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Calculations of high Rydberg states for the lithium atom

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We present calculations of high Rydberg states for the lithium atom by two different theoretical methods. The first method is based on the *R*-matrix theory to obtain the energy levels and the quantum defects for the $1s^2nd\ ^2D$ and $1s^2nf\ ^2F$ states and their adjacent continuum states. Then the quantum defect functions of the two channels are obtained which vary smoothly with energy based on quantum defect theory. The second method is based on the full core plus correlation method. Our results are compared with data in the literatures; especially the results of the *R*-matrix method are in excellent agreement with microwave measurements for the lithium atom.

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I. INTRODUCTION

In recent years, some advances have been made in theoretical and experimental research into the high-*l* Rydberg states of the lithium atom [1,2]. The Rydberg states of lithium consist of a two-electron core and a distant Rydberg electron, and are nearly hydrogenic. However, the more subtle features of their spectra deviate from the hydrogenic features. Such differences between the alkali-metal and hydrogenic spectra arise from the interaction between the excited electron and the alkali-metal core instead of a point Coulomb charge. The most obvious effect is the depression of the energies of the lower-*l* states, which arises from the polarization and penetration of the core by the Rydberg electron [3]. Cooke *et al.* [4] used a laser-excitation, optical-detection scheme to observe microwave transitions from the *nd* to the *nf* level for the lithium atom with principal quantum number *n* from 7 to 11. They obtained accurate transition frequencies and fine-structure intervals of the *d*,*f* states. In Ref. [5], there are also some experimental spectroscopic results of the energy levels for *nd* and *nf* Rydberg states with *n* from 7 to 9. Jaffé and Reinhardt [6] used a core potential constructed from a static Hartree-Fock term, a semiclassical exchange approximation, and a polarization term to calculate quantum defects. Using an adapted pseudopotential, they numerically integrated the Schrödinger equation to calculate quantum defects for the lithium atom. Using these reported quantum defects, Cooke *et al.* [4] have also calculated the *d*-*f* intervals of the lithium atom with *n* from 7 to 11, within about 15% with results in comparison with their microwave measurements. Here we present our calculations of high Rydberg states for the lithium atom by two different theoretical methods; especially the results of the *R*-matrix method are in excellent agreement with the microwave measurements within −0.5%.

Configuration-interaction (CI) theory and variational method have been very successful for low excited states of atomic and molecular systems. However, in the calculation of high Rydberg states, one encounters great difficulties. Countless Rydberg states and continuum states near the threshold must be taken into account in CI and variational calculations, and the problem of convergence induced by rounding errors is a formidable task. Therefore it is difficult to obtain an accurate energy level of a high Rydberg state with a traditional variational method. Quantum defect theory (QDT) [7–12] has been developed and applied successfully in the field of spectroscopy and collision phenomena in atomic and molecular systems. In the framework of QDT, the infinite excited states are classified as channels; e.g., in the ^2D channel of the lithium atom, there are infinite bound $1s^2nd\ ^2D$ excited states $(3 \leqslant n \leqslant \infty)$ and adjacent $1s^2\varepsilon d\ ^2D$ continuum states. In the energy range studied in this work, only the single-channel quantum defect theory is needed to deal with the energy levels of the Rydberg states for the lithium atom. The physical parameters of the channel (e.g., the quantum defect μ) are smooth functions of the energy, so Rydberg energy levels can be calculated through the quantum defect function (QDF) which depends weakly on the energy. In this work, QDFs of Rydberg states for the lithium atom are obtained by two different theoretical methods.

