

## Nonrelativistic energy of the ground state of $\text{Li}^-$ and the electron affinity of lithium\*

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The energy results of an extensive configuration-interaction calculation of the ground state of  $\text{Li}^-$  are reported. A quantitative assessment of all sources of truncation errors leads to a nonrelativistic energy estimate of  $-7.5004 \pm 0.0002$  a.u. An  $r_{ij}$  calculation on the ground state of  $\text{Li}^-$  yields a rigorous upper bound to the nonrelativistic energy of  $-7.500186$  a.u., in excellent agreement with the estimate from the configuration-interaction calculation. Consideration of relativistic contributions to the electron affinity of Li leads to an estimate of the electron affinity of Li of  $0.609 \pm 0.007$  eV.

### I. INTRODUCTION

Previously one of us (C.F.B.) performed a configuration-interaction (CI) calculation of the ground state of Be,<sup>1</sup> obtaining an energy 0.07 eV above the "experimental" value. By means of suitable extrapolation techniques it was possible to reduce this margin of error to 0.01 eV.<sup>1</sup> A subsequent  $r_{ij}$  calculation,<sup>2</sup> capable of obtaining an energy good to within 0.01 eV, confirmed the validity of the extrapolation techniques for Be. We have now carried out a still more accurate CI calculation of  $\text{Li}^-$ . Because of the peculiarities of the  $\text{Li}^-$  wave function, and also owing to the use of a larger basis set, we have obtained an estimated upper bound to the ground-state energy of  $\text{Li}^-$  lying 0.03 eV above our extrapolated value. We have also used the combined CI-Hy method<sup>2</sup> to do a 147-term calculation on the ground state of  $\text{Li}^-$  which yields a rigorous upper bound to the nonrelativistic energy of  $-7.500186$  a.u.,<sup>3</sup> in excellent agreement with the estimate from the CI calculation. Since both procedures are capable of giving results for the

energy good to better than 0.01 eV for four-electron systems, and in view of their excellent agreement, in these calculations we feel justified in ascribing an error of less than 0.01 eV to our value for the nonrelativistic energy of  $\text{Li}^-$ . Consideration of relativistic corrections does not modify this error estimate, so that a value of  $A(\text{Li})$  is computed *ab initio*, which is one order of magnitude more accurate than previous theoretical values and in excellent agreement with the latest experimental results.<sup>4</sup>

### II. NONRELATIVISTIC ENERGY OF $\text{Li}^-$

#### A. Configuration-interaction calculations

The one-electron basis set consists of  $9s7p4d3f$  energy optimized Slater-type orbitals (STO's) which has been transformed into approximate natural orbitals to ensure a rapid convergence of the CI series. The details of the calculation shall be reported elsewhere,<sup>5</sup> and an outline of the method is given in Ref. 1. The final 234-term wave function gives an energy of  $E = -7.499378$  a.u., which

TABLE I. Nonrelativistic energy of  $\text{Li}^-$  in a.u. (Li) by CI.

Present work		-7.49938
<i>L</i> -shell <i>spd</i> f STO truncation	-0.00003	
<i>9s7p4d3f</i> full CI truncation	-0.00003	
Overall <i>K</i> -shell error <sup>a</sup>	-0.00086	
<i>g</i> , <i>k</i> , and higher <i>L</i> -shell orbitals	-0.00007	
Total truncation error	-0.00099	
Nonrelativistic energy $\text{Li}^-$		$-7.50040 \pm 0.0002$
Nonrelativistic energy $\text{Li}^b$		-7.47807
Nonrelativistic $A(\text{Li})$		0.02233

<sup>a</sup> Taken as the energy error in a  $\text{Li}^+$  wave function expressed in our  $9s7p4d3f$  basis; see Ref. 1.

