

Relativistic configuration-interaction calculations for the $n = 2$ states of lithiumlike ions

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Term energies are determined for the $n = 2$ states of lithiumlike ions with nuclear charges in the range $10 \leq Z \leq 92$. These calculations are based on the relativistic no-pair Hamiltonian, which includes both the Coulomb and the retarded Breit interactions. Single-particle wave functions are expanded in a B -spline basis constructed from Dirac-Slater orbitals restricted to a finite cavity. The Hamiltonian matrix is evaluated and Davidson's method is used to determine the lowest few eigenenergies and eigenfunctions for each angular symmetry. Quantum electrodynamic and mass polarization corrections are also calculated. Precise agreement between theory and experiment for the $2s-2p$ transition energies is found throughout the Periodic Table.

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I. INTRODUCTION

Recently, we have developed a large-scale relativistic configuration-interaction (CI) calculation for two-electron ions [1,2]. This CI method is based on the no-pair Hamiltonian [3,4] and makes use of finite basis sets constructed from B splines [5]. A special two-electron code was used to calculate the energy levels of the ground and the $n = 2$ states of ions in the helium isoelectronic sequence [1,2]. These calculations have produced term energies in very good accord with results from relativistic many-body perturbation theory (RMBPT) [6,7] and in precise agreement with experiment throughout the Periodic Table after QED corrections are included. The success of the two-electron case has prompted us to develop a general, large-scale relativistic CI code that can be applied to any many-electron system. This is particularly timely in view of the recent high-precision measurements of the $2s-2p_{3/2}$ energy differences in Li-like through Ne-like uranium, which were made at the SuperEBIT facility at Lawrence Livermore National Laboratory [8]. The multiconfiguration Dirac-Fock (MCDF) method led to energies in poor agreement with these measurements [8]. While RMBPT gives excellent results for some of these uranium ions, convergence of the RMBPT energies for Be-like uranium is still poor [9]. The CI method provides an alternative approach that can be used to obtain high-precision solutions to the relativistic many-body problem.

Lithiumlike ions are the simplest many-electron systems other than the two-electron ions. The three-electron ion was chosen as a test case for our recently developed general CI code because of its simplicity and the availability of accurate experimental data and precision theoretical predictions. In this paper, we report the relativistic CI calculations of the $n = 2$ states of Li-like ions with

$10 \leq Z \leq 92$ using B -spline basis functions. These basis functions are solutions of the radial Dirac equation for an electron moving in a potential confined to a finite cavity. The modified spectrum cleanly separates into two discrete spectra: one with n positive-energy states and the other with n negative-energy states. As a result, positive-energy projection operators in the relativistic no-pair Hamiltonian can be accommodated easily by using only positive-energy states. Also, B -spline functions form a complete basis set for functions that can be approximated by piecewise polynomials of a fixed degree, so both continuum and bound-state contributions to the electron correlation are included. In this work, CI energies are combined with *ab initio* quantum electrodynamic (QED) and mass polarization corrections to obtain $2s-2p_{1/2}$ and $2s-2p_{3/2}$ transition energies.

In the following section, we present our version of the CI method using B -spline basis functions. We then discuss, in Sec. III, computational details including the generation of basis functions and the configuration-state functions employed. In Sec. IV, the treatment of QED corrections is described. Finally, in Sec. V, results of our CI calculations are presented and compared with experiment and with other theories.

II. THEORETICAL METHOD

The relativistic no-pair Hamiltonian is given by [3,4]

$$H = \sum_{i=1}^N h_0(i) + \Lambda_{++}(H_C + H_B)\Lambda_{++}, \quad (1)$$

where h_0 is the single-particle Dirac Hamiltonian for an electron moving in a nuclear Coulomb potential $V_{\text{nuc}}(r)$

$$h_0 = [c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1)mc^2 + V_{\text{nuc}}(r)], \quad (2)$$

H_C is the Coulomb interaction

$$H_C = \sum_{i>j}^N \frac{e^2}{r_{ij}}, \quad (3)$$

H_B is the retarded Breit interaction

$$H_B = -e^2 \sum_{i>j}^N \left[\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j \frac{\cos \omega r_{ij}}{r_{ij}} - (\boldsymbol{\alpha}_i \cdot \nabla_i)(\boldsymbol{\alpha}_j \cdot \nabla_j) \frac{\cos \omega r_{ij} - 1}{r_{ij}} \right], \quad (4)$$

and Λ_{++} is the positive-energy projection operator. Nuclear finite-size corrections are included by replacing the nuclear potential $V_{\text{nuc}}(r)$ in Eq. (2) by the potential of a two-parameter Fermi charge distribution. The eigenfunction $\Psi(JM)$ of an atomic state with angular momentum (J, M) and parity π is expressed as a linear combination of the many-electron configuration-state functions $\phi(\Gamma_K JM)$,

$$\Psi(JM) = \sum_K C_K \phi(\Gamma_K JM), \quad (5)$$

where Γ_K is a set of quantum numbers representing different electronic configurations and $\phi(\Gamma JM)$ are eigenstates of the total angular momentum operators J^2 and

