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Quasi-projection-operator calculation of inelastic resonances in He$^-$ and Li

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Feshbach resonances of electrons incident on He and Li$^+$ are calculated below the $3\,^3S$ target threshold by means of the inelastic quasi-projection-operator technique of Temkin and Bhatia. A configuration-interaction-type wave function is employed with up to 46 configurations. The calculations reveal, with reasonable accuracy, all presently observed Feshbach resonances. The method does not reveal shape resonances, but, for isoelectronic systems with greater nuclear charge, it is argued that shape resonances should become less important. This is already apparent in the case of Li, for which the authors calculate the known resonances and also predict higher resonances for which there are as yet no experimental data.

I. INTRODUCTION

Recent experiments[1,2] with substantially improved resolution have been carried out on the autoionization states of He$^-$ and Li. Brunt *et al.*[1] have observed states by electron impact excitation of metastable He up to the $n=4$ threshold with an incident energy spread of 15 meV, to be compared with previous transmission and metastable excitation experiments[3-6] with resolution from 36 to 50 meV. For lithium McIlrath and Lucatorto[2] observed the first optical absorption for excited states to core-excited (i.e., Feshbach) autoionizing levels of even parity. They used a 1-MW dye laser, tuned to the lowest resonance line, to excite a dense Li vapor, thereby producing an accurate far-uv absorption spectra of Li. Other previous experiments were conducted by Bruch *et al.*,[7] who used an ion beam time-of-flight method, and Ziem *et al.*,[8] who bombarded Li vapor by H$^+$ and He$^+$. Both experiments observed the energy spectrum of electrons emitted from the autoionizing states. Ederer *et al.*[9] observed the $^2P^o$ transitions through photon absorption from the Li ground state.

Theoretical work on the autoionization states of He$^-$ has been done by Nesbet,[10] who refined an earlier variational calculation of Oberoi and Nesbet[11] by including $n=3$ states and all energetically allowed open channels. His results in the region of the $2\,^1S \rightarrow 3\,^3S$ excitation threshold agree with the experimental work in that range except for the classification of the ^2D resonance. Burke *et al.*[12] dealt with resonances below the $3\,^3S$ state, in a close-coupling scattering calculation.

The present calculations are based on an extension of the quasiprojection method of Temkin *et al.*[13] The original method and calculations were confined to resonances below the first excited ($2\,^3S$) threshold and were applied to He$^-$ (Ref. 13), Li (Refs. 14 and 15), and Be$^+$, B^{2+}, C^{3+} (Ref. 15). The method has now been generalized to calculate resonances below any discrete threshold,[16] and it is this extended method that is employed here for calculations below all five thresholds (up to $3\,^3S$) of the He$^-$ and Li systems.

Before presenting the details of the calculation and results, we should emphasize that the method only reveals Feshbach resonances. However, within this restriction it is both powerful and accurate. Results for Feshbach resonances below the $3\,^3S$ threshold for He and Li$^+$ are given in Sec. III. We detail a specific case of an apparent $^2P^o$ resonance in He$^-$ which on more rigorous testing turned out to disappear. This vanishing was due to the use of more accurate target wave functions in the projection operators. The experience shows both the power and the caution that must be exercised in applying the quasi-projection-operator formalism.

Our method does not reveal shape resonances. However, we argue (we believe cogently) in Sec. III that the importance of shape resonances relative to Feshbach resonances will diminish for any isoelectronic series as the nuclear charge increases.

II. CALCULATIONS

The essence of the quasiprojection method[13] is the relaxation of the idempotency requirement of the Feshbach projection-operator formalism,[17] so that explicit (quasiprojection) operators $\hat{Q}$ can be constructed which preserve the correspondence of the eigenvalue spectrum of $\hat{Q}H\hat{Q}$ with resonant energies. One slight inconvience of the $\hat{Q}H\hat{Q}$ spectrum is that it can cause spurious states (i.e., eigenvalues not associated with resonances). However, the nature of these spurious states can be understood well, so that one can identify them in

TABLE I. Number and designation of spurious states in the quasiprojection technique for three-electron ions.[a]

Symmetry of autoionization state	$\nu+1$ Target state[a]	1 $2\,^3S(1s2s)$	2 $2\,^1S(1s2s)$	3 $2\,^3P(1s2p)$	4 $2\,^1P(1s2p)$	5 $3\,^3S(1s3s)$
$^2S^e$		0	2	2	3	3
Configurations of spurious states			$(1s^2\,2s)$ $(1s2s^2)$	$(1s^2\,2s)$ $(1s2s^2)$	$(1s^2\,2s)$ $(1s2s^2)$ $(1s2p^2)$	$(1s^2\,2s)$ $(1s2s^2)$ $(1s2p^2)$
$^2P^o$		0	0	0	3	3
Configurations of spurious states					$(1s^2\,2p)$ $(1s2s)^3S(2p)$ $(1s2s)^1S(2p)$	$(1s^2\,2p)$ $(1s2s)^3S(2p)$ $(1s2s)^1S(2p)$
$^2D^e$		0	0	0	1	1
Configurations of spurious states					$(1s2p^2)$	$(1s2p^2)$