<sup>b</sup> S. Larsson, Phys. Rev. **169**, 49 (1968).

is 0.10 and 0.13 eV lower than the ones obtained by Weiss,<sup>6</sup> and by Miller and Ruedenberg,<sup>7</sup> respectively. The truncation errors in the CI expansion are grouped into: (i) truncation of the *spdf* STO basis (saturation remainders), (ii) truncation of the full CI expansion expressed in our *9s7p4d3f* basis, and (iii) the energy effect of *g*, *h*, and higher harmonics. Reliable procedures to estimate these truncation errors have been advanced.<sup>1,8,9</sup> In Table I we describe the steps in the computation of the nonrelativistic energy of the ground state of  $\text{Li}^-$ .

### B. Combined CI-Hy calculation

The combined CI-Hy wave function for  $\text{Li}^-$  was specifically of the form

$$\Psi_{\text{Li}^-}(X_1, X_2, X_3, X_4) = \sum_{\kappa} C_{\kappa} \Phi_{\kappa}(X_1, X_2, X_3, X_4), \quad (1)$$

where

$$\Phi_{\kappa} = O(L^2)O_{\text{as}} \left( \chi r_{ij}^{\nu_{\kappa}} \prod_{s=1}^4 \varphi_{\kappa s}(\vec{r}_s) \right). \quad (2)$$

In Eq. (2),  $O(L^2)$  is an idempotent orbital-angular-momentum projection operator<sup>10</sup> and  $O_{\text{as}}$  is the projection operator which guarantees the antisymmetry of the wave function

$$O_{\text{as}} = (4!)^{-1} \sum_p (-1)^p P,$$

where the summation runs over all the  $4!$  permutations  $P$ , with  $p$  being the parity of the corresponding permutation  $P$ . Also,  $\chi$  is the spin function  $\chi = \frac{1}{2}(\alpha_1\beta_2 - \beta_1\alpha_2)(\alpha_3\beta_4 - \beta_3\alpha_4)$ . In Eq. (2),  $\varphi_{\kappa s}(r_s)$  refers to the  $s$ th basis orbital in the  $K$ th configuration. The orbital basis consists of STO's of the general form

$$\varphi(r) = \{(2\xi)^{n+1/2} / [(2n)!]^{1/2}\} r^{n-1} e^{-\xi r} Y_{l,m}, \quad (3)$$

where the set  $\{Y_{l,m}\}$  consists of normalized spherical harmonics in the Dirac phase convention.<sup>11</sup> Specifically, the basis set used was  $1s-4s$ ,  $1s'-8s'$ ,  $2p''-4p''$ , where the orbital exponents,  $\xi_s = 2.55$ ,  $\xi_{s'} = 0.42$ , and  $\xi_{p''} = 0.48$ , were taken from Weiss's calculation.<sup>6</sup> From this orbital basis and Hylleraas correlation factors  $r_{ij}^{\nu}$ ,  $\nu = 0, 1, 2$  we formed a 147-term wave function for the ground state of  $\text{Li}^-$  by forming almost all conceivable combinations of basis functions and retaining the energetically important terms. The final result was a 147-term  $\text{Li}^-$  wave function with energy of  $-7.500186$  a.u., in excellent agreement with the configuration-interaction estimate of  $-7.5004 \pm 0.0002$  a.u.

### III. ELECTRON AFFINITY

The existence of a stable  $\text{Li}^-$  ion was observed in a plasma study by Ya'akobi,<sup>12</sup> and an estimate of 0.6 eV was given for the lithium electron affinity. In the next experimental study,<sup>13</sup> the electron affinity of lithium was reported to be bound by the following values:  $0.65 < A(\text{Li}) < 1.05$  eV. The same authors concluded that  $A(\text{Li})$  was probably greater than 0.75 eV, in good agreement with Edlen's empirical estimate of 0.82 eV.<sup>14</sup> The most recent experimental studies now favor the original Ya'akobi estimate, and give an electron affinity of  $0.62 \pm 0.007$  eV.<sup>4</sup>