J_Z constructed from antisymmetrized product wave functions of one-electron Dirac orbitals. Expressed in terms of the expansion coefficients C_K , the energy functional is given by

$$E = \langle \Psi | H | \Psi \rangle = \sum_{K,L} C_K C_L \langle \phi_K | H | \phi_L \rangle = \sum_{K,L} C_K C_L H_{KL}. \quad (6)$$

Variation of the energy functional with respect to C_K , subject to the wave function normalization condition, leads to the CI equation

$$\sum_L (H_{KL} - \lambda \delta_{KL}) C_L = 0. \quad (7)$$

Here the contribution of the one-electron operator to diagonal matrix elements can be written as [10]

$$\left\langle \Psi \left| \sum_i h_0(i) \right| \Psi \right\rangle = \sum_K C_K^2 \sum_a q_a(K) I(aa), \quad (8)$$

where $q_a(K)$ is the occupation number of orbital a in the K th configuration and $I(ab) = \langle a | h_0 | b \rangle$ is the one-electron radial integral. Matrix elements of the two-electron operators between a pair of configuration-state functions are given by [11]

$$\begin{aligned} \langle \Gamma JM | H_C + H_B | \Gamma' J' M' \rangle &= \delta_{JJ'} \delta_{MM'} \sum_{\alpha_1, \beta_1, \alpha_2, \beta_2} (-1)^{\Delta P} N(\alpha_1 \beta_1 \alpha_2 \beta_2) \\ &\times \sum_{\Gamma} (\Gamma_{\alpha_1} \{ |\bar{\Gamma}_{\alpha_1} j_{\alpha_1} \rangle (\Gamma_{\beta_1} \{ |\bar{\Gamma}_{\beta_1} j_{\beta_1} \rangle (\bar{\Gamma}_{\alpha_2} j_{\alpha_2} | \} \Gamma'_{\alpha_2}) (\bar{\Gamma}_{\beta_2} j_{\beta_2} | \} \Gamma'_{\beta_2}) \\ &\times \sum_k \{ A_D^k (1 + \delta_{\alpha_1 \beta_1} \delta_{\alpha_2 \beta_2})^{-1} [j_{\alpha_1}, j_{\beta_2}]^{-1/2} X^k(\alpha_1 \beta_1 \alpha_2 \beta_2) \\ &- A_E^k (1 - \delta_{\alpha_1 \beta_1}) (1 - \delta_{\alpha_2 \beta_2}) [j_{\alpha_1}, j_{\alpha_2}]^{-1/2} X^k(\alpha_1 \beta_1 \beta_2 \alpha_2) \}. \end{aligned} \quad (9)$$

Here ΔP defines the phase of the matrix element, $N(\alpha\beta\gamma\delta)$ is the statistical factor, $(\Gamma_{\alpha} \{ |\bar{\Gamma}_{\alpha} j_{\alpha} \rangle$ denotes the fractional parentage, $[j_{\alpha}, j_{\beta}, \dots] = (2j_{\alpha} + 1)(2j_{\beta} + 1) \dots$, and A_D^k and A_E^k are recoupling coefficients for the direct and exchange matrix elements. The effective interaction strength $X^k(\alpha\beta\gamma\delta)$ for the Coulomb and Breit operators is given by [1]

$$\begin{aligned} X^k(\alpha\beta\gamma\delta) &= \langle \kappa_{\alpha} || C_k || \kappa_{\gamma} \rangle \langle \kappa_{\beta} || C_k || \kappa_{\delta} \rangle R_k(\alpha\beta\gamma\delta) + \langle \kappa_{\alpha} || C_k || \kappa_{\gamma} \rangle \langle \kappa_{\beta} || C_k || \kappa_{\delta} \rangle \\ &\times \frac{k(k+1)}{2k+1} \left[\frac{1}{2k-1} T(k, k-1) + \frac{1}{2k+3} T(k, k+1) - \frac{1}{2} X(k) \right] \\ &- \langle -\kappa_{\alpha} || C_k || \kappa_{\gamma} \rangle \langle -\kappa_{\beta} || C_k || \kappa_{\delta} \rangle \frac{(\kappa_{\alpha} + \kappa_{\gamma})(\kappa_{\beta} + \kappa_{\delta})}{k(k+1)} T(k, k). \end{aligned} \quad (10)$$

Formulas for reduced matrix elements $\langle \kappa || C_k || \kappa' \rangle$, Coulomb radial integrals $R_k(\alpha\beta\gamma\delta)$, and Breit integrals $T(k, k')$ and $X(k)$, $k' = k, k \pm 1$, are given in Ref. [1].

