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Note

Lifetimes and polarizabilities of low lying lithium S, P and D states

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Abstract

The radiative lifetimes, scalar and tensor polarizabilities of low lying S, P and D states of lithium are obtained using a Coulomb approximation. The calculated lifetimes agree very well with the handful of experimental values listed in the literature. The ground state polarizability is also close to the measured result. This method requires substantially less computational time than ab initio theory, thereby permitting the study of nearly 40 states.

Substantial progress has been made in modeling few electron atoms including lithium during the last decade [1–3]. Precise measurements of atomic properties of lithium therefore serve to test theory [4]. Indeed, laser spectroscopic measurements of isotope shifts yield results for the ^{6,7}Li nuclear radii that are substantially more accurate than those obtained from electron scattering [4,5]. Experiments are also being planned to examine radioactive isotopes including ^{11}Li that is believed to have two so-called halo neutrons [6].

Measurements of atomic lifetimes and polarizabilities provide a useful test of theoretically computed wavefunctions [7]. Unfortunately, many ab initio theoretical techniques require very considerable computer time and have therefore been largely used to only study the lithium 2P state [8–15]. This paper reports results obtained using a Coulomb approximation to examine nearly 40 of the energetically lowest states in lithium. This will facilitate experiments that up to now have only examined relatively few states.

The Coulomb approximation originally developed by Bates and Damgaard [16] has been used to study the other alkali atoms [17–20]. It simply models the potential seen by the valence electron by

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a Coulomb potential generated by the nucleus and inner core electrons. The calculated lifetimes and polarizabilities have been found to agree within a few percent with measured values for all but the lowest lying P states. This is not surprising as the spin–orbit interaction is largest for the lowest P states which are therefore not well modelled by a Coulomb potential.

The Hamiltonian describing the effect of an electric field E directed along the z direction on an atom is [21]

$$H = -\frac{1}{2}\left[\alpha_0 + \alpha_2\frac{3J_z^2 - \vec{J}^2}{J(2J-1)}\right]\frac{E^2}{2}, \tag{1}$$

where $\vec{J}$ is the electronic angular momentum. The second term vanishes when $J < 1$. α_0 and α_2 are the scalar and tensor polarizabilities, respectively, given by

$$\alpha_0 = \frac{r_0}{4\pi^2}\,\Sigma_{J'}\lambda_{JJ'}^2 f_{JJ'}, \tag{2}$$

$$\alpha_2 = \frac{r_0}{8\pi^2}\,\frac{1}{(2J+3)(J+1)}\Sigma_{J'}\lambda_{JJ'}^2 f_{JJ'}[8J(J+1) - 3X(X+1)], \tag{3}$$

where $X = J'(J'+1) - 2 - J(J+1)$. r_0 is the classical electron radius, $\lambda_{JJ'}$ is the wavelength for a transition between states J and J' and $f_{JJ'}$ is the transition oscillator strength.

In this work, the energies of all S, P, D and F states lying in excess of 760 cm^{-1} below the ionization limit of 43,487.19 cm^{-1} were used to compute the effective principal quantum numbers $n^{\star}$ [22]. The Schrodinger equation was then solved following the procedure of Bates and Damgaard [16] and the oscillator strengths were found. Very few reported oscillator strengths for lithium exist in the literature. The most accurate have been obtained using the Hylleraas variational method [1]. For the 2S–2P and 2P–3D transitions, values of 0.764787 and 0.63857 were obtained, respectively. Our results of 0.745 and 0.640 are in close agreement.

The various oscillator strengths were next used to determine the radiative lifetimes and polarizabilities that are listed in Table 1. Experimentally determined values of radiative lifetimes were only found for three of these states and are compared to the theoretically predicted results in Table 2. The most precise experimental result was determined by analyzing the long-range vibrational eigenenergies of the diatomic molecule Li_2 [27]. These high lying levels were produced in collisions of ultracold lithium atoms. The long-range component of the potential describing the levels of the A $^1\Sigma_u^+$ state has the form $V(R) = -C/R^3$ where C is proportional to the 2P radiative lifetime. This result agrees with that found by neutralizing a fast ion beam in a gas cell and then laser exciting the 2P state [26]. A movable detector then recorded the fluorescence as a function of the distance from the laser-atomic beam intersection point. These two experiments obtain results which differ sharply from that found by an earlier laser excitation measurement [23]. A considerable number of theoretical groups have calculated the 2P lifetime. These have been extensively reviewed in the articles referenced and are not discussed further here. For convenience, Table 2 only lists the values computed during the last decade. It is interesting to note that nearly all of the theoretical results obtained using a diverse array of techniques agree, although the result obtained using Hylleraas Variational theory has a much lower

Table 1
Lifetimes and polarizabilities of lithium low lying S, P and D states (a_o^3 is the Bohr radius cubed)