The first method is based on *R*-matrix theory [13–18]. In this method, the interactions of the scattered electron and the target (i.e., the electron-electron correlations) are considered in detail by coupling the target-state wave functions with the scattered electron wave functions. The energy levels and the quantum defects for the $1s^2nd\ ^2D$ and $1s^2nf\ ^2F$ states and their adjacent continuum states are calculated by *R*-matrix theory. Then the QDFs of the two channels are obtained, which vary smoothly with energy based on the QDT. The traditional variational method has an advantage in the calculation of low excited states, so our second method is based on the full core plus correlation (FCPC) method [19–26]. The quantum defects of the $1s^25l$ $(l=d,f)$ states are calculated, which will calibrate previous QDFs. We will also make calibrations using the experimental data [5]. Different sets of QDFs can be used to calculate energy levels of all the Rydberg states. To compare with experimental data in the literature, intervals of the *nd* and *nf* levels $(n=7-11)$ for the lithium atom are calculated. The *nd*-*nf* intervals based on the QDFs of the *R*-matrix method, the FCPC method, and the "experimental-calibration" method are in agreement with microwave measurements [4] within −0.5%, −1%, and 2.3%, respectively; we will discuss this in detail later. It is indicated that the combination of the *R*-matrix method and quantum defect theory is a very efficient method to study high Rydberg states of the lithium atom.

II. THEORY

Detailed descriptions of *R*-matrix theory were given in Refs. [13–18]; only a brief outline of this method will be given here. In *R*-matrix theory, a value a of the radial variable r is chosen such that the exchange interactions between the scattered electron and the target electrons are negligible for $r \geqslant a$, where a is the *R*-matrix box radius. Within the reaction zone ($r \leqslant a$), the interactions between the scattered electron and target electrons involve static electron-electron screening, dynamic polarizations, etc. It is a many-body problem, which is solved variationally for the whole system to obtain the logarithmic derivative boundary matrix $R(E)$. Outside the reaction zone ($r \geqslant a$), the scattered electron "feels" mainly the Coulomb potential. The present *R*-matrix code allows us to take the long-range static polarization potentials into account. The excited electron moves in the long-range multipole potential of the $(N-1)$-electron core, whose wave function is obtained by matching the boundary conditions. Therefore, the wave functions ψ_k of the energy eigenstates for the system can be expanded as

$$\psi_k = A \sum_{ij} a_{ijk} \Phi_i u_{ij}(r) + \sum_j b_{jk} \varphi_j, \tag{1}$$

where A is the antisymmetrization operator which accounts for electron exchange between the target electrons and the scattered electron, Φ_i are the channel functions obtained by coupling the target-state wave functions with the angular and spin functions of the scattered electron, the continuum orbitals u_{ij} represent the motion of the scattered electron, and φ_j are formed from the bound orbitals to ensure completeness and to include the short-range correlation effects.

We can easily perform an eigenchannel treatment of *R*-matrix theory [27–29]. We start with the logarithmic derivative boundary matrix $R(E)$, the physical eigenchannel parameters (eigen quantum defects μ and orthogonal transformation matrix U_{ia}), and the corresponding eigenchannel wave functions are calculated directly. Based on the compact set of eigenchannel parameters, atomic perturbed discrete Rydberg series, autoionizing states, and their adjacent continuum can be treated in an analytical unified manner without any numerical integration outside the *R*-matrix box. The detailed description of the eigenchannel treatment of *R*-matrix theory was given in Ref. [28].

According to QDT, the quantum defect μ should be a smooth function of the energy, and can be expressed in the following form:

$$\mu(\varepsilon) = \mu_0 + \mu_0' \varepsilon + \mu_0'' \varepsilon^2, \tag{2}$$

where ε is the energy relative to the first ionization threshold in a.u. The energy levels and the quantum defects for the $1s^2nd\ ^2D$ and $1s^2nf\ ^2F$ states and their adjacent continuum states are calculated by *R*-matrix theory. Then the QDFs of the two channels are obtained, which vary smoothly with the energy based on Eq. (2).

