$1\,^1S$, $2\,^1S$, and $2\,^3S$ States of Li^+†

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The ionization energy J, excluding the Lamb shift, of the ground state of Li^+ has been evaluated for determinants up to order $n=444$. We get $J(444)=610087.449$ cm^{-1}, and an extrapolated value $J(\infty)=610087.445$ cm^{-1}. For the $2\,^1S$ state we get a theoretical ionization energy of 118704.88 cm^{-1}, as against the experimental value of 120008.30 ± 0.10 cm^{-1} determined by Herzberg and Moore. It appears that the 8517.4 A line first measured by Series and Willis and later by Herzberg and Moore has been incorrectly identified as the $2\,^1S-2\,^1P$ transition. It should be looked for at 9584 A. For the $2\,^3S$ state our value for the ionization energy comes out 134044.12 cm^{-1}, in excellent agreement with the experimental value of 134044.19 ± 0.10 cm^{-1} determined by Herzberg and Moore.

THE Lamb shift of two-electron atoms has so far been verified to within 10% only, in the case of the ground state of helium. The limitation is due to its small magnitude of only -1.3 cm^{-1}, and the present experimental[1] uncertainty of ±0.15 cm^{-1}. In the case of the $1\,^1S$ state of Li^+, the Lamb shift is around 8 cm^{-1}, so that, with the increasing experimental accuracy,[2] it becomes of interest to evaluate its ionization energy. The $2\,^1S$ and $2\,^3S$ states of Li^+ are also of interest, since in their ionization energy Herzberg and Moore[2] have already achieved an experimental accuracy of ±0.10 cm^{-1}. We present here theoretical term-values for these states, including the mass-polarization and relativistic corrections, but not the Lamb shift correction. The principal results are:

1. An accuracy of 0.001 cm^{-1} has been achieved in the term-values of the three states, except for the Lamb shift.

2. The 8517.4 A line, first measured by Series and Willis[3] and later by Herzberg and Moore[2] has been incorrectly identified as the $2\,^1S-2\,^1P$ transition. It should be looked for at 9584 A.

3. The $2\,^3S$ term value comes out in excellent agreement with the experimental value of Herzberg and Moore.[2]

Results for the $1\,^1S$ state are shown in Table I. The solution was obtained by method B which is based on the method A described previously,[4,5] except that the eigenvalues ϵ were computed not by the *iteration* procedure of A, but by evaluating the determinant for various values of ϵ, and then proceeding to the root by Newton's method, followed by parabolic extrapolation. The extrapolated value for J of 610087.4450 cm^{-1} compares with the previous[4] extrapolated value of 610087.44 based upon orders n up to 203. Using the previous estimate of -7.83 cm^{-1} for the Lamb shift we again get 610079.61 cm^{-1} for the ionization energy. The experimental value, which previously was subject to an uncertainty of ±25 cm^{-1}, has now been determined by Herzberg and Moore[2] to be 610079.4 cm^{-1}

TABLE I. $1\,^1S$ state of Li^+. Values of the nonrelativistic ionization energy $-\epsilon^2$, the mass polarization correction $\epsilon^2(A/N)$, or $-\epsilon_M$, and the relativistic correction E_j. J denotes the theoretical value of the ionization potential, excluding the Lamb shift correction. $R_{Li}=109728.727$ cm^{-1}. Method B.

n	125	203	308	444	Extrapolated	Units
ω	10	12	14	16		
ϵ^2	7.279912842824	7.279913245733	7.279913354808	7.279913389891	7.279913408	a.u.
$\epsilon^2(A/N)$	0.28897848	0.28897654	0.28897604	0.28897588	0.2889758	a.u.
$\langle p_1^4\rangle$	310.54856	310.54838	310.54804	310.54777	310.54764	a.u.
$\langle\delta(r_2)\rangle$	6.851405	6.851699	6.851836	6.851906	6.85199	a.u.
$\langle\delta(r_{12})\rangle$	0.534244	0.533995	0.533877	0.533816	0.53374	a.u.
$-(2/\alpha^2)E_2$	0.856256	0.856095	0.856035	0.856003	0.85596	α^2 ry
$(2\epsilon^2-9)R_{Li}$	610072.5949	610072.6832	610072.7072	610072.7149	610072.7189	cm^{-1}
$-\epsilon_M$	-4.959769	-4.959736	-4.959727	-4.959725	-4.959723	cm^{-1}
E_j	19.7370	19.7124	19.7003	19.6938	19.6858	cm^{-1}
J	610087.3721	610087.4359	610087.4478	610087.4490	610087.4450	cm^{-1}
$\langle r_1\rangle$	0.572774284	0.572774189	0.572774164	0.572774155	0.572774150	a.u.
$\langle r_{12}\rangle$	0.862315610	0.862315442	0.862315399	0.862315384	0.862315376	a.u.
$\langle r_1^2\rangle$	0.446279294	0.446279101	0.446279045	0.446279025	0.446279015	a.u.
$\langle r_{12}^2\rangle$	0.927065505	0.927065029	0.927064888	0.927064840	0.927064811	a.u.

