Exact quantum defect theory approach for lithium in magnetic fields*

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We calculate the diamagnetic spectrum of lithium at highly excited states up to the positive energy range using the exact quantum defect theory approach. The concerned excitation is one-photon transition from the ground state 2s to the highly excited states np with π and σ polarizations respectively. Lithium has a small quantum defect value 0.05 for the np states, and its diamagnetic spectrum is very similar to that of hydrogen in the energy range approaching the ionization limit. However, a careful calculation shows that the spectrum has a significant discrepancy with that of hydrogen when the energy is lower than -70 cm^{-1}. The effect of the quantum defect is also discussed for the Stark spectrum. It is found that the σ transition to the np states in an electric field has a similar behavior to that of hydrogen due to zero interaction with channel ns.

Keywords: diamagnetic spectrum, quantum defect theory

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1. Introduction

A Rydberg atom in a magnetic field, one of the simplest realizations of a classically chaotic system, has been studied for many years.[1–5] In a pure magnetic field, the system has a rotational symmetry about the direction of the magnetic field. We can separate this orbital angular motion perpendicular to the magnetic field easily and reduce the problem to a two-dimensional one. For a low-lying atom in a weak magnetic field, the quadratic Zeeman term (usually called the diamagnetic term) is negligible. For a Rydberg atom in a magnetic field, with the increase of the magnetic intensity, the diamagnetic potential will be comparable with or even dominate over the Coulomb potential, and the system will gradually change form order to chaos.[5]

As the first element of alkali species, lithium is well studied experimentally and theoretically.[6–15] In 1973, Starace used a two-dimensional semiclassical approximation to examine the polarization spectrum of a hydrogen like atom in a strong magnetic field,[16] and the result is in excellent agreement with the experiment of Garton and Tomkins.[17] For the states above the ionization threshold, the hydrogen approximation can give a satisfactory result even when the quantum defect is not taken into account. In 1978, Lu *et al.* recorded quasi-Landau resonances of lithium atoms in magnetic fields up to 4.7 T, the spacing was only half of the cyclotron frequency rather than $3/2$ expected from the previous theory.[7] This hydrogen like feature was also confirmed by Iu *et al.* in the observation of the ordered structure in the spectrum of lithium in the range of -1 cm$^{-1} \leq E \leq 8$ cm^{-1} with a magnetic field of approximately 6 T.[18] In 1991, O'Mahony and Mota-Furtado calculated the positive-energy spectra of both hydrogen and lithium atoms in a field of 6.1 T.[19] The theory combines the quantum defect theory, the $\boldsymbol{R}$-matrix propagation, and the two-dimensional frame transformations. The results for hydrogen and lithium are nearly the same in the positive energy range. In the same year, Watanabe and Komine reported a successful implementation of the diabatic-by-sector method and applied it to the computation of positive-energy diamagnetic Rydberg spectra of the alkali-metal atoms in a laboratory magnetic field of 6 T.[20] The method provides the quantum defect parameters directly and opens up the possibility of accounting for various spectral features quantum mechanically. The quantum defect parameters are absorbed in the so-called $\boldsymbol{K}$-matrix.

In this paper, we use the exact quantum defect theory approach combined with the B-spline expansion techniques and the complex coordinate rotation method to study the spectral properties of lithium in an external magnetic field. As the quantum defect for the p channel is very small, especially for the high Rydberg states, it can be neglected. In most cases, lithium is a very good substitution for hydrogen since the latter has a too high ionization potential, which is not easy to access by one-photon absorption in laboratory. In the present work, we investigate how the hydrogen approximation depends on the excitation energy, below which the quantum defect effect has to be taken into account.

