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Diamagnetic spectra of alkaline earth barium in a magnetic field

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Abstract. We present theoretical diamagnetic spectra of Barium using R-matrix method combined with quantum defect theory. The nonhydrogenic character of the spectra is analyzed for Ba. Comparisons are made with similar calculations for hydrogen and with data of experiments in the l-mixing region and n-mixing region. The result shows that the theoretical results are in good agreement with the experimental ones.

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1 Introduction

Hydrogen and nonhydrogenic atoms are real physical systems whose behavior in external fields belongs to the fundamental problems in atomic physics. Over the past decades a great number of investigations on the atomic systems in magnetic fields have been carried out theoretically and experimentally and remarkable progresses have been made [1–4]. For example in 1969, Garton and Tomkins [5] in 1969 performed the first experiment on atoms in highly excited Rydberg states in an externally applied magnetic field and discovered the quasi-Landau resonances. These early experiments on alkaline-earth elements were important because they led to the discovery of many fundamental features of the quadratic Zeeman problem, including in particular those related to the chaotic behaviour of the underlying classical dynamics. However, they suffered from a hidden blemish, which was not initially appreciated. In all the early papers (both experimental and theoretical) it was assumed that

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the motional Stark effect, whose existence was uncovered and explained by Fano and Crosswhite [6], would have no significant influenced over the spectra of such heavy atoms. This has turned out not to be true. In fact, experiments with beams have shown that, under the conditions of the experiment performed by Garton and Tomkins [5], the spectra were strongly contaminated by motional Stark effects, to the extent that they do not really represent quadratic Zeeman structures. In fact, the first observation of a purely diamagnetic spectrum for Ba was reported by Elliott *et al.* [7] and to verify its interpretation. So far, there has been only one set of calculations since the work of Elliott *et al.*, namely those of Rao and Taylor [8]. In the present paper, we report a new set of calculations, which are based on similar principles, and we compare them both with earlier theoretical work and with the experimental data. We also note that recent experiments by Connerade and co-workers have led to new data on diamagnetic Stark spectra [9,10]. In absence of electric fields, however, the system possesses rotational symmetry. This allows us to reduce the problem to a two-dimensional one, but the remaining two-dimensional system is still nonseparable. Especially if the influence of the external field and the inner-atomic forces are comparable, which is the case for highly excited atoms under laboratory field strengths, the system becomes highly nonintegrable, and classically behaves chaotically [11]. Semiclassical techniques and full quantum theories have been developed to study the highly excited Rydberg atoms in magnetic fields. Du *et al.* [12] presented semiclassical closed orbit theory and studied the hydrogen atom in a magnetic field by semiclassical methods. A series of papers have been published [8,13] using the full quantum theories.

2 Model and method

In this work we study the spectra of Ba in a magnetic field by the R-matrix method with quantum defect theory that was developed by Halley, Delande and Taylor [14] and compare theoretical result with experimental one. This method combines a variant of the R-matrix method with quantum defect theory. The configuration space is divided into an inner region $(r \le a)$ and an outer region $(r \ge a)$. The boundary must be chosen large enough to encompass the multi-electron core, but also small enough for magnetic field terms in Hamiltonian to be neglected. In the outer region, we consider this system as a one-electron system. The Hamiltonian for outer electron of Ba in magnetic fields directed along the z-axis is given by (in atomic units)

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r} + \frac{\gamma L_z}{2} + \frac{\gamma^2}{8}(x^2+y^2), \qquad a \le r \le \infty, \tag{1}$$

where $\gamma = B/B_0$ and $B_0 = 2.35\times 10^5$ Tesla, $\gamma L_z/2$ and $\gamma^2(x^2+y^2)/8$ are the linear and quadratic Zeeman terms, respectively. The linear term $\gamma L_z/2$ provides a uniform shift for all the energy levels in a specified subspace of magnetic quantum number m, and so can be omitted. The physics in the inner region where $r \le a$, is very complicated, but according to quantum defect theory we only require the wavefunction solutions on the boundary $r = a$. This allows us to write each component of the inner region solution at a, as a linear combination of Coulomb functions,

$$F_l(a)=s_l(a)+\tan(\mu_l\pi)c_l(a). \tag{2}$$

Here $s_l(a)$ and $c_l(a)$ are energy normalized regular and irregular Coulomb functions respectively, evaluated at $r=a$ and μ_l is the quantum defect for angular momentum l. At energy E the Hamiltonian satisfies

$$\left(-\frac{1}{2}\nabla^2-\frac{1}{r}+\frac{1}{8}\gamma^2r^2\sin^2\theta\right)\Psi(r,\theta,\varphi)=E\Psi(r,\theta,\varphi), \qquad a\le r\le\infty. \tag{3}$$

