Anticrossing effects in Rydberg states of lithium in the presence of parallel magnetic and electric fields

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Rydberg states in lithium have been excited from the ground state by absorption of π-polarized photons in the presence of parallel electric F and magnetic B fields. The magnetic field strength ($B=3.11$ T) is high enough to reach the inter-n-mixing regime, and a small electric field strength ($F\simeq 25$ V/cm) is sufficient for the lowest state of the $n=30$ manifold to penetrate into the high-energy part of the $n=29$ manifold. The first anticrossing is thoroughly studied. Away from the anticrossing the spectrum exhibits two lines, but at the anticrossing a third component appears in the structure in the same energy range. This provides an experimental confirmation for the existence of pairs of almost-degenerate states with opposite parities in the high-energy part of the diamagnetic manifold of lithium. The two components of this doublet behave differently at the anticrossing. The experimental data have been interpreted in a global treatment in which core effects and intermanifold couplings are simultaneously taken into account. The different behavior of low- and high-lying states of the multiplet with respect to these two interactions is analyzed in detail.

I. INTRODUCTION

Over the last few years a complete understanding of the structure of the diamagnetic multiplet of the hydrogen atom has been achieved.[1-3] In the inter-l-mixing regime the diamagnetic interaction is treated to first order of perturbation theory within a given n manifold. This regime appears for magnetic field strength B satisfying

$$\gamma^2 n^7 \ll 1, \quad \gamma = B/B_c, \quad B_c = 2.35\times 10^5 \text{ T} . \tag{1}$$

The specific symmetry properties of the Coulomb potential give rise to the existence in the same n manifold of two classes of states, of which the highest-energy states are characterized by a rotational symmetry and the lowest-energy states by a librational symmetry.

When an electric field **F** parallel to the **B** field is applied, these two symmetries are preserved and the inter-l-mixing regime persists as long as

$$fn^5 \ll 1, \quad f = F/F_c, \quad F_c = 5.14\times 10^9 \text{ V/cm} . \tag{2}$$

With increasing electric field strength, states belonging to distinct classes behave differently; rotational states present a quadratic Stark effect whereas librational ones present a linear Stark effect.[4-6]

With increasing electric and magnetic field strengths, the manifolds spread over a larger energy range, and adjacent n manifolds overlap. Due to the different symmetries of the outermost states of the hydrogenic manifolds, the lowest states of the $n+1$ manifold are predicted to nearly cross the highest states of the n manifold. The existence of such avoided crossings with an almost negligible width has been confirmed by numerical calculations in the pure diamagnetic case ($F=0$) (Ref. 7) and in parallel fields.[8]

In the low-field regime the theoretical analyses initiated by Solov'ev[1] in the pure diamagnetic case, and by Braun and Solov'ev[9] for the parallel field problem, have been confirmed experimentally by investigating the lithium odd-parity spectra.[3,10-12] Due to the very small value of the quantum defect for $l=1$ states, $\delta_p=0.053$, the structure of the odd diamagnetic manifold recorded in lithium is identical to that calculated in hydrogen. For higher magnetic field strengths corresponding to the inter-n-mixing regime, narrow anticrossings are observed. Their non-negligible widths are ascribed to core effects in spite of the small value of δ_p.[4] When an electric field **F** parallel to **B** is added, odd- and even-parity states are coupled and the system departs strongly from hydrogenic behavior owing to the large value of the quantum defect for $l=0$ states, $\delta_s=0.4$. Nevertheless the global properties of the complete lithium manifold and the evolution of the structure with varying field strengths are similar to the corresponding ones of hydrogen. The ionic core induces alterations in the structure which persist even at high-field strengths.

Until now, no experimental investigation had ever been performed on atomic Rydberg states in the presence of parallel **B** and **F** fields beyond the inter-l-mixing regime. Furthermore, inter-n-mixing effects in diamagnetism of strongly nonhydrogenic systems—such as, for example, the even-parity states of lithium—remained unknown.

In the present experiment the magnetic field is kept constant and the anticrossing effects are induced by increasing the electric field. The evolution with **F** of energies of the $M=0$, $n\simeq 30$ states of lithium obtained by a diagonalization calculation is reported in Fig. 1. For $B=3.11$ T, the strength of the diamagnetic interaction within a given n manifold is $\gamma^2 n^4 \sim 1.4\times 10^{-4}$; **B** is strong enough to induce large intermanifold couplings ($\gamma^2 n^7 \sim 3.83$).

