	
$[(1s,2s)^3S,8p]$	N	68/68	11/16	13/13	2/6	8/8	102
$q=2.49$	$-\Delta E$	5.117 590	0.000 438	0.001 169	0.000 034	0.000 063	5.119 294
	$\lvert\psi_i\rvert^2$	0.987	0.103(−1)	0.196(−3)	0.269(−3)	0.544(−5)	
	α,β,γ	3.0, 1.06, 0.125	2.96, 0.86, 0.75	2.3, 2.0, 0.118	3.0, 1.05, 0.80	2.88, 3.2, 0.118	
$[(1s,2s)^3S,9p)$	N	68/68	13/18	11/15	2/6	8/8	102
$q=2.49$	$-\Delta E$	5.115 801	0.000 309	0.001 171	0.000 019	0.000 063	5.117 363
	$\lvert\psi_i\rvert^2$	0.990	0.772(−2)	0.204(−3)	0.145(−3)	0.545(−5)	
	α,β,γ	2.93, 1.14, 0.105	2.96, 0.95, 0.95	2.3, 2.0, 0.105		2.88, 3.2, 0.105	
$[(1s,2s)^3S,10p]$	N	68/68	10/19	9/17		9/9	96
$q=2.50$	$-\Delta E$	5.114 535	0.000 174	0.001 182		0.000 063	5.115 954
	$\lvert\psi_i\rvert^2$	0.995	0.434(−2)	0.206(−3)		0.550(−5)	

perimental result 64.260 eV or −5.11634 a.u. by about 0.0106 eV. For this state, it is found that slightly increasing the size of the first partial wave does not improve the energy appreciably. A large increase in the number of terms, however, is not feasible for reasons discussed before. The results for $n=8$ and 9 are −5.119294 and −5.117363 a.u., respectively, which agree remarkably well with the experimental values of −5.11914 and −5.11738 a.u. But the result for $n=7$, −5.122244 a.u., is substantially lower than the experimental result 64.121 eV or −5.12146 a.u. The reason for this unusual behavior is due to the presence of a "perturber" which has not been considered. Experimentally, the perturber is located between the $n=6$ and 7 resonances, therefore the results of this section for $n=6$ or higher must be taken with caution, especially the apparent excellent results for $n=8$ and 9.

D. The perturber

In Ref. 1, Ederer *et al.* had analyzed the data in the elastic region using the effective quantum numbers, and located the $[(1s2s)^3S, np]$ series. However, an extra line appeared at 64.046 eV which does not seem to fit in. The identity of this perturber has never been seriously studied in the literature. In this work, a detailed calculation is carried out for this state. The result of a 102-term, 11-partial-wave calculation gives −5.124253 a.u. This is remarkably close to the experimental position 64.046 eV (−5.12421 a.u.). This result is given in Table V.

Since this perturber is not a member of the $[(1s2s)^3S, np]$ series but is higher than many of the $[(1s2s)^3S, np]$ states, one must use a wave function which is essentially orthogonal to the $[(1s2s)^3S, np]$ states. The first partial wave in Table V is exactly orthogonal to $[(s,s)^3S, p]$, but the second and third partial waves are not. Therefore to avoid a variational break down in which case $[(1s, 3p)^1P, 2s]$ or $[(1s, 3p)^3P, 2s]$ may occur, we must build in a $2s$ vacancy in addition to the $1s$ vacancy in the third electron's coordinates. When this is carried out the calculation becomes straightforward. The lowest root of this secular equation should correspond to a poor $[(1s2s)^1S, 2p]$. The second lowest root gives an energy at −5.124253 a.u. as shown in this table. In this table, one notices that a two-partial-wave calculation gives an energy of −5.11542 a.u., substantially below the −5.11073 a.u. $\text{Li}^+(1s2s)^3S$ threshold.[20] This implies that the coupling of the $[(1s2s)^1S, 3p]$ and $[(1s2p)^1P, 3s]$ configurations is sufficient to produce a resonance lower than the $2\,^3S$ threshold.

From the above discussions, the most natural classification for this perturber should be the $[(1s2s)^1S, 3p]^2P$ state. However, a closer look at the last column of Table V suggests that there is an appreciable amount of mixing due to $[(1s2p)^3P, 3s]$ and $[(1s, 2p)^1P, 3s]$. In fact, the first three partial waves are not orthogonal to each other. If we combine the first and second, second and third, and first and third, the contributions to the normalization would be 0.800, 0.283, and 0.914, respectively. Hence it should be a $[(1s2s)^1S, 3p]$ state with substantial mixings.

