Quadratic Zeeman Effect for Nonhydrogenic Systems: Application to the Sr and Ba Atoms

P. F. O'Mahony and K. T. Taylor

Royal Holloway and Bedford New College, University of London, Egham, Surrey TW20 0EX, England

(Received 2 September 1986)

A method has been developed to calculate the spectrum over the l- and n-mixing regimes of an arbitrary nonhydrogenic system in an external laboratory-strength magnetic field. The original experimental results on Sr and Ba are explained in detail for the first time. The importance of quadratic Zeeman spectroscopy in the quantitative study of atomic structure is made clear.

PACS numbers: 32.60.+i, 31.50.+w

Garton and Tomkins,[1] in 1968, performed the first experiments on atoms in highly excited Rydberg states in an externally applied magnetic field. These experiments have stimulated new developments in both theoretical and experimental atomic physics because an atom in an external magnetic field provides the simplest example of a system where two disparate symmetries compete with one another. These symmetries are the cylindrical symmetry of the applied field and the spherical one of the Coulomb field. This competition results in a Hamiltonian which is nonseparable in any coordinate system.

This Letter reports the first calculations on Rydberg states of nonhydrogenic atoms in a uniform magnetic field that permit a detailed comparison with experimental spectra over the l- and n-mixing regimes for any atom.

The approach followed has hinged on two physical realizations. The first is that for magnetic fields of laboratory strength (5–50 kG or $\beta = 10^{-6}$ to 10^{-5} in atomic units), the quadratic Zeeman potential $\frac{1}{2}\beta^2 r^2 \sin^2\theta$ can, up to some radius r_0 equal to several hundred bohrs about the nucleus, be completely ignored in comparison to the potentials arising from the much stronger electron-nucleus and electron-electron interactions. This reduces the description of this inner region in the problem to that appropriate to a conventional multielectron atom completely free of any externally imposed fields. The second realization is that in the outer region (which extends in radial coordinates from r_0 to ∞ and in which the quadratic Zeeman potential is crucially important), only one electron of the atom will ever be found. Thus the Schrödinger equation for the complex atom in this outer region reduces to the one-electron form already investigated for hydrogen. These two physically distinct regions will now each be discussed separately in some detail.[2]

Since the magnetic field potential is a negligible term in the Hamiltonian over the inner region $0 \le r \le r_0$, we can acquire wave-function solutions to the Schrödinger equation there such that each solution corresponds to a fixed specific value of total orbital angular momentum L and total spin S. To progress further, this inner region must be divided into two subregions. The innermost of these, besides encompassing all but one of the atomic electrons, must also be sufficiently large so that low-lying excited configurations of the remaining electrons are entirely contained within it. Over the remaining part of the inner region the single electron present must, even for a fixed L, be described by a multicomponent wave function reflecting the various possible levels of excitation of the residual electrons of the atom. However, by the boundary of this region all but those components linked to the ground state of the residual ion will be considered to have undergone exponential decay and died away. For Sr and Ba atoms, the ground state of the residual positive ion is ^2S and so for a given L there remains only a single component corresponding to a specific value l of the orbital angular momentum of the single electron.

Near the boundary $r = r_0$, where only the Coulomb potential has significance, this single component can be written as a linear combination of energy-normalized regular and irregular Coulomb functions, $f_l(r)$ and $g_l(r)$, respectively; viz.,

$$P_l(r) = f_l(r) + \tan(\pi\mu_l) g_l(r) \qquad (1)$$

The quantity μ_l is the energy-dependent quantum defect and parametrizes the energy-dependent coupling between this component and those that die off exponentially before r_0 is reached. Generally for $l > 4$, μ_l is approximately zero.

It is appropriate to calculate solutions in the inner region for all values of L allowed by parity considerations, each time gaining a component of the form (1) on the outer boundary. Before long, however, there is some $L_{\max}$ with a corresponding $l_{\max}$ in (1) such that for $l > l_{\max}$ the angular momentum barrier is so large that the regular Coulomb function $f_l(r)$ evaluated at $r = r_0$ is completely negligible. This provides a valuable restriction on the amount of inner-region calculation necessary.

