

Term values of $1s2s2p\ ^4P^\circ$ for lithiumlike ions

Jung-Jiin Hsu, Kwong T. Chung,* and Keh-Ning Huang

*Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei, Taiwan 106, Republic of China
and Department of Physics, National Taiwan University, Taipei, Taiwan 106, Republic of China*

(Received 13 February 1991)

The best-known nonrelativistic energy of the term $1s2s2p\ ^4P^\circ$ of neutral lithium is improved to an accuracy of less than 1 cm^{-1} by using the Rayleigh-Ritz variational method with Slater-type basis functions. The relativistic, mass-polarization, and Lamb-shift effects are calculated perturbatively as first-order corrections to the nonrelativistic energy. Combined with best-known data from experiment, we attain the ionization potential $56\,460.0(2)\text{ cm}^{-1}$ for the term $1s2s2p\ ^4P^\circ$ of neutral lithium, compared to the experimental value of $56\,473(5)\text{ cm}^{-1}$ by Mannervik and Cederquist [Phys. Scr. **27**, 175 (1983)]. The discrepancy between theory and experiment is discussed. The relative term value of $1s2s2p\ ^4P^\circ$ for neutral lithium is calculated to be $463\,062.4(3.3)\text{ cm}^{-1}$ above the lithium ground state, compared with $463\,039(122)\text{ cm}^{-1}$ by Rassi *et al.* [J. Phys. B **10**, 3535 (1977)] from the ejected-electron spectrum. We have also extended the calculation to Li-like ions up to $Z=9$, where no experimental values are available.

PACS number(s): 31.20.Tz, 31.20.Di, 31.30.Jv

I. INTRODUCTION

The quartet system of doubly excited neutral lithium has been established by studying optical spectra from beam-foil measurements [1]. For higher members of the lithium isoelectronic sequence, many of the quartet transitions have also been observed and assigned. The interplay of related theoretical and experimental works has been reviewed by Berry [2] and more recently by Mannervik [3].

The term $1s2s2p\ ^4P^\circ$ is the lowest quartet of Li-like ions. It is metastable against both radiative deexcitations and autoionizations. Its relative term value above the ground term $1s^2s\ ^2S$ is therefore of significance in determining the term values for the quartet system of these ions.

Optical quartet-to-doublet transitions are difficult to observe experimentally. The relative term value $57.41(0.015)\text{ eV}$ of $1s2s2p\ ^4P^\circ$ for neutral lithium is given by Rassi *et al.* [4] from the ejected-electron spectrum. However, its uncertainty is too large to be used in the Grotrian diagram because optical levels in the quartet system of Li I have been explored [1] to within a few cm^{-1} ($1\text{ cm}^{-1}=0.124\text{ meV}$). Consequently, calculations with improved accuracy may play an important role in determining term values of the quartet system.

Theoretically, the challenge is to find a proper way to account for the correlations between the three electrons, each of them being in a different subshell. The most accurate calculation on the energy of $1s2s2p\ ^4P^\circ$ for Li I came from the configuration-interaction method (CI) with Slater-type orbitals performed by Bunge and Bunge [5] and later improved by Bunge [6]. In addition to a variational energy upper bound, they were able to find a pattern of convergence and estimate truncation-energy errors with an uncertainty of a few cm^{-1} . Assuming that the relativistic, radiative, and mass-polarization correc-

tions for $1s2snl$ and $1s2pnl$ states are equal to the corresponding ones for Li II $1s2s\ ^3S$ and Li II $1s2p\ ^3P^\circ$ cores, respectively, they calculated the nonrelativistic energies of the terms $1s2s3s\ ^4S$ and $1s2p3d\ ^4D^\circ$. Combined with other theoretical data and experimental transition energies to $1s2s2p\ ^4P^\circ$, they determined [6] the relative term value of $1s2s2p\ ^4P^\circ$ to be at $463\,062.0(7)\text{ cm}^{-1}$ or $57.4128(2)\text{ eV}$ above the Li ground state. There are also term values for $1s2s2p\ ^4P^\circ$ deduced from the quantum-defect analysis of the $1s2snd\ ^4D$ series. This has been done for Li I by Berry *et al.* [2,7] by fitting the experimental term values of $1s2snd\ ^4D$ ($n=3,4,5$) to the Ritz formula, and recently by Mannervik and Cederquist [1], who were able to observe and identify five more terms ($1s2snd\ ^4D$, $n=6-10$). The relative term value of $1s2s2p\ ^4P^\circ$ was determined to be at $463\,050(5)\text{ cm}^{-1}$ or $57.4113(6)\text{ eV}$, which is lower than that of Bunge [6]. The contributions from relativistic and mass-polarization effects were later studied by Chung [8]. One may combine Bunge's nonrelativistic energy [6] with Chung's relativistic corrections to obtain the relative term value of $1s2s2p\ ^4P^\circ$ for Li I at $463\,063.0(7)\text{ cm}^{-1}$ or $57.4130(2)\text{ eV}$; the discrepancy with that of Mannervik and Cederquist [1] still remains. It was queried [1] that variational calculations give only upper bounds for the energy and the error estimate given by Bunge [6] may be too small.

