Rydberg levels of lithium

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The electrostatic fine structure for singly excited lithium is accurately calculated using an effective potential method that has proven to be very useful for helium. Relevant properties of the two-electron Li^+ ionic core with finite nuclear mass are determined from variational wave functions. From these, nonrelativistic level shifts are obtained analytically, and the leading relativistic correction is applied. A comparison with recent experimental results is made.

I. INTRODUCTION

If we know enough about the long-range interactions of an electron with the two-electron Li^+ core, it is possible to calculate quite accurately the energy of any excited level of atomic lithium for "high enough" values of N and L using an effective potential formalism. The idea is that in these high Rydberg states the valence electron is excluded from the region containing the core so that it can be treated as distinguishable from the core electrons and also that only the asymptotic form of the interaction needs to be considered. The advantage of this technique over a direct, three-electron variational calculation is twofold: First, the two-electron core is much easier to handle numerically, and second, once the required properties of the core have been evaluated, any singly excited Rydberg state can be treated analytically. (We are essentially replacing a four-body problem by a tractable three-body problem plus a simple two-body problem.) This method builds on a history of similar calculations for excited helium [1], for which the one-electron core can be treated analytically and exactly.

II. HAMILTONIAN OF THE SYSTEM

We begin by writing the nonrelativistic Hamiltonian for the system of three electrons of unit mass and a nucleus of mass M and charge Z. (The charge of the nucleus is written explicitly here, although applications will be confined here to the case of $Z = 3$. It is not hard to extend the present calculation to more general positive ions with three electrons.) We assume that electron 3 is the valence electron and is much further from the nucleus than the other two. (Since this electron does not penetrate the core, exchange with the core electrons is negligible, and it may be taken to be distinguishable from them.) Then (in rydbergs) the Hamiltonian is

$$H = -\nabla_1^2 - \nabla_2^2 - \nabla_3^2 - \frac{1}{M}\nabla_M^2 - \frac{2Z}{|\mathbf{r}_1 - \mathbf{r}_M|} - \frac{2Z}{|\mathbf{r}_2 - \mathbf{r}_M|}$$
$$- \frac{2Z}{|\mathbf{r}_3 - \mathbf{r}_M|} + \frac{2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{2}{|\mathbf{r}_1 - \mathbf{r}_3|} + \frac{2}{|\mathbf{r}_2 - \mathbf{r}_3|} . \quad (1)$$

It is convenient to introduce coordinates ρ_1 and ρ_2 that measure the distance between each core electron and the nucleus and x, the distance between the valence electron and the center of mass of the core; these are

$$\boldsymbol{\rho}_{1,2} = m(\mathbf{r}_{1,2} - \mathbf{r}_M) ,$$
$$\mathbf{x} = m'\left[\mathbf{r}_3 - \frac{\mathbf{r}_1 + \mathbf{r}_2 + M\mathbf{r}_M}{M+2}\right] . \quad (2)$$

(The coordinate of the center of mass of the whole system has been dropped.) We have defined two reduced masses: $m = M/(M+1)$ is the reduced mass of one electron and the nucleus, while $m' = (M+2)/(M+3)$ is the reduced mass of the valence electron and the core. We write the Hamiltonian as the sum of three parts, $H_c, H_v,$ and V, representing, respectively, the core, the valence electron, and the interaction between them. These are

$$H_c = -\nabla_{\rho_1}^2 - \nabla_{\rho_2}^2 - K\nabla_{\rho_1}\cdot\nabla_{\rho_2} - \frac{2Z}{\rho_1} - \frac{2Z}{\rho_2} + \frac{2}{|\boldsymbol{\rho}_1 - \boldsymbol{\rho}_2|} ,$$

$$H_v = -q\left[\nabla_x^2 + \frac{2(Z-2)}{x}\right] , \quad (3)$$

$$V = 2q\left[\frac{1}{|\mathbf{x} - f\boldsymbol{\rho}_1 + g\boldsymbol{\rho}_2|} + \frac{1}{|\mathbf{x} - f\boldsymbol{\rho}_2 + g\boldsymbol{\rho}_1|}\right.$$
$$\left. - \frac{Z}{|\mathbf{x} + g(\boldsymbol{\rho}_1 + \boldsymbol{\rho}_2)|} + \frac{(Z-2)}{x}\right] .$$

Here $K = 2/(M+1)$, $q = m'/m \approx 1 + K^2/2$, $f = 2q/(2+K)$, $q = Kf/2$, and reduced rydberg units $(R = mR_\infty)$ are being used.

