Core-excited bound states of negative lithium

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Accurate solutions of the four-electron Schrödinger nonrelativistic equation for nuclear charge $Z = 3$ reveal the existence of two core-excited bound states of Li$^-$, which together with the ground state Li$^-$ $1s^2 2s^2$ are found to be the *only* long-lived negative lithium ions. The metastable Li$^-(1s2s2p\,^2)^5P$ state is 504.5 ± 2.0 meV below the (also metastable) $(1s2s2p)^4P^o$ state of Li. Another bound state Li$^-(1s2p\,^3)^5S^o$, lies 291.0 ± 2.0 meV below Li$(1s2p\,^2)^4P$ and it decays to the lower ^5P state with $\tau = 2.9$ nsec, emitting uv photons of $\lambda = 348.98 \pm 0.09$ nm. This is the first example of an electric dipole transition between bound states of atomic negative ions.

I. INTRODUCTION

Relatively intense beams of Li$^-$ have been produced for a number of years.[1] Undoubtedly, the only stable Li$^-$ ion,[2,3] the $1s^2 2s^2$ ground state, should be the main component and perhaps the only one present in these Li$^-$ beams. The existence of Li$^-$ in states other than $1s^2 2s^2$ or short-lived resonances ($\tau \simeq 10^{-13}$–10^{-15} sec) (Ref. 4) has not been reported so far.

The primary purpose of this paper is to inquire into the existence of long-lived[5] Li$^-$ ions other than the $1s^2 2s^2$ ground state. Calculations are carried out in the framework of Schrödinger's nonrelativistic equation for bound states. The eigenfunctions are approximated by means of moderate-size configuration-interaction (CI) expansions. An outline of the method employed is given in Sec. II.

Calculations show[6] that additional *stable* Li$^-$ states do not exist. The most likely candidate Li$^-(1s^2 2s 2p)^3P^o$, is apparently a 0.1-eV-wide resonance 0.15 eV above Li $1s^2 2s$ (the $^3P^o$ state is unbound[6] and the experimental data show[4] that there is a $^3P^o$ resonance just above Li $1s^2 2s$). Thus one should look for states which are *metastable* against autoionization. These are states lying below the onset of the continuum with the same LS symmetry and parity.[7] When transitions without spin change are possible, decay occurs most likely by electric dipole radiation into lower, bound, or continuum states including resonances.[8] Only when this mechanism is forbidden, does autoionization become dominant, taking place slowly ($\tau \simeq 10^{-5}$–10^{-7} sec in neutral systems)[7] on account of the small mixings of the adjacent continuum with states of different spin and orbital angular momentum. These occur due to the relativistic interactions in the atomic Hamiltonian. $M2$ radiative decay rates for systems similar to the ones to be considered here are comparatively negligible.[9]

One would normally expect Li$^-(1s^2 2p^2)^3P$ to be metastable and lying below Li $1s^2 2p$, just as H$^-(2p^2)^3P$ lies below H $2p$.[10] In fact, Li$^-(1s^2 2p^2)^3P$ is a resonance,[11] although analogous metastable states for Na$^-$, K$^-$, Rb$^-$, and Cs$^-$ do indeed exist.[11] Why is this so? The nature of binding in H$^-(2p^2)^3P$ is now clear[12]: The p-wave energy limit is unbound, with binding being achieved only after inclusion in the wave function of d orbitals localized in the innermost region of the electron charge distribution. Energy optimized d orbitals in Li$^-$-$(1s^2 2p^2)^3P$, on the other hand, stay localized too far out,[13] due to an apparent repulsion by the $1s^2$ core. And unlike the large correlation effects introduced by $ms \to nd$ excitations for $m \geq 2$, $n \geq 3$, the $1s \to 3d$ excitations, which are the only ones of the type present in Li$^-(1s^2 2p^2)^3P$, give negligible energy contributions. This is why Li$^-(1s^2 2p^2)^3P$ is unbound while the similar Na$^-$, K$^-$, Rb$^-$, and Cs$^-$ states are bound. $^3D^o$, ^3F, etc., metastable states are not likely to exist since they are already unbound in H$^-$ (Ref. 14).