For higher members of the lithium isoelectronic sequence, Chung [8] has studied the relativistic effect of low-lying quartet terms using nonrelativistic CI wave functions for $Z \leq 12$. Because for these ions the first few terms of $1s2pnl\ ^4L$ lie below the $1s2s\ ^3S$ limit and interact with the $1s2snl\ ^4L$ Rydberg series, it is difficult to determine the $1s2s\ ^3S$ limit using the quantum-defect analysis.

In this work we present improved nonrelativistic $1s2s2p\ ^4P^\circ$ term energy for Li-like ions up to $Z=9$ and establish its relative term value using the best-known theoretical and experimental data. In Sec. II we give a

brief account of our theory. Results are presented in Sec. III and summarized in Sec. IV.

II. THEORY

For an accurate assessment of the term energies of Li-like systems, we consider the Hamiltonian (in atomic units) given by [9]

$$H = H_0 + H_1 + H_2 + H_3 + H_4, \quad (1)$$

with

$$H_0 = \sum_{i=1}^3 \left[-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right] + \sum_{\substack{i,j=1 \\ i < j}}^3 \frac{1}{r_{ij}}, \quad (2)$$

$$H_1 = -\frac{1}{M} \sum_{\substack{i,j=1 \\ i < j}}^3 \nabla_i \cdot \nabla_j, \quad (3)$$

$$H_2 = -\frac{1}{8c^2} \sum_{i=1}^3 p_i^4, \quad (4)$$

$$H_3 = \frac{Z\pi}{2c^2} \sum_{i=1}^3 \delta(\mathbf{r}_i), \quad (5)$$

$$H_4 = -\frac{1}{2c^2} \sum_{\substack{i,j=1 \\ i < j}}^3 \frac{1}{r_{ij}} \left[\mathbf{p}_i \cdot \mathbf{p}_j + \frac{\mathbf{r}_{ij}(\mathbf{r}_{ij} \cdot \mathbf{p}_i) \cdot \mathbf{p}_j}{r_{ij}^2} \right], \quad (6)$$

where M is the nuclear mass in a.u., and $c=137.0360$. Here H_0 is the usual nonrelativistic Hamiltonian, and H_1 is the mass-polarization term. The rest come from the relativistic effect, and they are the mass variation, Darwin, and orbit-orbit interaction terms. The spin-orbit and spin-spin interaction operators will not be considered here because they do not affect the center of gravity of a term.

To solve Eq. (1), we first calculate the energy eigenvalue of H_0 using the Rayleigh-Ritz variational method. The term $1s2s2p^4P^o$ of Li-like ions lies lower than the $1s2s^3S$ ionization threshold, and there is no lower-quartet continuum to which it can autoionize. Therefore the Rayleigh-Ritz variational method is applicable for this calculation because the inner-shell vacancies are implicitly built in [10] as a direct consequence of the Pauli exclusion principle. In the case of neutral lithium, the term $1s2s3s^4S$ will also be considered; the Rayleigh-Ritz variational method is similarly applicable for this term. The basis functions in the trial wave function are chosen in the LS -coupling scheme as

$$\phi_\Omega = \sum_{m,n,k} C_{mnk} \mathcal{R}_{mnk}(r_1, r_2, r_3) \mathcal{Y}_{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{r}}_3) \chi(123), \quad (7)$$

where

$$\mathcal{R}_{mnk}(r_1, r_2, r_3) = r_1^m r_2^n r_3^k e^{-\alpha r_1} e^{-\beta r_2} e^{-\gamma r_3}, \quad (8)$$

$$\mathcal{Y}_{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{r}}_3) = \sum_{m_1, m_2, \mu, m_3} \langle l_1 m_1 l_2 m_2 | L_{12} \mu \rangle \langle L_{12} \mu l_3 m_3 | LM \rangle Y_{l_1 m_1}(\hat{\mathbf{r}}_1) Y_{l_2 m_2}(\hat{\mathbf{r}}_2) Y_{l_3 m_3}(\hat{\mathbf{r}}_3), \quad (9)$$