For diagonal matrix elements of the retarded Breit interaction $\langle ab | H_B(\omega) | ab \rangle$, the frequency ω is defined as

$$\omega = \begin{cases} \omega_{aa} = \omega_{bb} = 0 & \text{for the direct terms} \\ \omega_{ab} = \omega_{ba} = |\varepsilon_a - \varepsilon_b| / \hbar c & \text{for the exchange terms.} \end{cases} \quad (11)$$

For nondiagonal matrix elements $\langle ab | H_B(\omega) | cd \rangle$ where $\omega_{ac} \neq \omega_{bd}$, a frequency symmetrized Breit interaction as suggested by Mittleman [4] is used:

$$\langle ab | H_B(\omega) | cd \rangle \longrightarrow \frac{1}{2} [\langle ab | H_B(\omega_{ac}) + H_B(\omega_{bd}) | cd \rangle]. \quad (12)$$

Formulas for frequency-dependent Breit matrix elements can be found in Ref. [1].

III. NUMERICAL CALCULATIONS

A. Relativistic B -spline functions

B -spline basis functions for a Dirac electron in a model potential constrained to a cavity of finite radius were obtained using the method by Johnson, Blundell, and Sapirstein [5]. In this work, the model potential is taken to be the Hartree potential of the heliumlike $1s^2$ ground state. The choice of potential is found to be immaterial here, as we have saturated our CI calculations with all dominant configuration-state functions. Parameters for the Fermi charge distribution of the nucleus are taken from Johnson and Soff [12], except for thorium and for uranium, which are from Zumbro *et al.* [13,14]. The radius of the cavity was chosen so that the first few s and p states agree precisely with the actual eigenvalues of the unconstrained Hartree potential. A radius of 8 a.u. was used for orbitals with $\ell \leq 3$ for Ne^{8+} and the radius was gradually increased to 12 a.u. for $\ell = 6$ orbitals. A $1/Z$ scaling rule was used to determine the cavity radius for other ions. Within reason, the choice of the cavity radius is not critical.

In this work, 30 positive-energy B -spline orbitals are generated for each of the s , p , d , ... states inside the cavity. We included orbitals with $\ell = 0 - 6$ and used the first 19–20 orbitals for each of the angular symmetries in our calculations. Contributions from the remaining B -spline orbitals are found to be negligible.

B. Configuration-state functions

In our basic CI expansion, configuration-state functions (CSFs) include states arising from single and double excitations from reference states $1s^2 2s$ and $1s^2 2p$. For the $1s^2 2s$ state, we use 13 952 CSFs from $1snln'\ell'$ and $2snln'\ell'$ configurations with $\ell = \ell' = 0 - 6$. Contributions from states with $\Delta\ell = |\ell - \ell'| = 2$ are found to be insignificant. For the $1s^2 2p_{1/2}$ state, we employ 24 155 CSFs from $1snln'(\ell + 1)$ ($\ell \leq 5$) and $2pnln'\ell$ ($\ell \leq 6$). In both cases, up to 20 s , 20 p , 19 d , ..., 19 i orbitals are included in the basis set. For the $1s^2 2p_{3/2}$ state, the number of CSFs becomes rather large. To reduce the computational effort, we break the problem into two parts. First, we use 16 071 CSFs from $1snln'(\ell + 1)$ ($\ell \leq 5$) and $2pnln'\ell$ ($\ell \leq 6$) and restrict $nln'\ell$ in the latter configurations to be coupled to an angular momentum of $J = 0$ only (i.e., only two-electron excitations from the $1s^2$ core that preserve the core angular momentum are included). In this case, the B -spline basis set consists of the first 19 orbitals of each angular symmetry. Second, the same CI calculation is carried out with a smaller basis set that contains up to the f orbitals only, along with a separate CI calculation with 17 410 CSFs from the same configurations but with no restriction on the $nln'\ell$ couplings. Contributions to the correlation energy of the $1s^2 2p_{3/2}$ state from these core angular momentum changing configurations are then obtained by taking the differences of these two calculations. Even though we include up to the f orbitals only, these are very small corrections and

higher- ℓ contributions are completely negligible.

We have also included two additional corrections to the correlation energy: The first one is a small correction for the $1s^2 2p$ states from the $2pnln'\ell'$ configurations with $\Delta\ell = 2$ (e.g., $2pnsnd$, $2pnpnf$, ...). It is calculated from differences in energies obtained from two CI expansions with and without these configurations from a basis set with $\ell \leq 3$. Again, high- ℓ contributions are completely negligible. The other correction arises from three-electron excitations, which have been found to be quite small [15]. Here they are included by using a CI expansion that includes CSFs from three-electron excitations $3snln'\ell'$ and $3pnln'\ell'$ in addition to two-electron excitations $1snln'\ell'$, $2snln'\ell'$, and $2pnln'\ell'$ with $\ell, \ell' \leq 2$ and by subtracting the result of a similar CI calculation with the two-electron excitations only. Contributions from other triple excitations are expected to be insignificant.

