Relativistic all-order and multiconfiguration Hartree-Fock calculations of the 4*d*-4*f* energy separation in Li I

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We present a calculation of the 4*d*-4*f* energy separation in Li I using two advanced techniques in atomic structure theory, namely, the relativistic all-order method and the multiconfiguration Hartree-Fock (MCHF) method. The accuracy of our calculations was investigated by conducting a third-order many-body perturbation theory calculation that allowed us to evaluate the importance of fourth- and higher-order corrections. A large-scale MCHF calculation was performed using the active space method and the core-polarization approximation. The obtained results provide an important test of these methods against each other and are shown to agree with the most accurate available experimental data.

Neutral Li is one of the simplest yet nontrivial atomic systems whose atomic properties exhibit effects due to correlation in the motion of the electrons. In addition to being an interesting atomic system itself, Li I is widely used in plasma diagnostics. For instance, beams of lithium atoms have been successfully implemented for charge exchange measurements of edge ion temperature in tokamaks (see, e.g., [1,2]). Another example is provided by the measurement of plasma electric fields from the intensities of dipole-forbidden lines of Li I such as the 2*p*-4*f* or 3*p*-4*f* transitions [3–6]. For this specific method, knowledge of energy levels and, in particular, energy splittings becomes crucial due to strong dependence of the Stark level mixing on the latter.

The experimental energy levels of Li I are known with high accuracy. Radziemski *et al.* [7] used low-current hollow cathode sources and Fourier-transform spectrometry to determine the energies of all levels up to the principal quantum number $n=6$. With the uncertainty of 0.001 cm^{-1} to 0.0015 cm^{-1} for the 4*d* levels and 0.003 cm^{-1} for the 4*f* levels, the experimental value for the 4*d*-4*f* energy splitting was found to be (4.988 ± 0.003) cm^{-1} [7]. This value is deduced from all measured energy levels for the 4*d* and 4*f* terms. However, the authors of Ref. [7] mention that the high currents in the plasma source resulted in significant Stark shift of some levels, and thus the measured energies, while accurate, may not be those observed in field-free conditions. This issue was discussed in detail in Ref. [5], where another measurement of (5.1 ± 0.2) cm^{-1} was reported along with the comprehensive overview of the existing experimental values.

As far as the theoretical methods are concerned, the Li I energy spectrum was the subject of numerous studies. For instance, a recent review [8] contains a large number of references to high-precision results obtained by different computational techniques. The most accurate results, obtained using the Hylleraas-type expansion technique and taking into account the relativistic, mass-shift, and quantum-electrodynamic corrections, correspond to an energy splitting of 4.7 ± 0.7 cm^{-1} [8] which overlaps with the experimental value within error bars.

The goal of this paper is to test two advanced *ab initio* methods in atomic structure theory by comparing the calculated 4*d*-4*f* energy difference with the available benchmark experimental data [7]. The primary importance of this parameter is due to its significance in the determination of the electric field effects on forbidden lines. First, the calculation is performed with the relativistic all-order method. A third-order many-body perturbation theory (MBPT) is also used to evaluate the importance of the fourth- and higher-order corrections. Then, a nonrelativistic multiconfiguration Hartree-Fock (MCHF) method is implemented in two different approximations, both involving a large number of configurations. It will be shown that both theoretical methods provide good agreement with the experimental results.

In the present all-order approach, all single, double, and partially triple excitations of the single-configuration Dirac-Fock wave function are included to all orders of perturbation theory. The Li wave function is represented as an expansion

$$|\Psi_v\rangle = \left(1 + \sum_{ma} \rho_{ma} a_m^\dagger a_a + \frac{1}{2} \sum_{mnab} \rho_{mnab} a_m^\dagger a_n^\dagger a_b a_a \right.$$
$$+ \sum_{m \neq v} \rho_{mv} a_m^\dagger a_v + \sum_{mna} \rho_{mnva} a_m^\dagger a_n^\dagger a_a a_v$$
$$\left. + \frac{1}{6} \sum_{mnrab} \rho_{mnrvab} a_m^\dagger a_n^\dagger a_r^\dagger a_b a_a a_v \right) |\Phi_v\rangle, \quad (1)$$

where Φ_v is the lowest-order atomic state function, which is taken to be the *frozen-core* Dirac-Fock (DF) wave function of a state v. Substituting this expression into the many-body Schrödinger equation yields the coupled system of equations for the excitation coefficients ρ and the correlation energy δE_v. The determination of the energy is carried out by the iterative solution of these equations. The iteration procedure is completed when the correlation energy has converged to the required relative accuracy, set to be 10^{-5} in this calculation. The triple excitation term, given in the last line of Eq. (1), is included partially using the perturbative approach. We