For $F=0$, and $n=30$ and 31 manifolds overlap partially but the $n=29$ and 30 manifolds have not yet merged, the energy spacing between their outermost states

amounting to 1.5 cm^{-1}. Large core effects couple all the even-parity states, whether or not they belong to the same multiplet. The strength of this coupling, of the order of $\delta_s/n^3 \sim 1.5\times10^{-5}$, is not negligible compared to the diamagnetic interaction. Core effects are responsible for the existence, in the upper part of the multiplets, of pairs of almost degenerate states with opposite parity and possessing a rotational symmetry (in hydrogen odd- and even-parity rotational states are approximately equally spaced[9]). In the low-energy part of the multiplets, states with a librational symmetry are degenerate by pairs, a situation quite similar to that of hydrogen.

The two classes of states behave differently with increasing **F**: rotational states undergo a quadratic Stark effect and the librational states a linear Stark effect. As **F** increases librational states exhibit anticrossings, due to core effects; in the same multiplet all anticrossings appear at the same F value. For $B=3.11$ T the anticrossing widths are rather narrow. When **F** increases, the energy of the lowest librational state decreases rapidly, while the upper part of the $n=29$ manifold remains nearly unperturbed.

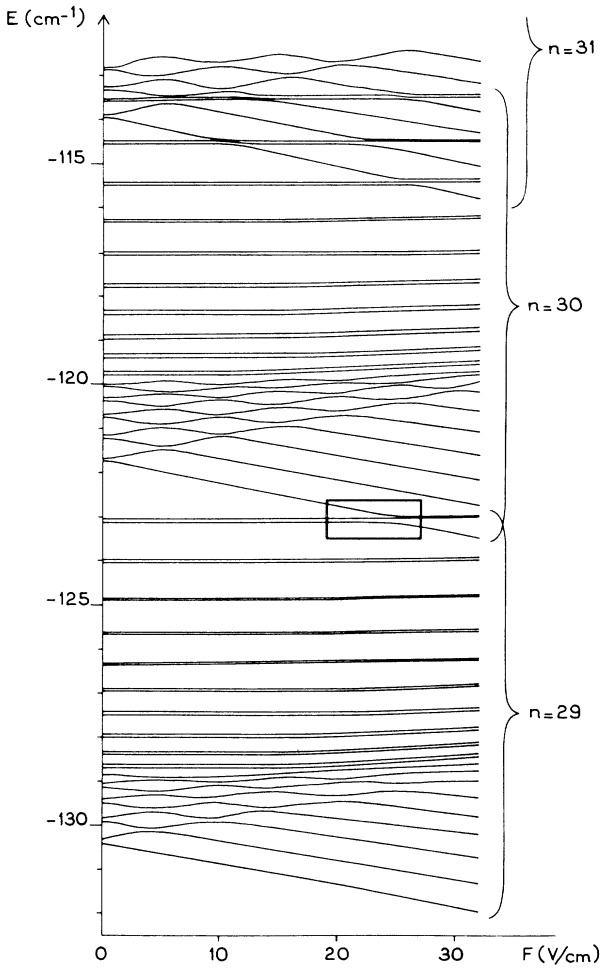

FIG. 1. Calculated energy diagram for the $n\simeq30$, $M=0$ states of lithium in the presence of a magnetic field $B=3.11$ T and of an increasing electric field **F** parallel to the magnetic field. The energies are referred to the zero-field ionization limit. The box shows the narrow anticrossing between the more excited doublet in the $n=29$ manifold and the lowest state of the $n=30$ manifold analyzed in detail in the present paper.

The present paper reports observation and analysis of the first anticrossing between the $n=29$ and 30 manifolds. This anticrossing occurs for a relatively small electric field strength $F\sim25$ V/cm ($fn^2\sim4.4\times10^{-6}$). Consequently, the electric field can be considered as a "probe" for the diamagnetic spectrum of a strongly nonhydrogenic system in the inter-n-mixing regime. Core effects and diamagnetic couplings between states belonging to different manifolds are both very strong interactions. Their effects are highly intricate and give rise to nonadditive contribution to the energy spectrum and thus cannot be treated independently. A diagonalization calculation on a large basis set including simultaneously these two interactions reproduces very nicely the experimental results. However, it does not allow one to disentangle the relative contributions of the different physical phenomena.

