

Lifetime and hyperfine structure of Li⁻ excited states

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The newly discovered excited states of Li⁻ are examined from a many-body point of view. Our result for the ⁵S^o lifetime includes the contribution of radiative autoionization. This removes one-third of the previous discrepancy between theory (our value = 2.7 ns) and experiment (= 2.3 ns). The first predictions of the hyperfine structures (hfs) of the Li⁻ ⁵S^o and ⁵P states are made, and the change in the hfs parameters as *p* electrons are removed is studied.

Very recent theoretical¹⁻⁶ and experimental^{7,8} advances have made possible the accurate prediction and verification of bound excited states in certain negative ions. These were shown to decay radiatively either to a lower bound state^{1,2,7,8} or to the continuum via radiative autoionization.^{3,9}

The significance of these exotic species to other fields of science such as chemical physics, solid-state physics, and astrophysics is evident. A proposal has already been made for the utilization of such metastable states for the construction of high-frequency lasers.⁹

The quantitative understanding of the properties of such states is minimal and most of it is contained in Refs. 1-9; except for the He⁻ 1s2s2p ⁴P^o state, whose structure and decay dynamics have been the subject of extensive investigations by Novick and collaborators over many years.¹⁰

The study of these states is more difficult than that of ordinary bound states: On the one hand, their diffuse wave functions, open shell character, small electron affinities, and the weak perturbations affecting their structure require large and flexible calculations.^{1-6,11} On the other hand, their preparation and observation require novel and sensitive experiments.^{7-9,12}

In this Brief Report we present the first prediction of the hyperfine structure of the Li⁻ 1s2s2p²⁵P and 1s2p³⁵S^o bound states and a result for the lifetime of the ⁵S^o state which includes the contribution of radiative autoionization

(RA)—previously neglected.^{1,2} This is the first time that the RA process has been confirmed as making a detectable contribution to a negative ion's lifetime. We note that the theoretical result of Bunge^{1,2} for the lifetime is $\tau = 2.9 \times 10^{-9}$ sec, while the experimental value^{5,6} is $\tau = 2.3 \times 10^{-9}$ sec. Our calculations yield (see Table I) $\tau = 2.7 \times 10^{-9}$ sec.

The wave functions of the ⁵P and ⁵S^o states which were employed for the calculation of the hyperfine structure and the lifetime were obtained variationally according to the methods described in detail elsewhere.¹³ We treated all electrons on an equal footing. The final correlated wave function which contained triple excitations was built from 113 (111) configurations, and is energetically accurate to 20 meV (17 meV) when compared with the most accurate² calculation available for the ⁵P (⁵S^o) state.

The above computation yields one-electron basis sets for the ⁵P and ⁵S^o states which are not orthonormal between them. To evaluate the dipole transition matrix elements, we took these nonorthonormality effects explicitly into account.¹⁴ From Table I, it can be seen that our wave functions yield good agreement (~ 1.5% difference) between the length and velocity forms, a typical accuracy achieved¹⁴ for the better calculations on the neutral and positive ions. It is also apparent from the table that neither the Hartree-Fock length nor velocity results are useful.

It can be observed that our result is in good agreement

TABLE I. Wavelength, transition probabilities, and lifetime of the Li⁻ ⁵S^o state.

λ (Å)	Theory		Experiment	
	This work 3490	References 1 and 2 3490	Reference 7 3489	Reference 8 3490
f_l	Hartree-Fock 0.315	Corr. 0.217	Corr. 0.212	
f_v	0.136	0.210	0.212	
$A_{av}^{discrete}$		$0.352 \times 10^9 \text{ sec}^{-1}$	$0.35 \times 10^9 \text{ sec}^{-1}$	
A^{RA}		$0.018 \times 10^9 \text{ sec}^{-1}$		
$\tau = \frac{1}{A^{discrete} + A^{RA}}$		$2.7 \times 10^{-9} \text{ sec}$	$2.9 \times 10^{-9} \text{ sec}^{-1}$	$2.28 \pm 0.05 \times 10^{-9}$ $2.3 \pm 0.1 \times 10^{-9}$

with that of Bunge,² who used a common (orthonormal) basis set for both states (which was smaller than the two basis sets used to establish the absolute energy) in calculating the electric dipole matrix element. The most likely source of the remaining theoretical-experimental discrepancy then appears to be the contribution from the process of radiative autoionization¹⁵ corresponding to the transition

$$1s2p^3^5S^o \rightarrow [1s2s2p\epsilon p]^5P + h\nu$$

(the $^5S^o$ channel is not allowed by symmetry). We have evaluated the integrated cross section for this process using continuum functions generated from the frozen core Hartree-Fock approximation¹⁶ in which the core was partially correlated. This removes approximately one-third of the discrepancy as is evident in Table I.