The true inner-region wave function that matches on to the wave function in the outer region is composed from all these differing l contributions. A vector $\mathbf{F}$ of radial parts can thus be written such that

$$\mathbf{F} = \mathbf{P} \cdot \mathbf{A}, \qquad (2)$$

where $\mathbf{P}$ is a diagonal matrix with elements $P_l(r)$ of Eq. (1) and $\mathbf{A}$ is a vector of numbers specifying the relative weighting of each $P_l(r)$ in the true wave function.

This weighting is governed by the direct action of the magnetic field potential in the outer region where the problem has been reduced to one electron moving under the combined influence of Coulomb and magnetic fields. Thus previous work on the hydrogen atom is relevant. The Hamiltonian over the region $r_0 \le r \le \infty$ takes a form identical to that for hydrogen which, in atomic units, is

$$H = -\tfrac{1}{2}\nabla^2 - r^{-1} + \beta l_z + \tfrac{1}{2}\beta^2 r^2 \sin^2\theta, \tag{3}$$

where $\beta = ehB/2mc$ and the magnetic field vector $\mathbf{B}$ is chosen to point along the z axis. This Hamiltonian is symmetric with respect to coordinate inversion and so parity is a good quantum number. In addition, since the potential does not depend on the azimuthal angle ϕ, it is also diagonal in the magnetic quantum number m.

In solving the corresponding Schrödinger equation in this outer region, we have chosen a method which is a variant of the R-matrix approach first employed in atomic physics by Burke, Hibbert, and Robb.[3] This rests on the ability of a finite number of suitably chosen basis functions to represent the wave function adequately over a limited region of space. In our work such basis functions have been obtained by diagonalization of the Hamiltonian (plus a surface term that arises because integration is confined to the outer region) over a set of linearly independent Sturmian functions $S^{\xi}_{nl}(r)$ satisfying *arbitrary* boundary conditions at $r = r_0$.

The basis functions have energies E_k and are denoted by ψ_k, where

$$\psi_k = \sum_{nl} C^k_{nl} S^{(\xi)}_{nl}(r) Y_{lm}(\theta,\phi) \tag{4a}$$

$$= \textstyle\sum_l d_{lk}(r) Y_{lm}(\theta,\phi). \tag{4b}$$

The energies E_k are the eigenvalues and C^k_{nl} the eigenvector components resulting from the diagonalization. In turn the Sturmian functions, already exploited advantageously by Clark and Taylor[4] in the hydrogen-atom magnetic field problem, are such that for a given orbital angular momentum quantum number l each satisfies the differential equation

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{\xi n}{r} - \frac{\xi^2}{4}\right] S^{(\xi)}_{nl}(r) = 0, \tag{5}$$

where n is an integer label with $n > l$ and ξ is a positive constant common to the basis.

A direct result of the R-matrix procedure (see Burke and Robb[5]) is that the R matrix, which relates the vector $\mathbf{F}$ of radial wave-function components given by Eq. (2) to the radial derivative of this vector on the boundary $r = r_0$, viz.,

$$\mathbf{F}(r_0) = \mathbf{R}\cdot\mathbf{F}'(r_0), \tag{6}$$

can be expressed as

$$R_{ll'} = \sum_k \frac{d_{lk}(r_0) d_{l'k}(r_0)}{E_k - E}, \tag{7}$$

where E is the total energy of the single last electron in the outer region and $l_{\max}$ provides the upper limit on both l and l'. It should be noted that Eq. (7), for a given field strength, is *independent* of the complexity of the atom in the inner region and once calculated can be used for an arbitrary atom.