To progress in resolving the intricacy of the problem, the respective influences of either intermanifold couplings produced by the magnetic field or core effects are separately analyzed in the first section of this paper. It is shown that states with different symmetry behave differently with respect to both interactions. Furthermore, it is pointed out that n-mixing effects partially cancel core effects in the lower-energy part of the multiplet, while they do not in the high-energy part.

The second section is devoted to the presentation of experimental results. The recorded spectra provide the first experimental confirmation for the existence, in the upper part of a pure diamagnetic multiplet of lithium, of pairs of nearly degenerate states with an opposite parity. An attempt is made to interpret the recorded anticrossing widths in a simple three-state model consisting of the lowest state of the $n=30$ multiplet and of the uppermost pair of states in the $n=29$ multiplet.

II. MAGNETIC-FIELD-INDUCED n-MIXING EFFECTS AND NONHYDROGENIC EFFECTS IN THE DIAMAGNETIC SPECTRUM OF THE RYDBERG STATES OF LITHIUM

The Hamiltonian for an atom having one optical electron in the presence of electric and magnetic fields parallel to the z direction is in atomic units

$$H=H_0+\Delta V+H_d+H_f\ , \tag{3}$$

where H_0 is the Hamiltonian for the field free hydrogen atom, ΔV represents the non-Coulombic effects due to the closed core shells, $H_d=\frac{1}{8}\gamma^2\rho^2$ is the diamagnetic interaction in cylindrical coordinates, and $H_f=fz$ is the Stark interaction.

Since the magnetic quantum number M is exact, the paramagnetic term $H_p=\gamma L_z/2$ has been disregarded (L_z

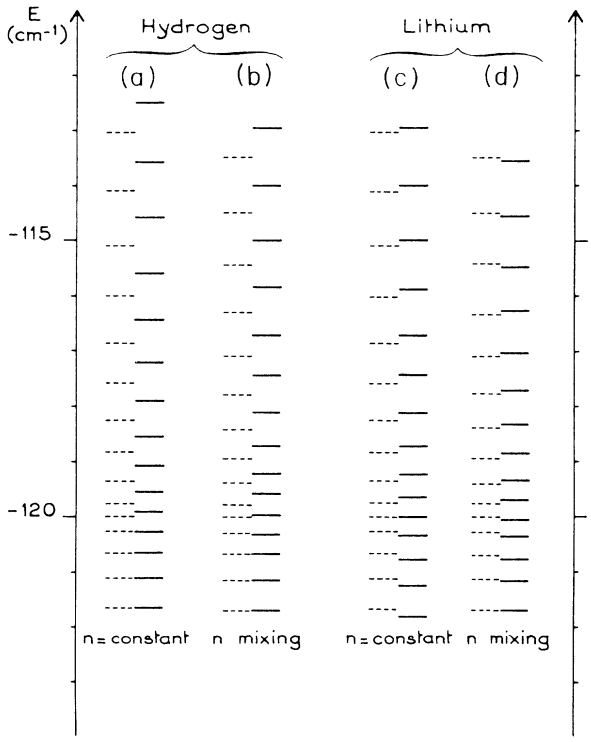

FIG. 2. Calculated structures for the diamagnetic manifolds $n=30$, $M=0$ in hydrogen [(a) and (b)] and lithium [(c) and (d)] obtained by diagonalization disregarding ($n=$const) or introducing (n-mixing) intermanifold couplings. The magnetic field strength $B=3.11$ T corresponds to $\gamma^2 n^7=3.83$. The energies are given with respect to the ionization limit. — — —, odd-parity states; ——, even-parity states.

is the z component of the angular momentum). Furthermore, only $M=0$ states are considered.

The eigenstates corresponding to the same eigenvalue $E_0=1/(2n^2)$ of H_0 constitute an n manifold, and H_0 does not couple different manifolds. The other three interactions present in Eq. (3) can be regrouped into two types of terms: the first ones $\Delta V(n)$, $H_d(n)$, and $H_f(n)$ describe intramanifold couplings, the second ones $\Delta V(n,n')$, $H_d(n,n')$, and $H_f(n,n')$ with $n\neq n'$ correspond to intermanifold couplings.

