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Relativistic, retardation, and radiative corrections in Rydberg states of lithium

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We have used third-order perturbation theory to calculate the effect of the Breit-Pauli relativistic interaction on the dipole polarizability of Li^+ ions of order α^2. Results are in good agreement with the value obtained by Johnson and Cheng [Phys. Rev. A **53**, 1375 (1996)]. In addition, the retardation (Casimir) corrections to singly excited $(1s^2\,NL)$ states of neutral lithium have been computed. When both of these corrections are added to the previously calculated Rydberg state energies, 1σ agreement is found with experiment [N. E. Rothery *et al.*, Phys. Rev. A **51**, 2919 (1995)]. Addition of radiative (Lamb-shift) corrections produces essentially exact agreement. [S1050-2947(97)04503-4]

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I. INTRODUCTION

Recently, accurate measurements have been made of several fine-structure intervals in singly excited lithium atoms [1], and accurate nonrelativistic calculations have also been reported [2]. The agreement between the two is fairly good, and the remaining discrepancies are of the order of $(Z\alpha)^2$, as would be expected for relativistic corrections. More recently, a relativistic configuration-interaction calculation of the dipole polarizabilities of two-electron atomic systems has been made [3], and about $\frac{3}{4}$ of the discrepancy in lithium has been removed.

In this paper we verify the results of Ref. [3] for the relativistic correction to the dipole polarizability of the Li^+ core using third-order perturbation theory and the Breit-Pauli relativistic operator, which is correct to order α^2. We carry out the intermediate-state sums appearing in the perturbation calculation by the use of pseudostates. In addition, we compute the effect of the retardation (Casimir) effect, again using pseudostates and applying the formalism of Au *et al.* [4]. These two corrections together bring theory and experiment into almost perfect agreement, to just outside their combined errors. The largest remaining correction is the Lamb shift, whose leading term (of order $Z\alpha^3$) we also compute.

II. NONRELATIVISTIC CALCULATIONS

Let us briefly review the standard method of evaluating the nonrelativistic energy shifts of Rydberg states of lithium-like systems [2]. The Hamiltonian (in atomic units with energies in rydbergs) of the three-electron system (with the nucleus taken as fixed and of atomic number Z) is

$$H_{\mathrm{NR}}=\left[-\nabla_1^2-\nabla_2^2-\frac{2Z}{r_1}-\frac{2Z}{r_2}+\frac{2}{r_{12}}\right]+\left[-\nabla_x^2-\frac{2(Z-2)}{x}\right]+\left\{-\frac{4}{x}+\frac{2}{|\vec{x}-\vec{r}_1|}+\frac{2}{|\vec{x}-\vec{r}_2|}\right\}. \tag{1}$$

Here r_i refers to the two core electrons, and x is the coordinate of the outer, Rydberg electron. The expression in the first set of brackets is the core Hamiltonian, that in the second set is the Hamiltonian of the Rydberg electron moving in the Coulomb field of the nucleus shielded by the two core electrons. The remainder (in curly brackets) is the perturbation due to the mutual interaction of core and outer electrons.

In Ref. [2] the perturbation theory is developed in detail, but here we are only interested in the leading asymptotic term. Expanding the interaction term of Eq. (1) in multipoles we find

$$H_{\mathrm{dip}}=\frac{2}{x^2}\,(\vec{r}_1+\vec{r}_2)\cdot\hat{\vec{x}} \tag{2}$$

as the leading (dipole) term for $x\gg r_i$. Second-order perturbation theory applied to this interaction leads to the well-known polarizability potential

$$V_2(x)=\sum_n \frac{\langle 0|H_{\mathrm{dip}}|n\rangle\langle n|H_{\mathrm{dip}}|0\rangle}{(E_0-E_n)}=-\frac{\alpha_1}{x^4}. \tag{3}$$

Strictly speaking, the quantities $|0\rangle$, E_0, $|n\rangle$, and E_n should be eigenvectors and eigenenergies of the core Hamiltonian, representing the ground and excited states, respectively. In practice we use normalized, approximate functions and energies obtained variationally. Hylleraas trial functions have been found [2] to give good convergence for the dipole polarizability α_1. The energy shift of a particular Rydberg state, due to this polarizability potential, is given by the expectation value of $V_2(x)$ in the corresponding hydrogenic state of appropriate Z.