TABLE V. Energy and wave function of the perturber $[(1s2s)^1S, 3p]^2p$ state of the lithium atom (in a.u.), $q=2.53$. For notations see Tables I and II.

	Angular waves	α,β,γ	N	$-\Delta E$	$\lvert\psi_i\rvert^2$
1	$[(s,s)^1S,p]$	2.96, 0.82, 0.67	27/33	5.108623	0.743
2	$[(s,p)^1P,s]$	3.00, 0.97, 0.65	6/16	0.006801	0.192
3	$[(s,p)^3P,s]$	2.95, 1.17, 0.55	14/16	0.003513	0.908(−1)
4	$[(s,p)^1P,d]$	3.02, 1.00, 0.65	10/15	0.002372	0.251(−1)
5	$[(p,p)^1S,p]$	3.60, 3.00, 0.47	15/21	0.001673	0.225(−3)
6	$[(s,p)^3P,d]$	3.02, 1.00, 0.80	8/15	0.000499	0.383(−2)
7	$[(p,d)^3P,s]$	2.60, 2.90, 0.35	9/9	0.000389	0.623(−4)
8	$[(d,d)^1S,p]$	4.00, 3.90, 0.47	2/5	0.000125	0.927(−5)
9	$[(p,d)^1P,s]$	2.70, 2.60, 0.60	3/9	0.000185	0.303(−4)
10	$[(p,d)^1P,d]$	2.22, 2.60, 0.65	5/8	0.000051	0.894(−5)
11	$[(s,d)^1D,f]$	3.00, 1.20, 1.15	3/6	0.000022	0.211(−4)
	Total		102	5.124253	

IV. OSCILLATOR STRENGTH AND RADIAL EXPECTATION INTEGRALS

In experimental observations, the intensity of an optical absorption line is directly proportional to the absorption cross section. If the initial state i and final state j are both discrete, this absorption cross section is[21]

$$\sigma_{\text{tot}}=\frac{4\pi^2}{137.036E_{ji}}\left|\langle j\,|\exp(i\vec{k}\cdot\vec{r})\vec{p}\cdot\hat{e}\,|\,i\rangle\right|^2, \tag{11}$$

where atomic units are used. E_{ji} is the energy difference for the initial and final state, $\hat{e}$ is the polarization of the incoming radiation, and

$$|\vec{k}\,|=E_{ji}/137.036\,. \tag{12}$$

If we assume $\vec{k}\cdot\vec{r}$ to be small, this expression becomes

$$\sigma_{\text{tot}}=\frac{8\pi^2}{137.036}E_{ji}\left|\langle j\,|\vec{r}\cdot\hat{e}\,|\,i\rangle\right|^2. \tag{13}$$

In the problem of interest, the initial state is the ground state of lithium, and the final state is the ^2P resonances. If we sum over S_z and M for the degenerate final states, there is no loss of generality in assuming a particular direction for the polarization vector $\hat{e}$. Choosing $\hat{e}$ to be in the z direction, we get

$$\sigma_{\text{tot}}=\frac{4\pi^2}{137.036}2E_{ji}\left|\langle j(M=0)\,|\,z\,|\,i\rangle\right|^2. \tag{14}$$

In this equation

$$f=2E_{ji}\left|\langle j(M=0)\,|\,z\,|\,i\rangle\right|^2 \tag{15}$$

is often called the oscillator strength of the j state. The autoionizing states are not pure discrete states, but it can be shown that if we integrate over the neighboring continuum of a narrow Feshbach resonance, Eq. (15) will still be valid.[22]

It should be pointed out, however, that in the resonances of interest, $\vec{k}\cdot\vec{r}$ is not necessarily very small, especially for high-n states. But this is somewhat compensated by the small radius of the ground state. Hence, Eq. (14) should give a reasonable approximation to the absorption cross section. With this in mind, the oscillator strengths of the ^2P resonances are calculated together with several radial expectation integrals. We define

$$\langle r^n\rangle_j=\left\langle j\left|\frac{r_1^n+r_2^n+r_3^n}{3}\right|j\right\rangle \tag{16}$$

and calculate the above for $n=-2,-1,1,2$. $\langle r\rangle$ gives the average radius of the system and $\langle r^2\rangle$ is directly related to the diamagnetic suspectability and scattering cross section of the atomic system.