Exact solutions of the Schrödinger equation do not exist; approximate solutions can be obtained from perturbation theory by writing $H=\mathcal{H}_0+H_1$. However, the choice of $\mathcal{H}_0$ is not unique. The spectra of different zeroth-order Hamiltonians, all including $H_d(n)$, are successively analyzed below. This allows one to evaluate respective influences of magnetic-field-induced inter-n-mixing effects $H_d(n,n')$ on the one hand, and on the other hand of the core effect $\Delta V(n)$ and $\Delta V(n,n')$. The corresponding energy diagrams obtained for the $n=30$, $M=0$ multiplet in the presence of the magnetic field $B=3.11$ T are presented in Fig. 2. H_f not being introduced in $\mathcal{H}_0$, even- and odd-parity states ($\pi_t=0$ or 1) are drawn separately.

A. Isolated diamagnetic multiplet in hydrogen

This case corresponds to $\mathcal{H}_0=H_0+H_d(n)$. The eigenvalues are obtained by diagonalizing $H_d(n)$, or equivalently the ρ^2 operator, within the subspace of unperturbed hydrogenic orbitals with fixed $n=n_0$ and $M=0$ values. The eigenvalues labeled in order of decreasing energy are written as

$$E_{n_0 k}=-\frac{1}{2n_0^2}+\frac{\gamma^2}{16}n_0^4\varepsilon_{n_0 k}\ , \tag{4}$$

where the reduced energy $\varepsilon_{n_0 k}$ does not depend on γ^2.

The diagram of energy states, presented in Fig. 2(a), exhibits clearly the existence of two classes of states:[1] (a) in the lower-energy part $0<\varepsilon_{n_0 k}<1$, odd- and even-parity states form doublets. States present a librational symmetry. (b) In the upper-energy part $1<\varepsilon_{n_0 k}<5$, odd- and even-parity states are approximately equally spaced, the highest state being an even-parity one. States present a rotational symmetry.

B. Inter-n-mixing effects in the diamagnetic manifold of hydrogen

Because of its large strength, the magnetic field **B** induces inter-n-couplings which cannot be disregarded, and $\mathcal{H}_0=H_0+H_d(n)+H_d(n,n')$. The eigenvalues of $\mathcal{H}_0$ are obtained by diagonalization; the basis states are eigenstates of H_0 and correspond to the nine manifolds $27\leq n\leq 35$. The results, presented in Fig. 2(b), demonstrate that the two classes of states behave differently with respect to n-mixing effects.

- In the low-energy part, energies are insignificantly modified; indeed the wave functions for these states are stretched along z direction and the states are scarcely affected by $H_d(n,n')$.[13,3]
- Energies of the most excited states are decreased by a quantity of the same order of magnitude as the spacing between two adjacent states; odd and even states behave similarly. The high-energy states of different n manifolds, localized in $z=0$ plane, where the diamagnetic interaction is the most important, are strongly coupled through $H_d(n,n')$.

The expansion of the eigenfunctions $\psi_{n_0 k}$ on the basis of unperturbed hydrogenic states is

$$\psi_{n_0 k}=\sum_{n,l} a_{nl}^{n_0 k}|n\ l\ M=0\rangle\ . \tag{5}$$

The weight of manifold n in the wave function of the state labeled k belonging to the n_0 manifold is equal to

$$A_n^{n_0 k}=\sum_l (a_{nl}^{n_0 k})^2\ . \tag{6}$$

For the highest state $k=1$ of the $n_0=30$ manifold, the weights of manifolds $n=29$, 30, and 31 are, respectively, equal to $A_{29}^{30,1}=0.106$, $A_{30}^{30,1}=0.743$, and $A_{31}^{30,1}=0.131$, which demonstrates the existence of a rather large n mixing. For the lowest state $k=30$, n-mixing effects are negligible, as it can be shown from $A_{30}^{30,30}=0.999$.

The change in the angular part of the wave function

$\psi_{n_0 k}$ arising from n-mixing effects is evaluated from the quantity

$$B_l^{n_0 k}=\sum_n n^{-3/2} a_{nl}^{n_0 k} . \tag{7}$$

It is shown that n-mixing effects induced by $H_d(n,n')$ do not change the l distribution in wave functions. Indeed n-mixing effects do not modify significantly wave functions of lower states and therefore do not change the l distribution. For the highest even state $B_{l=0}^{30,1}=0.003\,48$ and $B_{l=2}^{30,1}=-0.003\,58$ which do not significantly differ from the values $B'^{30,1}_{l=0}=0.003\,34$ and $B'^{30,1}_{l=2}=0.003\,42$ obtained by disregarding n-mixing effects.

