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Resonance calculations of $d-f$ intervals for the lithium Rydberg states*

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By using the energies of the $1s^2nd$ (n=3–5) and $1s^2nf$ (n=4–6) states for a lithium atom, calculated with the full core plus correlation method, quantum defect functions are obtained which vary smoothly with energy based on quantum defect theory. Then these functions are separately used to construct a system equation to calculate the energies and quantum defects of the $1s^2nd$ and $1s^2nf$ (n=7–11) states for the lithium atom. Separations between the centres of gravity of the nd and nf levels (n=7–11) are also predicted and compared with the experimental and theoretical data available in the literature.

Keywords: full core plus correlation method, quantum defect theory, energy intervals
PACC: 3130, 3110, 3270

1. Introduction

Recently, there has been increasing interest in the research of Rydberg atom, because it plays an important role in the fields of laser physics, plasma physics and astrophysics.[1] The structure of atomic Rydberg states is significant for the research of Coulomb long-range interaction among electrons inside atoms. High Rydberg spectra for open-shell atoms have long been recognized as a challenging problem for both experimental and theoretical work.

The advent of the tunable dye laser has made possible a variety of methods for the efficient production and detection of Rydberg states for atomic systems. As to theoretical aspect, configuration interaction calculations of atomic and molecular wavefunctions by variational techniques, via trial electronic wavefunctions, have been very successful for low excited states. However, in the calculating of highly excited or continuum states, one encounters several difficulties. The large number of required states, the poor orthogonality between states of the same symmetry, and the poor numerical convergence are major problems. On the other hand, for a Rydberg atom, with the increasing of the principal quantum number, the level spacing between different states becomes smaller and smaller, so it is difficult to obtain an accurate energy level of each state with traditional variational method. Quantum defect theory (QDT)[2] has evolved into the field of spectroscopy and collision processes in atoms and molecules, and this theory has been used to successfully calculate energy levels of highly excited or continuum states for atomic and molecular systems. Rydberg energy levels can then be evaluated insofar as some basic quantum defect parameters depending weakly on the energy of the system. This procedure may be useful for atomic systems where experiment has not yet provided information accurate enough to give quantum defect parameters.

Cooke *et al*[3] used a laser-excitation, optical-detection scheme to observe microwave transitions from the nd to the nf orbital levels for the lithium atom with principal quantum number n from 7 to 11. They obtained separations between the centres of gravity of the nd and nf levels. In Ref.[4], there are also some spectroscopic results for $d-f$ intervals with n from 7 to 9. Jaffe and Reinhardt[5] have used a core potential constructed from a static Hartree–Fock term, a semiclassical exchange approximation, and a polarization term to calculate quantum defects. Using this assumed pseudopotential, they numerically

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integrated Schrödinger equation to calculate quantum defects for the lithium atom. Using these reported quantum defects, Cooke *et al*[3] have also calculated the $d-f$ intervals of the lithium atom with n from 7 to 11.

Rydberg states of lithium consist of a two-electron core and a distant Rydberg electron, which are nearly hydrogenic. However, the more subtle features of their spectra are not hydrogenic. In particular, differences between the alkali and hydrogenic spectra arise from the interaction between the excited electron and the alkali 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 valence electron.[6] Naturally, we consider whether the QDT is adapted for Rydberg levels with higher angular momentum for the lithium atom. In this work, we apply the QDT to the lithium atom which has one $1s^2$-core and a non-paired nl ($l = d$ and f) electron in its Rydberg states. The ionization energy of atomic core corresponding to the second ionization threshold of system is very high, so the interaction of channels in the energy range is very weak. In this case, only the single channel quantum defect theory is needed to deal with the energy level structure of Rydberg states for the lithium atom. By using the single channel quantum defect theory, the Rydberg energy levels for the lithium atom can be predicted, then separations between the centres of gravity of different levels will also be calculated and compared with the above experimental and theoretical data available in the literature.

The choice of polarization effect is very sensitive to the calculation accuracy of the quantum defects, thus, the prediction of energy levels of Rydberg states. In this work, we take different polarization terms to see the influence of polarization on the quantum defect and energy level intervals, and then compare all the quantum defect and energy level intervals predicted by different methods with the data available in the literature.

2. Theory

For the highly excited states of a lithium atom, the level spacing between different states is small, so it is difficult to obtain an accurate energy level of each state with traditional variational method. The existing quantum defect theory can be used to deal with highly excited states. According to the quantum defect theory,[2] for the lithium atom, the nonrelativistic quantum defect μ can be determined from the following formula:

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

where n is the principal quantum number. The second term on the right-hand side of Eq.(1) denotes the effective principal quantum number in which ε is the energy relative to the first ionization threshold and obtained in this work by subtracting the core energy from the energy of a three-electron system

$$\varepsilon = E_{\rm tot}(1s^2 nl) - E_{\rm tot}(1s^2). \tag{2}$$

Here the symbol $E_{\rm tot}$ denotes the total energy, which includes the nonrelativistic upper bound and the relativistic and mass polarization corrections.

