

### Variational Calculation of the Ground State of the Lithium Atom\*

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The validity of the results obtained by Burke in an earlier article with the same title have been questioned by Larsson in a recent publication. The earlier calculations were reexamined and an error was found. The new results indicate a total energy of  $-14.9403$  Ry, as compared to the earlier results of  $-14.9559$  Ry, and an energy of  $-14.9561$  Ry calculated from experimental data. The new results are consistent with those of Larsson. The wave-function parameters for the more recent calculation with the addition of another term bringing the total energy to  $-14.9539$  Ry are given. An estimation by Burke of the error involved in the lack of proper symmetry of the wave functions of James and Coolidge is discussed.

In a paper<sup>1</sup> with the same title as this note, Burke has obtained results which show a rapid convergency towards the experimental value. These results are inconsistent with the results of Larsson.<sup>2</sup> Subsequently,<sup>3</sup> an error was found in Burke's original calculations. The error was contained in the calculation of the integral containing three odd powers of the interelectronic separation coordinates. The derivation of this integral was reported<sup>4</sup> earlier. The present co-authors independently recalculated the original function and the results and a discussion of the results is presented herein.

The wave function of Burke is of the form

$$\psi = \sum_{\nu} c_{\nu} \alpha_3 [\phi_{\nu}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \{A_{1\nu}(\alpha\beta\alpha - \beta\alpha\alpha) + A_{2\nu}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)\}], \quad (1)$$

where  $\alpha_3$  is the three-particle antisymmetrizer and  $c_{\nu}$ ,  $A_{1\nu}$ , and  $A_{2\nu}$  are variational parameters. The spatial functions  $\phi_{\nu}$  are of the form

$$\phi_{\nu}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = r_1^i r_2^j r_3^k e^{-(\alpha r_1 + \beta r_2 + \gamma r_3)} r_{23}^l r_{13}^m r_{12}^n. \quad (2)$$

The  $\phi$  set was restricted to contain only one  $r_{ij}$  term. The contribution from  $\phi_{\nu}$  with more than one  $r_{ij}$  term is not large as was found in L. The  $\phi_{\nu}$  used by Burke<sup>1</sup> are listed in Table I. Some of the terms are not symmetric in  $\vec{r}_1$  and  $\vec{r}_2$ . Burke used  $\phi_{\nu}$  that were symmetrized in  $\vec{r}_1$  and  $\vec{r}_2$ , i. e., he used  $\phi_{\nu}^S$  in the expression

$$\phi_{\nu}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{1}{2} \{ \phi_{\nu}(\vec{r}_1, \vec{r}_2, \vec{r}_3) + \phi_{\nu}(\vec{r}_2, \vec{r}_1, \vec{r}_3) \} + \frac{1}{2} \{ \phi_{\nu}(\vec{r}_1, \vec{r}_2, \vec{r}_3) - \phi_{\nu}(\vec{r}_2, \vec{r}_1, \vec{r}_3) \} = \phi_{\nu}^S + \phi_{\nu}^A. \quad (3)$$

Since  $\alpha\beta\alpha - \beta\alpha\alpha$  is antisymmetric in 1 and 2, we get

$$\alpha_3 \{ \phi_{\nu}(\alpha\beta\alpha - \beta\alpha\alpha) \} = \alpha_3 \{ \phi_{\nu}^S(\alpha\beta\alpha - \beta\alpha\alpha) \}, \quad (4)$$

i. e., it does not matter here if we use  $\phi_i$  or  $\phi_i^S$ ; but we get, since  $2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha$  is symmetric in 1 and 2,

$$\alpha_3 \{ \phi_{\nu}^S(2\alpha\alpha\beta - \beta\alpha\alpha - \alpha\beta\alpha) \} = 0. \quad (5)$$

Thus, Burke's requirement is equivalent to using only the spin function  $\alpha\beta\alpha - \beta\alpha\alpha$ . Furthermore, Burke combined terms 13 and 14 while Larsson treated them as separate (see Table II).

TABLE I. Wave-function parameters ( $\alpha = \beta = 2.69$ ).

