Relativistic and QED Energies in Lithium

Zong-Chao Yan[1,2] and G. W. F. Drake[2]
[1]*Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6*
[2]*Department of Physics, University of Windsor, Windsor, Ontario, Canada N9B 3P4*
(Received 3 April 1998)

High-precision variational results are reported for the total relativistic corrections, the anomalous magnetic moment corrections, and the electron-electron QED corrections in lithium up to orders $O(\alpha^4 mc^2)$, $O((\mu/M)\alpha^4 mc^2)$, $O(\alpha^5 mc^2)$, and $O((\mu/M)\alpha^5 mc^2)$ using fully correlated basis sets. Methods of estimating the dominant electron-nucleus QED term are discussed, and an extension of the Kabir-Salpeter formalism is found to yield good agreement with high-precision measurements for the ionization potential of the lithium ground state and the $1s^2 2s^2 S$-$1s^2 2p^2 P_J$ transition energies. [S0031-9007(98)06718-0]

PACS numbers: 31.15.Pf, 31.30.Jv, 32.10.Hq

Despite a long history of progress in calculations for the nonrelativistic eigenvalues of lithium [1,2], comparisons with experiment remain severely limited by the accuracy of the lowest-order relativistic corrections (the Breit interaction). In fact, matrix elements of the Breit interaction have never been calculated, except in the Hartree-Fock approximation or modifications of it [3]. The accuracy falls far short of what is required to reach spectroscopic accuracy. Similarly, the techniques of relativistic many-body perturbation theory (or relativistic configuration interaction methods) have been applied with great success to the heavier Li-like ions [4], but electron correlation effects are much too big to be treated satisfactorily for lithium and the lighter Li-like ions. Residual discrepancies between theory and experiment are often attributed to quantum electrodynamic (QED) effects such as the Lamb shift, but since other uncertainties in these calculations are as large as the QED effects themselves, there is no rigorous experimental basis for testing various proposed models of the QED shift, and the conclusions reached from such comparisons may be misleading. Thus only hydrogen, and more recently helium [5–7] (and other analagous two- and three-body systems), are sufficiently well understood to make meaningful comparisons for the QED shift in light atoms.

In this Letter, we present comprehensive high-precision calculations for the low-lying states of lithium, including all finite nuclear mass and lowest-order relativistic effects due to the Breit interaction. The results provide a firm basis for assessing various estimates of the QED shift in lithium, and by analogy in other low-Z atomic systems (Z is the nuclear charge).

The key to obtaining the necessary accuracy is the use of fully correlated variational wave functions in Hylleraas coordinates, including the full optimization of multiple distance scales. Our previous results [2] yielded nonrelativistic energies accurate to a few parts in 10^{12}. Difficulties in evaluating the more singular integrals required for the Breit interaction have now been overcome, resulting in computationally tractible expressions for the integrals [8].

With the integration problems solved, the leading relativistic correction of $O(\alpha^2)$ a.u. can now be calculated from expectation values of the Breit operator [5,9]

$$H_{\rm rel} = B_1 + B_2 + B_{3e} + B_{3Z} + B_5 + \frac{Z\pi\alpha^2}{2} \times \sum_{i=1}^{3} \delta(\mathbf{r}_i) - \pi\alpha^2 \sum_{i>j}^{3} \left(1 + \frac{8}{3}\,\mathbf{s}_i \cdot \mathbf{s}_j\right)\delta(\mathbf{r}_{ij}) + \frac{m}{M}\,(\tilde{\Delta}_2 + \tilde{\Delta}_{3Z}), \quad (1)$$

where $B_1 = -(\alpha^2/8)\sum_{i=1}^{3} \nabla_i^4$, B_2 is the orbit-orbit interaction, B_{3Z} is the spin-orbit interaction, B_{3e} is the spin-other-orbit interaction proportional to the spin sum $s_i + 2s_j$, and B_5 is the spin-spin interaction. Finite-nuclear-mass corrections of order $O(\alpha^2/M)$ a.u. come from the mass scaling of these terms, cross terms with the mass polarization operator, and the relativistic recoil terms $\tilde{\Delta}_2$ and $\tilde{\Delta}_{3Z}$ first derived by Stone [10]. The spin-dependent anomalous magnetic moment correction is