According to QDT,[2] quantum defect μ should be a smooth function of energy ε, and can be expressed by a weakly varying function of energy in the following form:

$$\mu = \mu_0 + \mu_0'\varepsilon + \mu_0''\varepsilon^2, \tag{3}$$

where the coefficients μ_0, μ_0' and μ_0'' for the lithium atom's $1s^2 nl$ systems are determined by using the energy ε obtained from Eq.(2) and the μ values obtained from Eq.(1). In this case the accurate total energies of the first three states for $1s^2 nl$ systems are very important to the accurate calculating of these basic quantum defect coefficients in Eq.(3).

For the first three states of the lithium atom's $1s^2 nl$ system, the total energies can be calculated using the full core plus correlation (FCPC) method.[7−16] This method has been given in detail by Chung,[7] and here we only give it a brief description. The nonrelativistic Hamiltonian H_0, and the perturbation operators H_1 (correction to the kinetic energy), H_2 (Darwin term), H_3 (electron–electron contact term), H_4 (mass polarization), 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 calculating the relativistic and mass-polarization corrections. The wavefunction of the three-electron system is constructed with the FCPC method in the LS coupling scheme as follows:

$$\begin{aligned}\Psi(1,2,3) =& A[\,\Phi_{1s1s}(1,2) \\ &\times \sum_i d_i r_3^i \exp(-\beta r_3) Y_{l(i)}(3)\chi(3) \\ &+ \sum_i C_i \Phi_{n(i),l(i)}(1,2,3)],\end{aligned} \tag{4}$$

where A is an antisymmerization operator. $\Phi_{1s1s}(1,2)$ is a predetermined $1s^2$-core wavefunction which is represented by a CI basis set.[7] The second term on the

right-hand side of Eq.(4) describes the core relaxation and the intershell correlation in the three-electron system.

By substituting the three coefficients μ_0, μ_0' and μ_0'' into Eq.(3), the quantum defect function which varies smoothly with energy based on QDT can be obtained. Combining Eq.(1) and Eq.(3), we can construct a system equation to solve all the energy levels of Rydberg states for the lithium atom. This equation is in the following form:

$$\varepsilon + \frac{1}{2(n-\mu_0-\mu_0'\varepsilon-\mu_0''\varepsilon^2)^2} = 0. \qquad (5)$$

Based on this equation, we can calculate the energy levels for all Rydberg states of the lithium atom. Inserting the principal quantum number n into the above equation, the corresponding energy ε can be calculated immediately; then substituting the calculated energy ε into Eq.(3), the quantum defect μ of this state can be obtained. The energy ε can be also used to calculate the separation between the centres of gravity of the nl and nl' states.

3. Results and discussion

In our calculation, the core energy $E_{\rm tot}$ $(1s^2) = -7.28051968$ a.u. is the same as that in Ref. [9]. Other total energies of $1s^2nd$ (n=3–5) and $1s^2nf$ (n=4–6) states calculated with FCPC method are also in agreement with those in Ref.[9]. These total energies together with the energy ε and the quantum defect μ are all listed in Table 1. The coefficients, μ_0, μ_0' and μ_0'' for the lithium atom's $1s^2nd$ and $1s^2nf$ states can be separately determined by solving Eq.(1) and Eq.(4). These calculated coefficients corresponding to different $1s^2nl$ states are also listed in Table 1.

Table 1. The total energies $E_{\rm tot}$, the energy ε, the quantum defect μ and corresponding coefficients μ_0, μ_0' and μ_0'' for the lithium atom's $1s^2nd$ (n=3–5) and $1s^2nf$ (n=4–6) states (in a.u.).

state	$E_{\rm tot}$	ε	μ	μ_0	μ_0'	μ_0''
$1s^23d$	–7.33613041	–0.0556107	0.001489	0.002094	0.01455	0.06594
$1s^24d$	–7.31179631	–0.0312766	0.001703			
$1s^25d$	–7.30053432	–0.0200146	0.001829			
$1s^24f$	–7.31177364	–0.0312540	0.0002534	0.0003201	0.001258	–0.02801
$1s^25f$	–7.30052195	–0.0200023	0.0002837			
$1s^26f$	–7.29440995	–0.0138903	0.0002972			

