Experimental Studies of a Diamagnetic Multiplet in Odd Rydberg States of Lithium

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The energy-level structure for $M_L = 0$ odd Rydberg states of lithium in a uniform magnetic field has been investigated experimentally. The whole structure of a diamagnetic multiplet excited from the ground state by π-polarized light has been recorded for the first time. Each multiplet is shown to exhibit two different behaviors; this provides an experimental confirmation for the existence of the two limiting approximate symmetries previously predicted for the diamagnetic Hamiltonian of atomic hydrogen. Furthermore, the observed spectra agree with diagonalization calculations.

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The theoretical problem of atomic hydrogen in a constant magnetic field has not been analytically solved when the diamagnetic interaction cannot be neglected. Indeed the corresponding Hamiltonian (in atomic units and with omission of the paramagnetic term $\frac{1}{2}\gamma L_z$)

$$H_B = H_0 + H_D = \tfrac{1}{2}p^2 - r^{-1} + \tfrac{1}{8}\gamma^2\rho^2, \qquad (1)$$

$$\gamma = B/B_C, \quad B_C = 2.35\times 10^5 \text{ T},$$

is not separable. Some advances have been recently achieved in the understanding of the diamagnetic interaction in low fields.[1] The existence of three independent integrals of motion,

$$L_z, \quad Q = L^2/(1-A^2), \quad \Lambda = 4A^2 - 5A_z^2, \qquad (2)$$

where the Runge-Lenz vector is

$$\mathbf{A} = (\mathbf{p}\times\mathbf{L}) - \mathbf{r}/r, \qquad (3)$$

has been deduced from classical perturbation theory. L_z is an exact motion integral, whereas Q and Λ are approximate motion integrals which are conserved within an accuracy of B^4.

The quantity Q is related to the energy E_0 of the unperturbed trajectories. The vector $\mathbf{A}$ is directed along the major axis of the Kepler ellipse; for a weak magnetic field its extremity moves slowly on the surface $\Lambda = \text{const}$. According to the sign of Λ this surface is either a onefold or a twofold hyperboloid, and therefore all perturbed trajectories split up into two classes: (i) $\Lambda > 0$ corresponds to a rotational motion of $\mathbf{A}$ around the $\mathbf{B}$ axis, and (ii) $\Lambda < 0$ corresponds to a librational motion of $\mathbf{A}$ along the $\mathbf{B}$ axis. These two types of motion are localized in two nonoverlapping domains.[2]

Equivalently, in quantum mechanics it has been shown that the effective operator H_D^{eff}, describing to first order in B^2 the diamagnetic interactions within the n manifold of atomic hydrogen $E_0 = -\frac{1}{2}n^2$, is given by[3]

$$H_D^{\text{eff}} = \tfrac{1}{8}\gamma^2\rho_n^2 = \tfrac{1}{16}\gamma^2 n^2(n^2+3+L_z^2+n^2\Lambda), \qquad (4)$$

with H_D^{eff} commutating with the total Hamiltonian H_B. From a group-theoretical point of view, the states of hydrogen with a constant energy E_0 present an exact O(4) symmetry, and H_D^{eff} is separable in ellipsoidal-cylindrical coordinates on a sphere in four-dimensional momentum space.[3,4] This separation has been exploited to obtain a complete classification of states in the weak-field limit. For the maximum Λ value the symmetry tends to the rotational type, associated with the coupling scheme $|nTm\rangle$, where T is the angular momentum (A_x, A_y, L_z); the parity of $|nTm\rangle$ is equal to $(-1)^{n+1+T+m}$,[5] and the diamagnetic energy can be expressed in terms of $T(T+1)$. For the minimum Λ value, the symmetry tends to the vibrational type described by the parabolic coupling scheme, A_z^2 being nearly an exact constant of motion; states with different parity are degenerate.[6]

The aim of this paper is to report experimental spectra obtained with Li atoms excited to Rydberg states in the presence of a magnetic field. For the field strengths studied the successive manifolds are well isolated, which corresponds to the "inter-l mixing regime." Furthermore, for odd states of Li, the quantum defects are equal to or smaller than $\delta p = 0.053$: Therefore the atomic system studied has a structure very close to that of hydrogen. The analysis of these spectra allows us to make evident for the first time the existence of two classes of states and to relate the constant of motion Λ to the general energy-level structure of a complete manifold.