[a] Note that this table corrects Table I of Ref. 16, where the $\nu+1=4,5$ entries for $^2P^o$ were erroneously given as 4 and 5.

advance, as we have done in Ref. 16. This is shown again in Table I, correcting an error in the number of spurious states of $^2P^o$ symmetry and also giving the (chief) configuration label of the spurious states. (In Table VI we display a particular spectrum of He$^-$ and see that the spurious-state configurations are indeed those which we were led to infer.[16])

The basic quasiprojector is the operator $\hat{P}$ defined as

$$\hat{P}=\sum_{n=0}^{\nu}\sum_{i=1}^{N+1}P_i^{(n)}\,, \tag{1}$$

where ν is the index of the highest energetically allowable target threshold, N is the number of target electrons, and n labels the target eigenfunctions. The $P_i^{(n)}$ are the respective target projectors given by

$$P_i^{(n)}=|\phi_n(x^{(i)})\rangle\langle\phi_n(x^{(i)})|\,, \tag{2}$$

where $x^{(i)}$ indicates the absence of the coordinates (including spin) of particle i. The above $\hat{P}$ acting on the scattering function ψ preserves its asymptotic form[13]:

$$\lim_{r_i\to\infty}\hat{P}\psi=\lim_{r_i\to\infty}\psi\,. \tag{3}$$

However, $\hat{P}^2\neq\hat{P}$. The closed-space $\hat{Q}$ operator is defined as

$$\hat{Q}_\nu=1-\hat{P}_\nu\,, \tag{4}$$

and the computation of resonances reduces to a Rayleigh-Ritz variational principle[13]:

$$\delta(\langle\hat{Q}_\nu\Phi,H\hat{Q}_\nu\Phi\rangle/\langle\hat{Q}_\nu\Phi,\hat{Q}_\nu\Phi\rangle)=0\,, \tag{5}$$

where in this calculation Φ is a bound configuration-interaction-type wave function for the three-electron system:

$$\Phi^{L,S}=\frac{\mathcal{A}}{\sqrt{3}}\sum_i C_i[R^{(1)}_{n_1l_1}R^{(2)}_{n_2l_2}R^{(3)}_{n_3l_3}Y^L(l_1l_2,l_3)+(1\leftrightarrow 2)]\chi^s(12;3)\,; \tag{6}$$

$\mathcal{A}$ is the antisymmetrization operator, $i=(n_1l_1,n_2l_2,n_3l_3)$, Y is the total angular eigenfunction, and χ^s is the total spin function. L and S are the total orbital and spin quantum numbers of the three-particle system. R_{nl} are the radial orbitals and in this work are expanded as follows:

$$R_{nl}=r^{-1}\sum_{j=1}^{n_l}a_jr^{m_j}e^{-z_jr}\,. \tag{7}$$

These functions are constructed to be orthonormal:

$$\int_0^\infty r^2R_{n'l'}R_{nl}\,dr=\delta_{nn'}\delta_{ll'}\,. \tag{8}$$

This requires $n_l=n-l$ terms for each series representation in Eq. (7). The integer m_j runs from $l+1$ to n, $l+1\leq m_j\leq n$, and the coefficients a_j are determined from the orthonormality condition (8). The nonlinear parameters z_j are determined by the optimization process of the $\hat{Q}H\hat{Q}$ matrix. The configurations used for ^2S, $^2P^o$, and ^2D symmetries are listed in Table II. Tables III and IV give the values of the coefficients a_j, exponents m_j, and optimized z_j for the R_{nl}.

The $\phi_n(x^i)$ in Eq. (2) are in principle supposed to be the exact eigenfunctions of He and Li^+. In most of our calculations we use approximations of the target plus the incident electron, i.e., product functions whose orbitals are optimized for He^- and Li. Such a choice is not as rigorous as that for orbitals optimized for the target wave functions, because they are poorer approximations of the exact eigenfunctions of He and Li^+; thus their effect is to *lower* the spectrum of the resonance positions. Weiss and Krauss[18] found it necessary to use such orbitals in their calculations of autoionizing states in Li. We test both types of orbitals by calculating the ^2S resonances in He^- with the two forms of $\phi_n(x^{(i)})$ described above. Using the He target orbitals, we obtain −2.192 a.u. for the resonance below $2\,^3S$ and −2.071 a.u. for the one below $3\,^3S$. These two positions became −2.193 and −2.077 a.u. when projecting out with the He^- orbitals. This indicates that the resonance positions do not seem to be very sensitive to the actual form of the target orbitals *when used in our generalized quasiprojection formalism*,[16] whereas the projection algebra is greatly simplified when one uses the orbitals of the $N+1$ electron system. However, if an apparent resonant eigenvalue should lie close to an unprojected (i.e., higher) threshold, then even a small shift in energy may take it above that threshold and thus negate its being a resonance. Precisely such a situation arose in the present calculation for a $^2P^o$ eigenvalue which lay below the $2\,^1S$ threshold of He. In such cases it is essential to be as rigorous as possible in carrying out the quasiprojection formalism.