and $\chi(123)$ denotes a quartet spin function. Here m , n , and k are non-negative integers, and Ω represents the coupling $[(l_1, l_2)^3 L_{12}, l_3]^4 L$ and the set of nonlinear parameters (α, β, γ) . We will refer to ϕ_Ω as a *partial wave*. The trial wave function is given by

$$\psi = \mathcal{A} \sum_{\Omega} \phi_\Omega, \quad (10)$$

\mathcal{A} being the antisymmetrization operator and is constructed by systematically increasing the number of partial waves in a manner of improving the angular correlation and radial expansion. Within each partial wave, the nonlinear parameters are optimized by minimizing the nonrelativistic energy; this procedure is similar to that used by Chung [11]. The convergence of energy can be seen as the number of partial waves in the trial wave function is increased. The truncation-energy error can then be estimated. Corrections to the nonrelativistic energy are calculated as first-order perturbations by using this wave function. The reduced-mass corrections are considered, when converting the energy from a.u. to cm^{-1} , by taking the appropriate value R_m from Table I for the Rydberg constant.

III. RESULTS AND DISCUSSIONS

A. Li

In recent studies of the relative term value of $1s2s2p^4P^o$ for neutral lithium, a discrepancy is found between theory and experiment. The theoretical value is based on the variational method, which gives upper bounds to the eigenvalues of a Hamiltonian. From the convergence of the upper-bound calculations, one may also extrapolate or estimate to obtain a more accurate

TABLE I. The Rydberg constant R_m used in this calculation.

Z	Isotope	R_m
3	^7Li	109 728.734
4	^9Be	109 730.634
5	^{11}B	109 731.846
6	^{12}C	109 732.298
7	^{14}N	109 733.015
8	^{16}O	109 733.552
9	^{19}F	109 734.146

solution to the eigenvalue equation. Unfortunately, Bunge's estimated value [6] lies 12 cm^{-1} or 5.5×10^{-5} a.u. above the experimental value given by Mannervik and Cederquist [1]. The discrepancy should be traced back to the ionization potential, which will be discussed later.

To study this discrepancy and reduce the possible errors in the extrapolation, the upper-bound calculation should converge to the level of 10^{-6} a.u. To avoid spurious convergence in this work, we perform calculations on two terms of different symmetry, $1s2s2p\ ^4P^\circ$ and $1s2s3s\ ^4S$. The latter is chosen because it converges faster in a full CI-expansion calculations than other quartets, and an accurate experimental transition energy of $1s2s2p\ ^4P^\circ - 1s2s3s\ ^4S$ is available for deducing a good term energy of $1s2s2p\ ^4P^\circ$ from the converged term energy of $1s2s3s\ ^4S$ (Fig. 1).

The energy convergences for $1s2s3s\ ^4S$ and for $1s2s2p\ ^4P^\circ$ are shown in Tables II and III, respectively. The wave functions in these tables are divided into two groups. The partial waves in group I are adopted to account for the angular correlation, and they are built up by the CI method. Those in group II are used to saturate the radial expansion for dominant partial waves in group I. This is achieved by using the partial wave with the same angular composition but a different set of nonlinear parameters. For example, the radial expansion of partial waves 1 and 2 in Table II is improved with partial waves 19, 20, and 21. The convergences of energies in this calculation can easily be seen from these two tables. The radial terms \mathcal{R}_{mnk} in each partial wave are chosen as follows. First, for a certain W , all terms with $(m+n+k) \leq W$ are used (see Tables II and III). This determines an energy contribution ΔE for the partial wave. To reduce the number of radial terms used, we then recalculate the energy contribution by successively adding each \mathcal{R}_{mnk} term until ΔE is essentially reached. Those terms with negligible contribution are thereby

dropped. In the partial wave of group I, the powers m , n , and k are started from their respective angular component l . This condition is relaxed in the partial waves of group II. Our upper bound to the term energy of $1s2s2p\ ^4P^\circ$, -5.367999 a.u., is lower than the value of -5.36780 a.u. by Ahlenius and Larsson [12] using Hylleraas coordinates, and -5.367917 a.u. by Froese Fischer [13] using the multiconfiguration Hartree-Fock method. In Table IV, the nonrelativistic energies are compared only with the best previous values given by Bunge and Bunge [6,5]. Nonrelativistic energy upper bounds calculated here for both $1s2s3s\ ^4S$ and $1s2s2p\ ^4P^\circ$ are accurate to about 10^{-6} a.u. Total term energies of these two terms are presented in Table IV along with mass-polarization and relativistic corrections.