This approach for the outer region has allowed us to use there—with minimal amendment—the computer programs written by Clark and Taylor[4] to examine the l- and n-mixing regimes in hydrogen. Some alterations result from the need to evaluate matrix elements of the Hamiltonian (3) over the limited radial range from r_0 to ∞ rather than from 0 to ∞. This breaks the selection rules on label n enjoyed by matrix elements of $1/r$ and r^2 in the Sturmian set. Nevertheless the new nonzero integrals are readily evaluated analytically and the overall banded structures of the Hamiltonian and overlap matrices remain, albeit with somewhat wider bandwidths than in the hydrogen problem. Moreover the limited radial range means that a smaller number of Sturmian functions is needed. Full details of the methods for these new integrals will be presented in a future publication.

Once calculations have been performed in the two regions there remains the problem of joining wave functions across the one-electron boundary. This is achieved by use of Eq. (6) above. Solution and derivative vectors $\mathbf{F}(r_0)$ and $\mathbf{F}'(r_0)$ are provided on the boundary from the inner-region side while expression (7) for the R matrix means that this depends entirely on the outer-region calculation. Thus Eq. (6) acts as a matching condition on the boundary between the regions and will be satisfied only at certain discrete energies E. On substituting (2) in (6) we obtain

$$(\mathbf{P} - \mathbf{R}\cdot\mathbf{P}')\cdot\mathbf{A} = 0. \tag{8}$$

The discrete energies are therefore those at which

$$\det(\mathbf{P} - \mathbf{R}\cdot\mathbf{P}') = 0, \tag{9}$$

and the vector $\mathbf{A}$ is also given by solution of (8) at each such energy.

In this matching of wave functions on the boundary $r = r_0$ we have been able to take full advantage of the efficient energy search algorithm due to Seaton[6] and the associated computer program. In Seaton's program, and indeed in all applications of the R-matrix method before this one, the R-matrix form (7) has resulted from calculations in the *inner* region surrounding the nucleus, and the vector (2) has been supplied by the *outer*-region calculation. The inversion of roles has necessitated some changes to Seaton's program but not of a fundamental nature.

For each wave function obtained and properly normalized, the coefficient A_1 gives the fraction of $L = 1$ character in it. The oscillator strength linking any such state to an $L = 0$ ground state is then simply proportional to $|A_1|^2$ times the field-free oscillator strength at the ener-

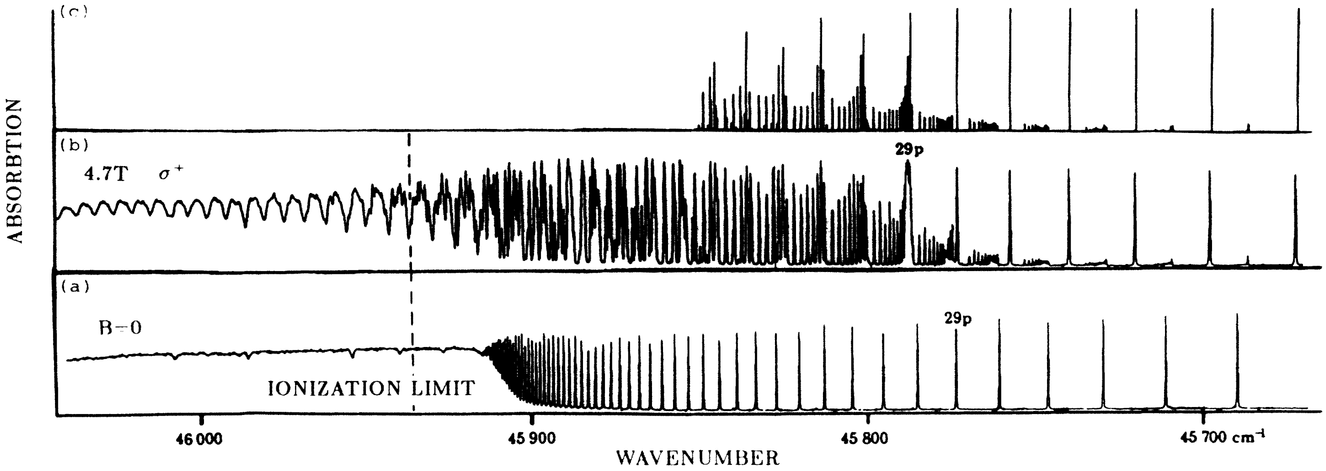

FIG. 1. Strontium absorption spectrum vs transition wave number from the ground state: (a) field-free spectrum; (b) experimental densitometer tracing for strontium in a magnetic field of 4.7 T; (c) theoretical photoabsorption spectrum in a field of 4.7 T. The theoretical results give the absolute oscillator strengths, but for n less than 29 the strongest lines have been reduced in size to facilitate comparison with the nonabsolute experimental measurements.

gy E of that state.