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2. Theory

To describe a single-electron atom in a magnetic field, the non-relativistic infinite-proton-mass Hamiltonian H for the Rydberg electron has the following form (in atomic units):[21,22]

$$H = \frac{p^2}{2} + V(r) + \frac{B}{2}L_z + \frac{B^2}{8}r^2\sin^2\theta, \tag{1}$$

where $V(r)$ is the atomic Coulomb potential considering the effects of valence electron polarization of the core system, B is the magnetic field strength in an atomic unit, θ is the angle coordinate of the Rydberg electron in the spherical coordinates, and $BL_z/2$ and $B^2r^2\sin^2\theta/8$ are the paramagnetic and the diamagnetic terms, respectively. To solve the Schrödinger equation

$$H\Psi = E\Psi, \tag{2}$$

it is more convenient to expand the wavefunction in radial basis $\{B_n(r)\}$ and spherical harmonic function basis $\{\mathrm{Y}_{lm}(\theta,\phi)\}$

$$\Psi(r,\theta,\phi) = \sum_{nl} C_{nl}\frac{B_n(r)}{r}\mathrm{Y}_{lm}(\theta,\phi), \tag{3}$$

where $\mathrm{Y}_{lm}(\theta,\phi)$ is the spherical harmonic function. For the atom in a magnetic field, m is a good quantum number, and the spherical harmonic function is reduced to the normalized associated Legendre function. The Schrödinger equation is expressed as

$$\left[-\frac{\mathrm{d}^2}{2\mathrm{d}r^2} + \frac{l(l+1)}{2r^2} + V(r) + \frac{B}{2}m + \frac{B^2}{8}r^2\sin^2\theta\right]\Psi = E\Psi. \tag{4}$$

Rather than using the model potential $V(r)$ [23] or the $\boldsymbol{R}$-matrix method including the quantum defects implicitly,[24] we employ an equivalent form for the central field potential[25–27]

$$V(r) = \frac{\lambda(\lambda+1) - l(l+1)}{2r^2} - \frac{1}{r}, \tag{5}$$

where $\lambda = l - \delta + \mathrm{Int}(\delta)$, and the quantum defects are explicitly enclosed. Here, $\mathrm{Int}(\delta)$ is the rounded nearest integer value of the quantum defect. We employ a reduced quantum defect to quantifiably describe the real contribution of the quantum defect for a given angular momentum channel. It is introduced in our previous work.[28]

In the present work, we will take the B-spline function as the radial basis. In addition, the complex coordinate is employed in our calculation. This method will supply complex eigenvalues with their imaginary parts corresponding to the natural linewidths of the absorptions. The basis function $B_n(r)$ in Eq. (3) is taken to be $B_n^k(r)$, which is the n-th B-spline function of order k.[29,30] It should be noted that the Hamiltonian matrix and its wavefunctions are parameterized by angular momentum quantum number l and magnetic quantum number m. Thus the Schrödinger equation can be transformed into the general eigenvalue problem

$$\boldsymbol{HC} = \boldsymbol{ESC}, \tag{6}$$

where $\boldsymbol{E}$ and $\boldsymbol{C}$ represent the eigenvalues and the eigenvectors to be solved, respectively, $\boldsymbol{H}$ is the Hamilton in the matrix form under the B-spline basis, and $\boldsymbol{S}$ is the overlap matrix. In the case of pure magnetic fields, The magnetic quantum number m and parity Π are two good quantum numbers.

3. Results and discussion

We first calculate the spectra for lithium and hydrogen π transitions in a magnetic field of 1 T (Fig. 1). The quantum defect of channel np is 0.05, while those of channel nf and higher angular momentum states are set to zero. The spectrum is determined completely by channel np since the neighbor states are excluded by the non-zero matrix element conditions. This unique feature makes it a good candidate element to study the hydrogen properties using a non-hydrogen atom, here for example, lithium. As the quantum defect of channel np is very small, the high states will behave like those in the hydrogen atom.

