Comment on the lifetime of the Li $1s2p^2\ ^2P$ state: How probable is radiative autoionization?

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The $1s2p^2\ ^2P$ state of lithium can autoionize by decaying radiatively into the adjacent continuum. The probability is smaller than the discrete transition probability to the ground state $1s^22p\ ^2P^o$ and equal to the decay probability to the $^2P^o$ Rydberg series. Our theoretical lifetime, $\tau = 0.041 \times 10^{-9}$ sec, differs from the experimental value of $\tau = 0.015 \pm 0.01 \times 10^{-9}$ sec. The mechanism of radiative autoionization affects the deexcitation dynamics of many valence excited states of *neutral* species.

I. INTRODUCTION

In a recent paper,[1] Fox and Dalgarno presented a theoretical result for the lifetime of the Li $1s2p^2\ ^2P$ state from large configuration-interaction (CI) calculations. Their value ($\tau = 0.054 \times 10^{-9}$ sec) is in substantial disagreement with a recent experimental value[2] ($\tau = 0.015 \pm 0.01 \times 10^{-9}$ sec).

In view of the seemingly high accuracies of both theory and experiment, we carried out a rigorous calculation of this lifetime taking into account all possible modes of decay. The Fox-Dalgarno calculation took only the $1s2p^2\ ^2P \rightarrow 1s^22p\ ^2P^o$ transition into account.

Our result, $\tau = 0.041 \times 10^{-9}$ sec, does not resolve the discrepancy and suggests that the experimental value is in error.

Examination of the energy spectrum of Li and its ions reveals that the $1s2p^2\ ^2P$ state cannot decay to the adjacent continuum (it lies at about 56.3 eV above the $Li^+\ 1s^2\ ^1S$ state[3]) via its own nonrelativistic Hamiltonian. Direct relativistic autoionization or indirect, via the other terms of the same configuration, is considered negligible.

However, there is another possibility for decay into the continuum and this is via the perturbation of electric dipole matter-radiation interaction. We shall call this process radiative autoionization (RA).

II. RADIATIVE AUTOIONIZATION IN NEUTRAL SPECIES

The phenomenon of RA in neutral species is analogous to the radiative Auger effect observed in positive ions in the x-ray region.[4-6] It is also analogous to the process of autodetachment computed previously[7] for the metastable ^3P states of the negative ions H^- and Na^- whose spectra do not have any bound states of $^3P^o$, $^3S^o$, or $^3D^o$ symmetry.

It is a one-photon two-electron emission transition with one of the two electrons ejected into the continuum. It is described by the following mechanism:

$$M^*_{\text{elec. dipole}} \rightarrow M^+ + e^- + h\nu \tag{1}$$

with

$$(E_{M^+} - E_{M^*}) = E_K + h\nu \equiv \Delta, \tag{2}$$

where E_K is the kinetic energy, M^* is the atomic (molecular) initial excited state, and M^+ is the final ionized state. The system $(M^+ + e^-)$ has different parity than M^*.

We note that mechanism 1 can, in principle, induce *molecular dissociation* if its probability is high. For instance, a hypothetical example is

$$He_2^-\ 1\sigma_g 1\sigma_u^2 1\pi_u^2\ ^2\Sigma^+ \xrightarrow{RA} He_2 1\sigma_g^2 1\sigma_u^2 + e^- + h\nu$$

$$\xrightarrow{D} 2He + e^- + h\nu.$$

In neutral atoms, inspection of the existing tables of atomic spectra[8] and of recently observed new excited states[3] reveals the existence of a few valence excited stable states for which RA is possible, e.g.,

$$\begin{aligned}
&C\ 2s2p^3\ ^3S^o \xrightarrow{RA} C^+\ 2s^22p^2P^o + e^- + h\nu,\\
&K\ 3p^54s^2\ ^2P^o \xrightarrow{RA} K^+\ 3p^6\ ^1S + e^- + h\nu,\\
&O\ 2s2p^5\ ^3P^o \xrightarrow{RA} O^+\ 2s^22p^3\ ^4S^o + e^- + h\nu,\\
&Li\ 1s2p^2\ ^2P \xrightarrow{RA} Li^+\ 1s^2\ ^1S + e^- + h\nu.
\end{aligned} \tag{3}$$