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[2] G. Herzberg and H. Moore, Can. J. Phys. **37**, 1293 (1959).
[3] G. W. Series and K. Willis, Proc. Roy. Soc. (London) **A71**, 27 4(1958).
[4] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).
[5] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

TABLE II. $2\,^1S$ state of Li^+. Method B.

n	125	203	308	444	Extrapolated	Units
ϵ^2	5.040854590529	5.040875812401	5.040876682847	5.040876731011	5.0408767341	a.u.
$\epsilon^2(A/N)$	0.021746512	0.021706552	0.021704559	0.021704396	0.021704379	a.u.
$\langle p_1^4\rangle$	213.71340	213.73890	213.74225	213.74268	213.74274	a.u.
$\langle\delta(r_2)\rangle$	4.516285	4.518347	4.518721	4.518798	4.518819	a.u.
$\langle\delta(r_{12})\rangle$	0.064492	0.064358	0.064316	0.064296	0.064275	a.u.
$-(2/\alpha^2)E_2$	0.075543	0.075439	0.075412	0.075402	0.075392	α^2 ry
$(2\epsilon^2-9)R_{\rm Li}$	118694.5714	118699.2287	118699.4198	118699.4303	118699.4310	cm^{-1}
$-\epsilon_M$	−0.3732378	−0.3725519	−0.3725177	−0.3725149	−0.3725146	cm^{-1}
E_j	6.7024	6.5541	6.5240	6.5175	6.5156	cm^{-1}
J	118700.9006	118705.4102	118705.5713	118705.5753	118705.5754	cm^{-1}
$\langle r_1\rangle$	1.64328918	1.64414988	1.64420169	1.64420415	1.64420426	a.u.
$\langle r_{12}\rangle$	2.84263332	2.84433838	2.84444118	2.84444606	2.84444628	a.u.
$\langle r_1^2\rangle$	4.6857173	4.6944635	4.6950662	4.6950987	4.6951003	a.u.
$\langle r_{12}^2\rangle$	9.4184005	9.4358263	9.4370284	9.4370932	9.4370965	a.u.

with a probable error of ± 5 cm^{-1}, or possibly ± 3 cm^{-1}. Clearly, further experimental refinement is needed, as well as a precise calculation of the Lamb shift.

In order to compare our results for the $2\,^1S$ state shown in Table II with experimental values, we use Dalgarno's estimate[6] of 177 for $\ln k_0$, giving a value for the Lamb shift of -0.69 cm^{-1}. This leads to a theoretical ionization energy of 118704.88 cm^{-1}, comparing with Winther's[7] approximate nonrelativistic value of 117900 cm^{-1} and Werner's[8] value of 118718 cm^{-1} deduced experimentally, but not with the value of 120008.30 ± 0.10 cm^{-1} given by Herzberg and Moore.[2] Taking the experimental term value of the $2\,^1P$ state as 108270.81 cm^{-1}, determined by Herzberg and Moore,[2] we get an interval of

$$118704.88-108270.81=10434.07\ cm^{-1} \qquad (1)$$

for the $2\,^1S-2\,^1P$ transition. This corresponds to a line at 9584 A, as against the 8517.4 A line first measured by Series and Willis,[3] and later by Herzberg and Moore.[2] It would be of interest to detect and measure the 9584 A line, and also to identify the 8517.4 A line.

In the case of the $2\,^3S$ state shown in Table III, we use an estimate by Dalgarno[6] of 168 for $\ln k_0$, giving a Lamb shift of -1.14 cm^{-1} and leading to a theoretical value for the ionization energy of 134044.12 cm^{-1}. This is in excellent agreement with the value of 134044.19 ± 0.10 cm^{-1} determined experimentally by Herzberg and Moore.[2]

In order to check our results for the $2\,^1S$ and $2\,^3S$ states we have recomputed them by an independent method C. In method C the wave function ψ is represented for the S states by

$$\psi=\exp(-\alpha r_1-\beta r_2)F(r_1,r_2,r_{12}) \pm\exp(-\alpha r_2-\beta r_1)F(r_2,r_1,r_{12}), \qquad (2)$$

$$\beta=Z, \quad \alpha^2=2\epsilon^2-Z^2, \qquad (3)$$

instead of the form[4] $\exp(-\epsilon r_1-\epsilon r_2)F(r_1,r_2,r_{12})$ used in method B. The r's are again represented by *perimetric* coordinates, and F is determined from the wave equation. The results are shown in Tables IV and V.

