

## Accurate theoretical prediction of the experimental ground-state total atomic energies

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Thirty-five configurations, built up from 15 orbitals obtained in multiconfigurational Hartree-Fock calculations, have been used in configuration-interaction calculations (involving 53 states with  $J=0$ ) for the two-electron systems He I, Li II, and Be III. The Hamiltonian operator consisted of the electronic,  $SL$ -nonsplitting, and fine-structure terms, and the results have been corrected by consideration of the appropriate nuclear mass effects. The accuracy of the resulting total energies is 99.986%, 99.994%, and 99.998%, respectively.

Accurate calculations of atomic total energies may be carried out within the framework of the Dirac-Breit-Hartree-Fock (DBHF) or the Dirac-Breit-Pauli-Hartree-Fock (DBPHF) formalisms. Inspection of the results obtained in both approaches led to conclusion<sup>1</sup> that, at least for light atoms (say, for  $Z < 50$ ), it could prove to be worthwhile to direct more efforts towards multiconfigurational Dirac-Breit-Pauli calculations.

Recently, the formulation for the evaluation of the matrix representation (in sets of appropriate functions) of the complete Hamiltonian operator was completed<sup>2</sup> and implemented in a computer program<sup>3</sup> that can be used for the accurate determination of total energies and/or energy levels of neutral or ionized atomic systems. The Hamiltonian operator considered consists of the electronic, the  $SL$ -nonsplitting (specific mass, mass variation, Darwin, spin-spin contact, and orbit-orbit) correction terms, and the fine- (spin-orbit and spin-spin dipole) and hyperfine-structure (magnetic dipole, electric quadrupole, and magnetic octupole) interactions. Their contributions to the matrix elements are corrected by consideration of the relativistic mass correction.<sup>4,5</sup> The total energies, after diagonalization of the interaction matrix, are then corrected for the normal mass effect.<sup>4,5</sup>

Test calculations have shown that different approaches are needed, in terms of the radial functions used, depending on whether the goal is the prediction of the energy-level spectrum or the total energy of the lowest state. In the first case it is sufficient to use a set of (orthonormal) radial functions consisting of the Hartree-Fock solutions

for the orbitals occupied in the lowest state and the required number of approximate functions for the excited orbitals to be considered; e.g., those excited functions may be obtained from single Slater-type orbitals, with orthonormalization of the complete set (including the functions of the occupied orbitals).<sup>6</sup> This approach, however, is not appropriate for the prediction of accurate total energies for lowest states (except when using very large numbers of configurations) and the use of orbitals, obtained in a multiconfigurational Hartree-Fock (MCHF) procedure,<sup>7</sup> is preferable.

Calculations have now been carried out for the two-electron systems He I, Li II, and Be III. The MCHF calculations have yielded a set of 15 orbitals ( $nl$ ,  $0 \leq l \leq 4$ ,  $l+1 \leq n \leq 5$ ), obtained from a total wave function, which was a straightforward extension of an existing function.<sup>8</sup> Those orbitals have been used to generate 35 configurations ( $n'l^n'l'$ ,  $l+1 \leq n \leq 5$ ,  $n \leq n' \leq 5$ ), which produce 53  $J=0$  levels. The configuration-interaction calculations, using these states and including all the interactions (except for the hyperfine-structure terms), have yielded the results presented in Table I, where the conversion from Hartrees to  $\text{cm}^{-1}$  has been carried out in each case using the appropriate  $2R_M$  factor (where  $R_M$  is the Rydberg constant for finite mass). Conversion of those results to eV [using the ratio  $(27.211\,608\, \text{eV}/(219\,474.635\,4\, \text{cm}^{-1}))$ ] yields the values 78.99, 198.08, and 371.61, which may be compared to the values 78.97, 198.05, and 371.57 obtained<sup>11</sup> in multiconfigurational Dirac-Fock calculations.

TABLE I. Total energies (in absolute value) of  $^1S_0$  states.

System <sup>a</sup>	Theoretical (hartrees)	Theoretical ( $\text{cm}^{-1}$ )	Experimental <sup>b</sup> ( $\text{cm}^{-1}$ )	Accuracy (%)
He I	2.903 384 5	637 131.9	637 219.6	99.986
Li II	7.279 967 9	1 597 643.4	1 597 739.1	99.994
Be III	13.657 171	2 997 220.0	2 997 278.1	99.998

<sup>a</sup>The atomic data (Ref. 10) (mass number and atomic mass) and the  $2R_M$  factors used are 4, 4.002 603 26, and 219 444.555 (for He); 7, 7.016 004 8, and 219 457.475 (for Li); and 9, 9.012 182 8, and 219 461.261 (for Be).

<sup>b</sup>Reference 9.

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