C. Evaluation of the Hamiltonian matrix

In large-scale CI calculations, we face the problem of setting up a huge Hamiltonian matrix with dimension as high as tens of thousands. The required number of angular recoupling coefficients is close to 10^9 . Direct calculations of the recoupling coefficients can easily use up to hundreds, or even thousands, of hours of CRAY-YMP supercomputer time. Hence the algorithms used to evaluate these hundreds of millions of matrix elements becomes the key to success of the CI calculations.

Recognizing that many matrix elements involving CSFs that differ by just the principal quantum numbers will have the same angular recoupling coefficients, we use the concept of angular momentum *channels* to simplify these calculations. An angular momentum channel is defined by an electronic configuration including coupling schemes but ignoring principal quantum numbers, except to distinguish between identical and nonidentical electrons with the same angular symmetry. Specifically, only recoupling coefficients between distinct channels are evaluated. We have successfully implemented the scheme of angular momentum channels into an existing general angular momentum recoupling program [10]. With this modified angular program, we are able to reduce the number of recoupling coefficients to be evaluated from hundreds of millions to tens of thousands such that the calculation of recoupling coefficients becomes a straightforward exercise.

It is also extremely expensive to calculate the millions and millions of Coulomb and Breit radial integrals in setting up the Hamiltonian matrix. To speed up the evaluation of radial integrals, we have designed our computer code in such a way that the same Hartree Y function is not recalculated from matrix element to matrix element. This is possible through careful orderings of the CSFs and leads to an order of magnitude increase in the speed of the calculation.

For full frequency-dependent magnetic and retardation corrections, the calculation becomes much more time consuming. As in our previous works on the ground

and $n = 2$ states of He-like ions [1,2], these corrections were calculated using a two-step approach. First, the off-diagonal Hamiltonian matrix elements were calculated with the unretarded Breit operator, while the diagonal matrix elements were evaluated with the retarded Breit operator to obtain the leading frequency-dependent Breit energies. Next, the corrections $\Delta B(\omega)$ from the off-diagonal matrix elements of the retarded Breit interaction were obtained by repeating the CI calculation described above with a smaller set of B -spline orbitals and subtracting this result from a similar calculation with a full, frequency-symmetrized Breit operator shown in Eq. (12). In general, contributions from these $\Delta B(\omega)$ terms are very small.

In the present relativistic CI calculations, atomic energy levels are obtained by solving for the first few eigenvalues of a dense, real, symmetric Hamiltonian matrix with dimensions ranging from 10 000 to 25 000. Even in symmetric storage mode, these matrices can take up to a few gigabytes of computer storage, making standard matrix diagonalization methods inappropriate for these calculations. Instead, we use Davidson's method [16] to solve our eigenvalue problem. Davidson's method is an iteration method based on perturbation theory and works very well here because our CI matrices are dominated by just a few configurations. Additionally, large CI matrices do not have to be stored in the fast memory of the computer for Davidson's method to work, making it possible to run our CI codes on CRAY-YMP supercomputers as well as on fast workstations with sufficient on-line disk space. We have adopted an implementation of Davidson's method by Stathopoulos and Fischer [17]. Typically, 10–20 iterations are sufficient to obtain the first few eigenvalues of the Hamiltonian.

IV. QUANTUM ELECTRODYNAMIC CORRECTIONS

In precision calculations of atomic energy levels, contributions from QED corrections are significant, especially for highly charged heavy ions. On the one hand, the evaluation of vacuum polarization presents no difficulty. Vacuum polarization energy corrections are domi-

nated by expectation values of the Uehling potential using screened wave functions. On the other hand, accurate evaluation of screened self-energies remains a challenging problem. In MCDF calculations of Li-like ions by Indelicato and Desclaux [18], electron self-energies were estimated by the Welton method [19]. In the work of Blundell [20], *ab initio* self-energies in a local screened potential were calculated using an algorithm developed with Snyderman [21,22], along with dominant contributions to QED corrections from electron-electron interactions. Recently, Persson *et al.* [23,24] have developed a method to calculate electron self-energy and vacuum polarization in a model potential based on a renormalization scheme that avoids the expansion of the bound electron propagator in terms of the external potential. In the present work, electron self-energies are calculated using the scheme of Cheng, Johnson, and Sapirstein [25], which is based on a method by Brown, Langer, and Schaefer [26]. Like Persson *et al.*, the effect of screening is included by the use of model potentials in our calculations. Specifically, Dirac-Slater (DS) potentials with Kohn-Sham average exchange for the $1s^2 2s$ state are used here to calculate one-electron self-energies. Nuclear finite-size effects are included by using a Fermi charge distribution nuclear model in the DS potential. Wichmann-Kroll corrections for vacuum polarization and higher-order QED corrections are taken from the tabulation by Johnson and Soff [12]. These point-Coulomb values are adjusted by a screening factor that is taken from the ratio of nonhydrogenic to hydrogenic values of the Uehling potential contributions. Total QED corrections for many-electron eigenstates are given by the sum of the calculated single-particle QED corrections, weighted by the fractional occupation number of each orbital as obtained from the eigenvectors of the CI calculation. We include QED corrections from the $1s$, $2s$, and $2p$ orbitals only, as contributions from higher- n orbitals are found to be unimportant.