After the Li $1s^2 2p$ threshold, the next Li$^-$ continuum with LS and parity not already present in the lower continuum starts at the metastable core-exicted Li$(1s2s2p)^4P^o$ state. This one is the lowest of a series of bound quartet states[15-18] located in an energy interval ranging from 57.413 eV[17] above the Li $1s^2 2s$ ground state up to the $(1s2p)^3P$ series limit at 66.672 95 eV. These quartet states are metastable against both autoionization and radiative decay to the doublet system. They may be produced either selectively, by electron impact bombardment of ground-state atoms,[7] or in a few of the lowest-energy states in hollow cathode tube experiments,[19] or in a myriad of states in the beam-foil excitation source.[20]

One may then ask whether Li$(1s2s2p)^4P^o$, which defines the onset of the $^5S^o$, $^5P^{o,o}$, $^5D^{o,o}$, etc., Li$^-$ continuum, may take an extra electron to form a metastable negative ion. The calculations pre-

sented in Sec. III show that only $Li^-(1s2s2p^2)^5P$ is below $Li(1s2s2p)^4P^o$.

The $Li(1s2p^2)^4P^e$ state, at 60.750 eV,[17] defines the onset of the $^{3,5}S^o$ Li^- continuum. The calculations presented in Sec. IV show that only Li^--$(1s2p^3)^5S^o$ is metastable against autoionization. This state, however, decays readily by $E1$ radiation into $Li^-(1s2s2p^2)^5P^e$ and into the $^5S^e$ and $^5P^e$ continuum. In Sec. V the calculation of the oscillator strength for the transition $^5S^o \rightarrow {}^5P^e$ is discussed.

The $Li(1s2p^2)^2P^e$ state, at 61.612 eV,[21] defines the onset of the $^1S^o$ Li^- continuum. Bound-state calculations analogous to those described in Secs. III and IV show that the lowest $^1S^o$ state of Li^- is embedded in the $^1S^o$ continuum and it will not be considered any further. The nature of binding of the extra electron is discussed in Sec. VI and conclusions are given in Sec. VII.

II. OUTLINE OF THE METHOD

In previous work[17,21] on core-excited states of neutral Li we arrived at the conclusion that relativistic, radiative, and mass polarization corrections ΔE_{rrmp} to the energy *differences* between these systems and singly excited $1s^2nl$ states should be considerably less than 0.000 037 a.u. $\simeq 1$ meV. The contributions E_{rrmp} to the *absolute* term values, however, are more than ten times ΔE_{rrmp},[17,21] $E_{rrmp} \simeq -0.000\,500$ a.u. $\simeq -13$ meV.

ΔE_{rrmp} contributions to electron affinities have been discussed before.[22] The bulk of the ΔE_{rrmp} term is believed to be given by its relativistic part which does not exceed 1 meV until $Z = 7$ in atomic nitrogen.[22] We have then assigned ΔE_{rrmp} $\pm 0.000\,037$ a.u. for the electron affinities (A's) of the Li^- ions, which is equivalent to writing

$$A = A_{nr} \pm 37 \ \mu\text{hartree}(\pm 1 \text{ meV}), \qquad (1)$$

where A_{nr} is the nonrelativistic electron affinity

$$A_{nr} = E_{nr}(\text{Li}) - E_{nr}(\text{Li}^-). \qquad (2)$$

The nonrelativistic energies E_{nr} are calculated variationally, by approximating the wave functions Ψ with moderate-size Cl expansions of about 300 terms

$$\Psi = \sum_{(K_p)}^{\approx 300} \Phi_K^{(p)} a_{K_p} \qquad (3)$$

based on (i) an energy optimized Slater-type orbital (STO) basis, (ii) orthogonal one-electron symmetry-adapted spin orbitals, with equivalence of partner orbitals in degenerate representations, and (iii) an N-electron basis with LS symmetry. In Eq. (1), the sum over the LS eigenfunctions $\Phi_K^{(p)}$ runs over the degenerate elements (p) of con-

figurations K.[23] The different degenerate elements of a given configuration may be associated with LS couplings of electron groups.[24]

In order to obtain an estimate of E_{nr}, the variational rigorous upper bounds E_u are supplemented with empirical truncation errors[25] ΔE_{STO} and ΔE_{Cl} in both the STO set and the Cl expansion:

$$E_{nr} = E_u + \Delta E, \qquad (4)$$

$$\Delta E = \Delta E_{STO} + \Delta E_{Cl}. \qquad (5)$$

Because of (i) the relatively small size of the STO sets employed here, and (ii) the required accuracy in E_{nr}, $\delta E = \pm 1$ meV, ΔE_{STO} may be estimated just by truncating a large energy optimized STO set. This set is tested at the level of Cl with single and double excitations (SDCl) only. Let $\Delta E_{STO}(\text{SD})$ denote the energy difference between SDCl's for the large and the reduced (final) STO sets. Then ΔE_{STO} is calculated as

$$\Delta E_{STO} = \Delta E_{STO}(\text{SD}) + \delta/2 \pm \delta/2, \qquad (6)$$

where δ is a negative correction which added to $\Delta E_{STO}(\text{SD})$ gives an empirical lower bound for ΔE_{STO}. The value of δ is inferred from previous experience[12,26] with exhaustive studies of patterns of convergence for the energy in negative ions.

