RAPID COMMUNICATION

An effective quantum defect theory for the diamagnetic spectrum of a barium Rydberg atom*

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A theoretical calculation is carried out to investigate the spectrum of a barium Rydberg atom in an external magnetic field. Using an effective approach incorporating quantum defect into the centrifugal term in the Hamiltonian, we re-examine the reported spectrum of the barium Rydberg atom in a magnetic field of 2.89 T [*J. Phys.* B **28** L537 (1995)]. Our calculation employs *B*-spline basis expansion and complex coordinate rotation techniques. For single photon absorption from the ground $6s^2$ to $6snp$ Rydberg states, the spectrum is not influenced by quantum defects of channels *n*s and *n*d. The calculation is in agreement with the experimental observations until the energy reaches $E = -60$ cm^{-1}. Beyond this energy, closer to the threshold, the calculated and experimental results do not agree with each other. Possible reasons for their discrepancies are discussed. Our study affirms an energy range where the diamagnetic spectrum of the barium atom can be explained thoroughly using a hydrogen model potential.

Keywords: diamagnetic spectrum, quantum defect, barium Rydberg atom

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1. Introduction

A hydrogen atom inside an external magnetic field constitutes an ideal system for the study of diamagnetism due to its pure Coulombic potential of the lone electron[1] in the unperturbed Hamiltonian. Such a system maintains rotational symmetry with respect to the direction of the magnetic field, providing fascinating opportunities for theoretical study especially when the diamagnetic potential is comparable to the Coulomb potential in magnitudes. This is in contrast to non-hydrogenic atoms, where incorporating core effects such as a non-zero polarizability remains a challenge in theoretical calculations. The usual approaches adopted include atomic potential models and $\boldsymbol{R}$-matrix methods.[2,3] Expansion into basis states is also used, for instance, with the generalized Laguerre function basis, the Sturmian basis, and the *B*-spline basis, as reported in the quantitative calculations of excited state atoms in external fields.[4–9] During the 1980s, Taylor and Clark performed an exact computation of the diamagnetic spectra for a hydrogen Rydberg atom using a large Sturmian basis.[4,5] Among the above mentioned choices, the *B*-spline basis derived from numerical analysis is often considered as the most efficient and accurate one for the spectrum calculation due to its simplicity in handling state coupling. It is widely used in quantum mechanical studies of atoms in external fields.[9]

In 1995, the Connerade group studied the active cancelation of the motional Stark effect in the barium diamagnetic spectrum.[10] They found that the motional Stark effect can be eliminated by applying a cancelation voltage and the reliability of their method is checked by the identification of the σ^+ and σ^- spectra even in the region of relatively high energy. Meng carried out a theoretical investigation in the same energy range,[11] however, was unable to explain the experiments well, especially in the region of high energy. She tried to attribute the discrepancy to magnetic field strength and performed her calculation at $B = 2.87$ T instead of $B = 2.89$ T used in the experiment. Nevertheless, discrepancies remain at the higher energy. From the experimental side, the agreement of σ^+ and σ^- spectra by an appropriate shift strongly supports the reliability of their observations. In the view of theoretical side, on the other hand, the core effect has been taken into account already in the calculation. It remains to clarify why this disagreement persists despite earnest effort from both sides. It is possible that the physical environment could be different from what it is believed to be, for instance, a nonzero electric field may result from leaking to the interaction region. Before concluding definitely, an alternative method should be adopted to revisit this issue and study the diamagnetic spectrum again.

This article reports our calculation of the one-photon absorption spectrum for a barium atom in a magnetic field of 2.89 T attempted at resolving the discrepancy between theory

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and experiment. Instead of the earlier mentioned theories, we adopt an effective approach which incorporates quantum defects into the angular momentum quantum numbers of the centrifugal potential part within a one electron description. The diamagnetic interaction then only couples the adjacent states with $L\pm 2$, causing the np states to absolutely predominate the spectrum. We keep the ns and nd states in the B-spline basis expansion and use the complex coordinate rotation technique to perform a numerical investigation.