V. RESULTS AND DISCUSSION

In Table I typical results of the Coulomb, Breit, and no-pair energies for the ground state of lithiumlike neon

TABLE I. Contributions to the total energy (a.u.) of the ground state of lithiumlike neon, $Z = 10$. E_C is the Coulomb energy, E_B is the Breit energy, and $E_{\text{no-pair}}$ is the energy from the no-pair Hamiltonian. The values listed in rows 2–6 are the increments obtained on adding configurations with successive ℓ orbitals. ΔE_{tail} and ΔE_{triple} are contributions from high- ℓ extrapolations and from three-electron excitations, respectively.

| Highest- ℓ orbitals | Number of configurations | E_C | E_B | $E_{\text{no-pair}}$ |
|-----------------------------|-----------------------------|-------------|-----------|----------------------|
| p | 3122 | -102.810645 | 0.011832 | -102.798813 |
| d | 5288 | -0.004026 | -0.000167 | -0.004193 |
| f | 7454 | -0.001054 | -0.000071 | -0.001125 |
| g | 9620 | -0.000382 | -0.000039 | -0.000421 |
| h | 11786 | -0.000167 | -0.000023 | -0.000190 |
| i | 13952 | -0.000083 | -0.000015 | -0.000098 |
| ΔE_{tail} | | -0.000137 | -0.000062 | -0.000199 |
| ΔE_{triple} | | -0.000039 | | -0.000039 |
| total | | -102.816533 | 0.011455 | -102.805078 |

are shown as functions of the angular momentum of orbitals included in the calculation. In the first two columns, orbital angular momenta and numbers of configurations included up to the indicated angular symmetry are listed. In columns 3–5 of the first row, we list under E_C , E_B , and $E_{\text{no-pair}}$ the Coulomb, Breit, and no-pair energies, respectively, obtained by using $1sn'sn's$, $1snpn'p$, $2sn'sn's$, and $2snpn'p$ basis states as described in Sec. III B. E_C is obtained by restricting the interaction to the Coulomb interaction only, $E_{\text{no-pair}}$ is the

value from the full no-pair Hamiltonian, and E_B is the difference between E_C and $E_{\text{no-pair}}$. In rows 2–6, we list the increments of these energies as obtained by successively adding more angular momentum states to the calculation. These tabulated values are extrapolated to infinity by assuming that the increments decrease as $a(\ell + 1/2)^{-k} + b(\ell + 1/2)^{-k-1}$, where $k = 4$ for Coulomb and $k = 2$ for Breit energies. Results of the extrapolated tails are listed in the seventh row. In the eighth row, corrections from three electron excitations as discussed

TABLE II. Coulomb and Breit contributions to the total energies (a.u.) of the $n = 2$ states of lithiumlike ions are given, together with frequency-dependent Breit corrections $\Delta B(\omega)$, the mass polarization corrections MP, and QED corrections.