Once a final STO set is decided upon, the full Cl expansion is approximated through several steps. Each step consists of two calculations, a 500-term Cl and a truncated 200-term Cl. The energy differences between these two calculations, ΔE_s, are added for all steps to give most of ΔE_{Cl}:

$$\Delta E_{Cl} = \sum_{(\text{all steps})} \Delta E_s + \Delta E_{UQ}(\text{small}). \qquad (7)$$

The meaning of the last term in Eq. (7) is discussed below. The first step in the search for an approximation to the full Cl is an SDCl supplemented with the leading triple and quadruple excitations.[25] In order to reduce the number of steps, *small* energy effects ΔE_{UQ} of a large number of unlinked (disconnected) quadruple excitations are obtained from approximate formulas[25,27] derived from variational and perturbative results.

For small systems such as the ones considered here, most of the effort, about 97% of both human and computer time, is spent in the optimization of the STO set.[28]

III. BOUND STATES BELOW THE $Li(1s2s2p)^4P^o$ THRESHOLD

Below $Li(1s2s2p)^4P^o$ there may exist $^5S^e$, $^5P^{e,o}$, $^5D^{e,o}$, etc., Li^- bound states. Of these, only Li^--$(1s2s2p^2)^5P^e$ has the extra electron in the valence shell. Among the other states, $Li^-(1s2s2p3s)^5P^o$

TABLE I. STO parameters for $Li^-(1s2s2p^2)^5P$. The functions marked with an asterisk form the critical $5s5p3d$ STO basis. Sequential optimization of additional STO's is sufficient to provide a fully optimized $7s7p5d4f2g1h$ basis, i.e., one which is stable upon cyclic reoptimization of any one of its members. About 97% of both human and computer time is spent in this stage of the calculation. The truncation energy errors are calculated as explained in Sec. II.

l	Outer-shell STO's		Truncation energy errors, in μhartree
0	$3s* = 1.66$; $2s* = 0.90$; $2s* = 0.667$; $4s* = 1.215$; $5s = 1.50$		
1	$3p* = 1.88$; $2p* = 1.23$; $2p* = 0.77$; $2p* = 0.338$; $4p* = 1.34$; $5p = 1.08$		13 ± 2
2	$3d* = 1.19$; $4d* = 1.30$; $3d* = 0.72$; $5d = 0.50$		
3	$4f = 1.13$; $5f = 1.25$; $4f = 0.74$; $6f = 2.20$		5 ± 1
4	$5g = 1.50$; $6g = 2.33$		10 ± 5
5	$6h = 1.80$		5 ± 2
≥ 6	Not included in the final wave function		8 ± 3
		Outer-shell subtotal	41 ± 13[a]
	Inner-shell STO's		
	$1s = 3.0$; $6s = 2.85$; $6p = 3.40$; $6d = 2.85$		106 ± 20
		Total ΔE_{STO}	147 ± 33

[a] Outer-shell STO truncation errors using the *full* basis.

should be the lowest one, since the order $3s < 3p < 3d$ is preserved in the core-excited states of neutral Li.[16,17] Since the $^5P^o$ state of Li^- was found to be unbound (Sec. III C), we conclude that the $^5S^e$, $^5D^{e,o}$, etc., Li^- states are unbound. In Secs. III A and III B the calculation of the bound $Li^-(1s2s2p^2)^5P^e$ state is described.

A. STO basis

It is convenient to develop a *critical* STO basis,[26] i.e., the smallest possible basis which would remain invariant after inclusion of additional STO's and further reoptimizations. The optimization procedure for the critical basis makes use of a good approximation to the full CI in the open shell and a frozen $1s$ orbital. A $5s5p3d$ STO basis was found to be adequate as a critical basis. In Table I we give the $7s7p5d4f2g1h$ STO basis and a breakdown of the truncation error ΔE_{STO} among the successive harmonic functions. We get $\Delta E_{STO} = 147 \pm 33$ μhartree. The uncertainty of 33

μhartree $\simeq 1$ meV is sufficient for our stated purposes, anticipating a negligible uncertainty in ΔE_{CI}. Because of the extended nature of the electron charge distribution in slightly bound negative ions, the number of energy optimized STO's exceeds[12] that one of significant natural orbitals (NO's),[29] and therefore the energy patterns of convergence for STO's do not follow those for NO's. Definite energy patterns of convergence for both STO's and NO's in the valence shell are associated with three distinct localization regions at $\langle r \rangle$ about 3, 5, and 7 bohr, respectively.