III. RELATIVISTIC CORRECTION TO THE POLARIZATION POTENTIAL

We wish to compute a correction to the energy shift of a Rydberg level of lithium due to the Breit-Pauli relativistic Hamiltonian of order α^2. Thus we must carry out a third-order mixed perturbation calculation, retaining the effect of the Breit-Pauli operator only to first order [5]. The Breit-Pauli perturbation is

$$H_{\mathrm{BP}}=\alpha^2\left\{-\frac{1}{4}[\nabla_1^4+\nabla_2^4]+\pi Z[\delta(\vec{r}_1)+\delta(\vec{r}_2)]\right.$$
$$\left.+2\pi\delta(\vec{r}_{12})+\frac{1}{r_{12}}[\vec{\nabla}_1\cdot\vec{\nabla}_2+\hat{\vec{r}}_{12}\cdot(\hat{\vec{r}}_{12}\cdot\vec{\nabla}_1)\vec{\nabla}_2]\right\}. \tag{4}$$

The complete third-order potential has the form

$$V_3(x)=\sum_{n,m}\frac{\langle 0|h|n\rangle\langle n|h|m\rangle\langle m|h|0\rangle}{(E_0-E_n)(E_0-E_m)}$$
$$-\sum_n\frac{\langle 0|h|n\rangle\langle n|h|0\rangle}{(E_0-E_n)^2}\langle 0|h|0\rangle, \tag{5}$$

where $h=H_{\mathrm{dip}}+H_{\mathrm{BP}}$. Keeping terms of order α^2 results in the following:

$$V_3^{\alpha^2}(x)=\sum_{n,m}\left[\frac{\langle 0|H_{\mathrm{dip}}|n\rangle\langle n|H_{\mathrm{BP}}|m\rangle\langle m|H_{\mathrm{dip}}|0\rangle}{(E_0-E_n)(E_0-E_m)}\right.$$
$$\left.+2\frac{\langle 0|H_{\mathrm{dip}}|n\rangle\langle n|H_{\mathrm{dip}}|m\rangle\langle m|H_{\mathrm{BP}}|0\rangle}{(E_0-E_n)(E_0-E_m)}\right]$$
$$-\sum_n\frac{\langle 0|H_{\mathrm{dip}}|n\rangle\langle n|H_{\mathrm{dip}}|0\rangle}{(E_0-E_n)^2}\langle 0|H_{\mathrm{BP}}|0\rangle$$
$$=-\frac{\Delta\alpha_1}{x^4}, \tag{6}$$

where we have taken account of the facts that the ground state has angular momentum $L=0$, the excited states n,m are $L=0$ or 1, and H_{BP} is rotationally invariant.

The summations in Eq. (6) are carried out using optimized pseudostates. For all the $L=0$ states we have chosen nonlinear parameters giving the best ground-state energy. For the $L=1$ pseudostates the nonlinear parameters were those maximizing the nonrelativistic polarizability α_1, Eq. (3), and Ref. [2]. The ∇^4 and $\delta(\vec{r})$ terms are larger than the other two in Eq. (4), but they are of opposite sign and, as noted by Weinhold [5], there is significant cancellation. Our best-converged result, obtained with 161 terms with $L=0$ and 165 terms with $L=1$, is $\Delta\alpha_1=-4.518\times10^{-5}$; this should be compared with $\Delta\alpha_1=-4.485\times10^{-5}$, the result of Ref. [3]. It is encouraging to see agreement to better than 1% between two distinct methods of calculation. We will show the effect of this correction on the Rydberg states of lithium below.