The predicted ionization potential (V_{IP}) of $1s2s2p\ ^4P^\circ$ is, therefore, given by

$$V_{IP}(1s2s2p\ ^4P^\circ) = E(1s2s\ ^3S) - E(1s2s2p\ ^4P^\circ) \\ = 56459.6(5)\text{ cm}^{-1}, \quad (11)$$

or semiempirically by

$$V_{IP}(1s2s2p\ ^4P^\circ) = E(1s2s\ ^3S) - E(1s2s3s\ ^4S) + \nu \\ = 56460.1(2)\text{ cm}^{-1}, \quad (12)$$

where $\nu = 34071.91(5)\text{ cm}^{-1}$ is the wave number of the interval $1s2s2p\ ^4P^\circ - 1s2s3s\ ^4S$ by Feldman *et al.* [14] based on the observation by Herzberg and Moore [15]. The total term energy $E(1s2s\ ^3S)$ is $-1121722.13(1)\text{ cm}^{-1}$ by Accad *et al.* [16], and the values of $E(1s2s2p\ ^4P^\circ)$ and $E(1s2s3s\ ^4S)$ are calculated in the present work. These are indicated in Fig. 1. In Eqs. (11) and (12), we have not included the Lamb-shift correction. The differences in the Lamb-shift contributions between the two- and three-electron systems are calculated for the ionization potentials to be $+0.7$ and -0.1 cm^{-1} , respectively [17]. The good agreement between the results from

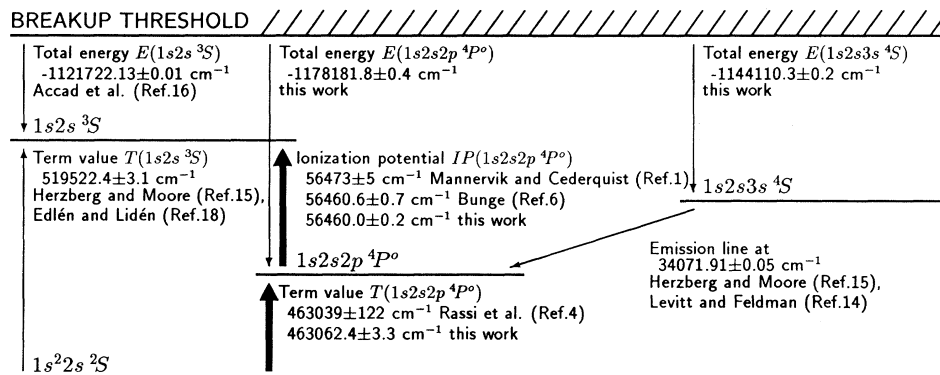


FIG. 1. The schematic diagram (not to scale) for the term energies, ionization potentials, and term values of neutral lithium. The total term energy of $1s2s2p\ ^4P^\circ$ can be obtained by direct calculation or by combining the total energy of $1s2s3s\ ^4S$ with the transition energy of $1s2s2p\ ^4P^\circ - 1s2s3s\ ^4S$. If we use the $1s2s2p\ ^4P^\circ$ and $1s2s3s\ ^4S$ energies from this work, the transition line would be $34071.5(6)\text{ cm}^{-1}$. The ionization potentials are given experimentally by Mannervik and Cederquist (Ref. [1]) and calculated by Bunge (for the $J=3/2$ level, Ref. [6]) and by the present authors. The term values of $1s2s2p\ ^4P^\circ$ are established from the ejected-electron spectrum by Rassi *et al.* (Ref. [4]) and from Eq. (13) with the ionization potential obtained in this work.

Eqs. (11) and (12) shows the consistency of our calculation. We conclude the value $V_{IP}(1s2s2p^4P^{\circ}) = 56460.0(2) \text{ cm}^{-1}$, including the Lamb-shift correction [17], from Eq. (12) because of its smaller uncertainty.

In Fig. 1, we compare the ionization potentials of $1s2s2p^4P^{\circ}$ from different approaches. The experimental value $56473(5) \text{ cm}^{-1}$ is deduced from spectroscopic data by Mannervik and Cederquist [1] using quantum-defect analysis. The value $56460.6(7) \text{ cm}^{-1}$ is calculated for the $J=3/2$ level by Bunge [6] using Eq. (12) with $\nu=34072.9 \text{ cm}^{-1}$. In that work, only nonrelativistic energies are considered. Replaced by the value [14,15] $\nu=34071.91(5) \text{ cm}^{-1}$ between centers of gravity of $1s2s2p^4P^{\circ}$ and $1s2s3s^4S$, it becomes $56459.6(7) \text{ cm}^{-1}$. Based on the results of Accad *et al.* [16] and the present calculation, the mass-polarization corrections for $1s2s^3S$ and $1s2s3s^4S$ are 0.30 and 0.33 cm^{-1} , respectively, and the relativistic corrections for these two terms are -135.21 and -136.26 cm^{-1} , respectively. The net contribution from the mass-polarization, relativistic, and Lamb-shift corrections [17] to $V_{IP}(1s2s2p^4P^{\circ})$ as given by Eq. (12) is 0.92 cm^{-1} . These additional corrections would bring Bunge's value to $56460.5(7) \text{ cm}^{-1}$, which is to be compared with our value $56460.0(2) \text{ cm}^{-1}$. The