The quantum defect functions which vary smoothly with energy can be easily obtained. The limit quantum defect of ^{2}D state is μ_0 listed in the second row of Table 1 as 0.002094 and that of ^{2}F state is μ_0 listed in the fifth row of Table 1 as 0.0003201. There are some other limit quantum defect values of ^{2}D and ^{2}F states of the lithium atom in the literature. For example, Johansson[4] fitted the experimental data to give limit quantum defect values: 0.001932 for ^{2}D state and 0.0003103 for ^{2}F state. And Lorenzen and Niemax[17] also gave limit quantum defect values: 0.002129 for ^{2}D state and –0.000077 for ^{2}F state by means of a Rydberg–Ritz fitting procedure. For the ^{2}D state, our extrapolated limit quantum defect lies between the theoretical value and the experimental value. For the ^{2}F state, our extrapolated limit quantum defect is in agreement with the experimental value of Johansson[4] to the fourth digit after the decimal point, but Lorenzen and Niemax[17] predicted a very small negative number; obviously the correctness of their prediction is open to suspicion. Then we can use Eq.(5) to accurately calculate high Rydberg levels of the lithium atom to the threshold. In Table 2, we list the energy ε and the quantum defect μ for the lithium atom's $1s^2nd$ and $1s^2nf$ (n=7–11) states. In order to check the accuracy of our calculations, we list our derived excitation energies for the $1s^2nd$ and $1s^2nf$ states of the lithium atom in Table 3 so as to compare them with experimental values in the literature. Firstly we calculate the total energy of the ground state $E_{\rm tot}(1s^22s) = -7.47867779$a.u. The excitation energy of the threshold is obtained by the relation $E_{\rm tot}(1s^2) - E_{\rm tot}(1s^22s)$, then by adding the obtained energy to the energy ε of the lithium atom's $1s^2nd$ ($n \geq 6$) states or $1s^2nf$ ($n \geq 7$) states, the corresponding excitation energy of each state is obtained. It is noted that if the reduced mass of the electron is taken into consideration, then the reduced Rydberg constant of Li is 109728.73cm^{-1} and it will be used throughout this work. Our calculated excitation energy of the threshold is 43487.27cm^{-1}, and in agreement with Moore's experimental value,

43487.19cm^{-1}.[18] For the 1s^{2}11d state, our excitation energy is 2 cm^{-1} higher than the experimental value, so further studies should be carried out either theoretically or experimentally for this state. For other states, our predicted excitation energies are in agreement with experimental values to the integer digit. As a whole, our results are in accord with experimental values very well. It is also shown that Eq.(5) is very effective for calculating the energy levels of Rydberg states for the lithium atom.

Using these data listed in Table 2, we can obtain $d-f$ intervals of the lithium atom through the relation $\varepsilon(1s^2nf)-\varepsilon(1s^2nd)$. The data in the literature are given in units of GHz. In order to make a straightforward comparison with the data in the literature, we convert the units of our present level intervals into GHz. A comparison of the previous experimental and theoretical data available in the literature with our calculated $d-f$ intervals is presented in Table 4. It is worth noting that our calculated values lie between earlier measurements[4] and later measurements.[3] When our theoretical prediction is compared with earlier measurements and theoretical calculations, the agreement between them becomes relatively poor, the discrepancy reaching 12%–18%. The discrepancy may be a consequence of choice of polarization term used in our calculation, which can influence the calculation accuracy of the quantum defects, and thus, the prediction of energy levels of Rydberg states. We can adjust the polarization term which is determined essentially by core polarization effects for a better fitting to the high-n $d-f$ intervals.

Table 2. The energy ε and the quantum defect μ of the lithium atom's 1s^2nd and 1s^2nf (n=7–11) states (in 10^{-3} a.u.).

state	ε	μ	state	ε	μ
1s^{2}7d	–10.20977529	0.001952	1s^{2}7f	–10.20496898	0.0003043
1s^{2}8d	–7.816376608	0.001984	1s^{2}8f	–7.813102688	0.0003086
1s^{2}9d	–6.175592749	0.002006	1s^{2}9f	–6.173266502	0.0003113
1s^{2}10d	–5.002023266	0.002023	1s^{2}10f	–5.000313121	0.0003131
1s^{2}11d	–4.133760576	0.002035	1s^{2}11f	–4.132467644	0.0003144

Table 3. Theoretical and experimental excitation energies for the 1s^2nd and 1s^2nf state of the lithium atom (in cm^{-1}).

	1s^2nd state		1s^2nf state	
n	Experiment [a]	This work	Experiment[b]	This work
3	31283.10	31283.885		
4	36623.39	36623.387	36628.33	36628.362
5	39094.94	39094.915	39097.53	39097.629
6	40437.32	40437.320	40438.86	40438.953
7	41246.5	41246.664	41247.65	41247.720
8	41771.3	41771.914	41772.58	41772.634
9	42131.3	42131.997	42132.43	42132.506
11	42578	42580.092		
12	42725	42725.011		

[a]Ref.[18]. [b]Ref.[4].