As an interesting aside we note that $\Delta\alpha_1(Z)$ has been calculated for a set of different values of atomic number Z up to 30 in Ref. [3]. For large Z this quantity can be well represented by the expression $\Delta\alpha_1(Z)=-4.86\times10^{-4}Z^{-2}$. For the one-electron atom the relativistic polarizability correction can be given exactly [6] as $\Delta\alpha_1(Z)=-28(Z\alpha)^2(\alpha_1/27)$. If we note that for the two-electron ions of interest here $\alpha_1\rightarrow 9Z^{-4}$ for large Z, then we can form the ratio of the two formulas as follows:

$$\frac{\left[-\dfrac{4.86\times10^{-4}}{Z^2}\right]}{\left[-\dfrac{28}{27}(Z\alpha)^2\dfrac{9}{Z^4}\right]}=\frac{5.207\times10^{-5}}{\alpha^2}=0.978. \tag{7}$$

This ratio is so close to 1 that we might almost have guessed the relativistic correction from the previous work. Presumably this simple relation reflects the fact that for high Z the two-electron ions become increasingly less correlated and hence more like two one-electron atoms scaled according to Z.

IV. RETARDATION CORRECTIONS TO RYDBERG STATE ENERGIES

Up to now we have considered the situation where the Rydberg electron is at a distance from the nucleus much greater than the radius of the two-electron core, in order to simplify the calculations in two ways. First, the asymptotic form of the interaction potential involving the multipole expansion is applicable. Second, exchange between the core electrons and the outer one can be neglected, since their wave functions do not overlap appreciably. When the distance between the Rydberg electron and the core is *very* large (greater than about $137a_0$) something new happens: it is no longer adequate to treat the interaction as purely Coulomb in character. This is because the delay due to the finite light propagation time between the core and the outer electron is comparable to the characteristic time $t=a_0/v$. This retardation (or Casimir) effect [7] brings in a new type of term [8] in the effective potential acting on the Rydberg electron that falls off like x^{-5}; for very large distances it replaces the ordinary nonadiabatic term that falls like x^{-6}. But for *fairly* large distances these asymptotic forms are not accurate, and it is in this more complicated intermediate region that the experimentally interesting wave functions lie.

We wish to calculate the shift in energy of a high Rydberg state of lithium $(1s^2NL)$ due to retardation. In [4] the following expressions are given for the modification of the effective potential producing the energy shift:

$$\Delta_{\mathrm{Ret}}^{\mathrm{NL}}=\frac{16}{\pi}\sum_n\frac{|\langle n|z_1+z_2|0\rangle|^2}{(E_n-E_0)^2}I_n, \tag{8}$$

$$I_n=\int_0^\infty\frac{dt}{(t^2+1)}\int_0^\infty\frac{dx}{x^6}R_{\mathrm{NL}}^2(x)$$
$$\times e^{-2z_nt}[3-5z_n^2+z_n^4+(6z_n-2z_n^3)t]$$
$$+\int_0^\infty\frac{dx}{x^6}R_{\mathrm{NL}}^2(x)\left[6z_n-\frac{z_n^3}{2}-\frac{3\pi}{2}\right], \tag{9}$$

where $z_n=\frac{1}{2}\alpha x(E_n-E_0)$. [In Eq. (9) we have inserted the parametric integral forms for the auxiliary functions f and g [9].) There are several possible ways to evaluate Eqs. (8) and (9), but we have chosen to evaluate analytically the integrals over the radial hydrogenic functions $R_{\mathrm{NL}}(x)$ first. Then we carry out the sum over the core index n, after which the integral over the parameter t is done numerically. The general expression for $R_{\mathrm{NL}}(x)$ is complicated, so we have cho-

TABLE I. Retardation corrections for lithium in MHz. Items in parentheses are from the approximate calculation of Ref. [10]; the present results should be correct to the number of figures given. $A[-B]$ means $A \times f10^{-B}$.