The rigorous study of the hyperfine structure of a negative-ion excited bound state is timely and challenging for a number of reasons. *Firstly*, one is probing for the first time the details of electronic structure in a many-electron system with an unusual structure. When reporting their experimental findings on the fine and hyperfine structure of He^- , Mader and Novick¹⁰ emphasized this point and called for an accurate theoretical treatment of this three-electron system. *Secondly*, if one provides reliable theoretical predictions, these can be used to guide the development and application of sensitive experimental techniques. For example, a combination of beam-foil and laser spectroscopic methods are currently being tested at Argonne^{7,17} for the detailed study of the Li^- states. *Thirdly*, one provides totally new information, whose derivation requires the application of completely general many-body theories of atomic structure.

The calculational approach we have taken is the following: Nonrelativistic LS -coupled correlated functions are used to evaluate the expectation value of the hyperfine structure operators. The fine-structure effects were neglected because, contrary to the He^- case where fine and hyperfine structure are of the same order of magnitude,¹⁰ our calculations of the relevant diagonal matrix elements showed that, in the Li^- and Li^+ cases, the hyperfine perturbation is much smaller.

The magnetic dipole hyperfine energy in the above approximation is given by $A_J \vec{I} \cdot \vec{J}$, where

$$A_J = G_{\text{en}} \frac{\mu_I}{IJ^*} \left(\frac{\lambda_S(J)}{\lambda_S(J^*)} \frac{g_e}{2} a_c + \frac{\lambda_I(J)}{\lambda_I(J^*)} a_l + \frac{\lambda_d(J)}{\lambda_d(J^*)} \frac{g_e}{2} a_d \right),$$

where, following Ref. 18, the λ 's are given in terms of Wigner $6j$ and $9j$ symbols as follows:

$$\lambda_S^{(J)} = -(-1)^{S+L+J} \left(\frac{2J+1}{J(J+1)} \right)^{1/2} \begin{Bmatrix} J & J & 1 \\ S & S & L \end{Bmatrix},$$

$$\lambda_I^{(J)} = -(-1)^{S+L+J} \left(\frac{2J+1}{J(J+1)} \right)^{1/2} \begin{Bmatrix} J & J & 1 \\ L & L & S \end{Bmatrix},$$

$$\lambda_d^{(J)} = \left(\frac{3(2J+1)}{J(J+1)} \right)^{1/2} \begin{Bmatrix} L & L & 2 \\ S & S & 1 \\ J & J & 1 \end{Bmatrix};$$

TABLE II. Correlated Li hyperfine structure constants (in a.u.).

Species	a_c	a_l^a	a_d^a
$\text{Li}^- 1s2p^3^5S^o$	35.366 ^b	0.0	0.0
$\text{Li} 1s2p^2^4P$	35.320 ^c	0.3094 ^c	0.0628 ^c
$\text{Li}^+ 1s2p^3P^o$	35.484 ^b	0.4778 ^b	-0.09849 ^b
$\text{Li}^{2+} 1s^2S$	36.0 ^d	0.0	0.0
$\text{Li}^- 1s2s2p^2^5P$	37.059 ^b	0.1850 ^b	0.03833 ^b
$\text{Li} 1s2s2p^4P^o$	37.423 ^e	0.3096 ^e	-0.0636 ^e
$\text{Li}^+ 1s2s^3S$	38.227 ^b	0.0	0.0

^aIn the restricted Hartree-Fock model, $a_l = \langle 2p | r^{-3} | 2p \rangle$,

$$a_d = \pm \frac{1}{5} \langle 2p | r^{-3} | 2p \rangle.$$

^bThis work.

^cReference 21.

^dNonrelativistic hydrogenic value.

^eReference 22.