The experiment has been performed on an atomic beam of Li. A pair of superconducting coils in the Helmholtz position created in the interaction region a magnetic field of strength up to 6 T. In this region, a laser beam propagating perpendicularly to the direction of the atomic beam excited the Li atoms to high-lying states in a one-photon absorption process. The populated states were detected by means of the field-ionization technique using an electric field directed parallel to the magnetic field. The electrons produced were accelerated and detected by a surface-barrier diode insensitive to the magnetic field. In order to

eliminate the motional electric field effects, the atomic beam was made parallel to the magnetic field. The detector was aligned with the atomic beam and was protected against corrosion by use of a gold-coated thin film of Collodion which stopped the atoms but was transparent to the accelerated electrons. The optical excitation was obtained by our successively doubling the frequency of a single-mode tunable pulsed dye laser[7] oscillating in the frequency range of the rhodamine-6G dye and mixing the resulting radiation (≈ 300 nm) with the fundamental of the Nd-doped yttrium-aluminum-garnet pump laser at 1.06 μm. The uv radiation had a linewidth of about 1 GHz and was tunable over a wide range in the region of the ionization limit of lithium ($\lambda \simeq 230$ nm).

Figure 1 shows a typical spectrum obtained with π-polarized light in the "inter-l mixing region" where the different manifolds do not overlap; the magnetic field strength is sufficient to resolve all the components. Each component, as usual, is labeled with an integer K: $K=1$ corresponds to the highest-energy level.[8]

For the first time, we have been able to observe experimentally a whole multiplet. The π $n=31$ manifold has been analyzed in detail. The positions and intensities of the lines have been compared with the calculated ones obtained by diagonalization of the matrix of the diamagnetic Hamiltonian of the Li atom[9] (Fig. 2). The agreement is rather good for the energies of the lines as well as their intensities. Comparison with the corresponding calculated spectrum for hydrogen [Fig. 2(c)] shows the influence of the perturbation caused by the non-Coulombic part of the Hamiltonian: One can notice that the intensities are much more sensitive to this perturbation than the energies are. Careful analysis of this spectrum reveals a peculiar repartition of the energies of the lines. In order to visualize this feature better, we have plotted in Fig. 3, curve a, the line spacing versus K for the $n=32$ manifold. The curve shows at $K=11$ a discontinuity which distinguishes two different behaviors.

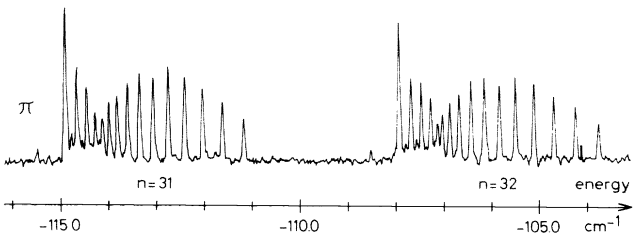

FIG. 1. Experimental recording of the diamagnetic multiplets in π polarization, with use of single-photon absorption from the ground state of Li ($B=1.94$ T). The energies are referred to the zero-field ionization limit.

From the experimental data we have calculated the Λ value for each K component of the studied n manifold. The results are shown in Fig. 3, curve b. The discontinuity seen in the energy-spacing curve (Fig. 3, curve a) is obviously linked to the change in the sign of Λ. Analytical approximate expressions for the energies of the outermost states of a given (n,M_L) diamagnetic multiplet have been derived in either a semiclassical approach[1,2] or a fully quantal one.[4,10] This leads us to introduce two different expansions for the diamagnetic energy [Eq. (4)] respectively valid for the upper ($\Lambda=\Lambda_{max}\simeq 4$) and the lower ($\Lambda=\Lambda_{min}\simeq 1$) states of the manifold. The K dependence is then given by quadratic functions of $K-K_0$ with $K_0=K_{min}$ and K_{max}, respectively:

$$\Delta E_D(n,K,M)=\Delta E_0+(K-K_0)\Delta E_1 + \tfrac{1}{2}(K-K_0)^2\Delta E_2. \quad (5)$$