$$\langle H_{\rm anom}\rangle = \gamma\left\langle 2B_{3Z} + \tfrac{4}{3}B_{3e} + \tfrac{2}{3}B_{3e}^{(1)} + 2B_5 + \frac{m}{M}\,\tilde{\Delta}_{3Z}\right\rangle. \quad (2)$$

with $\gamma = (\alpha/2\pi) + (-0.328\,47)(\alpha/\pi)^2 + \ldots$, and $B_{3e}^{(1)}$ is a spin-other-orbit term proportional to $s_i - s_j$. For doublet states, $-\pi\alpha^2\sum_{i>j}(1 + \frac{8}{3}\mathbf{s}_i \cdot \mathbf{s}_j)\delta(\mathbf{r}_{ij}) = \pi\alpha^2\sum_{i>j}\delta(\mathbf{r}_{ij})$ and the spin-spin expectation value $\langle B_5\rangle$ vanishes.

The above expectation values are calculated from nonrelativistic wave functions expressed in Hylleraas coordinates and solved variationally [2]. The Schrödinger Hamiltonian in scaled center of mass plus relative coordinates is

$$H = -\sum_{i=1}^{3}\left(\frac{1}{2}\,\nabla_i^2 + \frac{Z}{r_i}\right) + \sum_{i>j}^{3}\left(\frac{1}{r_{ij}} - \frac{\mu}{M}\,\nabla_i \cdot \nabla_j\right), \quad (3)$$

in units of $2R_M$, where $R_M = (1 - \mu/M)R_\infty$, and $\mu = mM/(m + M)$ is the electron reduced mass. The last

 0031-9007/98/81(4)/774(4)$15.00

mass polarization term is treated as a perturbation and the energy expanded in powers of μ/M up to order $(\mu/M)^2$ with the result

$$E_M(1s^2 2s^2 S) = -7.478\,060\,323\,650\,3(71) + 0.301\,842\,783\,02(25)\,(\mu/M) - 1.499\,788\,67(17)\,(\mu/M)^2, \quad (4)$$

$$E_M(1s^2 2p\ ^2P) = -7.410\,156\,531\,763(42) + 0.246\,738\,887\,5(70)\,(\mu/M) - 1.558\,84(14)\,(\mu/M)^2, \quad (5)$$

in units of $2R_M$. These results improve upon those reported previously [11]. The corresponding result for the Li^+ $1s^2\ ^1S$ core is [7]

$$E_M(1s^2\ ^1S) = -7.279\,913\,412\,669\,305\,9 + 0.288\,975\,786\,393\,99\,(\mu/M) - 1.277\,369\,377\,6(2)\,(\mu/M)^2. \quad (6)$$

In calculating expectation values of the Breit operators, it is computationally advantageous to transform the B_1 term to a less singular form, including finite mass corrections as described by Drake [6]. Similarly the δ-function term $\sum_i \delta(\mathbf{r}_i)$ is replaced by the global operator of Hiller-Sucher-Feinberg [12], including finite mass corrections [6], in order to improve the rate of convergence with basis set size. There then remains the evaluation of two types of singular integrals: integrals containing r_{ij}^{-2} in the integrands, which contain infinite expansions that converge as slowly as $\sum_k k^{-2}$, and integrals more singular than r_{ij}^{-2}. The rate of convergence must be improved for the first type of integrals and reduction formulas must be used to cancel analytically the singularities for the second type of integrals. The complete solution to these two problems is described in Ref. [8].

The convergence of the Breit operators with the number of terms N in the basis set is shown in Table I for the $1s^2 2s\ ^2S$ state. In the table and following equations, $\delta(\mathbf{r}_i)$ means $\sum_{i=1}^3 \delta(\mathbf{r}_i)$ and $\delta(\mathbf{r}_{ij})$ means $\sum_{i>j}^3 \delta(\mathbf{r}_{ij})$. A similar convergence study for the $1s^2 2p\ ^2P_J$ states is given in Ref. [13]. The complete matrix elements of the Breit operators for the $1s^2 2s\ ^2S$ and $1s^2 2p\ ^2P_{1/2}$ states are presented in Table II, together with a comparison with the previous work of Chung *et al.* [3]. For the spin-dependent operators, the $J = 3/2$ components are $(-\frac{1}{2})$ times the corresponding $J = 1/2$ components. Our calculations have dramatically improved the accuracy of Chung's [3] results by several orders of magnitude. The most significant change is that the total relativistic correction to the ionization energy of the ground state is $-1.280\,89(1) \times 10^{-5}$ a.u., as compared with Chung's value of -1.258×10^{-5} a.u. The change is 16% of our calculated QED shift.