The theory outlined above has, in this first application, been directed towards the heavy complex atoms Sr and Ba for which magnetic field experimental data exist. We have used experimental energies[7] for field-free states in $^1P^\circ$ and $^1F^\circ$ symmetries to determine the relevant μ_l's in (1) and experimental values[8] for oscillator strengths of field-free discrete transitions from the ^1S-component ground states of these atoms. In general, and especially for light atoms, these data can be provided by *ab initio* calculations using standard methods. This is all that is required to determine the spectrum in a laboratory magnetic field of arbitrary strength.

The calculated results are compared with the experimental measurements of Lu, Tomkins, and Garton[9] on Sr and Ba in Figs. 1 and 2, respectively. The striking differences between the Sr and Ba spectra in the presence of a magnetic field has long been a source of puzzlement. [Their field-free spectra are quite similar in this energy range as evidenced by the frames of Figs. 1(a) and 2(a).] We find that the differences are due to the perturbers "$4d5p$" in Sr and "$5d8p$" in Ba. In zero field the quantum defects of the $5snp$ and $5snf$ series in Sr each rise through unity as a result of the $4d5p\,^1P^\circ,^1F^\circ$ resonances. However this rise occurs predominantly at low n and the quantum defects of the $5snp$ and $5snf$ series are slowly varying at $n \approx 29$, being approximately 0.8 and 0.1, respectively. This results in the $5snp$ and $5snf$ levels being separated from the higher l's in the n manifold. These levels, in the presence of a magnetic field, can be associated with the strongest lines in the spectrum of Fig. 1(b) for $n < 29$.

In contrast, the $5d8p$ perturber in Ba lies in the vicinity of the ionization threshold and causes the zero-field quantum defects of the $6snp$ and $6snf$ series to change with energy in this region. Surprisingly, however, these

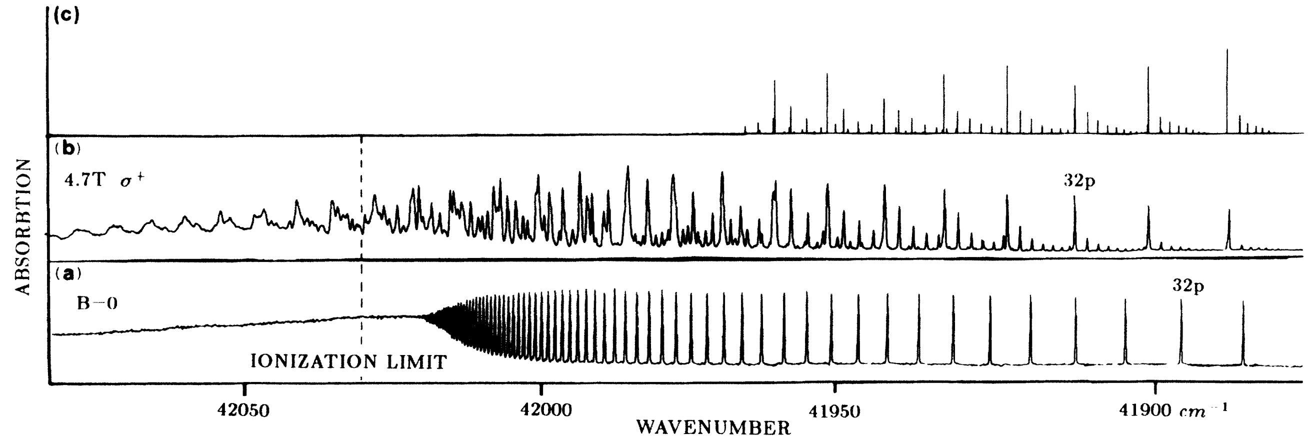

FIG. 2. Barium absorption spectrum vs transition wave number from the ground state: (a) field-free spectrum; (b) experimental densitometer tracing for barium in a magnetic field of 4.7 T; (c) theoretical photoabsorption spectrum in a field of 4.7 T.