Table 4. Theoretical and experimental separations between the centres of gravity of the nd and nf levels (n=7–11) for the lithium atom (in GHz).

n	our calculation	Expt.[a]	Expt.[b]	Other Theo.[c]
7	31.6215	30.2088	31.8	35.5
8	21.5397	20.4199	23.7	23.8
9	15.3048	14.4275	16.2	16.7
10	11.2513	10.5640		12.2
11	8.5064	7.960		9.14

[a]Ref.[3]. [b]Ref.[4]. [c]Ref.[5].

In Tables 5 and 6, we separately list the calculations of the quantum defect and the separations between the centres of gravity for the nd and nf levels of the lithium atom by using different methods. With no core polarization effect taken into account in the calculation of the total energy for the lithium atom's $1s^2nl$ state, the quantum defect of each state is very small and the intervals between nd and nf levels are minimal. Once the quadrupole polarization effect of the core is included in the calculation of the total energy upper bound for the $1s^2nl$ state, the quantum defect of each state appears a little larger and the intervals become broad, but the change is very small, which indicates that the contribution of quadrupole polarization effect of the core to the quantum defect is small. If the dipole polarization effect of the core is included in the calculation of the total energy, each quantum defect will be one order of magnitude greater than the previous calculations, and the intervals will become distinctly broad and exhibit good agreement with the later measurements,[3] which illustrates that the contribution of dipole polarization effect of the core to the quantum defect and intervals is very remarkable. When dipole and quadrupole polarization effects of the core are both taken into account in the calculation of the total energy, the quantum defect of each state and the intervals become a little larger again; in fact the present intervals are our calculations listed in Table 4. Owing to the fact that the first-order and second-order polarization effects of the core are considered at the same time, the present separations between the centres of gravity of the nd and nf levels for the lithium atom excel the later measurements[3] in accuracy. From Table 2 we find that the quantum defect of f wave is very small and approximates zero. Now the quantum defect of f wave is chosen as zero in the calculation of the separations between the nd and nf levels. The results are also listed in Table 6. In this case, the intervals are the broadest, interestingly, and the earlier measurements[4] and theoretical values[5] approach the present calculations, which suggests that the quantum defect of f wave predicted in Ref.[5] is smaller than the natural values and the intervals obtained in this way are broader than the true values. The quantum defect is determined essentially by core-polarization effects. In our FCPC method, dipole and quadrupole polarization effects are considered effectively in the whole CI variation calculation, so the quantum defect calculated from the accurate energy and the quantum defect extrapolated from quantum defect functions which vary smoothly with energy are both credible. It is also indicated that the present work is valuable for calculating the energy levels of Rydberg states for the lithium atom.

Table 5. The quantum defect μ for the lithium atom's $1s^2nd$ and $1s^2nf$ (n=7–11) states by using different methods.

state	No Polarization	Quadrupole Polarization	Dipole Polarization	Dip. and Qua. Polarization
$1s^27d$	0.0004580	0.0005068	0.001903	0.001952
$1s^28d$	0.0004787	0.0005283	0.001934	0.001984
$1s^29d$	0.0004934	0.0005435	0.001956	0.002006
$1s^210d$	0.0005041	0.0005546	0.001972	0.002022
$1s^211d$	0.0005122	0.0005630	0.001984	0.002034
$1s^27f$	0.0000282	0.0000313	0.0003016	0.0003043
$1s^28f$	0.0000291	0.0000320	0.0003057	0.0003086
$1s^29f$	0.0000301	0.0000330	0.0003083	0.0003113
$1s^210f$	0.0000313	0.0000341	0.0003101	0.0003131
$1s^211f$	0.0000328	0.0000355	0.0003114	0.0003144

Table 6. Separations between the centres of gravity of the nd and nf levels (n=7–11) for the lithium atom by using different methods (in GHz).

n	No Polarization	Quadrupole Polarization	Dipole Polarization	Dip. and Qua. Polarization	Method[a]
7	8.1561	9.0412	30.7367	31.6215	37.4905
8	5.7494	6.3508	20.9386	21.5397	25.5272
9	4.1817	4.6081	14.8787	15.3048	18.0960
10	3.1257	3.4386	10.9387	11.2513	13.2899
11	2.3922	2.6285	8.2704	8.5064	10.0569

[a] the quantum defect of f wave is chosen as zero.

4. Summary

By using the total energies of $1s^2nd$ (n=3–5) and $1s^2nf$ (n=4–6) states for the lithium atom, calculated from the FCPC method, quantum defect functions are obtained which vary smoothly with energy based on the quantum defect theory. Then these functions are separately used to construct a system equation to solve the energies and quantum defects for the $1s^2nd$ and $1s^2nf$ (n=7–11) states of the lithium atom. Separations between the centres of gravity of the nd and nf levels (n=7–11) are also calculated and compared with the experimental and theoretical data available in the literature. The results indicate that our theoretical method is very effective for calculating the energy levels of Rydberg states for the lithium atom with a $1s^2$-core.

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