For the lithium atom, the quantum defect μ can be determined from the formula

$$\mu = n - \frac{1}{\sqrt{-2\varepsilon}}, \tag{3}$$

where n is the principal quantum number. The second term on the right-hand side of Eq. (3) denotes the effective principal quantum number. Combining Eqs. (2) and (3), we can construct an equation to calculate all the energy levels of $1s^2nd$ and $1s^2nf$ Rydberg states for the lithium atom. This equation is in the following form:

$$\varepsilon + \frac{1}{2[n - \mu(\varepsilon)]^2} = 0. \tag{4}$$

The advantage of *R*-matrix theory is that the whole channel can be treated in an analytical unified manner and it gives the quantum defect the tendency to vary smoothly with the energy; the advantage of the traditional variational method is that it can give accurate results for the ground state and low excited states of atomic systems. The quantum defects of $1s^25l$ ($l=d,f$) states for the lithium atom are calculated with the FCPC method, which will calibrate the previous QDFs; namely, using the difference of the quantum defect of the $1s^25l$ ($l=d,f$) states between the *R*-matrix method and the FCPC method to calibrate the coefficient μ_0 in Eq. (2). In this work, the FCPC method is used to construct trial wave functions of $1s^2nl$ ($l=d,f$) low excited states for the lithium atom. This method has been given in detail by Chung [19], and here we only give it a brief description. The nonrelativistic Hamiltonian H_0 and the perturbation operators H_1 (relativistic correction to the kinetic energy), H_2 (Darwin term), H_3 (electron-electron contact term), H_4 (mass polarization), and H_5 (orbit-orbit interaction) are the same as those presented by Chung, and they will not be repeated here. These perturbation operators are used for the calculation of relativistic and mass-polarization corrections. The total energy $E_{\text{tot}}(1s^2nl)$ can be obtained by the variational principle with a trial wave function that is constructed with the FCPC method in the *LS* coupling scheme as follows:

$$\Psi(1,2,3) = A\left[\Phi_{1s^2\ ^1S}(1,2) \sum_i d_i r_3^i \exp(-\beta r_3) Y_{l(i)}(3) \chi(3) + \sum_j C_j \Phi_{n(j),l(j)}(1,2,3)\right], \tag{5}$$

where A is an antisymmerization operator. $\Phi_{1s^2\ ^1S}(1,2)$ is a predetermined $1s^2$ core wave function, which is represented by a CI basis set,

$$\Phi_{1s^2\ ^1S}(1,2) = A \sum_{kn,l} C_{knl} r_1^k r_2^n \exp(-\beta_l r_1 - \rho_l r_2) Y_l(1,2) \chi(1,2). \tag{6}$$

The angular part is

$$Y_l(1,2) = \sum_m \langle l,m,l,-m | 0,0 \rangle Y_{lm}(\theta_1,\varphi_1) Y_{l-m}(\theta_2,\varphi_2). \tag{7}$$

In Eq. (6), $\chi(1,2)$ is a two-electron singlet spin function. The linear and nonlinear parameters in Eq. (6) are determined by

TABLE I. The quantum defects of $1s^2nd$ ($n=3-5$) and $1s^2nf$ ($n=4-5$) states for the lithium atom of different theories and experiment.

	$1s^23d$	$1s^24d$	$1s^25d$	$1s^24f$	$1s^25f$
R matrix	0.001388	0.001554	0.001630	0.000112	0.000125
FCPC	0.001489	0.001703	0.001829	0.000253	0.000284
Expt.[a]	0.001475	0.001675	0.001766	0.000227	0.000270

[a] Reference [5].

optimizing the energy of the core; furthermore $E_{\text{tot}}(1s^2)$ can be calculated [19]. The factor multiplied by $\Phi_{1s^2\,{}^1S}(1,2)$ is a linear combination of the Slater orbitals for the valance electron. The second term on the right-hand side of Eq. (5) describes the inner-shell electron-electron correlation, dipole and quadrupole polarization effects of the core, etc., in the three-electron system.