quantum defects are both approximately zero (modulo one) in the energy range of interest around $n \sim 32$. This fortuitous coincidence explains the hydrogenic-type pattern that is observed in Ba in the presence of a magnetic field [Fig. 2(b)] in the inter-l- and inter-n-mixing regions.

The spectrum of Sr in the presence of a magnetic field should, however, be more typical of an arbitrary atom since the Ba spectrum results from an unusual coincidence in value of two important quantum defects.

In passing we point out that as $n = 29$ is approached in Sr, our calculations indicate a much more drastic redistribution of oscillator strength among levels than do the vapor experiments. This has important consequences for the use of magnetic rotation spectroscopy in measuring oscillator strengths.[10]

Some qualitative understanding of the spectra of Sr and Ba near $E = 0$ and above the ionization threshold exists but as yet no reliable theoretical approach has been developed to treat this region. The method worked out here for photoabsorption in nonhydrogenic systems should be readily applicable to photoionization in nonhydrogenic systems once a method has been found to handle the photoionization of hydrogen in a magnetic field.

In conclusion, we have described a general method to treat any nonhydrogenic system in laboratory magnetic fields of arbitrary strength. We have, for the first time, obtained excellent agreement with the original experiments of Garton and Tomkins on Sr and Ba. In doing so we have revealed in detail how the quadratic Zeeman spectroscopy of atoms can indirectly provide valuable information on symmetries (such as the $^1F^{\circ}$ in these cases) that are inaccessible in field-free single photoabsorption by ground-state atoms. We believe that our new theoretical understanding turns this spectroscopy into a quantative technique.

This work was supported in part by a research grant from the Science and Engineering Research Council, United Kingdom.

---

[1] W. R. S. Garton and F. S. Tomkins, Astrophys. J. **158**, 839 (1968).

[2] This approach is similar in spirit to that used by D. A. Harmin, Phys. Rev. Lett. **49**, 128 (1982), for atoms in external electric fields. However, he was able to utilize the separability of the Stark problem in parabolic and spherical coordinates. No comparable separability holds in the magnetic case.

[3] P. G. Burke, A. Hibbert, and W. D. Robb, J. Phys. B **4**, 153 (1971).

[4] C. W. Clark and K. T. Taylor, J. Phys. B **15**, 1175 (1982).

[5] P. G. Burke and W. D. Robb, Adv. Atom. Molec. Phys. **11**, 143 (1975).

[6] M. J. Seaton, J. Phys. B **18**, 2111 (1985).

[7] Sr energy levels: I. R. Rubbmark and S. A. Borgstrom, Phys. Scr. **18**, 196 (1978); M. A. Baig and J. P. Connerade, J. Phys. B **17**, L271 (1984). Ba energy levels: B. H. Post, W. Vassen, W. Hogervorst, M. Aymer, and O. Robaux, J. Phys. B **18**, 187 (1985); W. R. S. Garton and F. S. Tomkins, Astrophys. J. **158**, 1219 (1969).

[8] Sr oscillator strengths: W. R. S. Garton, J. P. Connerade, M. A. Baig, J. Hormes, and B. Alexa, J. Phys. B **16**, 389 (1983). Ba oscillator strengths: W. H. Parkinson, E. M. Reeves, and F. S. Tomkins, J. Phys. B **9**, 157 (1976).

[9] K. T. Lu, F. S. Tomkins, and W. R. S. Garton, Proc. Roy Soc. London, Ser. A **362**, 421 (1978).

[10] J. P. Connerade, private communication.