As we mentioned above, only the long-range part of the potential is to be retained. This involves the conventional multipole expansion of V for large x, although since we are not making the fixed-nucleus approximation the expansion is somewhat more complex than usual. The first three multipoles, the dipole, quadrupole, and octupole components, have the following forms:

$$V_1 = \frac{2q^2w}{x^2}\left[\frac{2+(Z-1)K}{2+K}\right]P_1(\hat{w}\cdot\hat{x}) \ ,$$

$$V_2 = \frac{2q^3}{x^3}\left[\rho_1^2 P_2(\hat{\rho}_1\cdot\hat{x})+\rho_2^2 P_2(\hat{\rho}_2\cdot\hat{x})\right.$$

$$\left.-\frac{4K+ZK^2}{(2+K)^2}w^2 P_2(\hat{w}\cdot\hat{x})\right] \ , \qquad (4)$$

$$V_3 = \frac{2q^4}{x^4}\left\{\frac{2-K}{2+K}[\rho_1^3 P_3(\hat{\rho}_1\cdot\hat{x})+\rho_2^3 P_3(\hat{\rho}_2\cdot\hat{x})]\right.$$

$$\left.-\frac{4K-2K^2-ZK^3}{(2+K)^3}w^3 P_3(\hat{w}\cdot\hat{x})\right\} \ ,$$

where $\mathbf{w}=\boldsymbol{\rho}_1+\boldsymbol{\rho}_2$.

III. THE EFFECTIVE POTENTIAL

In Ref. [1] the derivation of the effective potential has been given in detail for the case of neutral helium. In the present case, since the unperturbed Li^+ core is spherical-ly symmetric and sufficiently tightly bound, we can follow that discussion essentially step by step, and we will not repeat the details here. Let us just note that the method begins with the adiabatic approximation that results in the ordinary second-order polarization potentials as well as third- and fourth-order potentials. But for consistency it is necessary to include nonadiabatic terms as well. These come from the effect of the kinetic-energy operator of the valence electron interacting with the potential terms in various orders. They represent the inability of the core electrons to follow the motion of the outer electron exactly, and they correct the adiabatic approximation. We have previously reported [2] results which included only the first two terms in the asymptotic effective potential. We have now carried out the evaluation of all the core coefficients needed to evaluate the potential up to order $1/x^8$. Of course, the required accuracy of these higher terms is much less than for the dipole polarizability, which contributes the leading $1/x^4$ contribution to the effective potential.

The effective potential in which the valence electron moves is the following (up to order $1/x^8$):

$$U(x)=-\frac{\alpha_1}{x^4}+\frac{6q\beta_1-\alpha_2}{x^6}+\frac{\delta+16q^2\gamma_1/5}{x^7}+\frac{-\alpha_3+15q\beta_2-\epsilon+\alpha_1\beta_1-72q^2\gamma_1[1+L(L+1)/10]}{x^8} \ . \qquad (5)$$

The core coefficients $\alpha,\beta,\ldots$ are defined below.

$$S_{k,i}\equiv x^{2i+2}\sum_n \frac{\langle 0|V_i|n\rangle\langle n|V_i|0\rangle}{(E_n-E_0)^k} \ . \qquad (6)$$

(Here $\alpha_i=S_{1,i}$, $\beta_i=S_{2,i}$, and $\gamma_i=S_{3,i}$). The third-order polarizability has the following form:

$$\delta\equiv x^7\sum_{n,m}\frac{\langle 0|V_i|n\rangle\langle n|V_j|m\rangle\langle m|V_k|0\rangle}{(E_n-E_0)(E_m-E_0)} \ . \qquad (7)$$

(The values that (ijk) can take are all the permutations of $\{112\}$.) Finally, the fourth-order hyperpolarizability involving only dipole terms has the following form:

$$\epsilon\equiv x^8\sum_{n,m,p}\frac{\langle 0|V_1|n\rangle\langle n|V_1|m\rangle\langle m|V_1|p\rangle\langle p|V_1|0\rangle}{(E_n-E_0)(E_m-E_0)(E_p-E_0)} \ . \qquad (8)$$