At the top of the diamagnetic structure the analytical expression is almost similar to that given for a rigid rotator.[4] Since $K_{min}=1$ labels the upper state of the manifold, ΔE_1 is negative; furthermore, in order to describe a rigid rotator ΔE_2 must be positive. On the other hand, at the bottom of the structure the energy spectrum is similar to that of a harmonic oscillator

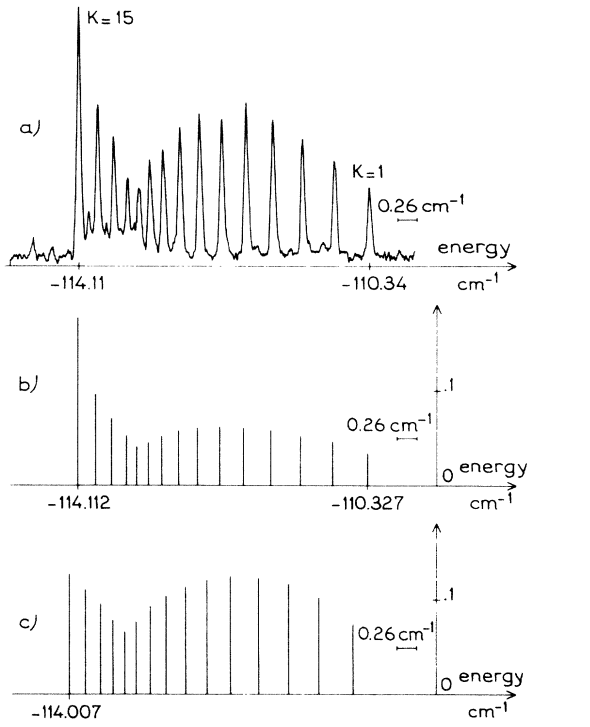

FIG. 2. Diamagnetic structure of the $n=31$ multiplet in π excitation ($B=1.94$ T): (a) Experimental recording for Li; (b) calculated diamagnetic spectrum for Li; (c) corresponding calculated spectrum for H.

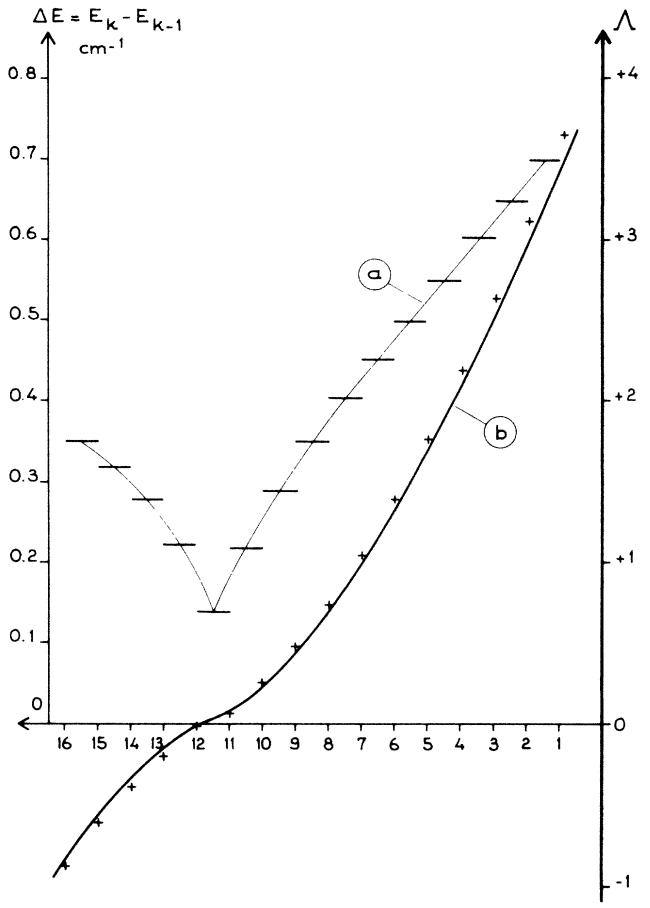

FIG. 3. Analysis of the $n=32$ diamagnetic π multiplet ($B=2.33$ T): Curve a, spacing between consecutive components vs the K value. Curve b, values of Λ deduced from experiment; crosses correspond to values of Λ determined by quantization of $L_\perp(\theta)$.

with anharmonic corrections.[4] In our development, ΔE_1 is associated with the fundamental frequency of the oscillator, and thus it must be positive, whereas ΔE_2, which corresponds to the anharmonic corrections, must be negative. The experimentally observed energy spacings for odd states of Li (Fig. 3, curve a) permit us to justify entirely the two developments introduced above [Eq. (5)]; indeed, for the two outermost parts of the manifold the spacings vary linearly with K: They increase with K for small values of K and decrease for large ones according to the different signs of ΔE_2.