The barium atom is studied extensively because it has two valence electrons, which makes it one of the best candidates to investigate electron correlations.[12–16] An added benefit for the barium atom concerns its quantum defect for the np channel, being very small or nearly zero. Its diamagnetic spectrum is thus analogous to that of hydrogen for one-photon excitation to np states as the selection rules $L' = L\pm 2$ prohibits intrusions from the neighboring ns and nd states, both of which possess considerable quantum defects. For higher angular momentum channels, the quantum defect values are very small and can be set to zero. This important feature provides an opportunity to study the fine detail of the slight difference between the effective quantum defects of hydrogen and barium atoms.

2. Theoretical calculation

The non-relativistic infinite-proton-mass approximation Hamiltonian for a Rydberg atom in a constant uniform magnetic field is as follows (with all variables in atomic units):[17,18]

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

where $V(r)$ is the Coulomb potential supplemented by polarization effects from the valence electron of the core system, B is the strength of the magnetic field in atomic unit, θ the angular coordinate of the Rydberg electron, and $BL_z/2$ and $(B^2r^2/8)\sin^2\theta$ are, respectively, the paramagnetic and diamagnetic terms. In order to solve the Schrödinger equation

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

it is more convenient to expand the wave function in terms of the spherical harmonic function basis $\{\mathrm{Y}_{lm}(\theta,\phi)\}$ as

$$\Psi(r,\theta,\phi) = \sum_l C_l \frac{R(r)}{r}\mathrm{Y}_{lm}(\theta,\phi), \tag{3}$$

with C_l being the expansion coefficient. Inside a uniform magnetic field, the magnetic quantum number m remains a good quantum number and the spherical harmonic function reduces to the normalized associated Legendre function. The Schrödinger equation is then expressed as

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

where $\Psi' = \sum_l C_l R(r)\mathrm{Y}_{lm}(\theta,\phi)$. Rather than using the model potential[13] or the $\boldsymbol{R}$-matrix method including the quantum defects implicitly,[18] we employ an effective form for the central field potential

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

where $\lambda = l - \delta + \mathrm{Int}(\delta)$ explicitly includes quantum defect, and $\mathrm{Int}(\delta)$ denotes the nearest integer value of δ. We employ a reduced quantum defect

$$\delta' = \delta - \mathrm{Int}(\delta) \tag{6}$$

to quantify its real contribution for a given angular momentum channel. To simplify the notation, we further ignore the prime and use δ instead in the following. Clearly, the potential $V(r)$ is now parameterized by non-zero quantum defects.

In this study, we employ the radial B-spline function as the basis. The Hamiltonian in the B-spline basis has a symmetric banded structure, which can significantly enhance the speed of numerical diagonalization when solving for its eigenvalues and eigenfunctions. In addition, a complex coordinate rotation is employed in our calculation to search the hidden resonance states. The radial wavefunction can be expanded in terms of the B-spline basis $\{B_0^k, B_1^k, \ldots, B_{N-1}^k\}$ and the reduced wavefunction in Eq. (4) takes the form

$$\Psi' = \sum_{nl} C_{nl} B_n^k(r)\mathrm{Y}_{lm}(\theta,\phi), \tag{7}$$

where $B_n^k(r)$ is the n-th B-spline function of order k as defined in Refs. [9], [19], and [20]. The corresponding Hamiltonian matrix and its wavefunctions are parameterized by the angular momentum quantum number l and magnetic quantum number m. Thus, the Schrödinger equation can be transformed into generalized eigenvalue problem

$$\boldsymbol{H}C = E\boldsymbol{S}C, \tag{8}$$

where E and C represent, respectively, its eigenvalue and eigenvector, $\boldsymbol{H}$ is the matrix form of the Hamilton in the B-spline basis, and $\boldsymbol{S}$ the overlap matrix. Accurate matrix elements are obtained rapidly through the employment of Gauss–Legendre integration. A Lanczos algorithm for the general eigen-problem applied to the matrix equation gives its eigenvalue E and eigenvector C.

3. Results and discussion

In our calculation, we take the following effective quantum defect values for the ns, np, nd and nf states, respectively,

$$\delta_{\mathrm{s}} = 0.2572,\ \delta_{\mathrm{p}} = 0,\ \delta_{\mathrm{d}} = -0.25,\ \delta_{\mathrm{f}} = 0.04, \tag{9}$$

unless they are specified otherwise. As barium is excited by the absorption of σ^+ or σ^- photons, only the $m = 1$ or $m = -1$ state is excited from the initial $m = 0$ state. For a direct comparison with the experimental spectrum, the theoretically calculated spectrum is convoluted with a Gaussian of a suitable width to account for the Doppler broadening and laser linewidth. The theoretical results are shown in Fig. 1, where the experimental results are shown as inverted in mirror style for easy comparison. We conclude that their agreement is almost perfect below the energy of $E = -60$ cm^{-1}. However, above this energy, the theoretical result does not seem to be capable of fully repeating the main features of the experimental data.

