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DIAMAGNETISM IN EXCITED STATES OF HYDROGEN

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Abstract. -The spectrum of high Rydberg states of atomic hydrogen in a magnetic
field has received much attention in the last few years. Although no experi­
mental work has been done, theoretical activity has elucidated major features
of the spectrum ranging in energy up to a few cyclotron frequency units below
the ionization threshold. In the weak field limit an unexpected richness of
structure has been uncovered by perturbative treatments based on the O(4)
symmetry of hydrogen. Though this symmetry is absent in the more complex atoms
for which experimental data is available, we believe that a comprehensive
theory of Rydberg diamagnetism will ultimately be phrased in hydrogenic lan­
guage. We review here the basic physics which motivates this hypothesis, the
experimental and numerical results which substantiate it, and the opportunities
it suggests for future investigations.

Modern interest in the diamagnetism of Rydberg states originates from the
experiments of Garton and Tomkins in 1969 [1]. Since then a number of experimental
groups [2-4] have taken up similar studies, and theoretical effort has produced
broad qualitative understanding of the phenomenon. However, there is at present no
comprehensive and quantitatively useful theory of Rydberg diamagnetism; and, perhaps
partly in consequence of this, the several experimental programmes seem to have
operated without a strong common focus. At this stage the most useful service
theorists can provide may be to enunciate the reasons why this sort of work is
important, and what experiments are then needed to further it. In our view,
diamagnetism offers a unique facility for exploring the dense spectral regions of
atoms and molecules near ionization thresholds, which is based on its great sen­
sitivity to the size of excitations. Exploitation of this facility is contingent
both on advances in theoretical understanding of non-separable dynamics, and on
parallel experimental studies. For fundamental, as well as practical reasons, the
atomic systems of greatest theoretical simplicity may be expected to yield the most
valuable results. This expectation is given encouragement by simple reasoning and
by historical analogy.
Fig. 1: Photoabsorption spectrum of barium in magnetic fields of various strength (as indicated). The absorbed photons are circularly polarized about the magnetic field axis. From [2], courtesy K. T. Lu.

The lowest frame of figure 1 shows a phenomenon which occurs universally in atomic and molecular spectra: a Rydberg series. Though it is here associated with a fairly complex atom, barium, similar series are observed in every atomic species; being always characterized by a formula for the frequency $v_n$ of the $n^{th}$ line,

$$v_n = v_\infty - \frac{\zeta^2}{(n-\mu)^2}.$$  

(1)

It is unnecessary to catalogue here the many qualifications which must be made about the utility of formula 1 - $v_\infty$ is the frequency at the series limit; $\zeta$ depends only on the degree of ionization; and $\mu$, the quantum defect, is essentially independent of $n$ - since major discrepancies from this simple description can be resolved by a multichannel treatment. Formula 1 accommodates an infinity of lines in terms of only three constants which are specific to the atom (one of which, $\zeta$, is only trivially so). This is a clear indication that the explanation of the form of Rydberg series must reside in a phenomenon which is independent of the many varied details of atomic structure. This explanation is of course well known: a Rydberg line series is associated with states in which a single electron moves progressively further from the residual ion core. At large electron-ion distances, the central Coulomb attraction - the expected universal feature - dominates the motion; at small distances, the particular atomic features come into play. These
latter are often difficult to describe in detail, but their net effect is summarized by the quantum defect \( \mu \). This states the adjustments made at short range to motion in a pure Coulomb field, through an expression for the radial wavefunction \( \psi_L(r) \) of the electron at long range:

\[
\psi_L(r) = f_L(r) \cos \mu_L - g_L(r) \sin \mu_L, \tag{2}
\]

\( f \) and \( g \) being regular and irregular solutions to the Coulomb equations of motion. Since \( \mu \) thus enters the wavefunction in the guise of a phase shift [5], it is appropriate to regard the core as a scatterer of Coulomb waves. This is the sense in which it may be said that the theory of Rydberg series is built entirely on hydrogenic foundations. It is by no means necessary to treat the effect of the core as weak, compared to the long range Coulomb force (which is anyway not the case). The success of quantum defect theories [6] is instead based on regarding non-Coulombic interactions as being effective only within a limited volume of configuration space (which is, until energy is sufficient for double Rydberg excitation [7], pretty much the case). Explanations are then provided both for the characteristic form of Rydberg series in terms of properties of motion in a central Coulomb field; and for the specific positions of lines (and irregularities), in terms of electron-core scattering.