Analytical expressions for the constants ΔE_i have been obtained from Eqs. (11) of Solov'ev[3] and Eqs. (16) and (18) of Herrick[4]; the corresponding experimental values for the multiplet $n=32$, $M_L=0$ have been deduced from the diamagnetic experimental shift of the three outermost components of this multiplet. The results are presented in Table I.

The experimental results agree very well with Herrick's theoretical values. Concerning Solov'ev's results a notable discrepancy is observed for the coefficient ΔE_2. In the latter semiclassical treatment, the values of Λ are determined from the quantization of the angular momentum component $L_\perp(\theta)$ perpendicular to the plane defined by **B** and **A**, θ being the angle between these two vectors. Using this quantization rule we have numerically calculated the different values of Λ. As shown in Fig. 3, curve b, they agree very well with the experimental data, which is somewhat contradictory to the discrepancy mentioned above. However, in the analytical computation of the quantization integral, Solov'ev introduced a quadratic approximation for the effective potential $U_{\text{eff}}(\theta)$ in the vicinity of its minimum value. This approximation

TABLE I. Values (in 10^{-3} cm^{-1}) of the coefficients appearing in the development of ΔE_D [Eq. (5)] for the components of the $n=32$, $M_L=0$ manifold (at $B=2.33$ T).

Coeff.	Expt.[a]	Herrick[b]	Solov'ev[c]	Quantization of $L_\perp$[d]	Solov'ev corrected[e]
			$\Lambda<0$		
ΔE_0	161	195	184	186	193
ΔE_1	378	386	343	375	379
ΔE_2	−38	−33	−99	−36	−29
			$\Lambda>0$		
ΔE_0	6213	6489	6873	6488	6489
ΔE_1	−733	−758	−763	−753	−758
ΔE_2	53	44	107.5	50	44

[a]Our experimental results.
[b]Equations (16) and (18) of Ref. 4.
[c]Equations (11) of Ref. 3.
[d]Quantization of the component $L_\perp(\theta)$ (Ref. 3).
[e]New analytical expression of the quantization integral.

is insufficient and it is necessary to take into account a higher-order term.[11]

We have performed, for the first time, a detailed experimental analysis of a complete diamagnetic quasihydrogenic manifold in the inter-l mixing regime. We have shown the existence of two different types of states depending on the sign of Λ; both types are nearly uncoupled. Our experimental values of diamagnetic energies confirm the validity of the expressions obtained by use of either the semiclassical theory or the more elaborate group-theory approach. The wave functions of states belonging to the different types (different signs of Λ) are localized in different regions of space: They do not interact strongly even in the inter-n mixing regime ($\gamma n^3 \approx 1$). The typical structure of a diamagnetic multiplet obtained in the low-field limit ($\gamma n^3 \ll 1$) is conserved even for values of γn^3 as high as 0.3 as has been observed in the present work. This feature is probably at the origin of the existence of the small anticrossing pointed out by Zimmerman, Kash, and Kleppner.[12] However, the above reported property cannot be used to predict the size of anticrossings of states belonging to the same type; therefore more sophisticated experimental investigations would be of great interest in the search for new symmetry properties of the Hamiltonian.

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[11]A careful analytical calculation has given for the upper-energy $M_L = 0$ states the expression

$$E_D(n,k,M_L=0) = \tfrac{1}{16}\gamma^2 n^2 (5n^2 - 4\sqrt{5}nk + \tfrac{9}{2}k^2), \qquad k = 0, 1, \ldots,$$

and for the lower states

$$E_D(n,k,M_L=0) = \tfrac{1}{16}\gamma^2 n^2 (2\sqrt{5}n + 4\sqrt{5}nk - 12k^2), \qquad k = 0, 1, \ldots.$$

The formulas differ from Solov'ev's but agree completely with those of Herrick (Ref. 4) and Braun (Ref. 10).

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