TABLE II. Configurations used[a] for both He^- and Li.

i	^2S	$^2P^o$	^2D
1	$1s^22s$	$1s^22p$	$1s^23d$
2	$1s2s^2$	$1s2s\,^1S2p$	$1s2s\,^3S3d$
3	$1s2s\,^3S3s$	$1s2s\,^3S2p$	$1s2s\,^1S3d$
4	$1s2s\,^1S3s$	$1s2s\,^1S3p$	$1s2s\,^3S4d$
5	$1s2p^2$	$1s2s\,^3S3p$	$1s2s\,^1S4d$
6	$1s2p\,^3P3p$	$1s2p\,^1P3s$	$1s2s\,^3S5d$
7	$1s2p\,^1P3p$	$1s2p\,^3P3s$	$1s2s\,^1S5d$
8	$2s2p^2$	$1s2p\,^1P4s$	$1s2s\,^3S6d$
9	$1s3s^2$	$1s2p\,^3P4s$	$1s2s\,^1S6d$
10	$1s3p^2$	$1s2s\,^1S4p$	$1s2p^2$
11	$1s3d^2$	$1s2s\,^3S4p$	$1s2p\,^3P3p$
12	$1s4s^2$	$1s2s\,^1S5p$	$1s2p\,^1P3p$
13	$1s4p^2$	$1s2s\,^3S5p$	$1s2p\,^3P4p$
14	$1s2s\,^3S4s$	$1s2p\,^1P3d$	$1s2p\,^1P4p$
15	$1s3s\,^1S4s$	$1s2p\,^3P3d$	$1s2p\,^3P5p$
16	$2s^23s$	$1s2p\,^1P4d$	$1s2p\,^1P5p$
17	$2s3s^2$	$1s2p\,^3P4d$	$1s3p\,^3P5p$
18	$2p^23s$	$1s3s\,^1S3p$	$1s3p\,^1P5p$
19	$2s3p^2$	$1s3s\,^3S3p$	$1s4p\,^3P5p$
20	$2s3d^2$	$1s3p\,^1P4s$	$1s4p\,^1P5p$
21	$1s2s\,^3S5s$	$1s3p\,^3P4s$	$1s3s\,^3S3d$
22	$1s2s\,^1S5s$	$1s3s\,^1S4p$	$1s3s\,^1S3d$
23	$1s3p\,^3P4p$	$1s3s\,^3S4p$	$1s3p^2$
24	$1s3p\,^1P4p$	$1s3p\,^1P3d$	$1s3d^2$
25	$1s4s\,^3S5s$	$1s3p\,^3P3d$	$1s3d\,^3D4s$
26	$1s4s\,^1S5s$	$1s3p\,^1P4d$	$1s3d\,^1D4s$
27	$1s4p\,^3P5p$	$1s3p\,^3P4d$	$1s3d\,^3D4d$
28	$1s4p\,^1P5p$	$1s3d\,^1D4f$	$1s3d\,^1D4d$
29	$1s5s^2$	$1s3d\,^3D4f$	$1s4p^2$
30	$1s5p^2$	$1s4s\,^3S4p$	$1s4d^2$
31	$1s4d^2$	$1s3s\,^3S5p$	$1s3s\,^3S4d$
32	$1s4f^2$	$1s3s\,^1S5p$	$1s3s\,^1S4d$
33	$1s3d\,^3D4d$	$1s4s\,^3S5p$	$1s3s\,^3S5d$
34	$1s3d\,^1D4d$	$1s4s\,^1S5p$	$1s3s\,^1S5d$
35	$1s3p\,^3P5p$	$1s3p\,^3P5s$	$1s3s\,^3S6d$
36	$1s3p\,^1P5p$	$1s3p\,^1P5s$	$1s3s\,^1S6d$
37	$1s2s\,^3S4s$	$1s3p\,^3P5d$	$1s3p\,^3P4p$
38	$1s2s\,^1S4s$	$1s3p\,^1P5d$	$1s3p\,^1P4p$
39	$1s2s\,^3S5s$	$1s3d\,^3D5f$	$1s3d\,^3D5d$
40	$1s2s\,^1S5s$	$1s3d\,^1D5f$	$1s3d\,^1D5d$
41			$1s3d\,^3D6d$
42			$1s3d\,^1D6d$
43			$1s5d^2$
44			$1s6d^2$
45			$1s4s\,^3S4d$
46			$1s4s\,^1S4d$

[a] For He^- 30 of the above configurations were used for all symmetries.