In calculating the oscillator strength, a 96-term ground-state wave function is used. The basis functions are the same as in Eq. (7) and the energy is $-7.476\,909$ a.u. This is inferior to the $-7.478\,025$ a.u.[19] obtained by Larsson and comparable to the 18-configuration multiconfiguration-Hartree-Fock (MCHF) result $-7.476\,90$ a.u. of Fisher.[23] The radial integrals of this ground state are also calculated. These results are given in Table VI.

It is interesting to note in this table that the perturber does have similar geometrical parameters as $[(1s2s)^3S, 3p]$ state. This gives further supportive evidence to the $[(1s2s)^1S, 3p]$ classification. These parameter are obtained without considering the dynamic-coupling effect. Therefore it should be subject to some small corrections.

TABLE VI. Oscillator strength and radial expectation values of r for ^2P resonances of lithium (in a.u.).

Energy states	Oscillator strength f	$\left\langle\frac{1}{r^2}\right\rangle$	$\left\langle\frac{1}{r}\right\rangle$	$\langle r\rangle$	$\langle r^2\rangle$
$[(2s2p)^3P, 1s]$	0.2797	6.3953	1.2993	2.1876	7.5152
$[(2s2p)^1P, 1s]$	0.7527(−2)	6.3028	1.2890	2.2662	8.3414
$[(1s2s)^3S, 3p]$	0.4656(−1)	6.3769	1.2333	4.0931	35.868
$[(1s2s)^3S, 4p]$	0.1698(−1)	6.3920	1.2120	7.0703	129.25
$[(1s2s)^3S, 5p]$	0.7907(−2)	6.3957	1.2028	10.990	342.74
$[(1s2s)^3S, 6p]$	0.4155(−2)	6.3977	1.1979	15.908	757.36
$[(1s2s)^1S, 3p]$ (perturber)	0.2720(−3)	6.2533	1.2214	3.8097	28.599
$[(1s2s)^3S, 7p]$	0.2337(−2)	6.3983	1.1952	21.539	1437.8
$[(1s2s)^3S, 8p]$	0.1204(−2)	6.3998	1.1929	29.305	2700.1
$[(1s2s)^3S, 9p]$	0.7203(−3)	6.4012	1.1915	37.787	4571.0
$[(1s2s)^3S, 10p]$	0.3863(−3)	6.4014	1.1903	47.640	7237.0
$[(1s1s)^1S, 2s]^2S$ Ground		10.083	1.9058	1.6632	6.1167

V. DYNAMIC COUPLING

If one compares the results of this calculation for the states $[(1s2s)^3S, 6p]$ and $[(1s2s)^3S, 7p]$ with the experimental result, the $6p$ states appears to be too high and the $7p$ state appears to be too low. This leads to the suspicion that it may have something to do with the appearance of a perturber in between. The study of the perturbation phenomena of a Rydberg series started as early as 1932.[24] More recently, Weiss[25] investigated the series perturbation of the Al I and Al II spectra by using a superposition of configuration technique. Ideally, if the basis functions for both the perturber and the $[(1s2s)^3S, np]$ could all be included in the construction of a huge secular equation, then all the eigenvalues of the Hamiltonian could be obtained. But in reality limitations such as the finite size of the computer code, computing machine time and the lost of numerical accuracy exist.

The basis function for the $[(1s2s)^3S, np]$ and the $[(1s2s)^1S, np]$ are essentially orthogonal, we can calculate these two series separately. However, each single result may not be an exact solution to the Schrödinger equation and there may be coupling between the states through the Hamiltonian. Since these states are good approximation to the final solution, the coupling calculation carries a slightly different meaning than the usual configuration interaction. For this reason, it is called dynamic coupling in this work.