TABLE I. Contributions to the energies of the $4d_{3/2}$ and $4f_{5/2}$ states in Li I (with respect to the ground state of Li II). The lowest- and second-order contributions are listed in rows labeled DF and II(SD), respectively. The third-order contribution is separated into the parts originating from the single-double excitations, III(SD), and triple excitations, III(pT). The contributions from the fourth and higher orders obtained using SD all-order method are listed in the next row. The correction of this value due to the partial inclusion of the triple term beyond the third-order contribution is given in the row labeled IV$^+$(pT). The experimental data are obtained by subtracting the ionization energy given in Ref. [12] from Ref. [7] values. All data are given in cm^{-1}.

Contribution	$4d$	$4f$	$4f$-$4d$
DF	−6859.399	−6858.594	0.804
II(SD)	−4.178	−0.642	3.536
III(SD)	−0.621	−0.113	0.508
III(pT)	0.060	0.010	−0.050
IV$^+$(SD)	−0.166	−0.027	0.139
IV$^+$(pT)	0.018	0.003	−0.015
Total(SD)	−6864.363	−6859.376	4.987
Total(SDpT)	−6864.285	−6859.362	4.922
Expt.	−6863.823	−6858.830	4.993

have conducted the calculation with and without this term to determine the significance of its contribution. We refer to the two corresponding sets of data as SD and SDpT, respectively. The SD energy value, while containing fourth and higher MBPT orders, omits certain third-order terms. We added these terms to the SD calculation to make it complete through third order. The SDpT approach is intrinsically complete through third order. We refer the reader to Refs. [9,10] for further details of the SD and SDpT methods. Our third-order energy calculation follows Ref. [11].

The results of our calculation are summarized in Table I. The lowest- and second-order contributions are listed in rows labeled DF and II(SD), respectively. The third-order contribution is separated into the parts originating from the single-double excitations, III(SD), and triple excitations, III(pT). The contribution of fourth and higher orders obtained using the SD all-order approach is listed in the next row. It is calculated as the difference of the SD all-order value, with the full restored third-order contributions, and the sum of the second- and third-order values. The correction to this value due to the partial inclusion of the triple term beyond the third-order contribution is given in the row labeled IV$^+$(pT). We note that there is no contribution from triple excitations into the second order. The totals are listed for both SD calculation, excluding all triple excitations, and SDpT calculation for comparison and to illustrate the discussion below. The total SD values are the sums of the DF, II(SD), III(SD), and IV$^+$(SD) and are listed in the row labeled Total(SD). The total SDpT values listed in the row labeled Total(SDpT) are the sums of all contributions listed in the first six rows of the table. The experimental data are obtained by subtracting the ionization energy given in Ref. [12] from Ref. [7] values. We find that the dominant contribution to the $4d$-$4f$ energy separa-

ration comes from the second order. The third-order contribution is on the order of the DF contribution, while the fourth- and higher-order corrections are small but significant for an accurate calculation. We investigated other possible small corrections, such as the effect of the Breit interaction and the contribution of higher-partial waves [we truncated all sums over excited states in Eq. (1) at $l_{max}=7$ in the third-order and the all-order calculations]. In second quantization, the Breit interaction can be separated into the "one-body" part, that can be incorporated into the calculations on the same footing as the DF potential, and the "two-body" part, that can be evaluated perturbatively (see Ref. [13] for details). We evaluated the "one-body" part of the Breit interaction using this approach by rerunning the all-order calculation with the modified basis set; its contribution was found to be 0.0005 cm^{-1}. The "two-body" part of the Breit interaction was evaluated in the second order and found to contribute at the level below 0.01 cm^{-1}.