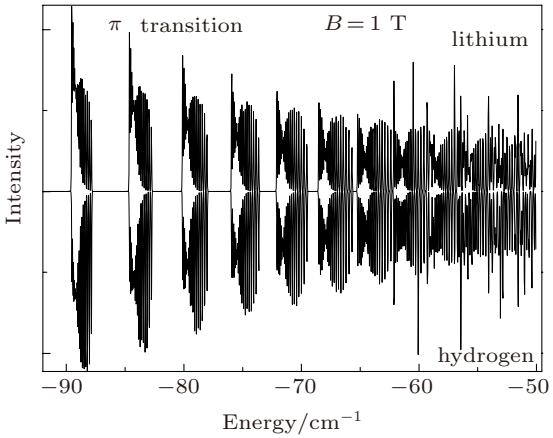


Fig. 1. The calculated π transition spectra for lithium and hydrogen in a magnetic field of 1 T. For this field, the spectra are very similar above -70 cm^{-1}, while below this threshold the non-hydrogenic properties are obvious.

A quantitative comparison of spectral calculation for the σ^+ transition between hydrogen and lithium in a magnetic field of 1 T is depicted in Fig. 2. It can be seen that the spectra are nearly the same except that the predominant peaks in the manifolds are different in intensity. It seems that the σ transition of lithium is similar to that of hydrogen. The difference is very hard to distinguish from the experimental observation solely if considering the saturation of signal in data acquisition. This is why many works take the potential model of hydrogen to explain the experimental spectrum of lithium in magnetic fields.[31] However the non-hydrogenic characters can be revealed by the exchange effects between the Rydberg and the core electrons,[32] resulting in anticrossing in the spectrum and the energy levels as well.[12]

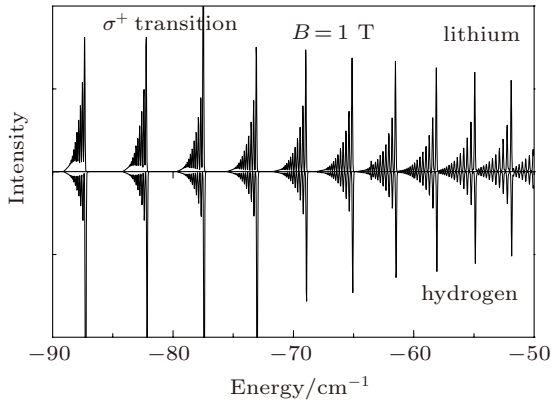


Fig. 2. The calculated σ^+ transition spectra for lithium and hydrogen in a magnetic field of 1 T. It can be seen that the spectra are nearly the same except that the predominant peaks in the manifolds are different in intensity.

This similarity in the diamagnetic spectra of lithium and hydrogen was also studied previously at $B = 6.113$ T.[33,34] In the calculation, the $\boldsymbol{R}$-matrix and the complex coordinate techniques are combined and applied to the diamagnetic spectrum even approaching the positive energies. The study extends from -30 cm^{-1} to $+30$ cm^{-1}. The spectrum calculated for hydrogen is in remarkable agreement with the spectrum observed in lithium, although there are still some unimportant discrepancies. We recalculate the spectra at the same conditions but for lithium and hydrogen respectively. The result is shown in Fig. 3. One can note that the spectral line positions are nearly the same. The only difference is the intensity of some lines. This discrepancy is very difficult to definitely recognize in experimental observation, because usually many experimental factors will influence the absorption signal intensities, for example, the fluctuation from the lower power or the atomic beam density.

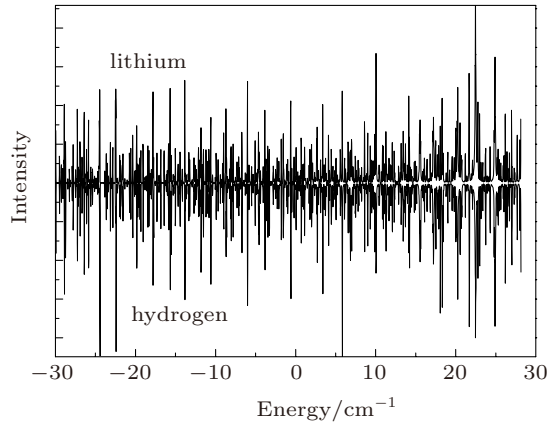


Fig. 3. The calculated π transition spectra for lithium and hydrogen in a magnetic field of 6.113 T. It can be seen that for the high energy states, for example, $E > -30$ cm^{-1}, the calculation based on the hydrogen potential model can explain the lithium spectrum very well.