$J^* = L + S$; g_e is the electronic g factor ($= 2.00232$).

$$G_{\text{en}} = \frac{2\mu_B \mu_N}{a_0^3},$$

which has a value of 95.4129 when A_J is in MHz and a_c , a_l , and a_d , which are, respectively, the expectation values of the contact, orbital, and spin-dipolar operators¹⁸ for J^* , are given in atomic units (a.u.). As is usual, μ_I is the nuclear dipole moment (in nuclear magnetons) and I is the nuclear spin.

The correlated results obtained for the J -independent Li^- parameters a_c , a_l , and a_d are shown in Table II. Due to the presence of open p and s subshells (particularly the $1s$), no striking differences with the Hartree-Fock values were noted (see Ref. 19 for contrary examples).

It is of interest to observe the behavior of the a 's as the least bound electrons are removed one at a time for the states of highest spin. In order for the trends to become evident, all such a 's have to be evaluated at the same level of approximation as was used for Li^- (otherwise these trends can be masked by other effects of the same order, such as reduced mass, relativistic, and QED corrections²⁰). Correlated results of $\text{Li} 4P, 4P^o$ are available from the work of Glass^{21,22}; for $\text{Li}^+ 3S, 3P^o$ the results were generated here, and the result of Li^{2+} is obtained from nonrelativistic hydrogenic theory. In comparing the results, shown in Table II, we see that with one exception ($\text{Li}^- 5S^o$), addition of a $2p$ electron reduces (slightly) the absolute value of all a 's.

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- ¹C. F. Bunge, Phys. Rev. Lett. 44, 1450 (1980).
²C. F. Bunge, Phys. Rev. A 22, 1 (1980).
³D. R. Beck, C. A. Nicolaides, and G. Aspromallis, Phys. Rev. A 24, 3252 (1981).
⁴C. A. Nicolaides, Y. Komninos, and D. R. Beck, Phys. Rev. A 24, 1103 (1981).
⁵D. R. Beck and C. A. Nicolaides, Chem. Phys. Lett. 59, 525 (1978).
⁶D. R. Beck, Phys. Rev. A 27, 1197 (1983).
⁷R. L. Brooks, J. E. Hardis, H. G. Berry, L. J. Curtis, K. T. Cheng, and W. Ray, Phys. Rev. Lett. 45, 1318 (1980); R. L. Brooks, J. E. Hardis, H. G. Berry, and L. J. Curtis, Bull. Am. Phys. Soc. 25, 1128 (1980).
⁸S. Mannervik, G. Astner, and M. Kisielinski, J. Phys. B 13, L441 (1980).
⁹C. A. Nicolaides and Y. Komninos, Chem. Phys. Lett. 80, 463 (1981).
¹⁰D. L. Mader and R. Novick, Phys. Rev. Lett. 29, 199 (1972); 32, 185 (1974); L. M. Blau, R. Novick, and D. Weinflash, Phys. Rev. Lett. 24, 1268 (1970).
¹¹A. V. Hazi and K. Reed, Phys. Rev. A 24, 2269 (1981).
¹²R. N. Compton, G. D. Alton, and D. J. Pegg, J. Phys. B 13, L651 (1980); R. V. Hodges, M. J. Coggiola, and J. R. Peterson, Phys. Rev. A 23, 59 (1981).
¹³D. R. Beck and C. A. Nicolaides, in *Excited States in Quantum Chemistry*, edited by C. A. Nicolaides and D. R. Beck (Reidel, Dordrecht, 1978), p. 105.
¹⁴C. A. Nicolaides and D. R. Beck, in *Excited States in Quantum Chemistry*, edited by C. A. Nicolaides and D. R. Beck (Reidel, Dordrecht, 1978), p. 143.
¹⁵C. A. Nicolaides and D. R. Beck, Phys. Rev. A 17, 2116 (1978).
¹⁶G. N. Bates, Comput. Phys. Commun. 8, 220 (1974).
¹⁷P. S. Ramanujam and H. G. Berry (private communication).
¹⁸O. Sinanoglu and D. R. Beck, Chem. Phys. Lett. 20, 221 (1973).
¹⁹D. R. Beck and C. A. Nicolaides, Int. J. Quantum Chem. S8, 17 (1974).
²⁰A. N. Jette, T. Lee, and T. P. Das, Phys. Rev. A 9, 2337 (1974).
²¹R. Glass, J. Phys. B 11, 3459 (1978).
²²R. Glass, J. Phys. B 11, 3469 (1978).