We use a spherical basis set expansion of the eigenfunctions Ψ in terms of radial functions $F_l(r)$ for angular momentum l, multiplied by spherical harmonic functions $Y_{lm}(\theta,\varphi)$. We therefore have

$$\Psi=\sum_l\frac{F_l(r)}{r}Y_{lm}(\theta,\varphi). \tag{4}$$

Substituting this expansion into the Schrodinger equation yields

$$\begin{aligned}&\sum_l\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{l(l+1)}{r^2}-\frac{2}{r}+\frac{1}{4}\gamma^2r^2\sin^2\theta\right)F_l(r)Y_{lm}(\theta,\varphi)\\&=2E\sum_lF_l(r)Y_{lm}(\theta,\varphi).\end{aligned} \tag{5}$$

To make the Hamiltonian in Eq. (5) hermitian in this reduced radial space, we must replace $\frac{\mathrm{d}^2}{\mathrm{d}r^2}$ in each partial wave by $\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\delta(r-a)(\frac{\mathrm{d}}{\mathrm{d}r}-B_l)$. We thus arrive at the new equation,

$$\begin{aligned}&\sum_l\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2}-\delta(r-a)(\frac{\mathrm{d}}{\mathrm{d}r}-B_l)+\frac{l(l+1)}{r^2}-\frac{2}{r}+\frac{1}{4}\gamma^2r^2\sin^2\theta\right)F_l^k(r)Y_{lm}(\theta,\varphi)\\&=2E_k\sum_lF_l^k(r)Y_{lm}(\theta,\varphi).\end{aligned} \tag{6}$$

Here we let

$$B_l=\frac{1}{F_l(a)}\frac{\mathrm{d}F_l(r)}{\mathrm{d}r}\bigg|_{r=a}, \tag{7}$$

where $F_l(r)$ is the solution to Eq. (5) at energy E. It can be proved that an eigenvalue E_k of Eq. (6) is coincident with E and that the corresponding eigenfunction components $F_l^k(r)$ coincide with $F_l(r)$. Multiplying Eq. (6) from the left by $Y_{l'm}^*$ and integrating over the solid angle $\mathrm{d}\Omega$ gives,

$$\begin{aligned}&\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2}-\delta(r-a)\left(\frac{\mathrm{d}}{\mathrm{d}r}-B_l\right)+\frac{l(l+1)}{r^2}-\frac{2}{r}\right)F_l^k(r)\\&\quad+\frac{1}{4}\gamma^2r^2\left(K_{ll-2}F_{l-2}^k(r)+K_{ll}F_l^k(r)+K_{ll+2}F_{l+2}^k(r)\right)\\&=2E_kF_l^k(r),\end{aligned} \tag{8}$$

where

$$K_{ll'} = \int Y^*_{lm} \sin^2\theta Y_{l'm} \mathrm{d}\Omega.$$

This is an eigenvalue equation which can be solved for (real) eigenvalues E_k and corresponding eigenfunction components $F^k_l(r)$.