0.5-cm^{-1} difference between the corrected Bunge's value and that of this work comes from Bunge's lower estimate for the nonrelativistic term energy of $1s2s3s^4S$. The disagreement between theory and experiment still remains. The discrepancy, 13 cm^{-1} , is too large to be explained as the truncation error of the theoretical result arising from the finite number of basis functions used in the calculation. Mannervik and Cederquist [1] obtained the ionization potential $V_{IP}(1s2s2p^4P^{\circ})$ by presenting a quantum-defect diagram with three series limits, 56490 , 56473 , and 56460 cm^{-1} . Our results favor the value 56460 cm^{-1} . It appears that further analysis is needed.

The relative term value $T(1s2s2p^4P^{\circ})$ to the ground state $1s^22s^2S$ can then be determined by

$$T(1s2s2p^4P^{\circ}) = T(1s2s^3S) - V_{IP}(1s2s2p^4P^{\circ}) \quad (13)$$

with the relative term value $T(1s2s^3S)$ established experimentally by

$$\begin{aligned} T(1s2s^3S) &= V_{IP}(1s^22s^2S) + V_{IP}(1s^21S) - V_{IP}(1s2s^3S) \\ &= 519522.4(3.1) \text{ cm}^{-1}, \end{aligned} \quad (14)$$

where $V_{IP}(1s^22s^2S) = 43487.19(2) \text{ cm}^{-1}$ by Edlén and Lidén [18], $V_{IP}(1s^21S) = 610079.4(3.0) \text{ cm}^{-1}$ and

TABLE II. The nonrelativistic energy upper bound (in a.u.) of $1s2s3s^4S$ for neutral lithium. Here W is the maximum allowed sum of the powers, $m+n+k$, and N is the number of selected radial terms for each partial wave; α , β , and γ are the optimized nonlinear parameters, and ΔE is the contribution by adding the partial wave to the trial wave function.

Partial wave	Angular coupling	W	N	α	β	γ	ΔE
Group I							
1	$[(s,s)^3S,s]$	6	48	2.3250	1.6250	0.3800	-5.20447230
2	$[(s,s)^3S,s]$	4	32	2.0600	1.0938	0.6300	-0.00001303
3	$[(s,p)^3P,p]$	7	45	3.1263	1.4175	0.8872	-0.00685721
4	$[(p,p)^3S,s]$	7	31	2.7000	2.5937	0.5850	-0.00116168
5	$[(p,s)^3P,p]$	7	39	1.3154	2.7056	0.7375	-0.00003533
6	$[(s,d)^3D,d]$	9	20	2.9469	1.2350	1.1475	-0.00002785
7	$[(d,d)^3S,s]$	9	26	4.3181	3.4543	0.3924	-0.00007760
8	$[(p,d)^3P,p]$	9	31	3.4650	2.2425	0.6000	-0.00006377
9	$[(p,p)^3D,d]$	8	20	2.8500	1.1250	1.0455	-0.00000018
10	$[(f,f)^3S,s]$	11	16	4.7381	4.8750	0.3780	-0.00001111
11	$[(s,f)^3F,f]$	11	16	2.5625	1.2600	1.1610	-0.00000486
12	$[(g,g)^3S,s]$	13	13	5.4050	5.0625	0.6000	-0.00000225
13	$[(s,g)^3G,g]$	13	8	2.9900	1.5000	1.5750	-0.00000118
14	$[(h,h)^3S,s]$	13	13	5.6478	6.1215	0.3150	-0.00000062
15	$[(s,h)^3H,h]$	13	13	3.0000	1.7425	1.6500	-0.00000031
16	$[(i,i)^3S,s]$	15	13	6.4050	6.3000	0.3000	-0.00000021
17	$[(s,i)^3I,i]$	17	13	2.8000	1.5000	1.3000	-0.00000010
18	$[(k,k)^3S,s]$	17	13	6.8000	6.5000	0.4000	-0.00000008
Group II							
19	$[(s,s)^3S,s]$	13	22	6.1000	3.7625	0.6000	-0.00000218
20	$[(s,s)^3S,s]$	4	10	3.0750	1.4625	1.0000	-0.00000029
21	$[(s,s)^3S,s]$	4	22	3.3863	1.9168	0.8550	-0.00000007
22	$[(p,p)^3S,s]$	12	22	5.8750	5.3375	0.4725	-0.00000462
23	$[(s,p)^3P,p]$	6	22	1.1685	3.1500	3.7925	-0.00000013
24	$[(d,d)^3S,s]$	13	20	5.1750	4.3700	0.5850	-0.00000063
25	$[(d,d)^3S,s]$	10	43	2.1591	1.3325	2.3704	-0.00000038
Total			571				-5.212738