To evaluate the contribution of the higher partial waves with $l > l_{max}$, we studied the convergence of the all-order values with l. The $l=6$ contribution is only 0.003 cm^{-1} and the $l=7$ contribution is 0.001 cm^{-1}. Since the correlation is dominated by the second-order contribution, we extrapolated the contribution of higher partial waves with $l>7$ in second order and found it to be 0.002 cm^{-1}. It is included in the present results.

The contribution from the mass-polarization corrections was estimated to be below 0.01 cm^{-1}. Our calculation is intrinsically relativistic, and we listed $4f_{5/2}$-$4d_{3/2}$ as the difference in Table I. We also conducted the same calculation for the $4f_{7/2}$ and $4d_{5/2}$ levels. We found no correlation correction contribution to $4d$ and $4f$ level fine structure at the 0.001 cm^{-1} level. The weighted average DF $4f$-$4d$ value differs from the $4f_{5/2}$-$4d_{3/2}$ value by 0.005 cm^{-1}. Therefore, all corrections except for the missing terms in the Coulomb correlation were found to be negligible at the level of 0.01 cm^{-1}.

In order to clarify the discussion of the omitted Coulomb correlation corrections, we separated out contributions originating from the single-double and triple excitations in Table I. Only two types of contributions are missing from the calculation: triple contributions that are omitted in the perturbative approach discussed above and all nonlinear terms, such as $S_1 \times S_2$, where S_1 and S_2 designate single and double excitations, respectively. We concluded that the SD nonlinear terms contribute −0.06 cm^{-1} to the $4f$-$4d$ difference using the method described in Ref. [14]. At the present time, we cannot evaluate missing triple terms (including nonlinear terms) for these states. However, such calculation was conducted for Na in Ref. [15]. It was found that nonlinear terms strongly cancel total contribution from the triple excitations (including the one from the third order). The case of Li differs from Na by the lack of the core triple contribution, which was omitted in Ref. [15]. However, it was found to be negligible in the latter work [14]. As a result, such cancellation may explain better agreement of our SD value for the splitting with experiment in comparison to our SDpT value.

The nonrelativistic MCHF method (for a detailed description see Ref. [16]) has been successfully applied to the calculation of atomic characteristics and spectroscopic proper-

ties of many low-Z elements, including neutral Li I [17]. However, in Ref. [17] the $4d$ and $4f$ states were not included in the calculations. In the MCHF approach, the atomic state is represented by an expansion over configuration state functions (CSFs)

$$\Psi(\gamma LS\pi) = \sum_i c_i \Phi(\gamma_i LS\pi), \sum_i c_i^2 = 1, \qquad (2)$$

where γ_i, L, S, and π denote, respectively, the configuration and its additional quantum numbers, the total orbital and spin momenta, and the parity. The CSFs are built from a basis of one-electron spin orbitals

$$\phi_{nlm_lm_s} = \frac{1}{r} P_{nl}(r) Y_{lm_l}(\theta, \phi) \chi_{m_s}. \qquad (3)$$

The orbital radial functions $P_{nl}(r)$ along with the mixing coefficients of Eq. (2) are optimized together for a stationary solution. The ensuing expansions and orbitals are then used in a configuration interaction calculation that accounts for all contributions to the Breit-Pauli (BP) Hamiltonian.

In this paper, two strategies for calculation of the $4d$-$4f$ splitting are implemented. The first one (method A) is close to the approach of Ref. [17] while the second one (method B) emphasizes core-polarization effects. A short description of both approaches is given in the following.

Method A. This approach is close to that used in [17] and therefore only the main ideas of the calculational method will be presented here. Two principal features of this approximation are (i) use of the MCHF active space method [16] and (ii) equivalent core correlation for the $4d$ and $4f$ electrons. The active one-electron orbitals were unrestricted up to $n=8$, that is, all $l \leq (n-1)$ orbitals were included in CSF expansions. For the larger n values up to $n_{max}=11$, the angular momentum was limited to $l \leq 7$. Furthermore, three atomic electrons were allowed to occupy all active orbitals with $n \leq 11$ provided at least one of the electrons has the principal quantum number $n \leq 4$. This approach results in a large number of included configurations, reaching 21 307 and 25 245 for the $4d$ and $4f$ cases, respectively.