For diamagnetism of hydrogen in the low-field limit, there exists an approximate constant of motion[1] $\Lambda=4A^2-5A_z^2$ ($\mathbf{A}$ is the Runge-Lenz vector) conserved with an accuracy of B^4. Matrix elements of Λ calculated on the hydrogenic basis are diagonal with respect to n and M; for fixed n and M, their values depend only on l. Consequently when the n-mixing effect is explicitly taken into account, the conservation of the l distribution in the wave function leads to the conservation of the approximate constant of motion Λ even far from the inter-l-mixing regime ($\gamma^2 n^7 \gg 1$) where consecutive manifolds overlap.[3] This conservation can be numerically shown by studying the quantity

$$\langle \Lambda_n^{n_0 k}\rangle=\sum_l \sum_{l'} a_{nl}^{n_0 k} a_{nl'}^{n_0 k} \langle nlM|\Lambda|nl'M\rangle / A_n^{n_0 k} , \tag{8}$$

which represents the partial contribution of the manifold number n to the mean value of Λ operator for the $\psi_{n_0 k}$ state. Indeed even in the upper part of the manifold where n-mixing effects are large, $\langle \Lambda_n^{n_0 k}\rangle$ is nearly independent of n. As an example $\langle \Lambda_{29}^{30,1}\rangle=3.846$, $\langle \Lambda_{30}^{30,1}\rangle=3.851$, and $\langle \Lambda_{31}^{30,1}\rangle=3.855$. All n manifolds which contribute significantly to the wave function of the $\psi_{30,1}$ state correspond to the same partial contribution to the mean value of Λ. Consequently the mean value of Λ operator

$$\langle \psi_{n_0 k}|\Lambda|\psi_{n_0 k}\rangle=\sum_n A_n^{n_0 k}\langle \Lambda_n^{n_0 k}\rangle$$

does not change when n-mixing effects are taken into account.

C. Isolated multiplet of hydrogen in parallel electric and magnetic fields

In this case $\mathcal{H}_0=H_0+H_d(n)+H_f(n)$, and states with opposite parity belonging to the same n-manifold are coupled through $H_f(n)$.

The two different symmetries observed in the pure diamagnetic multiplet ($\mathbf{F}=\mathbf{0}$) are preserved when the electric field is added in the direction parallel to the magnetic field, and there exists a new approximate constant of motion. Because of the very different spatial localization of their wave functions, states belonging to different classes behave differently. In the lower-energy part of the multiplet states degenerate by pairs undergo an important linear Stark effect. In the upper-energy part a quadratic Stark effect appears. However, states with opposite parity are only slightly coupled through the electric field.[9,5]

D. Diamagnetic structure of an isolated multiplet in lithium atom (core effects)

The studied Hamiltonian reduces to $\mathcal{H}_0=H_0+H_d(n)+\Delta V(n)$. In the inter-$l$-mixing regime the eigenstates are determined by diagonalizing $H_d(n)+\Delta V(n)$ in the basis of unperturbed hydrogenic states $|nlM\rangle$ with fixed $n=n_0$ and $M=0$ values. The non-Coulombic interaction $\Delta V(n)$ is expressed in terms of the quantum defects δ_l as[14]

$$\Delta V(n)=\sum_l |nlM\rangle \frac{\delta_l}{n^3}\langle nlM| . \tag{9}$$

This approximation, which disregards all but the first term in the expansion of $[\frac{1}{2}n^2-\frac{1}{2}(n-\delta)^2]$ is accurate enough to differentiate the contribution of core effects.

Because the total-parity operator commutes with $\mathcal{H}_0$, odd- and even-parity states can be analyzed independently, because $\delta_s \gg \delta_p$ core effects are especially manifested in the even-parity spectrum.

The structure of the diamagnetic multiplet depends on the relative strengths of the interactions $H_d(n)$ and $\Delta V(n)$. Consequently γ^2 cannot be isolated in the energy expansion of states, or, in other words, the reduced energy $\varepsilon_{n_0 k}$ [Eq. (4)] is γ^2 dependent. For each parity $\pi_t=(-1)^l$, different ranges for the magnetic field strength can be distinguished.