TABLE III. The nonrelativistic energy upper bound (in a.u.) of $1s2s2p^4P^\circ$ for neutral lithium. Here W is the maximum allowed sum of the powers, $m+n+k$, and N is the number of selected radial terms for each partial wave; α , β , and γ are the optimized non-linear parameters, and ΔE is the contribution by adding the partial wave to the trial wave function.

Partial wave	Angular coupling	W	N	α	β	γ	ΔE
Group I							
1	$[(s,s)^3S,p]$	11	131	3.8745	1.5110	1.9373	-5.360 583 60
2	$[(s,p)^3P,s]$	4	14	3.0030	0.9332	1.0660	-0.000 076 36
3	$[(s,p)^3P,d]$	11	151	2.1450	1.6500	1.7100	-0.006 201 40
4	$[(p,d)^3P,s]$	6	16	2.9880	3.5438	0.7108	-0.000 016 07
5	$[(p,p)^3S,p]$	8	30	3.6300	2.7830	0.9801	-0.000 760 89
6	$[(p,p)^3P,p]$	6	8	2.0250	1.3860	1.4190	-0.000 001 65
7	$[(p,p)^3D,p]$	6	5	2.3100	2.8067	1.2870	-0.000 000 17
8	$[(s,d)^3D,f]$	10	23	3.0000	1.9562	1.7364	-0.000 129 32
9	$[(d,f)^3P,s]$	10	50	4.0590	4.5980	0.6688	-0.000 086 83
10	$[(d,d)^3S,p]$	10	16	4.0000	3.4650	0.8978	-0.000 063 91
11	$[(p,d)^3P,d]$	8	16	3.1500	2.2000	1.4108	-0.000 011 48
12	$[(s,f)^3F,g]$	10	16	2.8500	2.1632	1.9500	-0.000 024 77
13	$[(f,g)^3P,s]$	10	15	4.5100	4.6200	0.9975	-0.000 006 95
14	$[(f,f)^3S,p]$	10	8	3.9600	4.7334	0.8400	-0.000 008 41
15	$[(p,p)^3D,d]$	8	11	3.8500	1.6200	1.9200	-0.000 005 16
16	$[(p,d)^3F,g]$	10	2	0.9500	4.9500	3.2340	-0.000 000 21
17	$[(d,f)^3P,d]$	10	1	4.5000	2.7600	1.1200	-0.000 000 45
18	$[(s,g)^3G,h]$	12	9	2.9250	2.4200	2.0625	-0.000 005 59
19	$[(g,h)^3P,s]$	12	11	5.5000	4.9020	0.9100	-0.000 001 75
20	$[(g,g)^3S,p]$	12	6	5.1600	4.6200	0.8550	-0.000 001 78
21	$[(s,h)^3H,i]$	14	7	3.0000	2.2000	2.1600	-0.000 001 67
22	$[(h,i)^3P,s]$	14	9	6.4000	5.2500	1.0800	-0.000 000 57
23	$[(h,h)^3S,p]$	14	2	5.9400	5.9800	0.8550	-0.000 000 35
24	$[(s,i)^3I,k]$	16	6	2.9925	2.5410	2.6173	-0.000 000 59
25	$[(i,k)^3P,s]$	16	7	6.3250	4.5000	1.2000	-0.000 000 18
26	$[(i,i)^3S,p]$	16	1	6.1712	6.1951	0.8494	-0.000 000 10
Group II							
27	$[(s,s)^3S,p]$	19	63	9.0000	2.3000	5.2465	-0.000 002 28
28	$[(s,p)^3P,d]$	19	108	2.0453	7.2518	7.0166	-0.000 004 82
29	$[(p,p)^3S,p]$	19	70	7.7500	5.2875	1.9250	-0.000 001 28
Total			812				-5.367 999

TABLE IV. Term energies (in a.u.) of $1s2s2p^4P^\circ$ and $1s2s3s^4S$ for neutral lithium.