The Rydberg spectra of atoms in magnetic fields also display characteristic forms, as can be seen in the upper frame of fig. 1. These again have explanation in terms of universal long range interactions. On the other hand, there are marked differences in detail in spectra of different atoms in the same magnetic field. These can be attributed to differences in the short range electron-ion interaction. However, it has not yet been possible to express as concisely as in formulae 1 and 2 the interplay of long- and short-range forces in this problem (except e.g. for the rightmost clusters of fig. 1, which can be described by perturbation theory). However, it is quite easy to show that, at least in the experiments done so far, the electron-core interaction is not appreciably changed by the presence of the magnetic field, and so can be described by the quantum defects obtained from field free spectra. On the other hand, the electron motion at large distances, which is subject only to magnetic and Coulomb forces, is profoundly affected by the magnetic field. The principal barrier to interpreting these spectra is thus the lack of understanding of how the high Rydberg states of a hydrogenic atom behave in a magnetic field.

At large distances from the core (presumed to have unit electrical charge), the wavefunction \( \psi \) for the Rydberg electron is a solution to the Schrödinger equation

\[
(-1/2 \nabla^2 - 1/r + \beta m + 1/2 \beta^2 r^2 \sin^2 \theta) \psi = E \psi, \tag{3}
\]

if the magnetic field is taken to lie along the z axis, and \( m = \hbar \). Equation (3) is written in atomic units; the effect of spin-dependent terms, which is usually not significant, is dealt with elsewhere [8]. In these units \( \beta = eB/2mc = \omega/2 \) is a small number for laboratory fields: for the topmost frame of fig. 1, \( \beta = 10^{-5} \). Since \( m \) is a constant of the motion we shall incorporate its contribution to eq. (3) in the total energy. Then at 10 Bohr radii \( a_0 \) from the nucleus, for instance, the change in the local potential caused by a 47kG field is of the order of \( 10^{-8} \) a.u., compared to atomic potentials there of the order 0.1 a.u. Clearly the quadratic term of the magnetic potential can be ignored over a significant range of \( r \), perhaps several hundred \( a_0 \). Within this range we can write the wavefunction in terms of the field free solutions of eq. (2):

\[
\psi(\vec{r}) = \sum \Gamma_A \Gamma_m \psi(m, \Gamma) \cdot \{f_L(r) \cos \mu_L - g_L(r) \sin \mu_L \}. \tag{4}
\]
Fig. 2: Calculated Lyman absorption spectrum of hydrogen in a 47kG magnetic field, for σ polarization. Oscillator strength vs. absolute energy for states of the:
a) principal series; b)-d) second-fourth series; e) all states in this energy range.
Fig. 3: The wavefunctions for the sixteen members of the principal series shown in fig. 2a, plotted as a function of distance from the nucleus on the ridge $\theta = \pi/2$. The coefficients $A$, and the allowed energies in the discrete spectrum $E$, are determined by boundary conditions at infinity. Though the relationship between the $A_2$, $\mu$, and $E$ is not adequately understood at present, eq. (4) indicates the possibility of using a magnetic field to determine the continuous dependence of quantum defects on energy. This could be of great use in unravelling complex spectra. Preliminary work along these lines has illustrated some effects of interseries perturbation in even parity states of barium [9]. However, the application of eq. (4) in the vicinity of ionization thresholds will require solution of the equations of motion out to much larger $r$. To some extent this can be done by numerical calculation, but in practical terms the situation is far from satisfactory. This contrasts somewhat unfavorably with recent advances [10] in the theory of the Stark effect on Rydberg states, in which the matching of short- and long-range solutions has been carried out in a general manner. Nevertheless some progress on the qualitative understanding on electron motion in combined Coulomb and magnetic fields has been made.