Let us assume we have two approximate orthonormal solution ψ_1 and ψ_2, belonging to two different series. One may construct a two-by-two secular equation

$$\begin{vmatrix} E_{11}-\lambda & E_{12} \\ E_{21} & E_{22}-\lambda \end{vmatrix} = 0 , \tag{17}$$

where

$$E_{ij} = \langle \psi_i | H | \psi_j \rangle . \tag{18}$$

The solution for λ is given by

$$\lambda_\pm = \frac{E_{11}+E_{22} \pm [(E_{11}-E_{22})^2 + 4|E_{12}|^2]^{1/2}}{2} . \tag{19}$$

Assuming $E_{11} > E_{22}$, then the shift in energy due to this coupling is

$$E_{22} - \lambda_- = \frac{E_{22}-E_{11} + [(E_{11}-E_{22})^2 + 4|E_{12}|^2]^{1/2}}{2} \geq 0 \tag{20a}$$

and

$$E_{11} - \lambda_+ = \frac{E_{11}-E_{22} - [(E_{11}-E_{22})^2 + 4|E_{12}|^2]^{1/2}}{2} \leq 0 , \tag{20b}$$

i.e., the higher root will be pushed up and the lower root will be pushed down due to the coupling of the two states. If ψ_1 and ψ_2 are good approximate solutions to H, then E_{12} should be small. In this case, if $E_{11} - E_{22}$ is large this shift will be insignificant. Only in the case where $E_{11} - E_{22}$ is small will this shift be appreciable.

Another point which is worth consideration is that in this work the energies of the higher states are obtained by optimizing the corresponding higher roots of the secular equation. When the optimized nonlinear parameters and configurations are different from those of the lower states, the orthogonality between the states will only hold approximately. This method is rigorously justified, however, based on the theorem proved by MacDonald.[26] In the case of the $7p$ resonance, we are optimizing the seventh root of the secular equation. This seems appropriate from examining the behavior of this eigenvalue in regards to the partial wave added. On the other hand, the perturber is also a ^2P resonance of $^2P^o$ symmetry. Even if the wave function of the $7p$ resonance appears to be orthogonal to the perturber, the solution to this seventh root is no longer a rigorous upper bound to the true resonance. In reality this orthogonality is only approximately maintained because the third partial wave of Table V obviously overlaps with the second partial wave of Table IV. This means that the solutions to the $7p$, $8p$, $9p$, and $10p$ resonances needs to be carefully reexamined. It can also be shown that in a coupling calculation, if the lowest few states lie very far from the perturber, they should not have much effect to the coupling result. To illustrate this point, let us consider a set of orthonormal states $\psi_1, \ldots, \psi_n$ which are the eigenfunctions of the same secular equation with eigenvalues E_{11}, $E_{22}, \ldots$, etc. Consider a perturber ϕ_0. Define

$$\langle \psi_i | \phi_0 \rangle = S_{i0} , \quad i = 1, \ldots, n \tag{21a}$$

$$\langle \psi_i | H | \phi_0 \rangle = H_{i0} , \quad i = 1, \ldots, n \tag{21b}$$

$$\langle \phi_0 | H | \phi_0 \rangle = H_{00} . \tag{21c}$$

Then the coupled secular equation becomes

$$D = \begin{vmatrix} E_{11}-\lambda & 0 & \cdots 0 & H_{10}-\lambda S_{10} \\ 0 & E_{22}-\lambda & \cdots 0 & H_{20}-\lambda S_{20} \\ & & & \cdot \\ 0 & 0 & \cdots 0 & \cdot \\ & & & \cdot \\ \cdots\cdots & \cdots\cdots & E_{nn}-\lambda & H_{n0}-\lambda S_{n0} \\ H_{01}-\lambda S_{01} & \cdots\cdots & H_{0n}-\lambda S_{0n} & H_{00}-\lambda \end{vmatrix} = 0 . \tag{22}$$

This equation gives

$$D=(E_{11}-\lambda)(E_{22}-\lambda)\cdots(E_{nn}-\lambda)(H_{00}-\lambda)-\sum_{i=1}^{n}\left(|H_{0i}-\lambda S_{0i}|^2\prod_{j\neq i}^{n}(E_{jj}-\lambda)\right)=0\,. \qquad (23)$$

Let us assume that E_{11}, $E_{22}\cdots E_{n-1,n-1}$ and H_{00} are very close together and very far from E_{nn}. If we are solving for λ in the region near H_{00}, then one term in the sum in Eq. (23) is much smaller than all other terms. Dropping this term, we get

$$D=(E_{11}-\lambda)(E_{22}-\lambda)\cdots(E_{nn}-\lambda)(H_{00}-\lambda)-\sum_{i=1}^{n-1}\left(|H_{0i}-\lambda S_{0i}|^2\prod_{j\neq i}^{n}(E_{jj}-\lambda)\right)=0\,. \qquad (24)$$

Clearly $(E_{nn}-\lambda)$ can be factored out from this equation. This implies ψ_n should have little effect on the solution of λ in the neighborhood of H_{00}.