IV. COMPUTATION OF THE CORE PARAMETERS

To evaluate the core parameters defined above we use the method of pseudostate summation. This has been widely used in the past, and we have employed it to evaluate the polarizabilities of helium and the hydrogen ion [3] as well as in a less thorough treatment of two-electron positive ions [2], and a treatment of two-photon transitions in hydrogen [4]. For the present application, we calculate the ground state of the two-electron ionic system using a Hylleraas type of correlated variational trial function. This function has angular momentum $L=0$ and the form

$$\Psi=e^{-a(\rho_1+\rho_2)}\sum_{l,m,n=0}^{\Omega}C_{l,m,n}\rho_1^l\rho_2^m\rho_{12}^n+[1\leftrightarrows2] \ , \qquad (9)$$

where Ω is an integer called the Pekeris number. Our best value of the energy was obtained for $a=4.8$ with 372 terms retained ($\Omega=14$). The pseudostate-summation technique uses a set of normalizable functions to approximate the complete sets of intermediate states in Eqs. (6)–(8). These have the Hylleraas form too, but with $L=1$–3. The $L=1$ and 2 states were shown in Ref. [2], and the $L=3$ F states are composed of two types of terms, $\Psi_F=\Psi_{sf}+\Psi_{pd}$, which are defined as follows:

$$\Psi_{sf}=\langle f+\bar{f}\rangle\left[\sqrt{5}\cos\left[\frac{3\theta_{12}}{2}\right]\mathcal{D}_3^{3+}-\sqrt{3}\cos\left[\frac{\theta_{12}}{2}\right]\mathcal{D}_3^{1+}\right]+(f-\bar{f})\left[\sqrt{3}\sin\left[\frac{\theta_{12}}{2}\right]\mathcal{D}_3^{1-}-\sqrt{5}\sin\left[\frac{3\theta_{12}}{2}\right]\mathcal{D}_3^{3-}\right] \ , \qquad (10)$$

$$\Psi_{pd}=\langle g+\bar{g}\rangle\left[\sqrt{15}\cos\left[\frac{\theta_{12}}{2}\right]\mathcal{D}_3^{3-}-\cos\left[\frac{\theta_{12}}{2}\right](1+2\cos\theta_{12})\mathcal{D}_3^{1+}\right]-(g-\bar{g})\left[\sqrt{15}\sin\left[\frac{\theta_{12}}{2}\right]\mathcal{D}_3^{3-}\right.$$

$$\left.+\sin\left[\frac{\theta_{12}}{2}\right](1-2\cos(\theta_{12})\mathcal{D}_3^{1-}\right] \qquad (11)$$

TABLE I. Best values of the core parameters used in constructing the effective potential. The upper entry in each case is for ^{6}Li and the lower one is for ^{7}Li.

α_1	β_1	γ_1	α_2
0.192 490 771	0.035 286 879	0.006 806 377	0.113 825 934
0.192 485 410	0.035 286 017	0.006 806 227	0.113 834 685

β_2	α_3	δ	ϵ
0.016 670 328	0.168 351 237	0.121 337 559	0.027 039 600
0.016 671 511	0.168 362 339	0.121 345 411	0.027 038 073

where

$$f(r_1,r_2,r_{12})=r_2^3\sum_{l,m,n}C_{lmn}r_1^l r_2^m r_{12}^n \exp^{-\gamma r_1 -\delta r_2} ,$$

$$g(r_1,r_2,r_{12})=r_1 r_2^2 \sum_{lmn}D_{lmn}r_1^l r_2^m r_{12}^n \exp^{-\alpha r_1 -\beta r_2} ,$$

$$\bar{f}(r_1,r_2,r_{12})=f(r_2,r_1,r_{12}) ,$$

$$\bar{g}(r_1,r_2,r_{12})=g(r_2,r_1,r_{12}) . \tag{12}$$

(As in [2] the rotational harmonics $\mathcal{D}$ appearing here are those defined by Bhatia and Temkin [5].) The nonlinear parameters in the P, D, and F functions are determined by maximizing the second-order polarizabilities of the

corresponding multipolarity. Our best values of the core parameters are shown in Table I.

V. OTHER CONTRIBUTIONS TO THE ENERGY AND RESULTS

From the core parameters of Table I the effective potential of Eq. (5) can be constructed explicitly. Numerically, this potential is

$$U(x)=-\frac{0.192\,485\,40}{x^4}+\frac{0.097\,881}{x^6}+\frac{0.143\,125}{x^7}$$
$$-\frac{0.428\,584+0.049\,005\,L(L+1)}{x^8} \tag{13}$$

for the case of ^{7}Li.