N	$L=N-1$	$L=N-2$	$L=N-3$	$L=N-4$	$L=N-5$	$L=N-6$
21	0.512914[−6]	0.784730[−6]	0.120167[−5]	0.184893[−5]	0.286846[−5]	0.450239[−5]
20	0.824531[−6]	0.128704[−5]	0.201008[−5] (0.24[−5])	0.315574[−5] (0.37[−5])	0.500108[−5]	0.803228[−5]
19	0.135954[−5]	0.216716[−5]	0.345638[−5]	0.554594[−5]	0.899641[−5]	0.148237[−4]
18	0.230336[−5]	0.375457[−5]	0.612534[−5]	0.100660[−4]	0.167579[−4]	0.284215[−4]
17	0.401893[−5]	0.671099[−5]	0.112235[−4]	0.189396[−4]	0.324660[−4]	0.569129[−4]
16	0.724279[−5]	0.124177[−4]	0.213463[−4]	0.371126[−4]	0.657790[−4]	0.119830[−3]
15	0.135305[−4] (0.16[−4])	0.238860[−4] (0.28[−4])	0.423474[−4] (0.50[−4])	0.761733[−4]	0.140352[−3]	0.267594[−3]
14	0.263198[−4] (0.31[−4])	0.480106[−4] (0.56[−4])	0.881605[−4] (0.10[−3])	0.164958[−3]	0.318213[−3]	0.641113[−3]
13	0.536064[−4]	0.101492[−3]	0.194088[−3] (0.23[−3])	0.380458[−3] (0.44[−3])	0.775800[−3]	0.167406[−2]
12	0.115116[−3]	0.227499[−3]	0.456352[−3]	0.946219[−3]	0.206712[−2]	0.487218[−2]
11	0.262951[−3]	0.546500[−3]	0.116111[−2]	0.258099[−2]	0.616036[−2]	0.163382[−1]
10	0.646286[−3]	0.142682[−2]	0.325464[−2]	0.790948[−2] (0.91[−2])	0.212477[−1] (0.24[−1])	0.653658[−1]
9	0.173556[−2]	0.412753[−2]	0.103097[−1]	0.282191[−1]	0.880362[−1]	0.119784
8	0.520102[−2]	0.135982[−1]	0.383258[−1]	0.122084	0.179089	
7	0.179285[−1]	0.531534[−1]	0.175064	0.285004		
6	0.744191[−1]	0.260226	0.492489			
5	0.397834	0.950122				

sen to simplify the analytic evaluation by working with functions of increasing numbers of nodes. That is, we fix $N-L$ at 1,2, . . . ,5; for each such choice the analytic form of $R_{\mathrm{NL}}(x)$ is simple, and this method includes the higher L values for each N for which the asymptotic method is best suited. Results of this calculation are shown in Table I, along with some earlier estimates [10].

V. LAMB-SHIFT CORRECTIONS

A good deal of work has been reported on the Lamb shift of atomic helium [11] and some on general two-electron ions such as Li^+ [12], which is the core of the lithium Rydberg atom that interests us here. But since we are only interested in the L-dependent fine-structure splitting of these Rydberg levels only the *change* in the Lamb shift of the two-electron core due to its interaction with the outer electron needs to be calculated. The main parts of the Lamb shift (mass renormalization, vacuum polarization, and radiative correction to the magnetic moment) can be written in terms of $\langle \delta(\vec{r}_1) + \delta(\vec{r}_2) \rangle$, and it is only necessary to calculate the dependence of these δ functions on the state of the outer electron. This idea has been developed previously [13] for the helium Rydberg states, where the core has only one electron. Smaller corrections due to the effect of the electric field of the Rydberg electron and of two-electron correlations will be omitted here; they have been discussed (for the case of helium) in Ref. [13].

Following [13] we can write the expression for the two-electron Lamb shift as

$$\Delta_{\mathrm{Lamb}}^{\mathrm{NL}} = \frac{8}{3} Z \alpha^3 \left\{ -2 \ln\alpha + \frac{19}{30} - \ln k \right\} \langle \delta(\vec{r}_1) + \delta(\vec{r}_2) \rangle. \tag{10}$$

Here the δ functions refer to the two core electrons but are influenced by the outer electron. We have already computed

TABLE II. Effect of the small corrections. Relativistic polarizability, retardation, Lamb shift, and the total including the uncorrected interval from [2], in MHz, for the $N=10$ manifold. The quantities in parentheses are estimated errors in the last figures retained.