TABLE III. Orbital parameters for He^-.

	m_j	a_j	z_j
$1s$	1	5.656 85	2.0
$2s$	1	0.827 05	1.590 47
	2	−0.243 49	0.528 61
$3s$	1	0.511 70	1.683 37
	2	−0.181 61	0.663 46
	3	0.002 73	0.235 07
$4s$	1	6.736 27	1.011 84
	2	−11.754 88	1.194 07
	3	2.404 28	1.137 93
	4	−0.019 74	0.777 93
$5s$	1	0.436 22	1.124 78
	2	−0.207 89	0.657 69
	3	−0.030 03	0.030 00
	4	0.012 84	0.400 0
	5	−0.000 29	0.400 0
$2p$	2	0.180 60	0.476 10
$3p$	2	0.855 16	0.963 70
	3	−0.008 57	0.346 58
$4p$	2	17.202 71	2.862 71
	3	−0.476 94	1.329 20
	4	0.000 27	0.363 72
$5p$	2	1.626 29	1.083 90
	3	−1.876 27	1.277 80
	4	0.025 08	0.699 70
	5	−0.000 15	0.395 40
$3d$	3	0.757 68	1.182 30
$4d$	3	0.001 37	0.633 38
	4	−0.000 03	0.163 05
$4f$	4	0.000 1	0.121 06

TABLE IV. Orbital parameters for Li.

	^2S			$^2P^o$			^2D		
	m_j	a_j	z_j	m_j	a_j	z_j	m_j	a_j	z_j
1*s*	1	10.392 30	3.0	1	10.392 39	3.0	1	10.392 30	3.0
2*s*	1	1.951 36	2.358 98	1	1.356 64	1.957 97	1	1.601 07	1.516 34
	2	−0.998 95	0.920 97	2	−0.809 52	0.843 25	2	1.526 60	1.029 02
3*s*	1	0.762 32	0.302 59	1	0.546 87	0.259 75	1	11.380 79	1.540 60
	2	−1.867 37	1.307 61	2	−1.302 22	1.277 95	2	−33.440 12	1.212 10
	3	−0.363 07	0.889 87	3	−0.287 58	0.841 77	3	33.106 62	1.580 00
4*s*	1	0.095 13	0.100 92	1	0.388 38	2.028 74	1	3.331 32	0.643 97
	2	−8.037 86	11.506 41	2	0.276 41	0.294 97	2	−7.641 31	0.820 08
	3	−6.790 15	5.131 39	3	−0.916 41	0.561 38	3	3.091 36	0.723 73
	4	−0.012 68	0.592 54	4	0.497 92	0.819 34	4	−0.648 47	0.795 48
5*s*	1	0.091 58	0.137 51						
	2	0.022 47	0.181 19						
	3	−0.281 44	0.459 30						
	4	0.118 93	0.585 05						
	5	−0.003 29	0.548 33						
2*p*	2	0.682 13	0.810 14	2	0.877 34	0.895 94	2	0.763 38	0.847 44
3*p*	2	0.373 92	0.950 41	2	0.347 93	0.929 80	2	0.231 36	0.800 32
	3	−0.010 52	0.345 25	3	−0.014 55	0.376 29	3	−0.011 01	0.346 07
4*p*	2	1.082 13	0.373 59	2	0.031 01	0.181 71	2	1.480 06	0.807 80
	3	−0.760 82	0.714 05	3	0.499 35	2.148 39	3	−0.495 50	0.714 05
	4	−0.046 37	0.549 19	4	−0.008 31	0.497 28	4	0.001 11	0.388 90
5*p*	2	6.614 50	1.083 90	2	0.178 48	0.479 22	2	6.424 23	1.083 90
	3	−5.119 53	1.277 80	3	−0.005 10	0.219 56	3	−5.119 81	1.277 80
	4	0.032 11	0.699 70	4	−0.019 70	0.473 66	4	0.039 80	0.699 70
	5	0.001 21	0.600 00	5	0.002 40	0.467 29	5	−0.001 61	0.600 00
3*d*	3	1.643 71	1.475 11	3	0.006 64	0.305 39	3	0.010 96	0.352 47
4*d*				3	0.130 56	0.707 09	3	0.140 81	0.730 92
				4	−0.000 43	0.396 06	4	−0.000 57	0.334 76
4*f*				4	0.030 88	0.750 00			
5*d*							3	0.445 99	0.737 60
							4	−0.108 20	0.764 99
							5	0.000 04	0.340 32
6*d*							3	0.153 31	0.736 06
							4	−0.042 57	0.750 78
							5	−0.000 01	0.232 73
							6	0.000 03	0.455 95

Therefore when we replaced the projector orbitals by optimized He (not He$^-$) orbitals, the eigenvalue was raised above the $2\,^1S$ threshold. We discuss further details of this specific calculation in Sec. III.

The optimization procedure used is that of Powell[19]; convergence of some positions versus the included number of configurations is illustrated in Table V.