Certain parts of the diamagnetic Rydberg spectra are easily understood. When the electron orbitals do not extend to sufficiently large $r$ — that is to say, when their principal quantum numbers $n$ are sufficiently small — the quadratic term in eq. (3) can be treated as a perturbation which couples states with the same $n$. The simple calculations which are required to carry this out give an excellent account of structures such as those on the low energy side of fig. 1. Hydrogen is unique among atoms as concerns this perturbative treatment, however, since in the absence of a field all levels with the same principal quantum number are degenerate. As a consequence, a weak magnetic field effects a splitting of levels into a pattern which except for a scale factor is independent of field strength, and redistributes oscillator strength among lines in a manner not dependent on field strength (up until perturbation theory breaks down). An example of such a pattern can be seen on the leftmost side of fig. 2e. Moreover, the perturbative Hamiltonian for a manifold of states with constant $n$ displays some unusual symmetries when expressed in terms of the parabolic states of the free atom [11], and it has in fact been shown to be exactly solvable in terms of Jacobian elliptic coordinates in momentum space [12]. If considered within a fixed $n$ manifold, the quadratic magnetic term of eq. (3) can be represented as a quadratic form in the Runge-Lenz and angular momentum vectors [12; C. J. Goebel and T. W. Kirkman, unpublished]. The resulting equations of motion resemble those of an asymmetric top. The highest lying state of a perturbed
Fig. 4: Wavefunctions for various states of fig. 2, plotted as a function of angle along their classical turning surfaces. The wavefunctions are symmetrical about 90°. The top row contains, from left to right, the wavefunctions for the first, fifth, tenth, and sixteenth members of the principal series shown in fig. 2a. The following rows show the corresponding members of the second, third, and fourth series appearing in fig. 2. The wavefunction in the bottom right hand corner is an exception, being the fifteenth member of the fourth series; the sixteenth member is strongly perturbed by a state of the second series, and its wavefunction does not fit the regular pattern.
manifold (e.g. that associated with the strongest line in the lowest cluster of figure 2e) tends to be localized around $\theta = \pi/2$. As this is the most repulsive part of the potential surface for fixed $r$, such localization seems somewhat surprising. It may perhaps be understood in analogy with the problem of stability of rotation of an asymmetric top, the top's rotation being stable if directed about the axis of either greatest or least moment of inertia.

The modulations of the spectra just above the ionization limit - the quasi-Landau resonances - have also been explained in terms of motion along this "ridge" of the potential surface, $\theta = \pi/2$ [13]. If the electron is considered to be confined on the ridge, it is found that the energy levels in the vicinity of the ionization threshold are spaced in energy by $1.5 \hbar \omega$; if one associates these levels with the peaks observed in the photoabsorption experiments, the predicted spacing is in good agreement with the data [14]. It thus seems, according the evidence from both ends of the spectrum, that electron motions on the potential ridge are of considerable importance. Though attention has been given to analogous phenomena in other problems as well [7,15], they are still not entirely understood. It is not clear, for example, why such intrinsically unstable motion should persist over rather large ranges of energy; nor, whether there exists any preferential mode of decay of a ridge state (which in this problem corresponds to escape of the electron to infinity along the direction $\theta = 0$). The experimental diamagnetic Rydberg spectra obtained to date do not show obvious traces of a governing dynamical principle which can be followed unambiguously from the lowest perturbative energy range, through the complex intermediate region, to and past the ionisation limit where the quasi-Landau resonances appear. The spectrum of hydrogen may, however, contain the essential clues as to how this gap is bridged.

A numerical calculation of a portion of the photoabsorption spectrum of hydrogen is shown in fig. 2e. It was obtained by diagonalizing the Hamiltonian of eq. (3) in a large ($\sim 1500$) basis of Sturmian functions, using a program written at the National Physical Laboratory and optimized for implementation on the CRAY-I computer at Daresbury Laboratory. The Sturmian basis displays a number of advantages over others which might be used in this problem; they have been listed elsewhere [8,16,17] but may be summarized here as completeness, sparseness, and flexibility. The spectrum shown is part of the Lyman series as it would be observed in absorption of $\sigma$ polarized light; the magnetic field strength, 47 kG, is the same as that in the top frame of fig. 1. The leftmost line cluster corresponds to the perturbed $n=23$ manifold of states with odd parity and $m = 1$; states of lower energy are not shown since they may be determined easily by perturbation theory and show no interesting differences from the pattern of $n = 23$. It should be kept in mind that states with this parity and $m$ value are constrained by symmetry to have an antinode on the ridge $\theta = \pi/2$. States for which parity - $m$ = odd necessarily have a node on the ridge; they do not show the quasi-Landau resonances above threshold and the oscillator strength below threshold is more evenly distributed [2,17]. The upper limit in energy of the lines shown is determined by the convergence of the calculations.