B. Electron affinity of Li $(1s2s2p)^4P^o$

In Table II the results for the electronic energy of $Li^-(1s2s2p^2)^5P^e$ are summarized. A 320-term CI expansion gives a rigorous upper bound to the nonrelativistic energy $E_u = -5.386346$ a.u. (Li). The truncation energy error ΔE_{CI} due to the truncation of the full CI, Eq. (7), is relatively small, $\Delta E_{CI} = -0.000040(5)$ a.u. Using ΔE_{STO}

TABLE II. Electronic energy for $Li^-(1s2s2p^2)^5P^e$, in a.u. (Li) and electron affinity of $Li(1s2s2p)^4P^o$. 1 a.u. $(^7Li) = 219457.48$ cm^{-1} = $27.20953(10)$ eV.

	Energy correction	Total energy
E_u, 320-term CI		-5.386346
ΔE_{CI}, Eq. (7)	$-0.000040(5)$	
ΔE_{STO}, Eq. (6)	$-0.000147(33)$ [a]	
E_{nr}, $Li^-(1s2s2p^2)^5P^e$		$-5.386533(38)$
E_{nr}, $Li(1s2s2p)^4P^e$		$-5.367992(37)$ [b]
Electron affinity[c]	$0.018541(76) = 504.5 \pm 2$ meV	

[a] Taken from Table I.

[b] Reference 18.

[c] Nonrelativistic value. Relativistic corrections to the electron affinity should be considerably less than ± 1 meV, Eq. (1).

TABLE III. STO parameters for Li$^-(1s2p^3)^5S^o$. The functions marked with an asterisk form the critical $1s4p3d$ STO basis. Sequential optimization of additional STO's is sufficient to provide a fully optimized $4s7p6d4f2g1h$ basis. The truncation energy errors are calculated as explained in Sec. II.

l	Outer-shell STO's		Truncation energy errors, in μhartree
1	$2p^* = 1.76$; $2p^* = 0.865$; $3p^* = 0.875$; $2p^* = 0.323$; $4p = 1.80$; $5p = 0.61$		15 ± 2
2	$3d^* = 1.16$; $4d^* = 1.30$; $3d^* = 0.68$; $3d = 0.38$; $5d = 2.10$		
3	$4f = 1.15$; $5f = 1.30$; $4f = 0.75$; $6f = 2.00$		5 ± 2
4	$5g = 1.50$; $6g = 2.35$		10 ± 5
5	$6h = 1.80$		5 ± 2
$\geqslant 6$	Not included in the final wave function		8 ± 3
		Outer-shell subtotal	43 ± 14 [a]
	Inner-shell STO's		
	$1s^* = 3.0$; $3s = 2.4$; $4s = 4.0$; $3s = 1.05$; $6p = 2.40$; $6d = 3.80$		105 ± 11
		Total ΔE_{STO}	148 ± 25

[a] Outer-shell STO truncation errors using the *full* basis.

$= -0.000\,147(33)$ from Table I, one arrives at the nonrelativistic energy $E_{nr} = -5.386\,533(38)$ a.u. (Li). The most accurate value for E_{nr} of Li-$(1s2s2p)^4P^o$ is $-5.367\,992(37)$ a.u. (Li) (Ref. 18), from which a nonrelativistic electron affinity $A_{nr} = 504.5 \pm 2.0$ meV is obtained. As discussed in Sec. II, the corresponding relativistic, radiative and mass polarization contributions should be considerably smaller than 1 meV.

C. Calculations on Li $(1s2s2p3s)^5P^o$

With the STO set of Table I truncated to $5s5p4d$ STO's and supplemented with a freely varying $3s$ STO we performed fairly complete Cl calculations in an attempt to obtain a bound Li$^-(1s2s2p3s)^5P^o$ state. We found that as the localization of the additional $3s$ STO extended away towards infinity the Cl energy approached the energy of Li-$(1s2s2p)^4P^o$ with the same $5s5p4d$ STO basis. This type of behavior is well documented in other examples of resonance states.^{22} Thus we conclude that Li$^-(1s2s2p3s)^5P^o$ is unbound, i.e., it is a

resonance as well as the other $^5S^e$, $^5D^{e,o}$, etc., Li$^-$ states, following our earlier reasoning.