With these results in hand, a comparison with experiment for the residual QED shift becomes meaningful to the full extent of the experimental accuracy. Two principal methods have been proposed to estimate the QED shift for many-electron atoms. In the first, the hydrogenic one-electron Lamb shift is evaluated at an effective value $Z_{\rm eff}$ for the nuclear charge. Various prescriptions have been put forward to calculate $Z_{\rm eff}$, but, as will be seen, they tend to give Lamb shifts that are too small. The second method is based on the formulation of Kabir and Salpeter [15], and extended to higher order by McKenzie and Drake [16]. It is similar in spirit to the method used by Indelicato and Desclaux [17]. In essence, the electron-nucleus Lamb shift ($\Delta E_{\rm L,1}$) is (nearly) the hydrogenic Lamb shift, except that a multiplying factor of $Z^3/\pi n^3$ is replaced by the correct electron density at the nucleus, and a corrected value for the Bethe logarithm is inserted. An electron-electron contribution $\Delta E_{\rm L,2}$ must also be included. The QED correction can then be written in the form

$$\Delta E_{\rm QED} = \Delta E_{\rm L,1} + \Delta E_{\rm L,\sigma} + \Delta E_{\rm L,2}\,, \quad (7)$$

where $\Delta E_{\rm L,1}$ is given by

$$\Delta E_{\rm L,1} = \frac{\pi}{Z^3}\left[\frac{xE_{\rm L}(1s_{1/2}) + E_{\rm L}(n\ell j)/n^3}{x + \delta_{\ell,0}/n^3}\right]\langle\delta(\mathbf{r}_i)\rangle_{1s^x n\ell}\,. \quad (8)$$

x is the number of $1s$ electrons and $E_{\rm L}(n\ell j)$ is the one-electron Lamb shift as recently discussed by Mohr [18], including the finite nuclear size correction. For $\ell > 0$, the lowest-order j-dependent part of $E_{\rm L}(n\ell j)$ comes from the anomalous magnetic moment correction which has

TABLE I. Convergence of the expectation values of the Breit operators (in atomic units) for the $1s^2 2s\ ^2S$ state of lithium with infinite nuclear mass and $\alpha^{-1} = 137.035\,989\,5(61)$. N is the size of basis set.

N	$B_1 \times 10^5$	$B_2 \times 10^5$	$\tilde{\Delta}_2 \times 10^5$	$\langle\delta(\mathbf{r}_i)\rangle$	$\langle\delta(\mathbf{r}_{ij})\rangle$
51	−418.352 291 0	−2.334 015 28	−697.105 826	13.840 926 910	0.548 953 75
121	−418.324 400 8	−2.322 013 04	−697.103 101	13.842 222 761	0.545 420 93
257	−418.323 843 9	−2.320 146 16	−697.132 304	13.842 513 464	0.544 668 19
503	−418.324 959 6	−2.319 705 43	−697.143 641	13.842 634 369	0.544 411 15
919	−418.322 494 7	−2.319 639 30	−697.140 568	13.842 608 088	0.544 356 64
1590	−418.322 103 2	−2.319 622 34	−697.140 587	13.842 608 125	0.544 344 10
2626	−418.322 105 6	−2.319 619 56	−697.140 703	13.842 609 541	0.544 330 62
Extrap.	−418.322 120 5(79)	−2.319 618 68(73)	−697.140 748(15)	13.842 609 642(55)	0.544 329 79(31)

TABLE II. Expectation values of the Breit operators and the Q term for the $1s^2 2s\,^2S$ and $1s^2 2p\,^2P_{1/2}$ states with infinite nuclear mass. Units are a.u.