Figure 2e shows similarities to the observed spectra of fig. 1, in that as energy increases the clusters of perturbed levels blend into a seemingly random pattern. On closer examination of fig. 2e, however, it is seen that the clusters interpenetrate without serious mutual perturbation. It is tempting to thus view this spectrum as a superposition of (nearly) independent line series; and as these series are conveniently ordered according to decreasing oscillator strength, it is quite straightforward to draw out their separate members. This has been done in frames a - d of fig. 2, which show respectively the members of what we shall call the principal, second, third, and fourth series. Higher series are difficult to distinguish on the basis of oscillator strength alone. It can be seen that the progression of oscillator strength along a series is not entirely regular; however, the most visible irregularities are associated with near coincidences of lines from separate series. Therefore one may conjecture that the complexity of the intermediate region of observed spectra is due in some part to
the presence of independent series with incommensurate frequencies. If so, each series, and each member within a series, ought to be characterized by a quantum number. A similar conjecture has been made on the basis of numerically observed non-crossings of energy levels in much higher magnetic fields [18].

These quantum numbers are defined in terms of the behavior of the wavefunction with respect to the potential ridge [19]. Figure 3 shows the wavefunctions for states of the principal series of fig. 2a, plotted along the ridge. It is seen that each successive state contains an additional node along the ridge, so that the position of a state within a series is determined by the degree of its excitation along the ridge. This holds true for the series of higher order, though perturbations can disturb the regularity of the progression. The distinction between series should thus be expected to be made by the form of motion across the ridge. Figure 4 shows wavefunctions for various series members, plotted along their respective classical turning surfaces. At large distances the wavefunctions of the principal series members are localized on the ridge; those of members of higher series have a local maximum on the ridge, but display structure tailing into the more attractive regions of the potential. The regularity of the "fall" off the ridge, in terms of the increasing number of nodes across the ridge with increasing series order, is reminiscent of the appearance of successive excited states in a potential well. The ordering is however entirely reversed, with the highest lying state being nodeless and localized in the most repulsive part of the potential.

In hydrogen, then, it appears that the intermediate spectral region may consist of large numbers of independent series, with the principal series evolving into the quasi-Landau resonances as the energy crosses the ionization limit. The spacings between members of the principal series, and indeed their absolute positions, agree well with the predictions of the two dimensional model [13,17]. Figure 2 clearly indicates that the effects of interseries perturbation become more pronounced with increasing series order. There is also a tendency for the perturbations to become stronger as the energy increases, through few conclusions can be drawn from the data at hand. Classical calculations [20] show the onset of "chaotic" electron motion at a certain energy (at about \(-3 \times 10^{-4}\) a.u. in fig. 2, according to calculations by Edmonds and Pullen), which takes place first in orbits which avoid the ridge. It is certainly to be expected that wavefunctions which do move well off the ridge will be more sensitive to the imminence of the ionization limit, since complete escape can take place only along \(\theta = 0\) or \(\pi\). Thus if the higher order series evolve into satellite features of the quasi-Landau resonances, those finer features would be expected to be damped more rapidly with increasing energy. This is at least consistent with observations. Definitive answers to these questions await an experiment.

We presume that for complex atoms the existence of quantum defects will disrupt this picture of series ordering, perhaps even beyond repair. However, it should be kept in mind that since all diamagnetic Rydberg spectra show the same features on a coarse scale, it is to be expected that the effects of competition Coulomb and magnetic forces at long range will be made manifest always in a similar way. It now seems probable that the quasi-Landau resonances are more intimately associated with the potential ridge than was previously imagined, and their analogues may appear in other similar systems. We are currently investigating atoms with small quantum defects, to view in detail the effect of minor departures from hydrogenic symmetry.

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