| Z | State | Coulomb | Breit | $\Delta B(\omega)$ | MP | QED | Total |
|-----|------------|------------|---------|--------------------|----------|---------|------------|
| 10 | $2s_{1/2}$ | -102.81653 | 0.01146 | -0.00003 | 0.00004 | 0.01035 | -102.79472 |
| | $2p_{1/2}$ | -102.23262 | 0.01213 | -0.00003 | -0.00010 | 0.00983 | -102.21080 |
| | $2p_{3/2}$ | -102.22428 | 0.01129 | -0.00003 | -0.00010 | 0.00985 | -102.20328 |
| 15 | $2s_{1/2}$ | -238.90654 | 0.04219 | -0.00015 | 0.00004 | 0.04397 | -238.82049 |
| | $2p_{1/2}$ | -237.95822 | 0.04516 | -0.00014 | -0.00019 | 0.04152 | -237.87187 |
| | $2p_{3/2}$ | -237.90369 | 0.04168 | -0.00014 | -0.00019 | 0.04164 | -237.82070 |
| 20 | $2s_{1/2}$ | -432.27343 | 0.10459 | -0.00040 | 0.00004 | 0.11980 | -432.04940 |
| | $2p_{1/2}$ | -430.95245 | 0.11269 | -0.00038 | -0.00034 | 0.11273 | -430.72775 |
| | $2p_{3/2}$ | -430.75752 | 0.10341 | -0.00038 | -0.00031 | 0.11316 | -430.54164 |
| 26 | $2s_{1/2}$ | -741.10042 | 0.23758 | -0.00099 | 0.00004 | 0.29408 | -740.56971 |
| | $2p_{1/2}$ | -739.31514 | 0.25689 | -0.00095 | -0.00044 | 0.27596 | -738.78368 |
| | $2p_{3/2}$ | -738.70765 | 0.23486 | -0.00096 | -0.00041 | 0.27726 | -738.19690 |
| 32 | $2s_{1/2}$ | -1135.5525 | 0.4535 | -0.0021 | 0.0000 | 0.5928 | -1134.5082 |
| | $2p_{1/2}$ | -1133.2775 | 0.4916 | -0.0020 | -0.0005 | 0.5552 | -1132.2332 |
| | $2p_{3/2}$ | -1131.7984 | 0.4480 | -0.0020 | -0.0005 | 0.5582 | -1130.7946 |
| 42 | $2s_{1/2}$ | -1990.5372 | 1.0575 | -0.0045 | 0.0001 | 1.4705 | -1988.0137 |
| | $2p_{1/2}$ | -1987.3673 | 1.1496 | -0.0042 | -0.0007 | 1.3734 | -1984.8492 |
| | $2p_{3/2}$ | -1982.6425 | 1.0420 | -0.0043 | -0.0007 | 1.3824 | -1980.2231 |
| 54 | $2s_{1/2}$ | -3363.9563 | 2.3241 | -0.0090 | 0.0001 | 3.3926 | -3358.2485 |
| | $2p_{1/2}$ | -3359.5290 | 2.5330 | -0.0086 | -0.0009 | 3.1604 | -3353.8451 |
| | $2p_{3/2}$ | -3345.6136 | 2.2796 | -0.0087 | -0.0009 | 3.1835 | -3340.1601 |
| 64 | $2s_{1/2}$ | -4826.8888 | 3.9858 | -0.0138 | 0.0001 | 5.9911 | -4816.9256 |
| | $2p_{1/2}$ | -4821.1998 | 4.3531 | -0.0135 | -0.0011 | 5.5711 | -4811.2901 |
| | $2p_{3/2}$ | -4791.9655 | 3.8895 | -0.0138 | -0.0010 | 5.6128 | -4782.4780 |
| 74 | $2s_{1/2}$ | -6617.2727 | 6.3721 | -0.0181 | 0.0001 | 9.8111 | -6601.1075 |
| | $2p_{1/2}$ | -6610.0683 | 6.9743 | -0.0180 | -0.0013 | 9.1105 | -6594.0028 |
| | $2p_{3/2}$ | -6554.1132 | 6.1792 | -0.0183 | -0.0012 | 9.1740 | -6538.7795 |
| 82 | $2s_{1/2}$ | -8319.7066 | 8.9433 | -0.0231 | 0.0001 | 14.0052 | -8296.7811 |
| | $2p_{1/2}$ | -8311.0829 | 9.8098 | -0.0229 | -0.0015 | 12.9944 | -8288.3031 |
| | $2p_{3/2}$ | -8221.3584 | 8.6216 | -0.0234 | -0.0013 | 13.0717 | -8199.6898 |
| 90 | $2s_{1/2}$ | -10301.765 | 12.254 | -0.028 | 0.000 | 19.486 | -10270.053 |
| | $2p_{1/2}$ | -10291.624 | 13.476 | -0.027 | -0.002 | 18.071 | -10260.106 |
| | $2p_{3/2}$ | -10151.991 | 11.735 | -0.028 | -0.001 | 18.147 | -10122.138 |
| 92 | $2s_{1/2}$ | -10846.716 | 13.218 | -0.029 | 0.000 | 21.094 | -10812.432 |
| | $2p_{1/2}$ | -10836.202 | 14.548 | -0.028 | -0.002 | 19.562 | -10802.122 |
| | $2p_{3/2}$ | -10680.800 | 12.635 | -0.029 | -0.001 | 19.632 | -10648.563 |

in Sec. IIIB are shown. Final Coulomb, Breit, and no-pair energies, including the extrapolated values and triple excitation corrections, are listed in the last row of the table. The computational procedure described above was applied to all ions covered in this study.

In Table II we present the total energies of the $n = 2$ states for 12 lithiumlike ions with Z in the range $10 \leq Z \leq 92$. Here Coulomb energies include contributions from two-electron excitations with $\Delta\ell = 2$ configurations and from three-electron excitations. These contributions are found to be non-negligible only for low- Z ions. Specifically, triple excitations contribute -4×10^{-5} , -2×10^{-5} , and -1×10^{-5} a.u. to the correlation energies of the $n = 2$ states of Ne^{7+} , P^{12+} , and Ca^{17+} , respectively, while $\Delta\ell = 2$ configurations contribute less than -1×10^{-5} a.u. to the Coulomb correlation energy for all ions studied in this work. Contributions to Breit energies from these corrections are found to be completely negligible.

In this work, mass polarization (MP) corrections are calculated from first-order perturbation theory using the eigenvectors from our CI calculations with the operator $H_{\text{MP}} = \frac{1}{M} \sum_{i < j} \mathbf{p}_i \cdot \mathbf{p}_j$, where M is the nuclear mass. For low- Z ions, our mass polarization corrections agree to within a few percent with results of the full-core plus correlation method (FCPC) by Chung [27].