III. RESULTS AND DISCUSSION

In Table VI we present the complete spectrum of eigenvalues for the 30-configuration calculation, including the spurious ones, for ^2S symmetry in He$^-$. The numbers of spurious states are seen to conform to the entries in Table I, and in most cases the largest configuration (also listed) of each spurious state shows obviously that it corresponds to an ordinary (nonresonant) scattering from a target state whose energy is lower than the three-electron eigenvalue in question. Note that for the ^2S states the spurious states are found to be the lowest that arise. As suspected,[16] however, we have found one case where the ordering is violated. In Li $^2P^o$ below the $3\,^3S$ threshold ($\nu = 4$) we find a spurious eigenvalue −4.803 a.u. with configuration $(1s2s)\,^1S;\ 2p|^2P^o\rangle$, which is higher than one real resonance $(1s3s)\,^3S;\ 3p|^2P^o\rangle$ at −4.806.

Table VII contains a compilation of all our (real) He$^-$ resonances (in eV relative to the He ground state). Without attempting to be complete, we have also included in the table other salient results, both experimental and theoretical, which give a good picture of the current situation. Re-

TABLE V. Convergence of resonances below the first excitation (2^3S) threshold of target for various symmetries.

Symmetry	System	Resonance number	Number of configurations 10	20	30
			Resonance positions (a.u.)		
$^2S^e$	Li	1	−5.4045	−5.4054	−5.4059
		2	−5.1848	−5.1971	−5.1977
		3	−5.1492	−5.1560	−5.1569
		4	−5.1365	−5.1492	−5.1498
				−5.1439	−5.1446
	He$^-$	1	−2.1913	−2.1928	−2.1930
$^2P^o$	Li	1	−5.2895	−5.3124	−5.3128
		2	−5.2501	−5.2559	−5.2567
		3	−5.1499	−5.1828	−5.1836
		4	−5.1213	−5.1480	−5.1487
		5	−5.1301	−5.1338	−5.1345
^2D	Li	1	−5.2167	−5.2304	−5.2338
		2	−5.1487	−5.1650	−5.1657
		3	−5.1141	−5.1363	−5.1375

ferring first to the lowest ^2S (Schulz) resonance, we see that our present value is in satisfactory accord with a previous calculation and experiment. We do not consider our present value to be as theoretically rigorous as our previous quasiprojection results,[13] particularly the one (19.386 eV) based on the open-shell target. The latter has been gratifyingly supported by the recent beautiful complex-rotation calculation of Junker and Huang,[20] even though the best present experimental value of Brunt *et al.*[1] is closer to our previous[13] closed-shell result (19.363 eV). The difference between our previous results and our present one (19.34 eV) can be taken as a measure of the effect of using He$^-$ rather than He orbital in our projectors, as explained above.

Above the $2\,^3S$ threshold there is a comparatively broad shape resonance at 20.3 which shows up as a feature about 0.6 eV wide in the experiment of Brunt *et al.*[1] Being a shape resonance (i.e., having the quantum numbers of the energetically accessible $2\,^3S$ itself), this state cannot (and does not) show up as a resonance in our quasiprojection formalism, whereas, in elaborate scattering calculations, such as those in Ref. 11 or Ref. 21, it does.

Beyond the broad shape resonance there is a small but sharp feature in the data of Brunt *et al.*[1] which has its onset at essentially the $2\,^1S$ threshold. They[1] have attempted to fit this feature by convoluting a linear combination of the $2\,^3S$ cross section[21] and $2\,^1S$ cross section[10] with their experimental resolution profile. The recognized resonantlike item in the theoretical cross sections is an enhancement of the ^2S eigenphase above the $2\,^1S$ threshold, which first appeared in the calculation of Burke *et al.*[12] The latter interpreted this enhancement as a virtual state of ^2S symmetry just below the $2\,^1S$ threshold. As alluded to in the Introduction and in Sec. II, our own calculation originally showed a

TABLE VI. Lowest ^2S eigenvalues of $\hat{Q}H\hat{Q}$ for He$^-$ 30-configuration calculation.[a] Results are in a.u.

Target state Symmetry	Energy	ν	^2S autoionization states Energy	Chief configuration	Status
$1\,^1S(1s^2)$	−2.9037	0	−2.193	$(1s2s^2)$	real
$2\,^3S(1s2s)$	−2.1754	1	−2.698	$(1s^22s)$	spurious
			−2.148	$(1s2s^2)$	spurious
$2\,^1S(1s2s)$	−2.1461	2	−2.147	$(1s^22s)$	spurious
			−2.145	$(1s2s^2)$	spurious
$2\,^3P(1s2p)$	−2.1333	3	−2.1302	$(1s^22s)$	spurious
			−2.1300	$(1s2s^2)$	spurious
			−2.128	$(1s2p^2)$	spurious
$2\,^1P(1s2p)$	−2.1250	4	−2.117	$(1s^22s)$	spurious
			−2.114	$(1s2s^2)$	spurious
			−2.096	$(1s2p^2)$	spurious
			−2.077	$(1s3s^2)$	real
$3\,^3S(1s3s)$	−2.0688				

[a] In order to be considered, the $(N+1)$-electron eigenvalue must be lower than the target threshold for the next higher ν. Only such eigenvalues are given here. Of those eigenvectors, the (chief) configuration must not be a spurious one, as given in Table I. Cf. also Ref. 16.