In the FCPC method, the orbital energy ε_{nl} can be calculated by subtracting the core energy from the energy of the three-electron system,

$$\varepsilon_{nl} = E_{\text{tot}}(1s^2nl) - E_{\text{tot}}(1s^2), \tag{8}$$

and the quantum defect μ can be calculated through Eq. (3).

For the $1s^2nl$ state, the fine-structure intervals come from the spin-orbit and spin–other-orbit interactions. The operators are

$$H_{\text{SO}} = \frac{3}{2\alpha^2}\sum_{i=1}^{3}\frac{\vec{l}_i\cdot\vec{s}_i}{r_i^3}, \tag{9}$$

$$H_{\text{SOO}} = -\frac{1}{2\alpha^2}\sum_{i\neq j}^{3}\left[\frac{1}{r_{ij}^3}(\vec{r}_i-\vec{r}_j)\times\vec{p}_i\right]\cdot(\vec{s}_i+2\vec{s}_j), \tag{10}$$

where α is the fine-structure constant. Then the total fine-structure intervals for the $1s^2nl$ state are defined as

$$\Delta E_{\text{FS}}^J = \langle 1s^2nl\,^2L_J|H_{\text{SO}}|1s^2nl\,^2L_J\rangle + \langle 1s^2nl\,^2L_J|H_{\text{SOO}}|1s^2nl\,^2L_J\rangle. \tag{11}$$

III. RESULTS AND DISCUSSION

For the *R*-matrix calculations of Li, we use the following set of basis orbitals calculated from the CIV3 code [30]. The target set is $1s$, $2s$, $2p$, $3s$, $3p$, $3d$, $4s$, $4p$, $4d$, $4f$, $\overline{5s}$, $\overline{5p}$, $\overline{5d}$, $\overline{5f}$, where nl ($n\leqslant 4, l\leqslant 3$) are spectroscopy orbitals, $\overline{5l}$ ($l\leqslant 3$) are polarized pseudo-orbitals including static polarization effects [29–32]. In order to obtain accurate results, we choose 27 target functions carefully, and take into account the long-range multipole potentials sufficiently. Then the energy levels and the quantum defects for the $1s^2nd\,^2D$ and $1s^2nf\,^2F$ states and their adjacent continuum states are calculated. Table I lists the quantum defects of $1s^2nd$ ($n=3-5$) and $1s^2nf$ ($n=4-5$) states by *R*-matrix calculations. In Table I the quantum defects of these states calculated by the FCPC method [19] and results derived from experimental data [5] are also listed and compared with *R*-matrix results. The experimental quantum defects are derived from the differences between the energy levels of $1s^2nl$ states and the first ionization threshold. Such differences may lose some significant figures so as to influence the accuracy of the quantum defects, which will be discussed later. Note that the reduced Rydberg constant of Li of 109 728.73 cm^{-1} is adopted in our calculations. In the FCPC calculations, various perturbation operators are used for the calculation of relativistic and mass-polarization corrections. These perturbation operators are considered for both the $1s^2$ core and the $1s^2nl$ state. For example, our calculated contribution from various perturbation operators to the total energy of the $1s^2$ core is -599.68μ a.u. and of the $1s^23d$ state is -599.88μ a.u. The contributions of these perturbation operators to the total energies of other $1s^2nl$ states are similar to those of the $1s^23d$ state; therefore we will not list them here. For the FCPC

TABLE II. Intervals calculated from different theoretical and experimental QDFs and the center-of-gravity results from Table IV of Ref. [4] of the *nd* and *nf* levels ($n=7-11$) for the lithium atom, and the data in parentheses are the relative differences between the present results and microwave measurements [4] (in GHz). (*LS* coupling scheme is used in our calculations.)