IV. BOUND STATES BELOW THE Li $(1s2p^2)^4P^e$ THRESHOLD

Below Li$(1s2p^2)^4P^e$ there may exist $^5S^o$ and $^3S^o$ Li$^-$ bound states, both of them with the same dominant configuration $1s2p^3$. Energy optimized $5s5p3d$ STO basis for the $^3S^o$ state leads to the $^4P^e$ state plus a free electron. We then conclude that Li$^-(1s2p^3)^3S^o$ is a resonance. In Secs. IV A and IV B the calculation of the bound Li$^-(1s2p^3)^5S^o$ state is described.

A. STO basis

Because of the absence of a $2s$ orbital (present in the $^5P^e$ state), the critical STO basis is just $1s4p3d$. The more extended nature of the electron charge distribution, however, extends the localization range where the orbital exponent optimization takes place, making the $^5S^o$ calculation of the

TABLE IV. Electronic energy for Li$^-(1s2p^3)^5S^o$, in a.u. (Li) and electron affinity of Li$(1s2p^2)^4P^e$. 1 a.u. (^{7}Li) = 219 457.48 cm^{-1} = 27.209 53(10) eV.

	Energy correction	Total energy
E_u, 200-term Cl		$-5.255\,890$
ΔE_{Cl}, Eq. (7)	$-0.000\,009(1)$	
ΔE_{STO}, Eq. (6)	$-0.000\,148(25)$ [a]	
E_{nr}, Li$^-(1s2p^3)^5S^o$		$-5.256\,047(26)$
E_{nr}, Li$(1s2p^2)^4P^e$		$-5.245\,351(37)$ [b]
Electron affinity [c]	$0.010\,696(63) = 291.0 \pm 2$ meV	

[a] Taken from Table III.

[b] Reference 18.

[c] Nonrelativistic value. Relativistic corrections to the electron affinity should be considerably less than ± 1 meV, Eq. (1).

TABLE V. Results for the $^5S^o \rightarrow ^5P^e$ transition in Li⁻: wavelength; length, velocity, and acceleration absorption f values; transition probability A_{ki}, line strength $S(i,k)$, and mean lifetime τ.

λ(nm)	348.98 ± 0.09
$f_{ik}^{(l)}$	0.212 ± 0.003[a]
$f_{ik}^{(v)}$	0.212 ± 0.003[a]
$f_{ik}^{(a)}$	0.205 ± 0.025[a]
f(estimated)	0.212 ± 0.006[b]
A_{ki}(10^8 sec⁻¹)	3.5 ± 0.1
$S(i,k)$	36 ± 1
τ(nsec)	2.86 ± 0.10

[a] The uncertainties are dispersion values in a set of increasingly accurate CI calculations, starting with 50-term CI expansions up to 120-term CI's.

[b] The estimated uncertainty takes into account the error analysis discussed in Ref. 18.

same degree of complexity as the one for the $^5P^e$ state. In Table III we give the $4s7p6d4f2g1h$ STO basis together with $\Delta E_{STO} = 148 \pm 25$ μhartree. The general comments in Sec. III A also apply here.

B. Electron affinity of Li $(1s2p^2)^4P^e$

In Table IV the results for the electronic energy of Li⁻$(1s2p^2)^5S^o$ are summarized analogously as those for the $^5P^e$ state in Table II. The electron affinity $A_{nr} = 291.0 \pm 2.0$ meV is slightly smaller than the one of He$(2p^2)^3P$ which amounts to 328 meV.[14,30] Thus a decrease of 38 meV in A_{nr} is obtained by both increasing the nuclear charge in one unit and placing one electron in a $1s$ orbital. Knowing that the binding energy of H⁻$(2p^2)^3P$ with respect to H$2p$ is less than 10 meV (Ref. 12), it is not surprising that He⁻$(1s2p^2)^4P$ is not bound.[22] The He⁻$(1s2p^2)^2P$ state, of course, lies still

TABLE VI. First 15 configurations of the Li⁻$(1s2s2p^2)^5P^e$ wave function expressed in terms of approximate natural orbitals. The convergence of A_{nr} slows down after the first 50 configurations. The electron detachment threshold is at $E(1s2s2p$ $^4P^o) = -5.367\,992(37)$ a.u. (Li).