	$1s2s2p^4P^\circ$		$1s2s3s^4S$	
	This work	Bunge and Bunge ^a	This work	Bunge ^b
Nonrelativistic energy				
E_{calc}	-5.367 999	-5.367 948	-5.212 738	-5.212 727
$E_{\text{estimated}}$	-5.368 001(2)	-5.367 992(37)	-5.212 739(1)	-5.212 741(3)
Mass-polarization and relativistic corrections				
$\langle H_1 \rangle$	-0.000 015 4		0.000 001 5	
$\langle H_2 + H_3 \rangle$	-0.000 604 0		-0.000 621 0	
$\langle H_4 \rangle$	0.000 009 2		0.000 000 1	
E_{total}	-5.368 611(2)		-5.213 358(1)	

^aReference [5].

^bReference [6].

TABLE V. Term energies (in a.u.) of $1s2s2p^4P^\circ$ for Li-like ions, $Z=4-9$.

	${}^9\text{Be}^+$	${}^{11}\text{B}^{2+}$	${}^{12}\text{C}^{3+}$	${}^{14}\text{N}^{4+}$	${}^{16}\text{O}^{5+}$	${}^{19}\text{F}^{6+}$
Nonrelativistic energy						
E_{calc}	-10.066 638	-16.267 594	-23.969 537	-33.171 990	-43.874 745	-56.077 688
$E_{\text{estimated}}$	-10.066 640(2)	-16.267 596(2)	-23.969 539(2)	-33.171 992(2)	-43.874 747(2)	-56.077 690(2)
Mass-polarization and relativistic corrections						
$\langle H_1 \rangle$	-0.000 032 2	-0.000 050 8	-0.000 076 0	-0.000 096 5	-0.000 117 2	-0.000 130 8
$\langle H_2 + H_3 \rangle$	-0.002 007 0	-0.005 078 5	-0.010 804 4	-0.020 410 9	-0.035 352 5	-0.057 314 8
$\langle H_4 \rangle$	0.000 034 5	0.000 084 9	0.000 169 0	0.000 295 0	0.000 471 4	0.000 706 6
E_{total}	-10.068 645(2)	-16.272 640(2)	-23.980 250(2)	-33.192 204(2)	-43.909 745(2)	-56.134 429(2)

$V_{\text{IP}}(1s2s^3S)=134\,044.19(10)\text{ cm}^{-1}$ by Herzberg and Moore [15]. The value $V_{\text{IP}}(1s^2^1S)=610\,079.6(2)\text{ cm}^{-1}$ was used by Bunge [6] referring to the value $610\,079.61\text{ cm}^{-1}$ calculated by Pekeris [19]. This value was also quoted later by Mannervik and Cederquist [1] and by Mannervik [3]. However, we retain the Herzberg-Moore value. From Eq. (13) we obtain the value $T(1s2s2p^4P^\circ)=463\,062.4(3.3)\text{ cm}^{-1}$, which is consistent with the value of $463\,039(122)\text{ cm}^{-1}$ given by Rassi *et al.* [4] from the ejected-electron spectrum. The large uncertainty, 3.3 cm^{-1} , in our value is primarily due to the uncertainty, 3 cm^{-1} , in $V_{\text{IP}}(1s^2^1S)$.

B. Be^+ up to F^{6+}

We have also calculated the term energy of $1s2s2p^4P^\circ$ for ions along the isoelectronic sequence. The trial wave function is composed of 834 linear parameters in 27 partial waves with the nonlinear parameters optimized for each Z . The results are presented in Table V. The absolute values of $\langle H_2 + H_3 \rangle$ and of $\langle H_4 \rangle$ are smaller than the earlier results by Chung [8]. This difference caused by the larger set of basis functions in the present calculation becomes larger as Z increases. In the case of F^{6+} , it is 38×10^{-6} a.u. for the absolute value of $\langle H_2 + H_3 \rangle$ and 4×10^{-6} a.u. for that of $\langle H_4 \rangle$. High-order relativistic corrections, which are an order of $(Z\alpha)^2$ smaller than the first-order correction, could be comparable to the mass-

TABLE VI. Relative term value (in 10^3 cm^{-1}) of $1s2s2p^4P^\circ$ to the ground state $1s^2s^2S$ for Li-like ions, $Z=4-9$. The uncertainties in this work do not include higher-order effects discussed in Sec. III B. The values and the undetermined constants X , B , and R in the column headed Kelly are quoted directly from Ref. [20].

	This work	Kelly
${}^9\text{Be}^+$	934.511 6(4)	1060.0
${}^{11}\text{B}^{2+}$	1570.888 6(4)	
${}^{12}\text{C}^{3+}$	2372.015 3(4)	$2377.1 + X$
${}^{14}\text{N}^{4+}$	3338.150 8(4)	$3344.07 + B$
${}^{16}\text{O}^{5+}$	4469.318 7(4)	$4670.0 + R$
${}^{19}\text{F}^{6+}$	5765.753 1(4)	

polarization correction when $Z > 9$. The intermediate coupling may also contribute to a shift in the term energy of high- Z ions.