The expansion of the effective potential is at best asymptotic, so we use the following conservative expression for the energy shift $\Delta(NL)$ away from the unperturbed energy $-R/N^2$:

$$\Delta(NL)=R\{(U_4+U_6+\tfrac{1}{2}[U_7+U_8])\pm\tfrac{1}{2}(U_7+U_8)\} , \tag{14}$$

where the reduced rydberg $R=3.289\,584\,678\times10^9$ MHz for ^{7}Li, and where U_k is the expectation value of that term in $U(x)$ which goes like x^{-k}. Since the unperturbed wave function of the outer electron is purely hydrogenic, these expectation values can be evaluated

TABLE II. Level shifts (in MHz) for ^{7}Li due to the effective potential terms U_k. The total and the error are obtained as described in Eq. (14).

N	L	U_4	U_6	U_7+U_8	Total	Error
5	4	−3216.239	8.723	−0.399	−3207.716	0.200
6		−2068.055	7.303	−0.501	−2061.003	0.251
7		−1380.858	5.491	−0.446	−1375.590	0.223
8		−959.211	4.077	−0.363	−955.316	0.182
9		−690.125	3.058	−0.288	−687.211	0.144
10		−511.674	2.332	−0.229	−509.457	0.115
6	5	−658.0174	0.6639	0.0062	−657.3504	0.0031
7		−456.6619	0.6018	0.0014	−456.0594	0.0007
8		−324.3128	0.4863	−0.0010	−323.8270	0.0005
9		−236.6280	0.3826	−0.0019	−236.2464	0.0010
10		−177.1181	0.3007	−0.0022	−176.8185	0.0011
7	6	−175.6392	0.0810	0.0012	−175.5576	0.0006
8		−128.6956	0.0773	0.0010	−128.6178	0.0005
9		−95.6986	0.0658	0.0007	−95.6325	0.0004
10		−72.5341	0.0541	0.0005	−72.4798	0.0003
8	7	−56.626 05	0.013 63	0.000 19	−56.612 33	0.000 10
9		−43.207 23	0.013 45	0.000 17	−43.193 70	0.000 09
10		−33.290 26	0.011 90	0.000 14	−33.278 29	0.000 07
9	8	−21.025 976	0.002 901	0.000 035	−21.023 058	0.000 018
10		−16.554 171	0.002 929	0.000 033	−16.551 226	0.000 017
10	9	−8.712 722	0.000 738	0.000 007	−8.711 981	0.000 004

analytically and exactly [6]. The expectation value of each term in the effective potential of Eq. (13) is shown in Table II, along with the total evaluated according to the prescription (14).

Since we have included U_8 it is not consistent to omit the effect of including α_1/x^4 to second order. That is

$$\Delta_2 = \sum_N \frac{\langle NL|\alpha_1/x^4|N'L\rangle\langle N'L|\alpha_1/x^4|NL\rangle}{E_N - E_{N'}} . \quad (15)$$

(States labeled with capital letters are eigenstates of H_v and refer to the valence electron, while those labeled with lower-case letters refer to the core.) The quantity Δ_2 can be obtained (by scaling α_1) from the previous results for helium [7] or from Drake and Swainson's explicit formula [8]. This is shown in Table III.

The last correction to be included here is the largest relativistic effect. It is derived from the nonrelativistic form of the Breit operator and is mainly due to the increase of mass with velocity [9]. But, as was pointed out in Ref. [9], to obtain the result correct to order K it is necessary to include an additional term. It may be worthwhile to outline the derivation of this correction [10].

In order to derive the leading relativistic term in the energy we treat the atom (as discussed in Ref. [10]) as a two-body system: the core and the valence electron. This simplification should give results which are accurate up to first order in K, which is adequate for the present pur-

pose. The two relevant terms in the Breit operator are

$$H_1 = -\frac{\alpha^2}{4}(m')^4 R_\infty \left[1 + \frac{K^3}{(2+K)^3}\right]\nabla_x^4 ,$$

$$H_2 = \frac{\alpha^2(m')^3 R_\infty K}{(2+K)}\frac{1}{x}\left[\nabla_x^2 + \frac{\partial^2}{\partial x^2}\right] . \quad (16)$$