L	Uncorrected shift	Relativistic polarizability	Retardation	Lamb shift	Total
4	−535.343(115)	0.1201	0.0654	−0.0251	−535.183(115)
5	−195.5397(11)	0.0416	0.0212	−0.0087	−195.4856(11)
6	−86.2932(3)	0.0170	0.0079	−0.0036	−86.2719(3)
7	−43.49739(7)	0.0078	0.0033	−0.0016	−43.4879(1)
8	−24.02231(2)	0.0039	0.0014	−0.0008	−24.0178
9	−14.013679(4)	0.0020	0.0006	−0.0004	−14.0115

TABLE III. Comparison of level differences for lithium, in MHz, between theory and experiment [1]. The standard deviations are experimental and theoretical combined in quadrature. ''Experiment'' refers to Ref. [1], ''theory'' means the present results, and Ref. [2] omits the present relativistic, retardation, and radiative corrections.

Interval	Experiment − Ref. [2]	Experiment − Theory	Standard deviation
$10G$-$10H$	−0.08	0.02	0.11
$10H$-$10I$	−0.0326	0.0003	0.0048

their expectation values in Sec. III using third-order perturbation theory, since such δ functions appear in the Breit-Pauli operator. Since the third-order perturbation theory expression involves the dipole term in the potential twice, the expectation value of $1/x^4$ must be evaluated. This is how the state of the outer electron manifests itself, since we are assuming here that the Bethe logarithm $\ln k$ depends only on the properties of the unperturbed Li^+ core. (There is a correction to this discussed, for the one-electron case, in Ref. [13]. In that case it is very small, and since it is fairly difficult to evaluate we will not worry about it here.) The two-electron Bethe logarithm has been evaluated as a function of Z in Ref. [12]: $\ln k=2.984\,128\,56+2\ln(Z-0.00615)$. From our previous discussion we know that the Lamb-shift correction to the Rydberg states of lithium must be proportional to the expectation value of $1/x^4$. In effect, this behaves like another correction to the dipole polarizability of the two-electron core.

VI. RESULTS AND DISCUSSION

From the preceding work we can write the relativistic corrections calculated here as

$$\Delta_{\mathrm{NL}}=[1.486\times10^5-3.103\times10^4]\left\langle\frac{1}{x^4}\right\rangle_{\mathrm{NL}}+\Delta_{\mathrm{ret}}^{\mathrm{NL}},\quad(11)$$

where the quantities in square brackets are the coefficients (in MHz) of the relativistic polarizability and Lamb-shift corrections, respectively. (We have converted from rydberg units to MHz using the value 1 $\mathrm{Ry}=3.289\times10^9$ MHz.) The hydrogenic expectation value $\langle 1/x^4\rangle_{\mathrm{NL}}$ is given analytically [14] as

$$\left\langle\frac{1}{x^4}\right\rangle_{\mathrm{NL}}=16\,\frac{(2L-2)!}{(2L+3)!}\left[\frac{3}{N^3}-\frac{L(L+1)}{N^5}\right],\quad(12)$$

while the retardation shift comes from Table I. In Table II we show the three types of corrections for the experimentally interesting case $N=10$ and their total in MHz. (It is simple to obtain results for other cases if needed.) Finally, in Table III, we compare the experimental fine-structure intervals for lithium [1] with the theoretical totals including the uncorrected values [2,15] and the three small corrections calculated here. It is clear that there is better agreement when the small corrections are included, although the almost perfect agreement is presumably fortuitous.

At present there are only two fine-structure intervals in lithium measured with enough precision to enable a comparison between theory and experiment to be made, and only one for which the present asymptotic calculation is good enough to begin testing the theory fairly rigorously. The lithium system is clearly not too difficult to handle theoretically, and higher-order corrections and more measurements seem to be warranted. This is a program that should be able to test both quantum electrodynamics and our computational techniques in a critical way.

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