Ionization energies from the present work for the $1s^2 2s$ ground state without QED corrections are compared with results from the FCPC [27] and RMBPT [28,29] in Table III. Our ionization energies are obtained by subtracting the heliumlike $1s^2$ CI energies [2] from the corresponding lithiumlike $1s^2 2s$ CI energies shown in Table II. The FCPC method employs nonrelativistic multiconfiguration interaction approach with optimized Slater-type basis functions. The effect of relativity is taken into account using first-order perturbation theory with the Breit-Pauli approximation. RMBPT starts from a Dirac-Fock basis and includes second- and third-order Coulomb corrections, the lowest-order Breit interaction with retardation, and second-order Breit corrections. For $Z = 10$, all three theories agree to within 5×10^{-5} a.u. For $Z = 15$ and 20, the FCPC results differ from the RMBPT and

TABLE III. Comparisons of the calculated ionization energies (a.u.) without QED corrections for the ground states of Li-like ions

| Z | Present work | RMBPT ^a | CCSD ^b | FCPC ^c |
|-----|--------------|------------------------|-------------------|-------------------|
| 10 | -8.78736 | -8.78733 | | -8.78731 |
| 15 | -22.48416 | -22.48410 | | -22.48367 |
| 20 | -42.55349 | -42.55334 | | -42.55059 |
| 26 | -75.19897 | -75.19865 | | |
| 54 | -360.7584 | -360.7550 | | |
| 74 | -724.2166 | -724.2057 | | |
| 92 | -1208.463 | -1208.449 ^d | -1208.451 | |

^aJohnson *et al.*, Ref. [28], except for $Z = 92$.

^bYnnerman *et al.*, Ref. [30].

^cChung, Ref. [27].

^dBlundell *et al.*, Ref. [29].

CI values by about 4.5×10^{-4} and 2.8×10^{-3} a.u., respectively, due to the neglect of higher-order relativistic corrections in the FCPC method. Ionization energies from the present work agree quite well with RMBPT, with differences ranging from 3×10^{-5} a.u. at $Z = 10$ to 1.4×10^{-2} a.u. at $Z = 92$. For lithiumlike uranium, RMBPT ionization energy is in very good agreement with the result of another relativistic many-body calculation that starts from a Dirac-Fock-Breit basis and is based on the coupled-cluster approach with single and double excitations (CCSD) [30]. Deviations at high Z between CI and the two RMBPT calculations are due mainly to differences in Breit energies. In RMBPT [29] and the CCSD [30], retardation energies are evaluated to first-order corrections only. From a perturbation theory point of view, frequency-dependent retarded Breit energies from our CI calculations contain not only first-order corrections but also contributions from higher-order Breit-Breit and Coulomb-Breit interactions. It appears that discrepancies in Breit energies between CI and the two RMBPTs are due mainly to higher-order Breit-Breit corrections that are included in CI but not in RMBPT and the CCSD. Similar differences in Breit energies have also been noted in heliumlike ions [1,2].

In Tables IV and V the $2s-2p_{1/2}$ and $2s-2p_{3/2}$ transition

TABLE IV. Theoretical and experimental $2s-2p_{1/2}$ transition energies (eV) for lithiumlike ions.

| Z | Present work | RMBPT ^a | CCSD ^b | MCDF ^c | Experiment | Reference |
|-----|---------------------|---------------------|---------------------|---------------------|------------|-----------|
| 10 | 15.8888 | 15.8885 | | | 15.8887(2) | [31] |
| 15 | 25.813 | 25.812 | | 25.806 | 25.814(3) | [32] |
| 20 | 35.963 | 35.964 | | 35.957 | 35.962(2) | [33] |
| 26 | 48.600 | 48.602 | | 48.597 | 48.599(1) | [34] |
| | | | | | 48.602(4) | [35] |
| 32 | 61.907 | 61.911 | | | 61.902(4) | [36] |
| 42 | 86.11 | 86.12 | | 86.13 | 86.10(1) | [36] |
| 54 | 119.82 | 119.84 | | 119.90 | 119.97(10) | [37] |
| 90 | 270.80 ^d | 270.85 ^d | | | | |
| 92 | 280.74 ^e | 280.84 ^e | 280.52 ^e | 281.88 ^e | 280.59(9) | [38] |

^aBlundell, Ref. [20].

^bYnnerman *et al.*, Ref. [30].

^cIndelicato and Desclaux, Ref. [18].

^dIncludes the 0.13-eV contribution from nuclear polarization [39].

^eIncludes the 0.19-eV contribution from nuclear polarization [39].

