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

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We present a calculation of the 4d-4f 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.

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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 plasma diagnostics. For instance, beams of lithium atoms

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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 contributions 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 separation 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 \( l_{\text{max}} = 7 \) 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 \( l > l_{\text{max}} \) 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-

### 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)

<table>
<thead>
<tr>
<th>Contribution</th>
<th>4d</th>
<th>4f</th>
<th>4f-4d</th>
</tr>
</thead>
<tbody>
<tr>
<td>DF</td>
<td>−6859.399</td>
<td>−6858.594</td>
<td>0.804</td>
</tr>
<tr>
<td>II(SD)</td>
<td>−4.178</td>
<td>−0.642</td>
<td>3.536</td>
</tr>
<tr>
<td>III(SD)</td>
<td>−0.621</td>
<td>−0.113</td>
<td>0.508</td>
</tr>
<tr>
<td>III(pT)</td>
<td>0.060</td>
<td>0.010</td>
<td>−0.050</td>
</tr>
<tr>
<td>IV*(SD)</td>
<td>−0.166</td>
<td>−0.027</td>
<td>0.139</td>
</tr>
<tr>
<td>IV*(pT)</td>
<td>0.018</td>
<td>0.003</td>
<td>−0.015</td>
</tr>
<tr>
<td>Total(SD)</td>
<td>−6864.363</td>
<td>−6859.376</td>
<td>4.987</td>
</tr>
<tr>
<td>Total(SDpT)</td>
<td>−6864.285</td>
<td>−6859.362</td>
<td>4.922</td>
</tr>
<tr>
<td>Expt.</td>
<td>−6863.823</td>
<td>−6858.830</td>
<td>4.993</td>
</tr>
</tbody>
</table>
ties of many low-Z elements, including neutral Li [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)

$$\Psi(\gamma L S \pi) = \sum_i c_i \Phi(\gamma L S \pi), \quad \sum_i c_i^2 = 1,$$

where $\gamma$, $L$, $S$, and $\pi$ 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

$$\phi_{nlm\pi} = \frac{1}{P} P_{nl}(r) Y_{lm}(\theta, \phi) \chi_{m\pi}.$$ 

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 $n_{\text{max}}=11$, 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 $n=4$ 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 $n=5$ shells were added, the optimization of the 4d and 4f states were performed separately using the fixed $n=4$ 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.

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 $\Delta E_{\text{BP}}=4.15 \text{ cm}^{-1}$ 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 $4l'nl''l''$ with $n',n''=5$ in the CSF expansion are in fact the core-core correlation orbitals that interact with $1s^2$ in the case of $1s^24f$. 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 $n=5-7$, $l=6$ 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 CSF’s. During the optimization, the core orbitals were kept fixed. Finally, to check the effect of core-core correlations, the $n=8,9$, $l=6$ 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 $\Delta E(MCHF)=4.95$ 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 4f $^2F$ 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 optimise 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 $\Delta E(\text{SD})=4.99$ cm$^{-1}$, $\Delta E(\text{SDpT})=4.92$ cm$^{-1}$, and MCHF (method B) value of $\Delta E(MCHF)=4.98$ cm$^{-1}$ agree well with the best experimental value of (4.98±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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