To determine the relative term value of $1s2s2p^4P^\circ$ above the ground state $1s^2s^2S$ for these ions, we cannot use Eq. (13) because an accurate $T(1s2s^3S)$ is difficult to derive from experiment for these ions. Instead, we consider the scheme given by

$$T(1s2s2p^4P^\circ) = V_{\text{IP}}(1s^2s^2S) + V_{\text{IP}}(1s^2^1S) - E(1s^2S) + E(1s2s2p^4P^\circ), \quad (15)$$

with the one-electron energy in the Dirac theory given by

$$E(1s^2S) = c^2 \left[\left(1 + \frac{Z^2\alpha^2}{1-Z^2\alpha^2} \right)^{-1/2} - 1 \right]. \quad (16)$$

The ionization potentials (IP's) are taken from Kelly's compilation [20]. The results are listed in Table VI. The Lamb-shift corrections to $1s^2S$ and $1s2s2p^4P^\circ$ are about the same order of magnitude [17]. Hence Eq. (15) has the advantage that it reduces the error of ignoring the Lamb-shift correction. This error, which we do not include in Table VI, is less than 10 ppm of the relative term value for each ion. Another source of errors may come from the uncertainty of the ionization potentials in Kelly's compilation [20]. In Table VI, we also list the relative term values given by Kelly [20], which shows the difficulty in determining the position of the quartet system in current compilation works.

IV. CONCLUSIONS

We have attained an accuracy of 10^{-6} a.u. in solving the nonrelativistic eigenvalue equation for the lowest quartet term, $1s2s2p^4P^\circ$, of three-electron systems. To obtain such an accuracy, we tried to saturate the radial basis functions and considered all possible angular correlations with l up to 7 for the orbital angular momentum of individual electrons. Our results showed that relativistic effects are important in making an accurate compar-

ison with experimental observations for neutral lithium. The relative term values of $1s2s2p\ ^4P^\circ$ are determined for the lithium isoelectronic sequence up to $Z=9$. Our results will help spectroscopic compilations in reducing the uncertainty in connecting the quartet system to the doublet energy spectrum.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Council of the Republic of China and by the U.S. National Science Foundation under Grant No. PHY90-20543.

*Present address: Department of Physics, North Carolina State University, Raleigh, NC 27695-8202.

- [1] S. Mannervik and H. Cederquist, *Phys. Scr.* **27**, 175 (1983), and references therein.
- [2] H. G. Berry, *Phys. Scr.* **12**, 5 (1975).
- [3] S. Mannervik, *Phys. Scr.* **40**, 28 (1989).
- [4] D. Rassi, V. Pejčev, and K. J. Ross, *J. Phys. B* **10**, 3535 (1977).
- [5] C. F. Bunge and A. V. Bunge, *Phys. Rev. A* **17**, 816 (1978); **17**, 822 (1978).
- [6] C. F. Bunge, *Phys. Rev. A* **23**, 2060 (1981).
- [7] H. G. Berry, E. H. Pinnington, and J. L. Subtil, *J. Opt. Soc. Am.* **62**, 767 (1972).
- [8] K. T. Chung, *Phys. Rev. A* **29**, 682 (1984).
- [9] H. Bethe and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957), p. 181.
- [10] K. T. Chung and B. F. Davis, in *Autoionization: Recent Developments and Applications*, edited by A. Temkin (Plenum, New York, 1985).
- [11] K. T. Chung, *Phys. Rev. A* **29**, 439 (1984).
- [12] T. Ahlenius and S. Larsson, *Phys. Rev. A* **18**, 1329 (1978).
- [13] C. Froese Fischer, *Phys. Rev. A* **41**, 3481 (1990).
- [14] P. Feldman, M. Levitt, and R. Novick, *Phys. Rev. Lett.* **21**, 331 (1968); M. Levitt and P. D. Feldman, *Phys. Rev.* **180**, 48 (1969).
- [15] G. Herzberg and H. R. Moore, *Can. J. Phys.* **37**, 1293 (1959).
- [16] Y. Accad, C. L. Pekeris, and B. Schiff, *Phys. Rev. A* **4**, 516 (1971).
- [17] C.-T. Chen and K.-N. Huang (unpublished).
- [18] B. Edlén and K. Lidén, *Phys. Rev.* **75**, L890 (1949).
- [19] C. L. Pekeris, *Phys. Rev.* **126**, 143 (1962).
- [20] R. L. Kelly, *J. Phys. Chem. Ref. Data* **16**, Suppl. 1 (1987).