TABLE VII. He$^-$ resonances: comparisons with other calculations and experiments.[a]

He target levels		He$^-$ resonances position (eV)								
Symmetry	Energy	Symmetry	Present	Other calculations			Experiments			
$(1s2s)\,^3S$	19.829	$^2S[1s(2s^2)]$	19.340	(19.363, 19.386)[b]	19.4[c]	19.387[d]	19.367 ± 0.007[e]	19.31 ± 0.03[f]	19.34 ± 0.02[g]	
		$^2P^o$ (shape)		20.17[h]	20.19[i]		20.3 ± 0.3	20.35 ± 0.3[j]	20.45 ± 0.05[k]	
$(1s2s)\,^1S$	20.616	^2S (virtual state)		20.616[l,m]			20.61 ± 0.009			
		^2D (shape)		20.85[h]			20.955	21.00 ± 0.05[k]		
$(1s2p)\,^3P$	20.964									
$(1s2p)\,^1P$	21.218									
		$^2S[1s(3s)^2]$	22.497	22.441[l]			22.45 ± 0.02	22.5 ± 0.05[j]	22.42 ± 0.08[g]	22.44[n]
		$^2P^o[1s(3s3p\,^3P)]$	22.687	22.608[l]			22.64 ± 0.04	22.60 ± 0.07[j]	22.66 ± 0.06[g]	22.60[n]
		$^2D[(1s3s\,^3S)nd]$	22.714	22.66[l]			22.70 ± 0.02			22.66[n]
$(1s3s)\,^3S$	22.719									

[a] Positions are calculated relative to the He ground state at −79.015 136 57 eV (1 Ry = 13.605 826 eV).

[b] Temkin *et al.* (Ref. 13).

[c] Sinfailam and Nesbet (Ref. 26).

[d] Junker and Huang (Ref. 20).

[e] Brunt *et al.* (Ref. 1).

[f] Kuyatt *et al.* (Ref. 24).

[g] Schulz (Ref. 25) and Sanche and Schulz (Ref. 3).

[h] Oberoi and Nesbet (Ref. 11).

[i] Fon *et al.* (Ref. 22).

[j] Pichanick and Simpson (Ref. 6).

[k] Ehrhardt and Willman (Ref. 22).

[l] Nesbet (Ref. 10).

[m] Berrington *et al.* (Ref. 21) and Burke *et al.* (Ref. 12).

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TABLE VIII. Positions in eV for Li and comparison with other calculations and experiments, where available.

Li$^+$ target levels	λ		Position relative to exact ground state This calculation[a]	Bhatia[a,b]	Position relative to Hartree-Fock energy of excited threshold This calculation	Weiss[c]	d	Experiments	e	Classification
	1	^2S	56.383	56.424	56.373	56.54	56.31	56.35[f]		$1s2s^2$
	2		62.043	62.156	62.033	62.03	61.992	61.995[f]		$(1s2s\,^3S)(3s)$
	3		63.159	63.425	63.149	63.23	63.135	63.19[g]		$(1s2s\,^1S)(3s)$[h]
	4		63.349		63.339	63.26	63.313	63.29[g]		$(1s2s\,^3S)(4s)$
	5		63.485		63.475	63.50	63.462	63.49[g]		$1s2p^2$[h]
	6		63.757		63.747		63.735	63.79[g]		$(1s2s\,^3S)(5s)$
	1	$^2P^o$	58.914	58.976	58.904	58.96		58.91[f]	58.91	$1s(2s2p\,^3P)$
	2		60.438	60.531	60.428	60.60		60.397[f]	60.396	$1s(2s2p\,^1P)$
	3		62.424	62.483	62.414	62.46		62.425[f]	62.419	$(1s2s\,^3S)(3p)$
	4		63.377		63.367	63.36		63.39[g]	63.356	$(1s2s\,^1S)(3p)$[h,i]
	5		63.758		63.748	63.77			63.753	$(1s2s\,^3S)(4p)$[i]
	1	^2D	61.064	61.177	61.054	61.11	61.062	61.06[g]		$1s2p^2$[h]
	2		62.914	63.008	62.904	62.98	62.899	62.93[g]		$(1s2s\,^3S)(3d)$
	3		63.676		63.666	63.62	63.565	63.59[g]		$(1s2s\,^3S)(nd)$
	4						63.865	63.89[g]		$(1s2s\,^3S)(5d)$
$1s2s\,^3S$	(64.445)				(64.455)					
	1	^2S	64.846							$(1s2s\,^1S)(4s)$
	2		65.009							$(1s2s\,^1S)(5s)$
	3		65.390							$(1s2p\,^3P)(3p)$[h]
	4		65.662							$(1s2p\,^3P)(4p)$[h]
	5		65.070							$(1s2p\,^1P)(3p)$[h]
	1	$^2P^o$	64.982	64.7[j]					64.6–65.1	$(1s2p\,^3P)(3s)$[h,i]
	2		65.145							$(1s2s\,^1S)(4p)$
	3		65.254	65.17[j]					65.25	$(1s2p\,^1P)(3s)$[h]
	4		65.309	65.28[j]				65.30		$(1s2p\,^3P)(3d)$[h]
	5		65.662	65.59[j]				65.66		$(1s2s\,^1S)(5p)$[i]
	6		65.907	65.87[j]				65.89		$(1s2p\,^1P)(3d)$[h,i]
	7		65.962							$(1s2p\,^3P)(4s)$[h]
	1	^2D	64.574		64.25	64.40	64.545			$(1s2s\,^1S)(3d)$
	2		64.900				64.832			$(1s2p\,^3P)(3p)$[h]
	3		65.390		65.066	64.94	65.366			$(1s2s\,^1S)(4d)$
	4		65.625				65.599			$(1s2p\,^1P)(3p)$[h]
	5		66.125							$(1s)(2p4p\,^3D)$[h]
$1s2s\,^1S$	(66.186)				(66.510)					
	1	^2S	66.263							$(1s2p\,^1P)(4p)$[h]
	1	$^2P^o$	66.452							$(1s2p\,^1P)(4s)$[h]
	1	^2D	66.588							$1s(2p4p\,^1D)$[h]