TABLE V. Theoretical and experimental $2s-2p_{3/2}$ transition energies (eV) for lithiumlike ions.

| Z | Present work | RMBPT ^a | MCDF ^b | Experiment | Reference |
|-----|----------------------|------------------------|----------------------|-------------|-----------|
| 10 | 16.0933 | 16.0931 | | 16.0932(2) | [31] |
| 15 | 27.205 | 27.205 | 27.197 | 27.206(3) | [31] |
| 20 | 41.028 | 41.028 | 41.021 | 41.029(2) | [31] |
| 26 | 64.567 | 64.568 | 64.560 | 64.566(2) | [34] |
| | | | | 64.567(4) | [35] |
| 32 | 101.051 | 101.055 | | 101.043(12) | [36] |
| 42 | 211.99 | 211.99 | 211.98 | 211.94(7) | [36] |
| 54 | 492.21 | 492.22 | 492.21 | 492.34(62) | [37] |
| 90 | 4025.11 ^c | 4025.25 ^c | | 4025.23(14) | [40] |
| 92 | 4459.31 ^d | 4459.70 ^{d,e} | 4460.09 ^d | 4459.37(35) | [8] |
| | | 4459.34 ^{d,e} | | | |

^aBlundell, Ref. [20], except for $Z = 92$.

^bIndelicato and Desclaux, Ref. [18].

^cIncludes the 0.15-eV contribution from nuclear polarization [39].

^dIncludes the 0.21-eV contribution from nuclear polarization [39].

^eJohnson *et al.*, Ref. [9].

energies from the present CI calculations are compared with experiment and with predictions from the MCDF method [18], RMBPT [9,20], and the CCSD [30]. Our CI results agree very well with RMBPT and experiment for all ions covered in this investigation. Results from the MCDF method are slightly outside experimental uncertainties. A closer examination of the differences in correlation energies between CI and RBMPT [28,29] shows that deviations for the $2s-2p_{1/2}$ transition in Coulomb energies range from 0.0003 eV at $Z = 10$ to 0.04 eV at $Z = 92$, while Breit energies differ by 0.0008 eV and 0.08 eV at $Z = 10$ and 92, respectively. For the $2s-2p_{3/2}$ energies, differences are 0.00014 eV and 0.01 eV for Coulomb energies at $Z = 10$ and 92, respectively, while deviations in Breit energies start from 0.00014 eV at $Z = 10$ and increase to 0.35 eV at $Z = 92$. As we shall show in the following, these discrepancies are partially canceled by differences in QED energies, resulting in closer agreements in transition energies between CI and RMBPT as shown in Tables IV and V. Without QED corrections, CCSD $2s-2p$ transition energies for lithiumlike uranium are essentially the same as those from RMBPT [29] and show similar differences in Breit energies when compared with the CI results.

In Table VI we compare our QED corrections for the $2s-2p$ transitions with those by Blundell [20]. In general, agreement between the two calculations is quite good,

especially for the $2s-2p_{1/2}$ transition. The biggest difference is at $Z = 90$ for the $2s-2p_{3/2}$ transition, where our QED correction is 0.57 eV below Blundell's value. Also shown here is the QED energy of the $2s-2p_{1/2}$ transition for lithiumlike uranium by Persson *et al.* [23,24], which is different from our result and Blundell's result by about 0.2 eV. While the use of model potentials to include correlation corrections to the QED energies in our work and in the work of Persson *et al.* is not as systematic as Blundell's approach, not all two-photon corrections are included in Blundell's calculations and his treatment of higher-order QED corrections is also incomplete. From these comparisons, it is clear that for high- Z ions such as thorium and uranium, QED corrections can be uncertain to 0.5 eV or more. But as discrepancies in Coulomb, Breit, and QED energies between RMBPT, the CCSD, and CI partially cancel each other, residual differences between all three calculations are, in general, too small to be detected by existing experiments. It thus appears that a complete treatment of higher-order QED corrections is needed to obtain high-precision transition energies.

In summary, we have successfully developed a large-scale, general-purpose relativistic CI code with B -spline basis functions for precision calculations of atomic structures. The code is applied to calculate the energy levels of $n = 2$ states of lithiumlike ions. Good agreement between the present work, RMBPT, and experiment has

TABLE VI. QED corrections (eV) for the $2s-2p$ transitions for lithiumlike ions.

| Z | $2s-2p_{1/2}$ | | | $2s-2p_{3/2}$ | |
|-----|---------------|-----------------------|------------------------------------|---------------|-----------------------|
| | This work | Blundell ^a | Persson <i>et al.</i> ^b | This work | Blundell ^a |
| 10 | -0.0143 | -0.0141 | | -0.0137 | -0.0135 |
| 15 | -0.067 | -0.066 | | -0.063 | -0.062 |
| 20 | -0.192 | -0.191 | | -0.181 | -0.178 |
| 32 | -1.025 | -1.016 | | -0.942 | -0.929 |
| 42 | -2.64 | -2.63 | | -2.40 | -2.37 |
| 54 | -6.32 | -6.29 | | -5.69 | -5.62 |
| 90 | -38.50 | -38.45 | | -36.44 | -35.87 |
| 92 | -41.69 | -41.68 | -41.92 | | |

^aReference [20].

^bReferences [23,24].

been attained. Work on more complex many-electron systems such as Be-like ions is in progress.

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