Configuration	Excitation	CI coefficient	Approximate energy[a] contribution (a.u.)	A_{nr}[b] (meV)
$s_1 s_2 p_1^2$		0.978	−5.363 88	−112
$s_1 s_2 p_2^2$	$p_1^2 \rightarrow p_2^2$	−0.133	−0.005 23	30
$s_1 p_1^2 d_1$	$s_2 \rightarrow d_1$	0.090	−0.003 44	124
$s_1 s_3 p_1 p_2$	$s_2 p_1 \rightarrow s_3 p_2$	0.085	−0.003 33	215
$s_1 s_2 d_1^2$	$p_1^2 \rightarrow d_1^2$	−0.079	−0.003 42	308
$(s_1 p_1)^3P (p_2 d_1)^3P$	$s_2 p_1 \rightarrow p_2 d_1$	0.040	−0.000 82	330
$(s_1 p_1)^3P (d_1 f_1)^3P$	$\rightarrow d_1 f_1$	0.022	−0.000 44	342
$(s_1 p_1)^3P (p_3 d_1)^3P$	$\rightarrow p_3 d_1$	−0.016	−0.000 27	349
$s_1 s_3 p_2^2$	$s_2 p_1^2 \rightarrow s_3 p_2^2$	0.015	−0.000 12	353
$(s_1 p_1)^3P (p_2 d_2)^3P$	$s_2 p_1 \rightarrow p_2 d_2$	0.015	−0.000 17	358
$s_1 s_3 p_2 p_3$	$s_2 p_1^2 \rightarrow s_3 p_2 p_3$	−0.014	−0.000 22	364
$(s_1 p_1)^3P (p_2 d_2)^3D$	$s_2 p_1 \rightarrow p_2 d_2$	−0.014	−0.000 17	368
$s_1 s_2 f_1^2$	$p_1^2 \rightarrow f_1^2$	−0.013	−0.000 21	373
$(s_1 p_1)^3P (d_1 f_1)^3D$	$s_2 p_1 \rightarrow d_1 f_1$	0.012	−0.000 13	377
$s_1 s_2 d_2^2$	$p_1^2 \rightarrow d_2^2$	0.012	−0.000 14	381
50-term CI				450
100-term CI				467
320-term CI				498.4
Full CI				499.5
Extrapolated A_{nr}(complete STO basis)				504.5 ± 2.0[c]

[a] Approximate energy contributions of each configuration.

[b] Contributions to A_{nr} of all configurations up to a given order.

[c] Data taken from Table II.

TABLE VII. First 15 configurations of the $\text{Li}^-(1s2p^2)^5S^\circ$ wave function expressed in terms of approximate natural orbitals. The convergence of A_{nr} slows down after the first 20 configurations. The electron detachment threshold is at $E(1s2p^2\,^4P^e) = -5.245\,351(37)$ a.u. (Li).

Configuration	Excitation	CI coefficient	Approximate energy[a] contribution (a.u.)	A_{nr}[b] (meV)
$s_1p_1^3$		0.961	$-5.221\,44$	-650
$s_1p_1p_2^2$	$p_1^2 \to p_2^2$	-0.228	$-0.017\,53$	-174
$s_1p_1d_1^2$	$\to d_1^2$	-0.132	$-0.009\,37$	81
$s_1p_2^3$	$p_1^3 \to p_2^3$	-0.041	$-0.000\,62$	98
$s_1p_2^2p_3$	$\to p_2^2p_3$	0.040	$-0.001\,15$	129
$s_1p_2d_1d_2$	$\to p_2d_1d_2$	-0.029	$-0.000\,79$	151
$s_1p_1p_3^2$	$p_1^2 \to p_3^2$	-0.025	$-0.000\,55$	166
$s_1p_1d_2^2$	$\to d_2^2$	-0.022	$-0.000\,51$	179
$s_1p_1f_1^2$	$\to f_1^2$	-0.020	$-0.000\,48$	192
$s_1p_1^2p_2$	$p_1 \to p_2$	-0.015	$-0.000\,05$	194
$s_1d_1^2f_1$	$p_1 \to d_1^2f_1$	-0.014	$-0.000\,21$	200
$s_2p_1^2p_4$	$s_1p_1 \to s_2p_4$	-0.013	$-0.000\,95$	226
$s_2p_1^2p_3$	$\to s_2p_3$	0.013	$-0.000\,66$	244
$s_1p_2d_1^2$	$p_1^3 \to p_2d_1^2$	-0.009	$-0.000\,04$	245
$s_2p_1^2p_2$	$s_1p_1 \to s_2p_2$	0.008	$-0.000\,21$	251
30-term CI				265
200-term CI				285.7
Full CI				286.0
Extrapolated A_{nr}(complete STO basis)				291.0 ± 2.0[c]

[a] Approximate energy contributions of each configuration.
[b] Contributions to A_{nr} of all configurations up to a given order.
[c] Data taken from Table IV.

higher than $\text{He}^-(1s2p^2)^4P$; i.e., it is a resonance,[22,26] notwithstanding claims by experimentalists[31] about the existence of a long-lived doublet of He^-.