TABLE VIII. *(Continued.)*

[a] These positions are calculated relative to the Li ground state at −14.956 05 Ry. (1 Ry = 13.605 826 eV).
[b] Results of Bhatia (Ref. 15).
[c] Results of Weiss (quoted in Ref. 2).
[d] McIlrath and Lucatorto (Ref. 2).
[e] Ederer *et al.* (Ref. 9).
[f] Ziem *et al.* (Ref. 8).
[g] M. Rødbro, R. Bruch, and P. Bisgaard, J. Phys. B 12, 2413 (1979).
[h] Cf. discussion of these resonances in text.
[i] Our classification disagrees with other theoretical classifications of Refs. c and j above.
[j] Cooper *et al.* [Ref. 12. Their energy scale is with respect to the Morse-Young-Haurwitz ground-state energy (−7.2225 a.u.), which is 1.56 eV above the experimental ground state.]

$^2P^o$ resonance at 20.564 eV. This was thought to be associated with the blip feature observed[1] at 20.16 eV. However, after conversations with Professor F. H. Read and Dr. G. C. King and careful inspection of the predicted cross section of Berrington *et al.*,[21] it was clear that this feature must be due primarily to the virtual ^2S state associated with the $2\,^1S$ threshold which had arisen in the previous calculations.[12,20,21] Since our original calculations were based on optimized He$^-$ rather than He orbitals in our quasiprojection operator, the reality of this ostensible $^2P^o$ resonance became an important issue. Therefore we redid the calculations with optimized He (i.e., target) orbitals. In addition we included up to 60 configurations in the total wave function and made further variations in the nonlinear parameters. The effect of these changes was dramatic: use of He orbitals immediately shifted the eigenvalue above the $2\,^1S$ threshold, and even with our most elaborate wave function the eigenvalue never descended below 20.67 eV! We conclude that there is no $^2P^o$ resonance; but the experience taught us to use caution in inferring resonances from nonoptimized target projectors. It is nevertheless gratifying that the quasi-projection-operator formalism allows such a more rigorous calculation to be carried out.

There are no resonances between the $2\,^1S$ and $2\,^3P$ thresholds, but above the latter we do find three Feshbach resonances which are clearly revealed in experimental data as well as the 1978 calculation of Nesbet.[10]

Another shape resonance, ^2D, shows up above the $2\,^1S$ threshold in the data of Brunt *et al.*[1] (elsewhere as well[22]) and also comes out of the calculation of Oberoi and Nesbet[11] but is (by definition) excluded from our calculation.

The inability of our formalism to deal with shape resonances shows that the quasi-projection-operator formalism is by itself not tantamount to a full scattering calculation. However, the following argument cogently indicates that for a given isoelectronic system the importance of shape (relative to Feshbach) resonances must decrease as the charge Z on the nucleus increases. This occurs because shape resonances, which arise by virtue of potential barriers, depend ultimately on the centrifugal or electron-electron repulsion. But these repulsive potentials are independent of Z, whereas Feshbach resonances, which depend strongly on the interaction with the core, also depend strongly on Z. Since our main interest is dominantly in (strongly) ionic targets,[23] we feel that the neglect of shape resonances in our formalism is not an important practical omission.