n	*R*-matrix QDF	FCPC QDF	"Expt." QDF[a]	Expt.[b]	Expt.[c]	Other theory[d]
7	30.0753 (−0.44%)	30.8451 (2.11%)	29.9043 (−1.01%)	30.2088	31.8 (5%)	35.5 (17.5%)
8	20.3473 (−0.36%)	20.8628 (2.17%)	20.2326 (−0.92%)	20.4199	23.7 (16%)	23.8 (16.6%)
9	14.3873 (−0.28%)	14.7493 (2.23%)	14.3067 (−0.84%)	14.4275	16.2 (12%)	16.7 (15.8%)
10	10.5391 (−0.24%)	10.8029 (2.26%)	10.4803 (−0.79%)	10.5640		12.2 (15.5%)
11	7.947 (−0.16%)	8.145 (2.32%)	7.902 (−0.73%)	7.960		9.14 (14.8%)

[a] Calculated from quantum defects of $1s^25l$ ($l=d,f$) states derived from the experimental data [5].

[b] Center-of-gravity results calculated from transition frequencies and fine-structure intervals of microwave measurements [4].

[c] Center-of-gravity results calculated from the differences between the energy levels of the *nd* and *nf* states of the experiment [5].

[d] Center-of-gravity results calculated from Ref. [6].

TABLE III. Theoretical and experimental fine-structure intervals $\Delta E = E_{5/2} - E_{3/2}$ for $1s^2nd$ $(n=3-5)$ states and $\Delta E = E_{7/2} - E_{5/2}$ for $1s^2nf$ $(n=4-5)$ states of the lithium atom (in cm^{-1}).

State	FCPC	Other theory[a]	Expt.[b]	Expt.[c]	Moore[d]
$1s^23d$	0.03616	0.03607	0.039	0.03608	0.04
$1s^24d$	0.01518	0.01522	0.015	0.01519	0.02
$1s^25d$	0.00784	0.00779	0.008	0.00776	0.01
$1s^24f$	0.00761	0.00761			
$1s^25f$	0.00390	0.00390			

[a] Calculated from hydrogenic theory (Ref. [3]).
[b] Reference [5].
[c] Reference [34].
[d] Reference [35].

method, based on Eq. (5), $E_{\mathrm{tot}}(1s^2nl)$ can be defined as

$$E_{\mathrm{tot}}(1s^2nl) = \overline{E}_{\mathrm{tot}}(1s^2) + \overline{\varepsilon_{nl}}, \tag{12}$$

where $\overline{E}_{\mathrm{tot}}(1s^2)$ is the corresponding energy of the $1s^2$ core in the three-electron calculations, which may be different from $E_{\mathrm{tot}}(1s^2)$ in the Li^+ calculations,

$$\overline{E}_{\mathrm{tot}}(1s^2) = E_{\mathrm{tot}}(1s^2) + \delta \tag{13}$$

where δ is a negative difference due to the contribution of the trial three-electron wave function shown as the second term of the right-hand side of Eq. (5) because of three identical electron properties. Therefore the true orbital energy $\overline{\varepsilon_{nl}}$ should be expressed as

$$\overline{\varepsilon_{nl}} = \varepsilon_{nl} - \delta. \tag{14}$$

Although δ is only a tiny fraction in $\overline{E}_{\mathrm{tot}}(1s^2)$, it should be significant to $\overline{\varepsilon_{nl}}$ or ε_{nl} in Eq. (8). The true orbital energy $\overline{\varepsilon_{nl}}$ is higher than the orbital energy ε_{nl}. Thus, the FCPC quantum defects are overestimated and provide the upper limits of the quantum defects. The R-matrix method avoids the issue mentioned above and provides the lower limits of quantum defects.