In the present work, the lowest and second lowest, $3p$ and $4p$ resonances lie 0.188, 0.133, 0.059, and 0.025 a.u. away from the perturber, respectively. On the other hand, the highest state, $10p$ is only 0.008 a.u. higher than the perturber.

Based on these considerations, I carried out a coupling calculation for the ^2P resonant states. These results are given in Table VII. In this table, the results for the lower-five states are obtained with all eleven states included in the coupling, whereas the higher-six states are obtained by using a seven-by-seven coupling. In this seven-by-seven coupling, the lowest solution is −5.134 63 a.u. which agree closely with the −5.134 55 a.u. result in this table obtained by coupling all eleven states.

VI. RESULTS AND DISCUSSION

In Table VII, the observed positions of ^2P Li in Ref. 1 are also given along with the results from dynamic coupling. As expected the lowest-three states are not effected by this coupling. For the lowest resonance, the present work is higher than the experimental value by 0.000 78 a.u. or 0.021 eV. The discrepency may conceivably come from two sources: the incompleteness of the basis functions used and the effect of coupling with the open channel. For the second resonance, the discrepency is 0.041 eV, much larger than the rest of the resonances investigated. Since no substantial improvement can be obtained by including more angular partial waves or increasing linear parameters, one must conclude that the Feshbach shift due to coupling with the open channel for this state is much larger than that of the other resonances. For higher resonances, the width and the Feshbach shifts are usually much smaller. The resonance positions for these higher states obtained from the saddle-point technique should give an excellent approximation to the true resonances. This can be seen from the close agreement of our calculated results with those of experiment. Although after the coupling this agreement appears to be worse for the perturber and for the $[(1s2s)^3S, np]$ states with $n=8$ to 10, I believe the coupled results are more sound theoretically, and the overall pattern of agreement is more consistent.

Theoretically, the $^2P^o$ resonances of Li have been investigated by Barden *et al.*[10] using a model potential method, by Bhatia and Temkin using a

TABLE VII. Coupling of perturber $[(1s2s)^1S, 3p]^2P$ with the $[(1s2s)^3S, np]^2P$ states of lithium atoms, (in a.u.).

States	E(Expt.)[a]	E_0 (before coupling)	E_0-E (in eV)	E_c (after coupling)	E_c-E (in eV)
$[(2s2p)^3P, 1s]$	−5.312 97	−5.312 185	0.021	−5.312 185	0.021
$[(2s2p)^1P, 1s]$	−5.258 36	−5.256 864	0.041	−5.256 870	0.041
$[(1s2s)^3S, 3p]$	−5.184 01	−5.183 387	0.017	−5.183 390	0.017
$[(1s2s)^3S, 4p]$	−5.149 57	−5.149 100	0.013	−5.149 193	0.010
$[(1s2s)^3S, 5p]$	−5.134 98	−5.134 334	0.018	−5.134 549	0.012
$[(1s2s)^3S, 6p]$	−5.127 70	−5.126 683	0.028	−5.127 359	0.009
$[(1s2s)^1S, 3p]$ (perturber)	−5.124 21	−5.124 253	−0.001	−5.123 687	0.014
$[(1s2s)^3S, 7p]$	−5.121 46	−5.122 244	−0.021	−5.121 219	0.007
$[(1s2s)^3S, 8p]$	−5.119 14	−5.119 294	−0.004	−5.118 839	0.008
$[(1s2s)^3S, 9p]$	−5.117 38	−5.117 363	0.0005	−5.117 065	0.009
$[(1s2s)^3S, 10p]$	−5.116 34	−5.115 954	0.011	−5.115 843	0.014

[a] The experimental results are converted from Ref. 1 using $E_{\text{ground}}=-7.478\,025$ a.u. and 1 a.u. = 27.2095 eV.

TABLE VIII. $^2P^o$ resonances of the lithium atom in the elastic scattering region (in eV).