The domination of Feshbach resonances for higher Z is already evident in the cleaner-cut resonant structure exhibited by lithium. Not only does the larger nuclear charge emphasize Feshbach resonances, but it lowers resonances relative to their parent (target) threshold. However, this greater separation has the one negative effect of exacerbating the question of the optimum energy relative to which one chooses to refer one's calculated results. We have consistently favored referring all eigenvalues to the exact (i.e., experimental) target energies.[13] The results in the second and third columns of Table VIII, which also include those of Bhatia,[15] are determined in this way. (The calculation of Bhatia is only for resonances below the $2\,^3S$ threshold.) The results of Weiss (quoted in Refs. 2 and 9) refer the energy scale to the Hartree-Fock energies of the target excited states. (Those energies are also given in Table VIII.) This will have the effect of lowering the resonant energies relative to the exact target ground state; our results so determined are given in column 5 of Table VIII and compared to those of Weiss, which are in column 6. One sees that our results so normalized are indeed lower (with one or two exceptions) than Weiss's. It would also seem that the results of columns 5 and 6 are closer to the experiment; however, on closer examination one sees that the higher states and higher symmetries are actually *too low* compared to experiment. [Compare for example the ^2D resonances below the $(1s2s)\,^1S$ level.] In addition, the sparseness of the alternately computed spectrum, compared to our own and the experimental spectrum, reinforces our opinion that the full quasiprojection formalism[13] plus normalization of results relative to exact threshold energies provides a superior framework for calculating resonances in the inelastic regime.

In Table IX we give our additional calculated resonances (and their configurations) for Li. These are predicted results which have not as yet been observed; note that states lie between the $2\,^1P$ and $3\,^3S$ states of Li$^+$ and that there are no autoionization states between the $2\,^3P$ and $2\,^1P$ thresholds; it will be of interest to see if these predictions are borne out by future experiments.

Particular attention should be given to those resonances marked by h and a in the last column of Tables VIII and IX, respectively. The configuration of those resonances shows that they fall below a target-state threshold even lower than the target state of which they are chiefly composed. Taking for example the $(1s2s)\,^1S(3s);\,^2S$ resonance at (calculated) energy 63.159 eV, one sees that its parent target state is clearly the $2\,^1S(1s2s)$ level of Li$^+$; nevertheless it falls below the $2\,^3S(1s2s)$ state. An essential point that we have tried to make previously [16,23] is that in a close-coupling calculation, one would have to include this $2\,^1S$ state explicitly in the close-coupling total wave function in order to get that resonance. In contrast, in a quasiprojection calculation one does not include the $\nu=1$ state in $\hat{Q}H\hat{Q}$. In fact, by including $\nu=1$, the resonance (although it would still occur) would be less accurately given, because the true resonance necessarily contains some $(1s2s)\,^3S(3s)\,^2S$ component which would be excluded in the $\nu=1$ calculation. (We should add that all such resonances occuring in a particular $Q_{\nu'}$ calculation that have already been accounted for in $\nu<\nu'$ calculations are not counted again; they are discarded along with spurious states, as listed in Table I, for example.)

TABLE IX. Additional predicted autoionization states for Li.

Li$^+$ target levels			Position relative to the exact ground state, this calculation	Classification
$1s2p\,^3P$			(66.706)	
$1s2p\,^1P$			(67.642)	
	1	^2S	70.615	$1s3s^2$
	2		61.839	$1s3p^2+1s3d^2$ [a]
	3		72.220	$(1s3s\,^3S)(4s)$
	4		72.330	$(1s3s\,^1S)(4s)$ [a]
	5		73.173	$(1s)(3p4p\,^3S)$ [a]
	6		73.390	$(1s)(3p4p\,^1S)$ [a]
	7		73.445	$(1s3s\,^3S)(5s)$ [a]
	8		73.690	$(1s3s\,^1s)(5s)$ [a]
	1	$^2P^o$	72.708	$1s(3s3p\,^3P)$
	2		73.119	$1s(3s3p\,^1P)$ [a]
	3		73.333	$1s(3pnd\,^3P)$ [a]
	4		73.663	$1s(3pnd\,^1P)$ [a]
	5		73.803	$1s(3s4p\,^3P)$
	6		73.900	$1s(3s4p\,^1P)$ [a]
	1	^2D	71.431	$1s3p^2$ [a]
	2		71.731	$1s(3s3d\,^3D)$
	3		71.839	$1s(3s3d\,^1D)$ [a]
	4		72.111	$1s3d^2$ [a]
	5		72.601	$(1s3s)\,^3S(4d)$
	6		72.685	$(1s3s)\,^1S(4d)$ [a]
	7		73.118	$(1s3p)\,^3P(4p)$ [a]
	8		73.200	$(1s3p)\,^1P(4p)$ [a]
	9		73.445	$1s(3d4d\,^3D)$
	10		73.581	$(1s3s)\,^3Snd$
	11		73.744	$1s(3d4d\,^1D)$ [a]
	12		73.799	$(1s3s)\,^1Snd$ [a]

[a] Cf. discussion in text.

In conclusion, we believe that these calculations have shown that the concept of inelastic quasiprojector operators[16] is viable and a useful technique, even at the practical calculational level. It is our next intention to calculate widths of these resonances, since the width is also an indispensible item for astrophysical and plasma diagnostics.[16,23]

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