TABLE III. $2\,^3S$ state of Li^+. Method B.

n	70	125	203	308	Extrapolated	Units
ϵ^2	5.110697342274	5.110726469186	5.110727348631	5.110727371956	5.1107273726	a.u.
$\epsilon^2(A/N)$	0.017625081	0.017569979	0.017568153	0.017568102	0.017568100	a.u.
$\langle p_1^4\rangle$	218.24445	218.29584	218.30201	218.30277	218.30287	a.u.
$\langle\delta(r_2)\rangle$	4.559183	4.563103	4.563694	4.563781	4.563797	a.u.
$-(2/\alpha^2)E_2$	0.0142407423	0.0142221163	4.0142217400	0.0142217402	0.0142217402	α^2 ry
$(2\epsilon^2-9)R_{\rm Li}$	134022.0839	134028.4760	134028.6690	134028.6741	134028.6743	cm^{-1}
$-\epsilon_M$	−0.30250118	−0.30155547	−0.30152413	−0.30152324	−0.30152322	cm^{-1}
E_j	17.2248	16.9431	16.8960	16.8886	16.8873	cm^{-1}
J	134039.0062	134045.1175	134045.2635	134045.2612	134045.2613	cm^{-1}
$\langle r_1\rangle$	1.49290908	1.49384497	1.49389148	1.49389330	1.49389336	a.u.
$\langle r_{12}\rangle$	2.55952916	2.56137316	2.56146506	2.56146865	2.56146878	a.u.
$\langle r_1^2\rangle$	3.7644784	3.7730713	3.7735674	3.7735895	3.7735904	a.u.
$\langle r_{12}^2\rangle$	7.5655424	7.5826559	7.5836454	7.5836895	7.5836913	a.u.

[6] A. Dalgarno (private communication).
[7] A. Winther, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **27**, No. 2 (1952).
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TABLE IV. 2 ^1S state of Li^+. Method *C*.

n	35	56	84	120	Extrapolated	Units
ϵ^2	5.040659018	5.040788836	5.040838683	5.040859189	5.040874	a.u.
$\epsilon^2(A/N)$	0.02376	0.02248	0.02201	0.02184	0.02172	a.u.
$\langle p_1{}^4\rangle$	213.7057	213.7434	213.7502	213.7502		a.u.
$\langle\delta(r_2)\rangle$	4.516337	4.518397	4.518768	4.518777		a.u.
$\langle\delta(r_{12})\rangle$	0.068708	0.067165	0.066218	0.065620	0.0645	a.u.
$-(2/\alpha^2)E_2$	0.082954	0.080261	0.078353	0.077194	0.0757	α^2 ry
$(2\epsilon^2-9)R_{\rm Li}$	118651.65	118680.14	118691.08	118695.58	118698.9	cm^{-1}
$-\epsilon_M$	−0.40783	−0.38577	−0.37781	−0.37479	−0.3729	cm^{-1}
E_j	6.5626	6.4870	6.4896	6.5035		cm^{-1}
J	118657.81	118686.24	118697.19	118701.71	118705.0	cm^{-1}
$\langle r_1\rangle$	1.644921	1.644492	1.644328	1.644261	1.644212	a.u.
$\langle r_{12}\rangle$	2.845892	2.845021	2.844692	2.844558	2.844461	a.u.
$\langle r_1{}^2\rangle$	4.69943	4.69695	4.69592	4.69548	4.69514	a.u.
$\langle r_{12}{}^2\rangle$	9.44566	9.44078	9.43874	9.43786	9.43717	a.u.

TABLE V. 2 ^3S state of Li^+. Method *C*.

n	35	56	84	120	Extrapolated	Units
ω	4	5	6	7		
ϵ^2	5.110726346	5.110726971	5.110727216	5.110727310	5.110727369	a.u.
$\epsilon^2(A/N)$	0.01758840	0.01757503	0.01757042	0.01756889	0.01756817	a.u.
$\langle p_1{}^4\rangle$	218.29631	218.30113	218.30252	218.30289	218.30302	a.u.
$\langle\delta(r_2)\rangle$	4.563349	4.563675	4.563775	4.563798	4.563804	a.u.
$-(2/\alpha^2)E_2$	0.014270	0.014247	0.014234	0.014228	0.014222	α^2 ry
$(2\epsilon^2-9)R_{\rm Li}$	134028.449	134028.586	134028.640	134028.661	134028.673	cm^{-1}
$-\epsilon_M$	−0.301872	−0.301642	−0.301563	−0.301537	−0.301524	cm^{-1}
E_j	16.9176	16.8957	16.8887	16.8872	16.8868	cm^{-1}
J	134045.065	134045.180	134045.227	134045.246	134045.260	cm^{-1}
$\langle r_1\rangle$	1.49389828	1.49389505	1.49389397	1.49389359	1.49389338	a.u.
$\langle r_{12}\rangle$	2.5614790	2.5614722	2.5614700	2.5614692	2.5614688	a.u.
$\langle r_1{}^2\rangle$	3.7736093	3.7735996	3.7735940	3.7735918	3.7735906	a.u.
$\langle r_{12}{}^2\rangle$	7.5837288	7.5837100	7.5836987	7.5836940	7.5836918	a.u.

The purpose of these calculations were merely to provide a rough check, since, with the exception of ϵ, the results for the 2 ^1S and 2 ^3S states appear here for the first time. When the ratios of the differences deviated markedly from constancy no extrapolation was made. It is seen that, to the accuracy of the low orders n used, the results obtained by method *C* are in agreement with those obtained by method *B*.

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