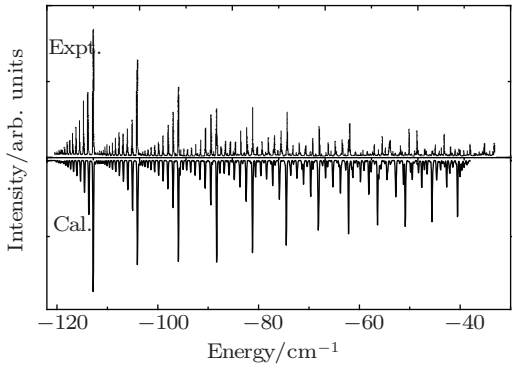


Fig. 1. Computed and observed spectra for σ^+ transition.

Below the energy $E = -60$ cm^{-1}, the detailed structures from theoretical calculations are similar for every manifold n. It is not yet quite clear why the abrupt change for the spectrum line occurs above -60 cm^{-1}. It is perhaps partly due to the fluctuation of the signal because the interaction between the atom and the laser light is rather weak, or the laser power is reduced further into the ultraviolet region at this energy range. The author of Ref. [10] argued that an unnoticed electric field could make the σ^+ and σ^- spectra identical, from the point of view of our theoretical computation. it is hard to attribute the abnormal behavior to the inadequacy of our model calculation.

As shown in Eq. (1), the value of the quantum defect for the channel np is taken to be zero. If the nf channel does not play an important role for the spectrum in the energy range of interest, the spectrum should therefore become completely the same as that of a hydrogen atom. We therefore perform calculations for the hydrogen atom as well and compare with an analogous calculation keeping only the nf quantum defect nonzero. The results are shown in Fig. 2, indeed the two spectra are nearly identical. This comparison shows that the quantum defect for the channel nf does not affect the spectrum much.

A second important numerical study is to investigate the contributions of the channels ns and nd. According to the selection rules for the Hamiltonian matrix elements, the channels ns and nd are not involved in this interaction at all. If this is true, we can draw a happy conclusion that the barium atom behaves exactly like a hydrogen atom in this energy range. This is important especially when studying atoms in extremely strong magnetic fields since a hydrogen atom can be used for the theoretical treatment instead. The dependence of the calculated spectrum on quantum defects of the channels ns and nd is shown in Fig. 3. The spectrum is insensitive to the above two quantum defect values. This follows the previous discussion that the transition matrix elements between the adjacent channels are zero.

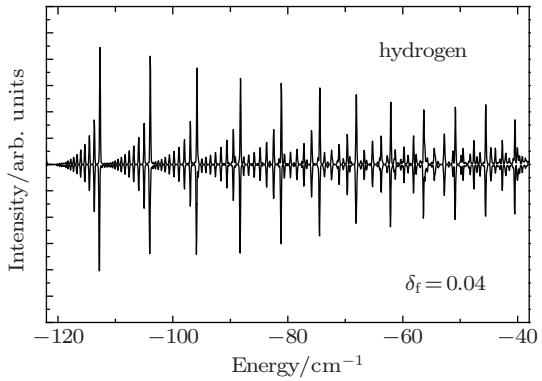


Fig. 2. The dependence of the calculated spectra on the quantum defect of the channel nf. The hydrogen spectrum is shown upwards and the barium calculation with $\delta_f = 0.04$ is mirrored for comparison. The spectrum is indeed insensitive to the quantum defect n_f at all in this energy range.