Based on the R-matrix method, the QDFs of ${}^2D$ and ${}^2F$ channels are obtained through the quantum defects of the finite $1s^2nd\ {}^2D$ and $1s^2nf\ {}^2F$ bound states and phase shifts of the $1s^2\varepsilon d\ {}^2D$ and $1s^2\varepsilon f\ {}^2F$ continuum states, which vary smoothly with energy as follows:

$$\mu(\varepsilon;{}^2D) = 0.001\,783\,1 + 0.007\,958\,6\varepsilon + 0.016\,546\varepsilon^2, \tag{15}$$

$$\mu(\varepsilon;{}^2F) = 0.000\,148\,1 + 0.001\,170\varepsilon + 0.000\,778\,4\varepsilon^2. \tag{16}$$

The quantum defects of the $1s^25l(l=d,f)$ states calculated from the FCPC method are used to calibrate the above QDFs. The FCPC QDFs are

$$\mu(\varepsilon;{}^2D) = 0.001\,982\,1 + 0.007\,958\,6\varepsilon + 0.016\,546\varepsilon^2, \tag{17}$$

$$\mu(\varepsilon;{}^2F) = 0.000\,307\,1 + 0.001\,170\varepsilon + 0.000\,778\,4\varepsilon^2. \tag{18}$$

The quantum defects of $1s^25l$ $(l=d,f)$ states derived from the experimental data [5] are also used to calibrate R-matrix QDFs. The "experimental" QDFs are

$$\mu(\varepsilon;{}^2D) = 0.001\,919\,1 + 0.007\,958\,6\varepsilon + 0.016\,546\varepsilon^2, \tag{19}$$

$$\mu(\varepsilon;{}^2F) = 0.000\,293\,1 + 0.001\,170\varepsilon + 0.000\,778\,4\varepsilon^2. \tag{20}$$

In Table II the intervals of the nd and nf levels $(n=7-11)$ for the lithium atom are calculated by different sets of QDFs and compared with the center-of-gravity results listed in Ref. [4]. The center-of-gravity results derived from the differences between the experimental energy levels [5] are larger than microwave experimental results [4] by more than 5%. It should be very careful to take the differences between the energy levels because of significant figure losses. It is interesting to note that the intervals of the "experimental" QDF are less than the microwave data within about −1%. The "experimental" QDF provides better quantum defects in comparison with the quantum defects of the nd and nf levels $(n=7-9)$ derived directly from the differences between the energy levels and the first ionization

TABLE IV. Theoretical and experimental fine-structure intervals of $1s^2nl$ $(n=7-11, l=d,f)$ states for the lithium atom (in MHz). (LS coupling scheme is used in our calculations.)

	d splittings			*f* splittings		
n	This work	Other theory[a]	Expt.[b]	This work	Other theory[a]	Expt.[b]
7	85.14	85.18	84.87	42.58	42.59	41.99
8	57.02	57.07	56.97	28.53	28.53	28.05
9	40.04	40.08	40.04	20.04	20.04	19.96
10	29.18	29.22	28.60	14.61	14.61	13.60
11	21.92	21.95		10.97	10.98	

[a] Calculated from hydrogenic theory (Ref. [3]).
[b] Reference [4].

TABLE V. Theoretical and experimental transition frequencies between the nd and nf levels ($n=7-11$) for the lithium atom, and the data in parentheses are experimental data [4] (in MHz).

n	$d_{3/2}$-$f_{5/2}$		$d_{5/2}$-$f_{5/2}$		$d_{5/2}$-$f_{7/2}$	
7	30102.05	(30235.31)	30016.91	(30151.04)	30059.49	(30193.03)
8	20365.21	(20437.67)	20308.19	(20381.18)	20336.72	(20409.23)
9	14399.87	(14440.08)	14359.83	(14400.12)	14379.87	(14420.08)
10	10548.26	(10572.64)	10519.08	(10545.1)	10533.69	(10558.61)
11	7953.9		7932.0		7942.9	(7956.3)