3 Results and discussion

We present the p- and f-wave quantum defects of barium in Fig. 1, where the solid squares indicate the quantum defects which are obtained by the following methods from the free-field experiment [15]. The full curves are the results of a least squares fitting to these values. Unlike other Rydberg series, the barium $^1P_0$ series in the energy region near the ionization threshold are strongly influenced by an intruder $5d8p\ ^1P_0$ level [16]. We used a function to fit the quantum defect of the $^1P_0$ series as follows,

$$\delta(E) = \begin{cases} a+bE+\frac{1}{\pi}\left(\pi+\arctan\left(\frac{\Gamma/2}{E_R-E}\right)\right), & \text{if } E>E_R, \\ a+bE+\frac{1}{\pi}\arctan\left(\frac{\Gamma/2}{E_R-E}\right), & \text{if } E\leq E_R, \end{cases}$$

where E_R=42000±1 cm^{-1}, $\Gamma/2$=75±1 cm^{-1}. The energy E is in cm^{-1} and where parameters a,b are found by fitting the experimental data. E_R and $\Gamma/2$ are the position of the 5d8p perturbing resonance and its half-width, respectively. The ^1F_o series quantum defect could be fitted to a simple 2$^{\mathrm{nd}}$-order polynomial. Considerably the Ba atoms are excitated from the

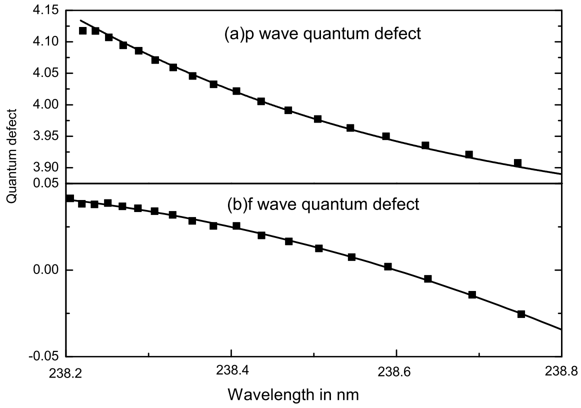

Figure 1: The p-wave and f-wave quantum defects of barium. The full curve in each case is the result of a least-squares fitting of the field-free experimental data. The solid squares represent the field-free experimental data.

singlet ground state in experiment, and in the case of the pure magnetic field, where parity is a good quantum number. Dipole transitions from the initial 6^1S_0 states are only allowed for odd total parity states but not even total parity states for the matrix element of the dipole operator to be non-vanishing.

Only odd l may exist in the final state, so the values of the p- and f-wave quantum defect are required. For higher l series the quantum defects can be considered to be zero.

We calculate the even z-parity spectra of barium and hydrogen with $m = \pm 1$ in a magnetic field strength of $B = 2.87$ Tesla. Note that this is different from the experimental data of $B = 2.89$ Tesla [7]. We adopt different magnetic field strength in calculating the spectra and found best agreement between calculation and experiment for a magnetic field strength of $B = 2.87$ Tesla which is within the experimental error $B = 2.89 \pm 0.03$. Figs. 2 and 3 show the numerically computed $\sigma^\pm$ spectra of barium. The σ^+ spectrum can be obtained by displacing spectra σ^- an appropriate paramagnetic shift. The l- and n-mixing regions were covered in the energy region of interest in this work. In the l-mixing region, the states with different l are strongly mixed, but the principal quantum number n is still can be considered as a good quantum number. The positions and intensities of the lines are in good agreement with those from the experiment in this region. In the n-mixing region, n can no longer be regarded as good quantum number, the spectrum becomes much more complicated in this region. The degree of agreement with the experiment is not quite as good as compared to the l-mixing region. Fig. 4 displays the computed spectrum of barium, together with those for hydrogen in the same field strength and over approximately same ranges of principal quantum numbers. We can see the spectra of barium has similarities with that of hydrogen in the l-mixing region. This is due to the small p and f quantum defects of barium in that range. There are more differences in the n-mixing region than in the l-mixing region. This embodies the effect of the muti-electron structure of barium. Over the whole wavelength range under consideration, the spectra in each cluster fall off monotonically in strength as one goes to shorter wavelengths