For O, this decay mechanism complements the usual ones discussed and analyzed before.[9,10] However, we estimate that, due to the small overlap $\langle \epsilon p | 2p \rangle$ (ϵp, $2p$ are Hartree-Fock orbitals) and the small Δ, its probability is very small. Of course, many other atomic states can be thought of as candidates for RA especially those with large Δ (i.e., inner hole states such as the $B\ 1s2s^22p^2\ ^2P$) or those for which other important decay channels are closed (e.g., He^- $1s2p^2\ ^2P \rightarrow He\ 1s^2 + e^- + h\nu$). The Li $1s2p^2\ ^2P$ state which we examined is a borderline case.

III. CALCULATION OF THE Li $1s2p^2\ ^2P$ LIFETIME: AN APPLICATION OF A FIRST-ORDER THEORY OF OSCILLATOR STRENGTHS (FOTOS)

The calculation of the Li $1s2p^2\ ^2P$ lifetime was carried out within the general scheme of a recently developed many-body theory of photoabsorption called FOTOS.[11-13] The Fermi sea[11,12] of the Li ^2P state is spanned by the $1s2p^2$ configuration only. Then, the first-order symmetries (FOS) of $^2P^o$ overall symmetry, which are dictated by *symmetry quantization*, are s^2p, spd, p^3. The transitions of interest can be obtained by imposing the *radial* (*energy*) *quantization* on the s^2p FOS. It follows that decays can occur to the discrete spectrum, i.e., the $1s^2np\ ^2P^o$ Rydberg series, and to the continuous spectrum, i.e., the autoionizing $1s[(2s2p)\ ^3P^o]\ ^2P^o$ and scattering $1s^2\epsilon p\ ^2P^o$ states. Thus, the lifetime of the Li $1s2p^2\ ^2P$ state is given by

$$\tau = \left(\sum_{n=2}^{\infty} A_n(^2P \rightarrow 1s^2np\ ^2P^o) + \int_0^{\Delta} dE\, A_E(^2P \rightarrow 1s2s2p\ ^2P^o, 1s^2Ep\ ^2P^o) \right)^{-1} . \quad (4)$$

From the computational point of view, apart from the Hartree-Fock (HF) orbitals for the discrete and autoionizing states, Slater-type-orbitals (STO) were used to describe electron correlation in initial ($1s2p^2\ ^2P$) and final states. The FOTOS analysis indicates that correlation is relatively unimportant for these Li transitions (i.e., the HF f values are fairly accurate). For example, the ground state of $^2P^o$ symmetry was expanded in terms of only 11 vectors while the $1s2p^2\ ^2P$ in terms of 8. The HF coefficients were 0.9999 and 0.9974, respectively.

The continuum states were approximated by a Coulomb function,[14] $R(E;Z_{\text{eff}})$. Since the matrix elements involving Coulomb functions are very sensitive to the choice of the effective nuclear charge Z_{eff}, this choice was made consistent by utilizing the well-known property of the continuity of the oscillator strength across the ionization threshold. Since electron correlation effects on the transition amplitudes of the $1s2p^2\ ^2P \rightarrow 1s^2np, Ep$ transitions are very small, the continuity condition was practically reduced to

$$\lim_{n\to\infty} n_{\text{eff}}^3 |\langle np|2p\rangle|^2 = \lim_{E\to 0} |\langle Ep|2p\rangle|^2 . \quad (5)$$