However, this hydrogen approximation is broken immediately by the introduction of an electric field if the electric field couples the states of neighboring angular momenta, since the quantum defect of channel ns has a rather large value of 0.4.[10] Specially, for the σ irradiated np states, the coupling with the neighboring ns states has a zero matrix element, resulting in that the non-zero quantum defect of ns has no effects on the Stark spectrum. It is shown in Fig. 4, where the electric field is taken to be $F = 50$ V·cm^{-1}.

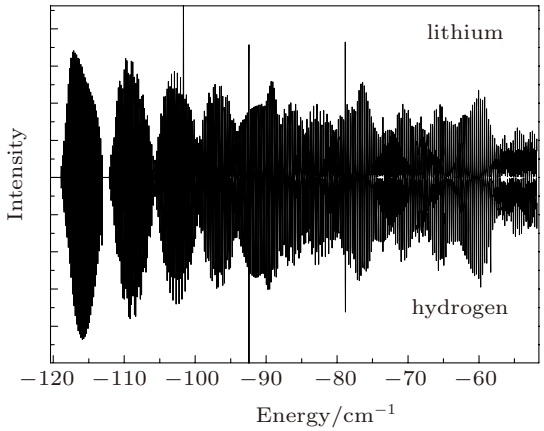


Fig. 4. The calculated σ^+ transition spectra for lithium and hydrogen in an electric field of $F = 50$ V·cm^{-1}. Due to a zero coupling with the np states, the quantum defect of the ns states will not affect the spectrum at all.

However, for the π transition, the ns and np states have a non-zero coupling. It makes the lithium Stark spectrum deviate from the hydrogen one, as depicted in Fig. 5. The interaction matrix elements between the neighboring channels are expressed as

$$\begin{aligned} V^m_{l,l-1} &= \langle l,m|F\cos\theta|\,l-1,m\rangle \\ &= \sqrt{\frac{l^2-m^2}{(2l+1)(2l-1)}}F, \end{aligned} \tag{7}$$

from which we can see that for the σ transition to the np states, the matrix elements are zero. This special feature will help us to simplify the study of the Stark spectrum of lithium.

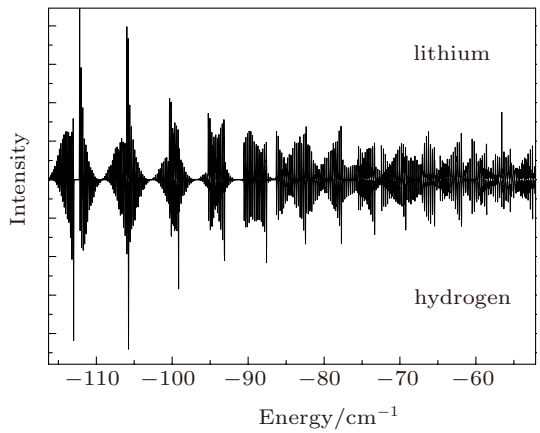


Fig. 5. The calculated π transition spectra for lithium and hydrogen in an electric field of $F = 50$ V·cm^{-1}. Due to the non-zero coupling with the np states, the quantum defect of the ns states will distort the spectrum.

4. Conclusion

We adopt the exact quantum defect theory to calculate the diamagnetic spectrum of lithium at highly excited states. Owning to a small quantum defect in the *n*p channel, the spectrum of lithium in a magnetic field is very similar to that of hydrogen, especially at higher energies. Another reason for this feature is that the diamagnetic spectrum of the *n*p states is immune to the quantum defects of the neighboring *n*s and *n*d states due to the non-zero matrix element condition. This similarity is broken by the introduction of an electric field or the transition concerning the *n*s state, but it is excluded for the σ transition to the *n*p states owning a zero coupling.

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