Operator	$1s^2 2s^2 S$	$1s^2 2p^2 P_{1/2}$
B_1	−0.004 183 221 205(79)	−0.004 127 280 433 2(90)
B_2	−0.000 023 196 186 8(73)	−0.000 021 110 238 5(48)
	−0.000 023 3[a]	−0.000 021 3[a]
B_{3e}		0.000 004 014 992 20(99)
B_{3Z}		−0.000 005 030 101 04(65)
$B_{3e}^{(1)}$		0.000 002 478 390 2(69)
$\tilde{\Delta}_2$	−0.006 971 407 48(15)	−0.006 848 916 194(77)
$\tilde{\Delta}_{3Z}$		0.000 001 799 199(82)
$\langle\delta(\mathbf{r}_i)\rangle$	13.842 609 642(55)	13.676 195 49(13)
$\langle\delta(\mathbf{r}_{ij})\rangle$	0.544 329 79(31)	0.532 281 42(51)
	0.570[a]	0.559[a]
Q	0.021 778(21)	0.022 997 5(88)
$\tilde{B}_1$[b]	−0.000 709 541 080(80)	−0.000 695 360 464(33)
	−0.000 707 5[a]	−0.000 693 3[a]

[a]Reference [3].
[b]$\tilde{B}_1 = B_1 + Z\pi\alpha^2\langle\delta(\mathbf{r}_i)\rangle/2$

already been included through Eq. (2). The anomalous magnetic moment part of $E_{\rm L}(n\ell j)$ must therefore be omitted for $\ell > 0$. The term $\Delta E_{{\rm L},\sigma}$ is the first-order correction in a $1/Z$ expansion of the three-electron Bethe logarithm

$$\Delta E_{{\rm L},\sigma} = -\frac{4}{3}\,\alpha^3 Z \ln\left[\frac{Z - \sigma(1s^x n\ell)}{Z}\right]^2 \langle\delta(\mathbf{r}_i)\rangle_{1s^x n\ell}\,, \tag{9}$$

with $\sigma(1s^2 2s\,^2S) = -0.008\,42(1)$ and $\sigma(1s^2 2p\,^2P) = 0.001\,65(1)$ [16]. The $\pm 10\%$ uncertainty assigned to $\Delta E_{{\rm L},\sigma}$ is the dominant source of uncertainty in the calculation. Finally, the two-electron QED shift from the Araki-Sucher terms is

$$\Delta E_{\rm L,2} = \alpha^3\left(\frac{14}{3}\ln\alpha + \frac{164}{15}\right)\langle\delta(\mathbf{r}_{ij})\rangle - \frac{14}{3}\,\alpha^3 Q\,, \tag{10}$$

where the Q term is defined by

$$Q = (1/4\pi)\lim_{\epsilon\to 0}\langle r_{ij}^{-3}(\epsilon) + 4\pi(\gamma + \ln\epsilon)\delta(r_{ij})\rangle\,. \tag{11}$$

γ is Euler's constant, ϵ is the radius of a sphere about $r_{ij} = 0$ excluded from the integration, and a summation over $i > j$ from 1 to 3 is assumed. The Q term was a major source of uncertainty in previous work [16]. The accurate variational values quoted in Table II should be used in place of the $1/Z$ expansion values used previously. Although the $1/Z$ expansion for Q rapidly improves in accuracy with increasing Z, it gives the wrong sign for $Z = 3$ due to numerical cancellation. A detailed analysis of the Q term in Hylleraas coordinates for three-electron systems will be presented in a future publication.

Table III lists the contributions to the ionization energy of $\mathrm{Li}(1s^2 2s\,^2S)$. It is clear that all terms are well established relative to the experimental accuracy, with the Bethe log screening correction $\Delta E_{{\rm L},\sigma}$ being the dominant source of uncertainty. The electron-electron term $E_{\rm L,2}$ turns out to be too small to be significant, due in part to a cancellation with the Li^+ core. The numerical values are $E_{\rm L,2}(\mathrm{Li}^+\ 1\,^1S) = -0.251\,98 \times 10^{-5}$ a.u. and $E_{\rm L,2}(\mathrm{Li}\ 2\,^2S) = -0.258\,31 \times 10^{-5}$ a.u. However, the contributions from $E_{\rm L,1}$ $E_{{\rm L},\sigma}$ are important in bringing theory and experiment into agreement.