State	$n^\star$	Lifetime (ns)	Polarizability (a_o^3)	
			α_0	α_2
$2S_{1/2}$	1.58854		1.623E2	
$3S_{1/2}$	2.59619	3.046E1	4.133E3	
$4S_{1/2}$	3.59836	5.870E1	3.526E4	
$5S_{1/2}$	4.59929	1.090E2	1.782E5	
$6S_{1/2}$	5.59979	1.861E2	6.587E5	
$7S_{1/2}$	6.59992	2.957E2	1.968E6	
$8S_{1/2}$	7.59959	4.439E2	5.072E6	
$9S_{1/2}$	8.59957	6.361E2	1.154E7	
$2P_{1/2}$	1.95938	2.713E1	1.178E2	
$3P_{1/2}$	2.95564	2.057E2	2.835E4	
$4P_{1/2}$	3.95441	3.600E2	2.734E5	
$5P_{1/2}$	4.95387	5.481E2	1.434E6	
$6P_{1/2}$	5.95323	8.039E2	5.340E6	
$7P_{1/2}$	6.95312	1.151E3	1.623E7	
$8P_{1/2}$	7.95166	1.562E3	4.173E7	
$9P_{1/2}$	8.95341	2.172E3	1.023E8	
$2P_{3/2}$	1.95940	2.713E1	1.178E2	3.874E0
$3P_{3/2}$	2.95564	2.057E2	2.835E4	− 2.173E3
$4P_{3/2}$	3.95441	3.600E2	2.735E5	− 2.074E4
$5P_{3/2}$	4.95387	5.481E2	1.433E6	− 1.068E5
$6P_{3/2}$	5.95323	8.039E2	5.339E6	− 3.909E5
$7P_{3/2}$	6.95312	1.151E3	1.623E7	− 1.180E6
$8P_{3/2}$	7.95166	1.561E3	4.173E7	− 2.987E6
$9P_{3/2}$	8.95341	2.172E3	1.023E8	− 7.441E6
$3D_{3/2}$	2.99864	1.453E1	− 1.504E4	1.147E4
$4D_{3/2}$	3.99848	3.337E1	3.093E6	− 5.355E5
$5D_{3/2}$	4.99843	6.378E1	7.464E6	− 1.055E6
$6D_{3/2}$	5.99841	1.086E2	3.208E7	− 4.777E6
$7D_{3/2}$	6.99820	1.706E2	9.881E7	− 1.477E7
$8D_{3/2}$	7.99711	2.535E2	2.179E8	− 3.072E7
$9D_{3/2}$	8.99633	3.596E2	4.510E8	− 5.871E7
$3D_{5/2}$	2.99865	1.453E1	− 1.510E4	1.645E4
$4D_{5/2}$	3.99849	3.337E1	3.103E6	− 7.678E5
$5D_{5/2}$	4.99843	6.378E1	7.473E6	− 1.509E6
$6D_{5/2}$	5.99842	1.086E2	3.460E7	− 9.300E6
$7D_{5/2}$	6.99820	1.706E2	9.881E7	− 1.477E7
$8D_{5/2}$	7.99711	2.535E2	2.179E8	− 4.389E7
$9D_{5/2}$	8.99633	3.596E2	4.516E8	− 8.404E7

Table 2
Comparison of experimental and theoretical lifetimes

State	Lifetime (ns)	Method	References
2P	27.29(4)	Laser excitation	[23]
	27.22(20)	Delayed coincidence	[24]
	26.99(16)	Photoassociation	[25]
	27.11(6)	Beam-gas-laser	[26]
	27.102(7)	Photoassociation	[27]
	27.10	Coupled-cluster	[8]
	27.30	CA	[9]
	27.08	CI	[10]
	27.10	CI-Hylleraas	[11]
	27.10	FCPC	[12]
	27.25	QMC	[13]
	27.10	RMBPT	[14]
	27.10	MCHF	[15]
	27.117301(36)	HV	[1]
	27.13	This work	
3S	29.72(17)	Beam-gas-laser	[26]
	30.46	This work	
3D	14.60(13)	Beam-gas-laser	[28]
	14.8(19)	Ion beam excitation	[29]
	14.5(7)	Laser excitation	[30]
	14.60	CI-Hylleraas	[11]
	14.58	FCPC	[12]
	14.584322(68)	HV	[1]
	14.53	This work	

CA = Coulomb approximation; CI = Configuration interaction; FCPC = Full core plus correlation; QMC = Quantum Monte Carlo; RMBPT = Relativistic many body perturbation theory; MCHF = Multiconfigurational Hartree Fock; HV = Hylleraas variational method.

uncertainty. This result agrees with our computed value and with the most precise measured values.

The beam-gas laser method has also been used to determine the lifetime of the 3S state [29]. The result is within about 2% of our computed value. Unfortunately, no theoretical predictions for the 3S state were found in the literature. For the 3D state, several measurements have been made. The result found using laser excitation [28] has a substantially lower uncertainty than that found by colliding an ion beam into a target and observing the fluorescence produced from a multitude of decay channels involving many excited states [29]. All of the theoretical predictions including our result agree with the most precise measured value.