Terms	<i>i</i>	<i>j</i>	<i>k</i>	<i>l</i>	<i>m</i>	<i>n</i>	$\alpha$
1	0	0	1	0	0	0	0.64
2	0	0	1	0	0	2	0.64
3	1	0	1	0	0	0	0.64
4	1	1	1	0	0	0	0.64
5	0	0	1	0	0	1	0.64
6	0	0	0	0	0	0	1.5
7	1	0	0	0	0	0	1.5
8	0	0	2	0	0	0	0.64
9	0	0	1	0	0	0	1.5
10	0	0	0	1	0	0	0.64
11	0	0	1	1	0	0	0.64
12	0	0	0	1	0	0	1.5
13	1	0	0	1	0	0	0.64
14	0	1	0	1	0	0	0.64
15	2	0	1	0	0	0	0.64

Comparing the basis set with that of James and Coolidge<sup>5</sup> one finds that the latter contains the function  $\{ijklmn, \gamma\} = \{201000, 0.65\}$ . This function is missing in B and when it was added in Larsson's calculation the energy  $-14.9542$  Ry was obtained, an improvement from 83.3 to 97.9% of the correlation energy. The large contribution from this term was also obtained by James and Coolidge.<sup>5</sup> In Burke's recalculation this term was included, yielding an energy of  $-14.9539$  Ry. The improved result of L is consistent with the fact that he has added an additional variational parameter in breaking up terms 13 and 14 into a single term.

The wave function of Burke was constructed so as to have the correct spin-angular-momentum symmetry,  $\langle \vec{S}^2 \rangle = \frac{3}{4}$ . This was not the case for the JC wave function. In B, as well as in a recent publication,<sup>3</sup> the energy error arising from this lack of symmetry was said to have been estimated.

The effect of  $^4S$  admixture in their wave function was thoroughly discussed by James and Coolidge in a subsequent paper.<sup>6</sup> Using the notation of L the JC terms Nos. 9 and 10 were

$$\psi_9 = \alpha_3 \{ \phi_9(\alpha\beta\alpha) \},$$

$$\psi_{10} = \alpha_3 \{ \phi_9(\beta\alpha\alpha) \}.$$

$C_9\psi_9 + C_{10}\psi_{10}$  has correct spin-angular-momentum symmetry if  $C_9$  and  $C_{10}$  are restricted so that  $C_{10} = -C_9$ . The latter construction was used by Burke and will necessarily make the energy poorer than if the coefficients are determined variationally and not better as was indicated in B. James and Coolidge<sup>6</sup> estimated the difference to be  $0.0004$  eV  $\approx 3 \times 10^{-5}$  Ry. The energy can,

however, be lowered by annihilation of the quartet part and then further improved by again varying  $C_9$  and  $C_{10}$  in the purified wave function. The latter case will, of course, be equivalent to using two spin functions as in L. From Table I in L we also see that the difference between the worst energy in this discussion, namely, the one using only one spin function as in B and the best energy, using two spin functions, is very small. In the case of the term discussed above, the difference should be between  $4 \times 10^{-5}$  and  $6 \times 10^{-5}$  Ry in agreement with the estimation by JC. The estimation in B is, therefore, incorrect.

The above should not be taken to mean that it is not possible to converge upon the exact wave function by employing only one spin function. Instead, as was pointed out in L and probably is well known, it is sufficient to use only one spin function. The energy difference when using one or two spin functions in the way mentioned above, will therefore decrease to zero when the basis set is extended towards completeness.<sup>2</sup>

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TABLE II. Ground-state energies.

No. of terms	- Energy (Ry = $e^2/2a_0$ )	
	Burke's result	Larsson's result
1	14.8358	14.8358
2	14.8696	14.8696
3	14.8849	14.8850
4	14.9102	14.9103
5	14.9331	14.9331
6	14.9349	14.9349
7	14.9349	14.9349
8	a	14.9356
9	a	14.9356
10	14.9395	14.9395
11	14.9397	14.9397
12	14.9397	14.9397
13	}	14.9397
14		14.9410
15	14.9539	14.9542
$\infty^b$	14.9561	14.9561

<sup>a</sup>In Burke's recalculation the terms 8-10 were done in the order 9, 10, and 8 with the respective negative energies of 14.9387, 14.9395, and 14.9395 Ry.

<sup>b</sup>Energy value calculated from experiments [C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. 127, 830 (1962)].

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<sup>1</sup>E. A. Burke, Phys. Rev. 130, 1871 (1963) (referred to as B in this paper).

<sup>2</sup>S. Larsson, Phys. Rev. 169, 49 (1968) (referred to as L).