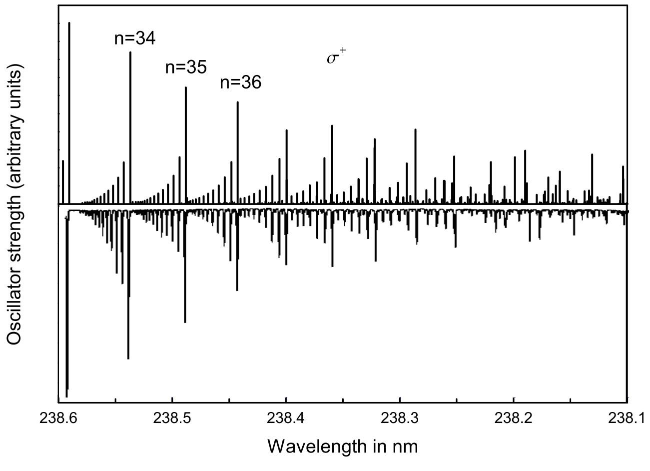

Figure 2: Upper frame: the theoretical σ^+ photoabsorption spectrum for barium in a magnetic field strength of 2.87 Tesla. Lower frame: the experimental spectrum with a magnetic field strength of 2.89 Tesla.

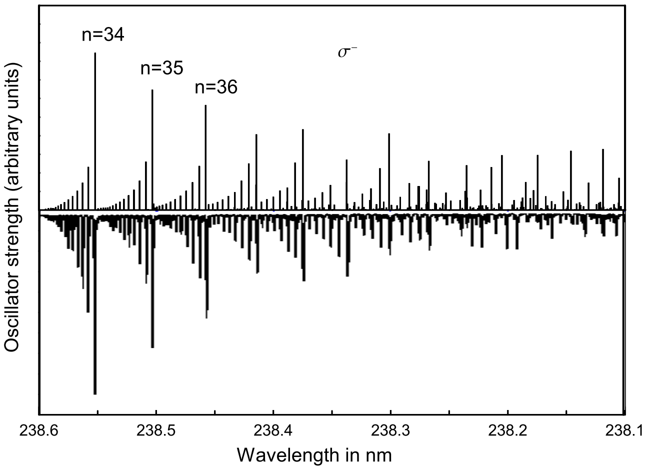

Figure 3: Upper frame: the theoretical σ^- photoabsorption spectrum for barium in a magnetic field strength of 2.87 Tesla. Lower frame: the experimental spectrum with a magnetic field strength of 2.89 Tesla.

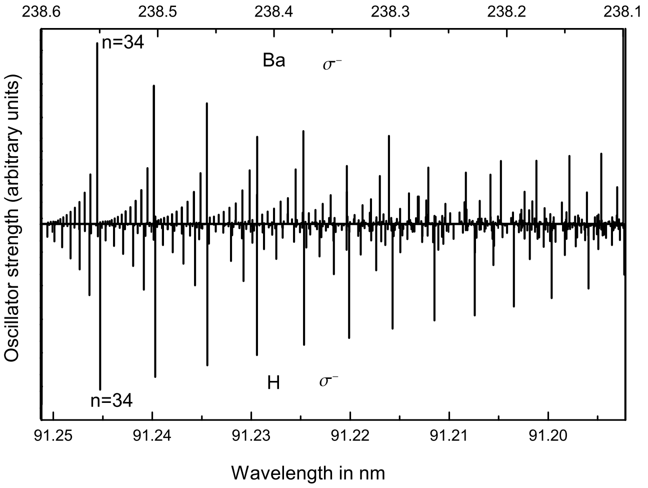

Figure 4: Upper frame: the theoretical σ^- photoabsorption spectrum for barium in a magnetic field strength of 2.87 Tesla. Lower frame: the theoretical spectrum of hydrogen in a magnetic field strength of 2.87 Tesla.

and becomes increasingly complicated and dense. For the same principal quantum number n (e.g. $n = 34$) the corresponding wavelengths are different for barium and hydrogen since each has a different first ionization energy. The ionization energy of barium and hydrogen are 42034.90 cm^{-1} and 109678.82 cm^{-1}, respectively.

In summary, we have calculated the diamagnetic spectra of alkaline earth barium in a magnetic field encompassing the l-mixing, and n-mixing regions and have compared the results with those for the hydrogen atom. Since the ratio of the diamagnetic shift to the spacing between adjacent field free Rydberg states scales as $\gamma n^{7/2}$, the spectra increase in complexity considerably as n increases. The difference between Ba and H is due to the fact that Ba has the core-effect and the character of many electrons. This system can help us to understand the relationship between classical mechanics and quantum mechanics.

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