The optimization was performed in two stages. First, for the CSFs with $n \leq 4$ all orbitals up to $4f$ were simultaneously optimized on the $3d$ ^2D, $4d$ ^2D, and $4f$ ^2F terms. The latter three orbitals as well as $1s$ were kept spectroscopic, i.e., the number of nodes N was fixed to be $N=n-l-1$. In order to enhance the $4d$ state, the $3d$ term was given a lower relative weight of 0.3. In the second step, when $n \geq 5$ shells were added, the optimization of the $4d$ and $4f$ states was performed separately using the fixed $n \leq 4$ orbitals from the first step. This method guarantees equivalence of the core correlation for both $4d$ and $4f$ electrons. On each subsequent step determined by addition of the next shell, all $n>4$ orbitals were varied until reaching the prescribed convergence while keeping all other orbitals fixed. These results are referred to below as the MCHF. Then the Breit-Pauli interaction matrix with contributions from mass-polarization corrections was computed and diagonalized, thereby producing the BP eigenfunctions and eigenvalues.
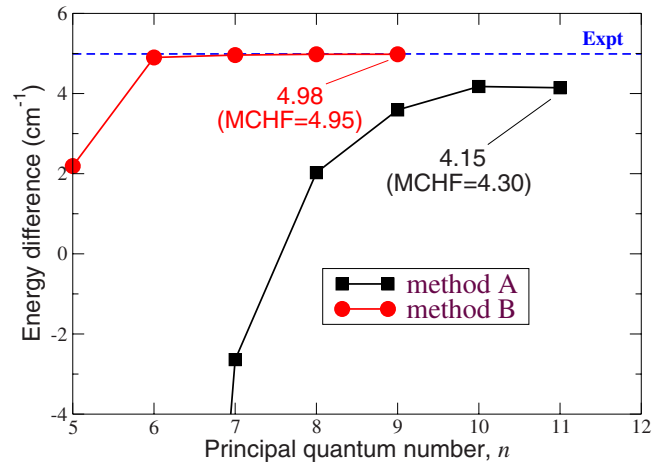

FIG. 1. (Color online) Theoretical $4d$-$4f$ energy difference vs the maximum principal quantum number of the orbital set n. The active space method results are shown by squares; the core-polarization results are shown by circles. The experimental value of $\Delta E = 4.988$ cm^{-1} [7] is shown by the horizontal dashed line.

The calculated energy difference vs the highest principal quantum number included in the calculations is shown in Fig. 1. Although the results demonstrate a reasonably fast convergence, this approach does not reproduce the experimental $4d$-$4f$ energy difference: The value extrapolated to $n=\infty$ is $\Delta E_{BP}(A) \approx 4.15$ cm^{-1} which is about 0.8 cm^{-1} below the data of Ref. [7]. It is also interesting to note that for $n=6$ and 7, the $4f$ term has lower energy than $4d$, and thus only the introduction of higher-n orbitals produces a correct level order. Finally, the relativistic corrections are found to contribute about 0.15 cm^{-1} to the energy difference.

Method B. In method A, the orbitals $4ln'l'n''l''$ with $n', n'' \geq 5$ in the CSF expansion are in fact the core-core correlation orbitals that interact with $1s^2$ in the case of $1s^2 4l$. Their contribution, however, cancels in the energy difference, at least to the first order, and therefore their importance for the present calculation is largely reduced. In order to accentuate those effects that contribute most to the energy splitting, with core polarization being the most prominent, we carried out another large-scale calculation of the $4d$-$4f$ separation. Hence, the correlation orbitals for the $1s^2$ core are first generated using the "natural orbital expansion" [18]

$$\Psi(1s^2\ ^1S) = c_1 \Phi(1s^2\ ^1S) + c_2 \Phi(2s^2\ ^1S) + c_3 \Phi(2p^2\ ^1S)$$
$$+ c_4 \Phi(3s^2\ ^1S) + c_5 \Phi(3p^2\ ^1S).$$