<sup>3</sup>R. F. Gentner and E. A. Burke, Phys. Rev. 176, 63

(1968).

<sup>4</sup>E. A. Burke, J. Math. Phys. 6, 1691 (1965). As pointed out in Ref. 31 of Ref. 3 the numerical values of  $l$  and  $j$  in Eq. (5) and  $L$  and  $J$  in Eq. (21) should be interchanged.

<sup>5</sup>H. M. James and A. S. Coolidge, Phys. Rev. 49, 688 (1936) (referred to as JC).

<sup>6</sup>H. M. James and A. S. Coolidge, Phys. Rev. 55, 873 (1939).

### Spin Orientation of Photoelectrons: Erratum and Addendum\*

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An effect overlooked in a recent calculation is pointed out and included in the theory. The resulting corrections amount to less than 1%.

A recent paper,<sup>1</sup> called I in the following and dealing with the alternative spin orientations of photoelectrons ejected by circularly polarized light, regrettably overlooked a well-known phase normalization requirement on the photoelectron wave functions. It seems worthwhile to rectify this error and evaluate its consequences, also because the calculation of I applies to a variety of experiments, one of which has been successfully performed.<sup>2</sup>

In calculations of the probability of alternative final channels for an outgoing particle, the outgoing large- $r$  wave-function term  $\exp(ikr)$  of a scattering eigenstate must have the same phase as the corresponding term of a free-particle wave function.<sup>3</sup> In our problem, this phase normalization allows for the influence of electron scattering by the atomic field and specifically for the influence of spin-orbit coupling after the photoabsorption proper. By disregarding this phase normalization, paper I took into account the spin-orbit coupling influence only upon the photoabsorption but not in later stages of the process. The latter influence is weak owing to the weakness of the coupling itself, but it would suffice to produce some spin polarization if the major influence upon photoabsorption were absent.

Appropriate phase normalization multiplies the real wave function  $P(\epsilon p j'; r)$  in (I1) by a factor  $\exp(i\delta_j')$ , where  $\delta_j'$  indicates the phase shift of  $P$ . We need not know the actual values of  $\delta$  for the alternative  $j'$  values but only their difference

$$\delta = \delta_{1/2} - \delta_{3/2} = \pi \Delta\tau \sim 0.1 \text{ rad}, \quad (1)$$

where  $\Delta\tau$  is defined by (I8). Renormalization of the wave function  $P$  causes factors  $\exp(i\delta_{3/2})$  and  $\exp(i\delta_{1/2})$  to be inserted in front of  $R_3$  and  $R_1$ , respectively, in (I3). The same insertion in (I4) prevents this equation from being satisfied exactly. The squares of matrix elements in (I5) must now be interpreted as absolute squares, owing to the complex character of the corrected matrix (I3); moreover, the real parameter  $x$  defined by (I6) must be replaced by the complex parameter

$$z(\epsilon) = \frac{x - ie^{-i\frac{1}{2}\delta} (\sin\frac{1}{2}\delta)^{\frac{2}{3}}(x-2)}{1 + ie^{-i\frac{1}{2}\delta} (\sin\frac{1}{2}\delta)^{\frac{2}{3}}(x-2)} \\ = \frac{x + (\sin\frac{1}{2}\delta - 3i \cos\frac{1}{2}\delta)(\sin\frac{1}{2}\delta)^{\frac{2}{3}}(x-2)(x+1)}{1 + (\sin\frac{1}{2}\delta)^{\frac{4}{3}}(x-2)(x+1)} \quad (2)$$

and the polarization formula (I5) itself becomes

$$P(z) = P(x, \delta) = (1 + z + z^*) / (2 + |z|^2) \\ = \frac{1 + 2x}{2 + x^2} + \frac{8}{9} \frac{(x-2)(x+1)}{2 + x^2} \sin^2\frac{1}{2}\delta. \quad (3)$$

These corrected results differ from those of I by terms proportional to  $\sin\frac{1}{2}\delta \sim 0.05$  or  $\sin^2\frac{1}{2}\delta \sim 0.002$ . The corrections also vanish at  $x=2$  and  $x=1$  where  $R_1$  and  $R_3$  vanish, respectively. (This result reflects the circumstance that the scattering eigenchannels with  $j' = \frac{1}{2}$  and  $j' = \frac{3}{2}$  no longer interfere when either of their probability amplitudes vanishes.) The maximum of  $P$  lies near