By explicit computation of n_{eff} and $\langle np|2p\rangle$ for $n \leq 7$ and extrapolation to large n we obtained a $Z_{\text{eff}} = 1.01$. The overlap integrals $\langle Ep|2p\rangle$, which in fact give rise to RA for most examples of Eq. (3), were done analytically using the integral representation of the Coulomb function[14] and an expansion of the $2p$ HF function in terms of $2p$ STO's. The overlap integral is then given by a sum of integrals of the type

$$I = \int_0^{\infty} r^3 dr\, e^{-\zeta r} R(E;Z_{\text{eff}}) = \frac{2}{E^2} \left(\frac{Z_{\text{eff}}(1+\nu^2)}{(1-e^{-2\pi\nu})} \right)^{1/2} \frac{(2\mu-\nu)}{(\mu^2+1)^3} e^{-2\nu \cot^{-1}\mu} \quad (6)$$

with

$$\nu \equiv Z_{\text{eff}}/\sqrt{2E}\ , \quad \mu \equiv \zeta/\sqrt{2E}\ .$$

I reduces to a constant in the limit $E \rightarrow 0$.

TABLE I. Oscillator strengths for the Li $1s^22p^2P^o \rightarrow 1s2p^2\ ^2P$ transition. Note that, due to the orbital structure and symmetry of the states involved, the effect of electron correlation is very small. The three forms yield comparable results in the HF and FOTOS approximations (see Ref. 16 for a similar case involving K-shell electrons). Our FOTOS computations employed wave functions obtained from a 11×11 CI with optimized virtuals for the ground state and a 8×8 CI for the excited state.

This work						
Hartree Fock			FOTOS			Reference 1
f_L	f_V	f_A	f_L	f_V	f_A	f_L
0.128	0.126	0.163	0.134	0.122	0.158	0.121

The results of our Li computations are presented in Tables I and II, together with the experimental lifetime of Buchet *et al.*[2] and the theoretical f value for the $1s^22p^2P^o \rightarrow 1s2p^2\ ^2P$ transition and corresponding lifetime of Fox and Dalgarno.[1] It is seen that RA is a factor-of-10 less probable than the discrete transition at 207 Å. In the length formulation, it has an 8% contribution to the total transition probability while another 9% is taken up by the Rydberg series. In the velocity formulation, these percentages become 11% and 10%, respectively.

We point out that the Rydberg-series contribution for $n > 7$ was estimated by employing the small-r expansion for the hydrogenic np in the overlap integral $\langle np|2p\rangle$. Two infinite series result, multiplying a constant factor which was deduced from $\langle 7p|2p\rangle$, one depending on n^{-3} and the other on n^{-5}, which were evaluated using tabulated Riemann ζ functions.[15] The Rydberg $n = 3-7$ members decrease the lifetime due to the $1s2p^2 \rightarrow 1s^22p$ transition by about 10% and the $n = 8-\infty$ members by another 0.6%.

TABLE II. Transition probabilities and theoretical lifetime of the Li $1s2p^2\,^2P$ state from FOTOS calculations (length and velocity forms) and comparison with previous theory and experiment. Radiative autoionization contributes 8%–11% and the Rydberg series another 9%–10%. $\Delta \equiv E(\mathrm{Li}^+\ 1s^2\,^1S) - E(\mathrm{Li}\ 1s2p^2\,^2P) = 2.07$ a.u. The integrated continuum transition probability includes a contribution of 1.2×10^8 sec^{-1} from the $1s[(2s2p)^3P^o]\,^2P^o$ autoionizing state and $(3 \times 10^{-6}) \times 10^8$ sec^{-1} from the $1s[(2s2p)^1P^o]\,^2P^o$ autoionizing state (length form).