	Theory					Experiment			
Author	Present[a] work	Wakid *et al.* (Ref. 8)	Bhatia (Ref. 7)	Barden *et al.* (Ref. 10)	Weiss (Ref. 5)	Ederer[c] *et al.* (Ref. 1)	Cantu *et al.* (Ref. 2)	Pegg *et al.* (Ref. 3)	Ziem *et al.* (Ref. 4)
$[(2s2p)^3P, 1s]$	58.931	58.914	58.976	58.96	58.965	58.910(6)	58.909(3)	58.91(3)	58.912(10)
$[(2s2p)^1P, 1s]$	60.437	60.438	60.531		60.599	60.396(3)	60.392(3)	60.40(3)	60.397(10)
$[(1s2s)^3S, 3p]$	62.436	62.424	62.483		62.458	52.419(3)	62.417(3)	62.42(3)	62.425(10)
$[(1s2s)^3S, 4p]$	63.366	63.377[b]			63.364	63.356(8)	63.358(3)		63.35(3)
$[(1s2s)^3S, 5p]$	63.765	63.758[b]			63.772	63.753(3)	63.755(3)		
$[(1s2s)^3S, 6p]$	63.960					63.951(3)	63.956(3)		
$[(1s2s)^1S, 3p]$	64.060					64.046(8)	64.052(3)		
$[(1s2s)^3S, 7p]$	64.128					64.121(3)	64.118(3)		
$[(1s2s)^3S, 8p]$	64.192					64.184(3)	64.181(3)		
$[(1s2s)^3S, 9p]$	64.241					64.232(6)	64.228(3)		
$[(1s2s)^3S, 10p]$	64.274					64.260(6)	64.258(3)		

[a] The ground-state energy of Li is taken as −7.478 025 a.u. (see Ref. 19). Other constants used in this table are 1 a.u. $= 27.2095$ eV, 1 bohr $= 0.529\,1770$ Å, fine-structure constant $= 1/137.036$, 1 $\text{Ry}_\infty = 13.6058$ eV.

[b] The classification of the fourth and fifth states of this reference is different from the present work. They imply a different wave function is obtained.

[c] The number in the parentheses gives the uncertainty in the last digits quoted. We have only included the errors due to repeatability, the absolute error may be larger by 0.005 eV (see Ref. 1).

quasi-projection-operator method[7] (QPO), by Wakid *et al.*[8] using a generalized QPO, and by Weiss.[5] A comparison of the theoretical and experimental results in the literature is given in Table VIII. In comparing the theoretical results, those of Wakid *et al.* appear to be particularly impressive. However, this is possibly the result of cancellation of errors.[27] For example, for the lowest resonance, if we use the same 104-term basis function as in the present work, but carry out a QPO calculation with the optimized target state. We get −5.314 57 a.u. This is *lower* than the experimental result of 58.910 eV by 0.044 eV. If we adopt the method in Ref. 8, this energy will be lower somewhat more. (In case of He^-, the two QPO methods give results differing by 0.03 and 0.16 eV for two different resonances. See Ref. 8). Therefore, the reason that their result does not fall below that of the experiment must be because the basis functions are not complete. In the present work, the $[(1s2s)^1S, 3p]$ resonance is located at 64.060 eV, higher than their result by 0.687 eV. The results of Weiss are also impressive. However, no detail of this work is given in the literature for meaningful comparison.

To my knowledge, there is no published theoretical results for states higher than the $[(1s2s)^3S, 5p]^2P$ in the elastic scattering region. The results of these states in the present work are higher than those of Ref. 1 by an average of 0.010 eV. This discrepancy can be probably improved slightly by including more correlation into the wave function. It is also interesting to note that the average "absolute error" for the six states are 0.010 eV in the experiment of Ref. 1. Overall speaking, the result of the present work must be considered as quite good.

In conclusion, we have calculated the $^2P^o$ autoionizing states of the lithium atom in the elastic scattering region using a saddle-point technique. Our result clearly suggests that this method is capable of generating highly accurate results, especially for higher members of the Feshbach resonances. Since this method is applicable in inelastic region as well as multiply excited region, the next step will be to investigate the resonances in the inelastic scattering region.

ACKNOWLEDGMENT

This work was supported in part by the North Carolina Board of Science and Technology.

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