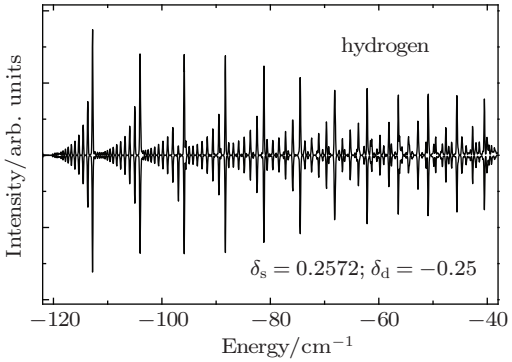


Fig. 3. The dependence of the calculated spectrum on quantum defects for the channels ns and nd. Indeed they are insensitive to the two quantum defects.

Since the effective quantum defects for barium atoms are close to zero for the concerned transitions, it is not so easy to draw physical conclusions from the spectrum feature. A non-zero quantum defect couples different angular momentum channels resulting in avoided crossings for the energy levels. It is generally believed that the diamagnetic spectrum reveals these avoided-crossing properties by tracing a series of spectra at different magnetic field values. We calculate therefore the diamagnetic spectrum for barium in the small energy range (from -97 cm^{-1} to -90 cm^{-1}) from $B = 3.06$ T to $B = 3.16$ T and compare this with hydrogen in the same magnetic fields. The results are shown in Fig. 4. Figure 4(a) displays the diamagnetic map for hydrogen, where the sub-manifolds belonging to the adjacent principal quantum numbers n and $n + 1$

cross directly and show no evidence of any collisions. However, figure 4(b), which shows the same results for barium, is very different. Due to the non-zero quantum defect for the channel *n*f, a clear avoided crossing can be found between the spectral lines from different manifolds of *n*, even though the value for the quantum defect is very small. This effect for the quantum defect is not observable if the energy levels do not collide. Although the levels meet at a certain magnetic field, a single spectrum alone cannot provide direct information on their interaction. An ideal approach to investigate this is to record the diamagnetic spectrum map at a series of magnetic fields. The level repulsion feature of the spectral lines then amplifies the effect of a non zero quantum defect in the spectrum, aiding us to reveal the general phenomenon for the diamagnetic spectrum of an atom with a non-zero quantum defect.

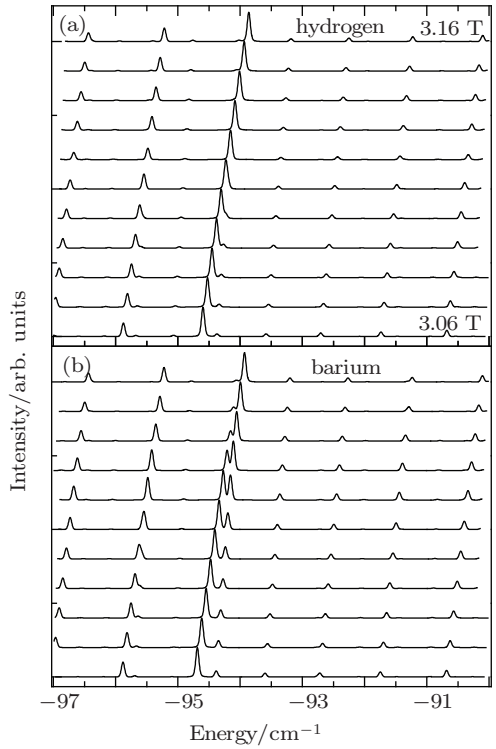


Fig. 4. Diamagnetic spectrum maps for (a) hydrogen and (b) barium atoms. For the hydrogen atoms, the neighboring manifolds do not interact and the spectral lines cross each other directly; while for the barium atoms, even for a very small quantum defect for the channel *n*f, its impact on the spectrum feature is significant.

4. Conclusion

In summary, we reinvestigate the photoabsorption spectra of a barium atom in a strong magnetic field of $B = 2.89$ T. Within the one-photon dipole coupling scheme, only the *n*p Rydberg states are directly excited. This treatment thus avoids the unnecessary complications from the intermediate states in the multi-step excitation configurations and keeps the effects of neighboring quantum channels away. Incorporating the effective quantum defects into the angular part of the centrifugal term, our calculation employs a B-spline basis expansion and complex coordinate rotation and gives satisfactory explanations for the experimental results over considerable energy range. As the quantum defects for the barium atoms are nearly equal to zero, we find it is difficult to obtain useful information from the single photon absorption spectrum alone. A more powerful approach points to the investigation of the diamagnetic spectrum maps, which can reveal avoided level crossings due to non-zero quantum defects.

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