With this correlated core, the $3d$, $4d$, and $4f$ orbitals were added to form $\Psi(1s^2\ ^1S)nl$ and were optimized on the ^2D and ^2F terms. Then the $4s$, $4p$, and $n=5-7$, $l \leq 6$ orbitals entered the expansion only as core-polarization orbitals, i.e., at least one nl orbital with $n \leq 3$, $l \leq 1$ was present in the CFS's. During the optimization, the core orbitals were kept fixed. Finally, to check the effect of core-core correlations, the $n=8,9$, $l \leq 6$ orbitals were added with all three excitations included; however, only $n=8,9$ orbitals were allowed to vary here. In this calculation, the total number of included

configurations was 26 580 for the $4d$ case and 32 346 for the $4f$ case.

Although the final number of configurations included in this approach is larger than that in method A, the energy difference between the $4d$ and $4f$ terms converges much faster than in method A which is obviously due to the principal contribution from the core-polarization effects. As seen in Fig. 1, for $n=6$ the calculated energy difference is already very close to the experimental value, while for method A the theoretical result at the same n has a wrong sign. Addition of the $n=8-9$ CFS's, which were included to test the core-core correlation contribution, lowers the total energy of the $4d$ and $4f$ states by about 500 cm^{-1} for $n=8$ and about 100 cm^{-1} for $n=9$. The energy difference, however, remains essentially unaffected for both $n=8$ and $n=9$ with the value of ΔE(MCHF)$=4.95$ cm^{-1}. This clearly confirms a negligible effect of the core-core correlations compared to the core-polarization contribution on energy difference in this approach. The Breit-Pauli corrections that were determined similar to method A do not noticeably change the MCHF result, slightly increasing the energy difference to a value of $\Delta E=4.98$ cm^{-1}.

The $4d$ and $4f$ electrons are well outside the $1s^2$ core and the change in the core from replacing the $4d$ electron by a $4f$ electron will be a minor perturbation at best. As a result, the energy from the core (including both correlation and relativistic effects) will cancel to first order in the calculation of the energy difference, and the relativistic effects on this difference will be of low importance for such a light atom as Li I. The problem facing method A is cancellation. This was addressed to some extent by using the same $n=4$ orbital basis for both the $4d$ ^2D and $4d$ ^2F wave functions. With this basis, the nonrelativistic energy difference was only 0.63 cm^{-1} with the relativistic and mass-polarization corrections increasing this by 0.01 cm^{-1}. The subsequent calculations had a different orbital basis for $4d$ and $4f$, each optimized for the nonrelativistic energy. This improved the contribution to correlation to 4.30 cm^{-1} but the relativistic and mass-polarization correction now reduced the energy difference by 0.15 cm^{-1}. This basis set dependence is due to the fact that the relativistic and mass-polarization corrections are not computed as perturbative corrections as done by Pekeris [19], for example, but rather are included in the interaction matrix. Method B addresses this issue by limiting the contribution from correlation in the core to the $n=3$ orbital set and then optimizes the orbitals for $4d$ ^2D and $4f$ ^2F independently (as in method A) but limiting correlation to core-valence correlation thus concentrating more directly on the difference in energy and the wave function coming from the outer regions of the atom. Clearly in this case, for method A, the relativistic and mass-polarization corrections are better computed perturbatively but at issue also is the fact that variational methods optimize the total energy. Since so little of the total energy in the present case comes from the relaxation of the core and core polarization, an exceedingly large basis would be needed before the optimization process would target these contributions. Method B does so directly.

The calculated relativistic all-order perturbation theory values of ΔE(SD)$=4.99$ cm^{-1}, ΔE(SDpT)$=4.92$ cm^{-1}, and MCHF (method B) value of ΔE(MCHF)$=4.98$ cm^{-1} agree well with the best experimental value of (4.988 ± 0.003) cm^{-1} [7]. We discussed the importance of different contributions in the all-order theory approach and showed that the account of the core-polarization effects provides both higher accuracy and faster convergence in the MCHF method.

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