Table IV lists the various contributions to the $2\,^2S$-$2\,^2P_J$ transition energies, and compares the sum with the recent high-precision measurements of Sansonetti *et al.* [19]. The contributions from $E_{\rm L,1}$, $E_{{\rm L},\sigma}$, and $E_{\rm L,2}$ all play an important role in the comparison. The agreement with experiment is within the estimated accuracy of these terms, and is noticeably better than for the ionization energy in Table III. The total calculated QED energy shifts (excluding spin-dependent anomalous magnetic moment terms) are 0.2459(30) cm^{-1} for the $2\,^2S_{1/2}$ state and -0.0586 cm^{-1} for the $2\,^2P_{1/2}$ state (relative to the Li^+ core). The difference of $-0.3045(30)$ cm^{-1} brings theory and experiment into agreement for the $2\,^2S$-$2\,^2P$ transition

TABLE III. Contributions to the ionization energy of $^7\mathrm{Li}(1s^2 2s\,^2S)$, relative to $^7\mathrm{Li}^+(1s^2\,^1S)$.

Contribution	Value (a.u.)
Nonrel. energy	−0.198 146 910 981 0(71)
μ/M	0.000 016 501 717 748(20)
$(\mu/M)^2$	−0.000 000 001 438 906 9(10)
Breit interaction α^2	−0.000 012 808 924(96)
Breit interaction $\alpha^2\mu/M$	0.000 000 009 44(14)
$E_{\rm L,1}$, α^3	0.000 001 391 73(5)[a]
$E_{{\rm L},\sigma}$, α^3	−0.000 000 208(20)
$E_{\rm L,2}$, α^3	−0.000 000 063 249(38)
Total	−0.198 142 09(2)
Ionization energy	0.198 142 09(2)
Experiment[b]	0.198 142 03(2)
Difference	0.000 000 06(3)

[a]Uncertainty due to the finite nuclear size contribution of $1.79(5) \times 10^{-9}$ a.u. for a nuclear radius of 2.392 ± 0.03 fm.
[b]Reference [14].

TABLE IV. Contributions to the $1s^2 2s\,^2S$-$1s^2 2p\,^2P_J$ transition energies for ^{7}Li, in units of cm^{-1}. (Anom. mag.: anomalous magnetic moment.)

Contribution	2^2S-$2^2P_{1/2}$	2^2S-$2^2P_{3/2}$	Center of gravity
Nonrel. energy	14 903.159 696 3(93)	14 903.159 696 3(93)	14 903.159 696 3(93)
μ/M	−2.111 225 46(12)	−2.111 225 46(12)	−2.111 225 46(12)
$(\mu/M)^2$	−0.000 005 30(19)	−0.000 005 30(19)	−0.000 005 30(19)
Breit interaction α^2	2.904 930(29)	3.239 116(29)	3.127 721(22)
Breit interaction $\alpha^2\mu/M$	−0.000 094(41)	−0.000 173(41)	−0.000 147(31)
Anom. mag. α^3	−0.000 777 434 2(13)	0.000 388 717 10(63)	0
Anom. mag. $\alpha^3\mu/M$	0.000 000 034 8(17)	−0.000 000 017 38(83)	0
$E_{L,1}, \alpha^3$	−0.347 95(1)	−0.348 19(1)	−0.348 11(1)
$E_{L,\sigma}, \alpha^3$	0.031 6(30)	0.031 6(30)	0.031 597(44)
$E_{L,2}, \alpha^3$	0.011 874 1(91)	0.011 874 1(91)	0.011 874 1(91)
$E_{L,2}, \alpha^3\mu/M$	−0.000 002(13)	−0.000 002(13)	−0.000 002(13)
Total transition energy	14 903.648 0(30)	14 903.983 1(30)	14 903.871 4(30)
Experiment[a]	14 903.648 130(14)	14 903.983 468(14)	14 903.871 689(10)
Difference	−0.000 1(30)	−0.000 4(30)	−0.000 3(30)

[a]Reference [19].

with a residual discrepancy of only $-0.0001(30)$ cm^{-1}. The QED shift is in accordance with Feldman and Fulton's [20] result of -0.30 cm^{-1} based on Hartree-Fock wave functions. However, it is more than a factor of 4 larger than the estimate of Chung *et al.* [3].