threshold because of more significant figure losses as n increases. The quantum defects of the Rydberg d states calculated by FCPC QDF are overestimated, so the intervals of the FCPC QDF are a little larger than microwave experimental results within about 2.2%. In the FCPC calculations, most of the relativistic effects have been taken into account, giving very accurate results for energies of various levels. Other corrections like Lamb shift and retardation are omitted in our calculations. Bhatia and Drachman [33] have used third-order perturbation theory to calculate the effect of the Breit-Pauli relativistic interaction on the dipole polarizability of the Li^{+} core. In addition, the retardation (Casimir) corrections to singly excited $1s^2nl$ states of neutral lithium have been computed. These two corrections together bring theory and experiment [1,2] into almost perfect agreement, to just outside their combined errors. Addition of radiative (Lamb-shift) corrections produces essentially exact agreement. The energies of high Rydberg states calculated from FCPC QDF with inclusion of the contributions of these high-order corrections are helpful to obtain more accurate energies, which may improve the comparison with the experimental results. The intervals of the R-matrix QDFs are a little less than those of microwave experimental data within −0.5%. It is indicated that the present R-matrix QDF is the most effective method to calculate the intervals of energy levels of high Rydberg states for Li.

According to the theory of Condon [3], the product of fine-structure intervals and n^3 should be a constant. In practical calculations, this constant turns to be a fine-structure function varying smoothly with the energy. Using the previous FCPC wave functions, fine-structure intervals of $1s^2nd$ ($n=3-5$) and $1s^2nf$ ($n=4-5$) states are calculated and compared with other theoretical and experimental data in Table III. Our calculation results are in good agreement with the available data. Then the fine-structure functions of the $1s^2nd$ and $1s^2nf$ Rydberg series can be obtained based on FCPC results. In Table IV the calculated fine-structure intervals of $1s^2nl$ ($n=7-11, l=d,f$) states are compared with data in the literature. Our calculations are all between the intervals of hydrogenic theory [3] and experimental data [4]. In particular the calculated fine-structure intervals of $1s^2nf$ states agree with the intervals of hydrogenic theory very well. Note that the experimental fine-structure interval of the $1s^210f$ state is 13.60 MHz which might be a misprint. Table V lists the calculated transition frequencies between the nd and nf levels ($n=7-11$) of the lithium atom based on our results in Tables II and IV. Our calculated transition frequencies are in good agreement with the microwave measurements [4] within −0.5% which is consistent with the accuracy of Table II.

It is natural to consider whether the present approach is suitable for higher l quantum numbers. In our method, the quantum defect is the most important physical parameter used to calculate energies of Rydberg states. For Rydberg states of lithium with higher l quantum numbers, the spectra are almost hydrogenic; therefore the quantum defects of these states are very small. It is difficult to ensure enough significant figures in the calculation to obtain accurate quantum defects of higher l quantum numbers; therefore our method encounters great difficulties when extended to Rydberg states of lithium with higher l quantum numbers. Drachman and Bhatia [2] have used an effective potential method to calculate Rydberg levels of singly excited lithium with higher l ($l \geqslant 4$) quantum numbers; they also made high-order relativistic corrections [33], and their calculation results agree with experimental values very well [1]. The method of Drachman and Bhatia is the more effective method to calculate Rydberg levels of singly excited lithium with higher l ($l \geqslant 4$) quantum numbers.

In summary, the R-matrix method is effective for the calculation of high Rydberg states of lithium with lower l quantum numbers; especially the calculated nd-nf intervals by the R-matrix method are in excellent agreement with the microwave measurements within −0.5%. Although the present calculated quantum defects by the R-matrix method have not been converged absolutely yet, the differences of the quantum defects can be calculated precisely, with the evidence of the excellent agreement with "microwave measurements" for the nd-nf intervals. The subtle features of alkali-metal spectra deviate from the hydrogenic one, because of factors like the polarization and penetration of the core by the Rydberg electron, which can be described as a quantum defect. Therefore the topic of absolute convergence for the quantum defect by the R-matrix method deserves further study, which is beyond the scope of the present paper and will be reported in future.

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