Very little theoretical or experimental work has been done to determine polarizabilities except for the ground state. The most precise value of 164.0(3.4) a_o^3 was obtained by deflecting an atomic beam using inhomogeneous electric and magnetic fields [31]. Table 3 shows that our result as well

Table 3
Comparison of measured ground state polarizability to theoretical values.

Polarizability $\alpha_0(2S_{1/2})\ a_o^3$	Method	References
164.0(34)	E-H gradient balance	[31]
170.3	MCHF	[32]
164.1	CI-Hylleraas	[11]
164.1	FCPC	[33]
164.8	TDGI	[34]
164.2	Coupled-cluster	[35]
162.3	This work	

MCHF = Multiconfigurational Hartree Fock; CI = Configuration interaction; FCPC = Full core plus correlation; TDGI = Time dependent gauge invariant method.

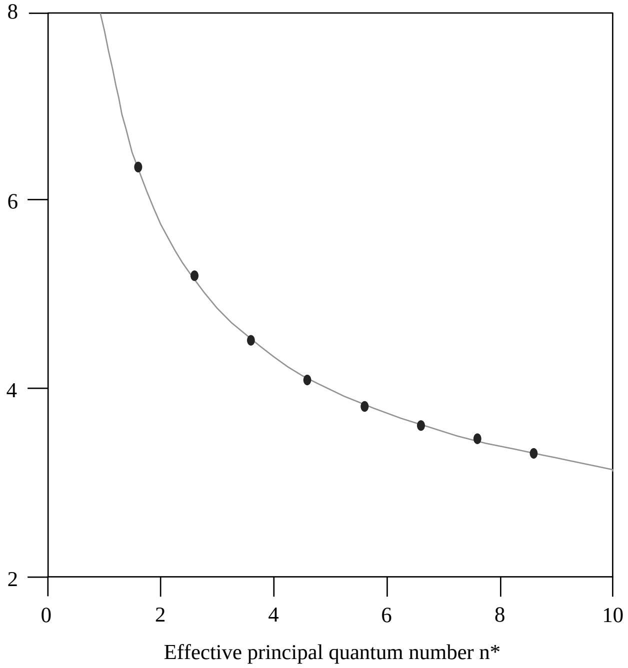

Fig. 1. Dependence of polarizability α_0 upon effective principal quantum number $n^\star$ for the (2–9)$S_{1/2}$ states. The curve is given by $\alpha_0/{n^\star}^7 = 1.438 + 6.431{n^\star}^{-0.574}$, where α_0 is in units of a_o^3 and a_o is the Bohr radius.

as those computed using a variety of theoretical techniques are consistent with the measured value. The only exception is an early calculation using multiconfigurational Hartree Fock theory [32].

The polarizability is predicted to scale as ${n^\star}^7$ for highly excited states where effects of the inner core electrons are negligible [36]. Fig. 1 shows a plot of α_0 for the (2–9)$S_{1/2}$ states. A function $\alpha_0/{n^\star}^7 = A + B{n^\star}^C$ was fitted to the data yielding $A = 1.438$, $B = 6.431$ and $C = -0.574$. The scalar polarizabilities computed using this function lie within 1% of the computed values.

Recently, precise values of Stark shifts have been obtained for the lithium D lines. These experiments are reviewed in Ref. [7]. A laser beam excited atoms as they passed through a uniform electric field and also in a field free region. The frequency shift of the laser beam required to excite the atoms in the field and field free regions was then measured. The group of Hunter found $\alpha_0(2P_{1/2}) - \alpha_0(2S_{1/2}) = -37.14(2)\ a_o^3$ [37]. This agrees with a result of $-37.26a_o^3$ obtained using the Configuration Interaction-Hylleraas technique [38]. This is 20% above the value $-44.5a_o^3$ found using our calculated polarizabilities. Similarly, Windholz et al. determined $\alpha_0(2P_{3/2}) - \alpha_0(2S_{1/2}) = -37.29(40)\ a_o^3$ and $\alpha_2(2P_{3/2}) = 1.64(44)\ a_o^3$ [39]. Our corresponding value for $\alpha_2(2P_{3/2})$ is 3.87 a_o^3. A similar discrepancy between the measured polarizabilities of the lowest P states and those computed using a Coulomb approximation has been found for other alkali atoms [18,19]. This discrepancy arises because the fine structure is largest for the lowest P state and is not adequately accounted for by the Coulomb potential. However, it has been shown that the polarizabilities of higher states computed using a Coulomb approximation are within a few percent of measured values.

In conclusion, the oscillator strengths, lifetimes and ground state polarizability computed using the Coulomb approximation technique are within a few percent of the best experimental data. With the exception of the few results computed using Hylleraas Variational theory, the accuracy of the results presented in this paper are comparable to those found using a number of different techniques that require extensive computation time. Hence, we have been able to study nearly 40 different states of lithium. These results should motivate further theoretical study as well as facilitate measurements of the lifetimes and polarizabilities of excited states lying above the 2P state.

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