Since the Bethe log screening uncertainty cancels for the $2\,^2P_{1/2}$-$2\,^2P_{3/2}$ fine structure splitting, the calculated value is more accurate. The result is 0.335 273 1(4) cm^{-1} as reported previously [13].

In summary, we have obtained theoretical values for all the lower order contributions to the energies of the $2\,^2S_{1/2}$ and $2\,^2P_J$ states of lithium with uncertainties close to the experimental accuracy. This allows a definitive comparison between theory and experiment for the residual QED shift. The good agreement suggests that a similar method of calculation can be applied to other many-electron atoms, and that results based on a screened nuclear charge tend to give QED shifts that are much too small. Further improvements in the QED theory, especially for the Bethe logarithm, would now be well justified.

This work was supported by the Natural Sciences and Engineering Research Council of Canada. Z. C. Y. was also supported by the National Science Foundation through a grant for the Institute for Theoretical Atomic and Molecular Physics at Harvard University and Smithsonian Astrophysical Observatory.

[1] F. W. King and M. P. Bergsbaken, J. Chem. Phys. **93**, 2570 (1990); J. Pipin and D. M. Bishop, Phys. Rev. A **45**, 2736 (1992); A. Lüchow and H. Kleindienst, Int. J. Quantum Chem. **51**, 211 (1994); G. Pestka and W. Woźnicki, Chem. Phys. Lett. **255**, 281 (1996).

[2] Z.-C. Yan, M. Tambasco, and G. W. F. Drake, Phys. Rev. A **57**, 1652 (1998), and earlier references therein.

[3] K. T. Chung, Phys. Rev. A **44**, 5421 (1991); Z.-W. Wang, X.-W. Zhu, and K. T. Chung, Phys. Scr. **47**, 65 (1993).

[4] See J. Sapirstein, Rev. Mod. Phys. **70**, 55 (1998) for a comprehensive review.

[5] G. W. F. Drake and Z.-C. Yan, Phys. Rev. A **46**, 2378 (1992).

[6] G. W. F. Drake, in *Long-Range Casimir Forces: Theory and Recent Experiments on Atomic Systems*, edited by F. S. Levin and D. A. Micha (Plenum, New York, 1993).

[7] G. W. F. Drake, in *Atomic, Molecular, and Optical Physics Handbook*, edited by G. W. F. Drake (AIP, New York, 1996).

[8] Z.-C. Yan and G. W. F. Drake, J. Phys. B **30**, 4723 (1997).

[9] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, New York, 1957).

[10] A. P. Stone, Proc. Phys. Soc. London **77**, 786 (1961); **81**, 868 (1963).

[11] Z.-C. Yan and G. W. F. Drake, Phys. Rev. A **52**, 3711 (1995).

[12] J. Hiller, J. Sucher, and G. Feinberg, Phys. Rev. A **18**, 2399 (1978).

[13] Z.-C. Yan and G. W. F. Drake, Phys. Rev. Lett. **79**, 1646 (1997).

[14] C. E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analysis of Optical Spectra*, NBS, National Standards Reference Data Series C13:48:34 (U.S. GPO, Washington, DC, 1970).

[15] P. K. Kabir and E. E. Salpeter, Phys. Rev. **108**, 1256 (1957).

[16] D. K. McKenzie and G. W. F. Drake, Phys. Rev. A **44**, R6973 (1991); **48**, 4803(E) (1993).

[17] P. Indelicato and J. P. Desclaux, Phys. Rev. A **42**, 5139 (1990).

[18] P. J. Mohr, in *Atomic, Molecular, and Optical Physics Handbook* (Ref. [7]).

[19] C. J. Sansonetti, B. Richou, R. Engleman, Jr., and L. J. Radziemski, Phys. Rev. A **52**, 2682 (1995).

[20] G. Feldman and T. Fulton, Ann. Phys. (N.Y.) **240**, 315 (1995).