V. THE TRANSITION $\text{Li}^-(1s2p^3)^5S^\circ \to \text{Li}^-(1s2s2p^2)^5P^e$

From Tables II and IV we get a nonrelativistic transition energy of 0.130 499(38) a.u. (Li) which corresponds to a wavelength $\lambda = 349.10 \pm 0.09$ nm. Assuming $\text{Li}^+(1s2s)^3S$ and $\text{Li}^+(1s2p)^3P$ cores for $\text{Li}^-\,^5P$ and $^5S^\circ$, respectively, one gets a relativistic, radiative, and mass polarization correction to the transition energy of $-0.000\,045$ a.u., which leads to the corrected wavelength (in nm):
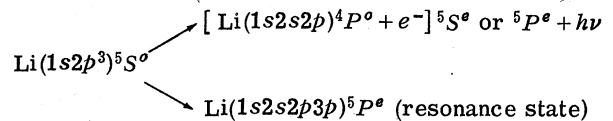
$$\lambda = 348.98 \pm 0.09 . \tag{8}$$

This is the first example of an electric dipole transition between bound states of a negative ion.

The calculation of oscillator strengths together with empirical error bounds has been discussed before.[18] The results for the $^5S^\circ \to {}^5P^e$ transition

are given in Table V. Since the negative ions have very extended electron charge distributions one might expect unusually large oscillator strengths and consequently very short mean lifetimes. Surprisingly, this is not the case, the mean lifetime for electric dipole decay of $^5S^\circ \to {}^5P^e$ being $\tau = 2.86 \pm 0.10$ nsec, corresponding to a normal mean lifetime in uv spectra.

Another mode of decay of $\text{Li}^-(1s2p^3)^5S^\circ$ is radiative autoionization[32] into the $^5S^e$ and $^5P^e$ continuum and resonance states

$$\text{Li}(1s2p^3)^5S^\circ \nearrow\!\!\!\!\!\!\quad [\text{Li}(1s2s2p)^4P^\circ + e^-]\,^5S^e \text{ or } {}^5P^e + h\nu$$
$$\searrow \text{Li}(1s2s2p3p)^5P^e \text{ (resonance state)}$$

with $\lambda \geqslant 406.4(1)$ nm.

$\text{Li}^-(1s2s2p^2)^5P^e$ is metastable. Selection rules for autoionization[7] indicate that the three fine structure levels $(J = 1, 2, 3)$ decay to the continuum with the same parity and J mainly through the

spin-orbit interaction. Neutral Li$(1s2s2p)^4P^o$ autoionizes[33] with $\tau = 4.5 \pm 1.5$, 0.45 ± 0.15, and 0.14 ± 0.07 μsec for $J = \frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$, respectively. The analogous Be$(1s2s2p^2)^5P^e$ state should have a comparable mean lifetime, and Li$^-(1s2s2p^2)^5P^e$ must have a much longer mean lifetime than the Be isoelectronic state, on account of well-established Z-dependent trends[9] for autoionization lifetimes.

VI. NATURE OF BINDING IN CORE-EXCITED Li$^-$

Both the $^5P^e$ and the $^5S^o$ states are bound at the sp-energy limit, but while the $^5P^e$ state is stable already at the Hartree-Fock level of approximation, the $^5S^o$ state is not. In Tables VI and VII we illustrate the build up of the electron affinity with growing Cl expansion size. It is seen that, relative to the Cl expansion, A_{nr} converges more quickly in the $^5S^o$ state than in the $^5P^e$ state. However, this is not an impediment for achieving comparable accuracy in both calculations since an adequate convergence is reached with moderate-size Cl expansions. More determinant of the degree of accuracy are the STO truncation errors in both the neutral and the negative atoms.

The present results and similar ones to be referred to below suggest the following rules for the formation of certain bound negative ions:

(i) A neutral atom in configuration (core) $2s2p$ and highest multiplicity always accepts a $2p$ electron to form a negative ion (core) $2s2p^2$ at the highest possible multiplicity. Examples are Li$^-(1s2s2p^2)^5P^e$ and Be$^-(1s^22s2p^2)^4P^e$ (Refs. 34, 35).