There have been, on the other hand, a large number of theoretical estimates made of this quantity.<sup>15,16</sup> The values obtained have fallen between 0.4 and 1.0 eV. In probably the best previous theoretical calculation, Weiss<sup>17</sup> obtained 0.62 eV with an estimated uncertainty of 0.10 eV for  $A(\text{Li})$ . Weiss obtained his binding energy of the additional electron in  $\text{Li}^-$  by attempting to calculate the correlation-energy correction directly.<sup>18</sup> Our calculations are in the spirit of the Weiss<sup>17</sup> and other recent calculations,<sup>19</sup> and we have attempted to reduce the uncertainty in the theoretical estimates by doing large scale CI and CI-Hy calculations as described in Sec. II. With the estimates of the nonrelativistic energy of  $\text{Li}^-$  as given in Sec. II, a consideration of relativistic effects leads us to a final estimate of  $A(\text{Li})$  which has an order of magnitude less uncertainty than that of Weiss.<sup>17</sup>

#### A. Consideration of relativistic effects

Clementi<sup>20</sup> gives the  $K$ -shell part of the correlation energy of lithium as 0.0005 a.u. Since the lithium correlation energy is given by Veillard and Clementi<sup>21</sup> as 0.00055 a.u., this leaves  $\sim 0.00005$  a.u. as the relativistic correction for a  $2s$  electron. Since the major part of the relativistic energy of  $\text{Li}$  and presumably  $\text{Li}^-$  is made up of contributions of  $K$ -shell electrons which should cancel when computing electron affinities, we take  $0.00005$  a.u.  $\approx 0.0014$  eV as the relativistic contribution to  $A(\text{Li})$  and ascribe an uncertainty of  $\pm 0.0014$  eV to this estimate. Note that the relativistic correction to the electron affinity is small and does not significantly affect our estimates.

#### B. Final estimates

Adding the relativistic correction to the CI estimate of Table I gives a final CI estimate of  $A(\text{Li})$  to be  $0.02238$  a.u.  $= 0.609$  eV, and the nonrelativistic and relativistic energy error estimates combine to  $0.00025$  a.u.  $\approx 0.007$  eV. The combined CI-Hy result for the nonrelativistic energy of  $\text{Li}^-$ ,

7.500186 a.u., combined with a similar CI-Hy calculation for the ground state of lithium<sup>22</sup> ( $E = -7.478023$  a.u.), gives a nonrelativistic  $A(\text{Li}) = 0.02216$  a.u. Adding the relativistic correction gives a final CI-Hy estimate for  $A(\text{Li})$  of 0.2221 a.u. = 0.604 eV, in excellent agreement with the CI estimate. Since the  $\text{Li}^-$  energy computed by the CI-Hy procedure is an upper bound to the nonrelativistic energy of  $\text{Li}^-$ , further lowering the  $\text{Li}^-$  nonrelativistic energy will bring the CI-Hy estimate closer to the CI estimate; so we give as our final estimate for the electron affinity of lithium:

$$A(\text{Li}) = 0.609 \pm 0.007 \text{ eV}$$

in excellent agreement with the latest experimen-

tal result of  $A(\text{Li}) = 0.620 \pm 0.007$  eV.<sup>4</sup>

#### IV. CONCLUSION

Theoretical CI extrapolation techniques and improved *ab initio* CI-Hy techniques have been combined to give a theoretical estimate of the electron affinity of lithium which has a probable accuracy an order of magnitude better than the best previous theoretical estimates of unmeasured electron affinities and in excellent agreement with recent improved experimental results.

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<sup>18</sup>The Hartree-Fock (HF) approximation, which assumes that each electron in an atomic system interacts with an *average field* produced by the remaining electrons and the nucleus, leads to an  $A(\text{Li})$  of  $-0.123$  eV; i.e., it predicts  $\text{Li}^-$  to be unstable. Therefore, in order to account for the stability of the negative ion, it is necessary to correct the HF energies with terms which describe the detailed way in which electrons mutually correlate their motions.

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