	Transition probabilities (sec^{-1})			Lifetime of the Li $1s2p^2\,^2P$ state (sec)		
	FOTOS		Ref. 1			Experiment
	Length	Velocity	Length	This work	Ref. 1	(Ref. 2)
$1s2p^2\,^2P \rightarrow 1s^22p\,^2P^o$	208×10^8	189×10^8	185×10^8	0.040×10^{-9} (length)	0.054×10^{-9}	$0.015 \pm 0.01 \times 10^{-9}$
$\rightarrow 3p$	13.5	13.9		0.042×10^{-9} (velocity)		
$\rightarrow 4p$	3.8	4.0				
$\rightarrow 5p$	1.7	1.8				
$\rightarrow 6p$	0.9	1.0				
$\rightarrow 7p$	0.5	0.5				
$\rightarrow \sum_{n=8}^{\infty} np$	1.5	1.7				
$\rightarrow \int_0^{\Delta} dE$	19.1	26.2				
Total	249×10^8	238.1×10^8				

IV. CONCLUSION

The herein proposed deexcitation mechanism for neutral species of radiative autoionization is not sufficiently probable to explain the existing discrepancy between theory[1] and experiment[2] for the lifetime of the Li $1s2p^2\,^2P$ state. In view of the completeness of our calculation, we consider the theoretical value of $\tau = 0.041 \times 10^{-9}$ sec to be a reasonably accurate one. This and other preliminary studies on RA[17] indicate that this phenomenon might be a non-negligible component of the decay dynamics of a certain class of excited states, producing continuous radiation over a wide range of short wavelengths. For example, it may be important in the radiative deexcitation of $Ne^+ 1s2s^22p^6\,^2S$ which has been studied before through approximation.[5] Along isoelectronic sequences, it is more probable on the neutral end due to the larger magnitude of the overlap integrals of the discrete with the continuum orbitals.

[1] J. L. Fox and A. Dalgarno, Phys. Rev. A 16, 283 (1977).

[2] J. P. Buchet, M. C. Buchet-Poulizac, H. G. Berry, and G. W. F. Drake, Phys. Rev. A 7, 922 (1973).

[3] T. J. McIlrath and T. B. Lucatorto, Phys. Rev. Lett. 38, 1390 (1977).

[4] T. Åberg and J. Utriainen, Phys. Rev. Lett. 22, 1346 (1969).

[5] T. Åberg, Phys. Rev. A 4, 1735 (1971).

[6] V. O. Kostroun and G. B. Baptista, Phys. Rev. A 14, 363 (1976).

[7] G. W. F. Drake, Astrophys. J. 184, 145 (1973); 189, 161 (1974); V. L. Jacobs, A. K. Bhatia, and A. Temkin, Astrophys. J. 191, 785 (1974); R. F. Stewart, G. A. Victor, and C. Laughlin, J. Phys. B 8, 1603 (1975).

[8] *Atomic Energy Levels*, U. S. Natl. Bur. Stand. Circ. No. 467, edited by C. E. Moore (U. S. GPO, Washington, D.C., 1949).

[9] C. A. Nicolaides, Nucl. Instrum. Methods 110, 231 (1973); D. R. Beck and C. A. Nicolaides, in *Proceedings of the Fourth International Conference on Atomic Physics, Abstracts of Contributed Papers, Heidelberg, 1974,* edited by J. Kowalski and H. G. Weber (Heidelberg U.P., Heidelberg, 1974).

[10] P. M. Dehmer, W. L. Luken, and W. A. Chupka, J. Chem. Phys. 67, 195 (1977); H. P. Garnir, Y. Baudinet-Robinet, and P. D. Dument, Phys. Lett. 59A, 431 (1977).

[11] C. A. Nicolaides and D. R. Beck, Chem. Phys. Lett. 36, 79 (1975).

[12] D. R. Beck and C. A. Nicolaides, Int. J. Quantum Chem. Suppl. 10, 119 (1976).

[13] D. R. Beck and C. A. Nicolaides, Phys. Lett. 61A, 227 (1977).

[14] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957), p. 21.

[15] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegum (Dover, New York, 1965).

[16] C. A. Nicolaides and D. R. Beck, J. Chem. Phys. 66, 1982 (1977).

[17] C. A. Nicolaides and D. R. Beck (unpublished).