(ii) A neutral atom in configuration (core) $2p^2$ always accepts a $2p$ electron to form a negative ion (core)$2p^3$. Examples are Li$^-(1s2p^3)^5S^o$ and Be$^-(1s^22p^3)^4S^o$ (Ref. 35). Also, He$^-(2p^3)^4S^o$ is bound.

Although the range of applicability of rules (i) and (ii) is exhausted by the examples given above, their relevance lies in that they suggest the existence of similar negative ions for the higher alkali and alkali-earth[34] elements. Furthermore, the rule (ii) may be extended by including one or two $2s$ electrons. In the first case we have B$^-(1s^22s2p^3)^5S^o$ (Ref. 22), Al$^-(1s^22s^22p^63s3p^3)^5S^o$ (Ref. 22), etc., and in the second case we have the well-known[3] negative ions of the C group.

VII. CONCLUSIONS

The calculations in Secs. III and IV show the existence of two new bound states of negative lithium. Li$^-(1s2s2p^2)^5P^e$ is metastable and has an electron affinity of 504.5 ± 2 meV. The other
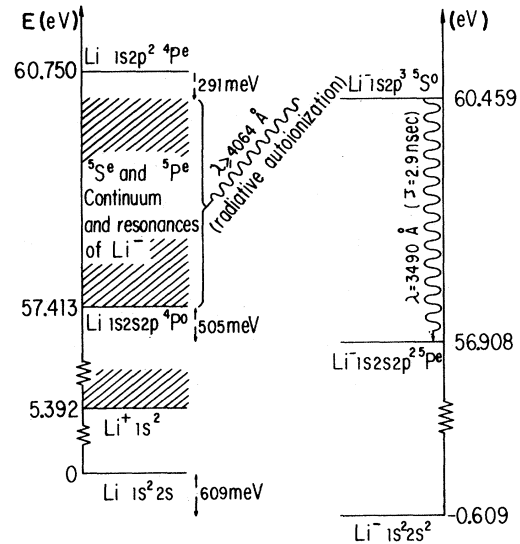

FIG. 1. Energy diagram of bound Li$^-$ ions and photoionization thresholds. The electron affinity of Li $1s^22s$ is from J. S. Sims et al., Phys. Rev. A 13, 560 (1976); the ionization potential is from C. E. Moore, Natl. Bur. Stand. (U.S.) Circular No. 467 (U.S. GPO, Washington D.C., 1949), slightly corrected in the light of the most recent values for the fundamental constants. The absolute term values of Li$(1s2s2p)^4p^o$ and Li$(1s2p^2)^4p^e$ are from Ref. 17 and the others may be deduced from Tables II, IV, and V.

bound state is Li$^-(1s2p^3)^5S^o$, with an electron affinity of 291.0 ± 2 meV. It decays with $\tau = 2.9$ nsec to Li$^-(1s2s2p^2)^5P^e$ emitting uv photons of $\lambda = 349.0(1)$ nm; decay into the $^5S^e$ and $^5P^e$ continuum is also possible [$\lambda \geq 406.4(1)$ nm].

Furthermore, additional calculations (Secs. III and IV) and the arguments given in the Introduction suggest that the ground state Li$1s^22s^2$, and the two core-excited states just mentioned, are the *only* bound states of negative lithium. In Fig. 1 we show, in an energy diagram, the absolute term values of pertinent states of Li and Li$^-$ and $E1$ decays of Li$^-$ ions. It now remains to be seen whether experimentalists can produce and detect these core-excited Li$^-$ ions which should readily be identified by the $^5S^o \leftrightarrow\, ^5P^e$ transition at $\lambda = 349.0(1)$ nm. There is also the possibility of making a direct measurement of the electron photodetachment threshold of Li$^-(1s2s2p^2)^5P$, e.g., by laser photoelectron spectroscopy.[3] One may even attempt laser photodetachment of Li$^-(1s2s2p^2)^5P$ into the higher excited quartet Li$(1s2p^2)^4P$ [$\lambda = 322.6(1)$ nm]. The mean lifetime of Li$^-(1s2p^3)^5S^o$ is so short ($\tau < 2.9$ nsec) that a direct measurement of its binding energy can only be attempted at the place of its production. After this work was submitted for publication, we identified Li$^-$ in beam-foil experiments.[36]

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