We are only interested here in the first-order effect of these operators, so only their expectation values in the appropriate hydrogenic states must be calculated. These are easily obtained by rewriting the differential operators as follows:

$$\nabla_x^2 = -\frac{H_v}{q} - \frac{2}{x} ,$$

$$\frac{\partial^2}{\partial x^2} = \nabla_x^2 - \frac{2}{x}\frac{\partial}{\partial x} + \frac{L(L+1)}{x^2} . \quad (17)$$

The hydrogenic expectation values needed here are

$$\left\langle\frac{H_v}{q}\right\rangle = -\left\langle\frac{1}{x}\right\rangle = -\frac{1}{N^2} ,$$

$$\left\langle\frac{1}{x^2}\right\rangle = \frac{1}{N^3(L+\frac{1}{2})}, \quad \left\langle\frac{1}{x^3}\right\rangle = \frac{1}{N^3 L(L+\frac{1}{2})(L+1)} ,$$

and

$$\left\langle\frac{1}{x^2}\frac{\partial}{\partial x}\right\rangle = 0 \quad \text{for } L\neq 0 . \quad (18)$$

Inserting these in the formulas for H_1 and H_2 and expanding the K-dependent factors, we get the following expression for the leading relativistic correction:

$$\Delta_{\text{rel}} = \frac{\alpha^2 R}{N^3}\left[\frac{3}{4N}\left[1 - \frac{K}{6}\right] - \frac{2}{2L+1}\right] , \quad (19)$$

where we have replaced R_∞ by R and have kept terms up to order K^2, even though they appear only in the L-independent term, will not contribute to the L-dependent fine structure, and are very small in any case. Equation (19) is evaluated and the relativistic shifts are displayed in Table III.

A sample of these fine-structure splittings for the $N=10$ manifold is shown in Table IV. They are com-

TABLE III. Second-order corrections, leading relativistic corrections, and the final total shift for ^{7}Li in MHz.

N	L	Δ_2	Δ_{rel}	Final total
5	4	-0.448	-101.218	-3309.381 ± 0.200
6		-0.338	-78.849	-2140.190 ± 0.251
7		-0.242	-58.774	-1434.606 ± 0.223
8		-0.175	-43.956	-999.446 ± 0.182
9		-0.129	-33.375	-720.714 ± 0.144
10		-0.097	-25.790	-535.343 ± 0.115
6	5	-0.0248	-46.0819	-703.4571 ± 0.0031
7		-0.0201	-38.1392	-494.2186 ± 0.0007
8		-0.0154	-30.1323	-353.9747 ± 0.0005
9		-0.0117	-23.6659	-259.9240 ± 0.0010
10		-0.0090	-18.7122	-195.5397 ± 0.0011
7	6	-0.0023	-23.8534	-199.4133 ± 0.0006
8		-0.0019	-20.5620	-149.1818 ± 0.0005
9		-0.0016	-16.9444	-112.5784 ± 0.0004
10		-0.0012	-13.8122	-86.2932 ± 0.0003
8	7	-0.00030	-13.54381	-70.15644 ± 0.00010
9		-0.00026	-12.01526	-55.20922 ± 0.00009
10		-0.00022	-10.21888	-43.49739 ± 0.00007
9	8	-0.000051	-8.245930	-29.26904 ± 0.00002
10		-0.000046	-7.471035	-24.02231 ± 0.00002
10	9	-0.000011	-5.301687	-14.013679 ± 0.000004

TABLE IV. Fine-structure splittings in the $N=10$ manifold of ^{7}Li. The theoretical errors are obtained by summing in quadrature.

Interval	Energy shift (MHz)	Experiment[a] (MHz)
10G-10H	339.80 ± 0.11	339.7186 ± 0.0031
10H-10I	109.2466 ± 0.0011	109.2140 ± 0.0047
10I-10K	42.7958 ± 0.0003	
10K-10L	19.47508 ± 0.00007	
10L-10M	10.00863 ± 0.00002	

[a]Reference [11].

pared with the results being reported in an accompanying paper [11]. Notice that the experiment and theory are not in accurate agreement for the $10H$-$10I$ interval. The discrepancy, however, is not larger than might be expected for the uncalculated relativistic and retardation terms. In the helium case [12] these are of order $(\alpha Z)^2$ smaller than the leading polarizability correction and reduce the splitting. Terms of this order are being investigated now.

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