For $\gamma=0$, the $|n_0 l=0 M=0\rangle$ state (or the $|n_0 l=1 M=0\rangle$ state), which has a nonzero quantum defect, lies below "the incomplete $\pi_t=+1$ (or $\pi_t=-1$) manifold" composed of all the $|n_0 l' M=0\rangle$ states with $l'\geq 2$ (or $l'\geq 3$) and with a zero quantum defect. The energy gap is equal to

$$\Delta E(n_0 l,\gamma=0)=-\frac{\delta_l}{n_0^3} \quad \text{for } l=0 \text{ or } 1 . \tag{10}$$

For sufficiently low magnetic field, the $|n_0 l=0 M=0\rangle$ state (respectively $|n_0 l=1 M=0\rangle$ state) can be considered as uncoupled from the incomplete $\pi_t=+1$ (or $\pi_t=-1$) manifold. This state undergoes a diamagnetic shift which, calculated to first order of nondegenerate perturbation theory, varies linearly with γ^2:

$$\Delta E(n_0 l,\gamma)=-\frac{\delta_l}{n_0^3}+\frac{\gamma^2}{8}\langle \rho^2\rangle_{n_0 l M=0} \quad \text{for } l=0 \text{ or } 1 . \tag{11}$$

In the same γ range, states of the incomplete $\pi_t=+1$ (or $\pi_t=-1$) manifold are mixed through $H_d(n)$. Their energies calculated to first order of the degenerate perturbation theory increase linearly with γ^2 but, compared to the hydrogenic ones, are shifted towards lower values. This low-field approximation is valid as long as the $|n_0 l=0 M=0\rangle$ state (or $|n_0 l=1 M=0\rangle$ state) has not penetrated into the incomplete $\pi_t=+1$ (or $\pi_t=-1$)

manifold, that is for

$$B \ll B_{n_0 l} = \gamma_{n_0 l} B_c \ , \tag{12a}$$

where $\gamma_{n_0 l}$ satisfies

$$\Delta E(n_0 l, \gamma_{n_0 l}) = 0 \quad \text{for } l = 0 \text{ or } 1 \ . \tag{12b}$$

The order of magnitude of $\gamma_{n_0 s}$ (or $\gamma_{n_0 p}$) can be obtained by using hydrogenic radial functions to evaluate the mean value $\langle \rho^2 \rangle_{n_0 l M=0}$ with $l=0$ (or $l=1$). The analytical expressions are

$$n_0^7 \gamma_{n_0 s}^2 = \tfrac{24}{5} \delta_s \ , \tag{13}$$

$$n_0^7 \gamma_{n_0 p}^2 = 8 \delta_p \ . \tag{14}$$

For even- and odd-parity states in lithium, the limiting field strengths $B_{n_0 l}$ are, respectively, equal to $B_{30s} = 2.20$ T and $B_{30p} = 1.03$ T.

When γ is in the range of $\gamma_{n_0 s}$ (or $\gamma_{n_0 p}$), the $|n_0\, l=0\, M=0\rangle$ state (or $|n_0\, l=1\, M=0\rangle$ state) cannot be considered as isolated any longer, and the complete $\pi_t = +1$ (or $\pi_t = -1$) manifold has to be treated as a whole. Then the reduced energies of all the states $\varepsilon_{n_0 k}$ [Eq. (4)] depend on γ^2. The way the nonhydrogenic character spreads over the manifold depends on the symmetry of the diamagnetic states: rotational and librational states behave differently when the penetration occurs.

When $\gamma \gg \gamma_{n_0 s}$ (or $\gamma \gg \gamma_{n_0 p}$) core effects become less significant, and a nearly hydrogenic behavior is observed: reduced energies again become γ^2 independent and converge towards the hydrogenic values.

Above, odd and even manifolds have been analyzed independently. However, their relative positions are also very important because they govern the evolution of the structure when an electric field is added in the B direction. Noticeable variations in the structure of the diamagnetic manifold are observed when the s state penetrates into the manifold. Two typical structures are described below.

For $B = 2.33$ T ($\gamma^2 n^7 \simeq 2.15$), the odd manifold is quasihydrogenic. At this B strength the s state is still isolated from the incomplete even manifold. Reduced energies of all the even states are shifted below the hydrogenic values. This induced a quasidegeneracy in the rotational part of the total (even plus odd) manifold and, on the other hand, a breaking of the hydrogenic degeneracy in the librational part, where odd and even states alternate.[15] This situation has been experimentally observed:[12] with increasing but weak electric field, collective anticrossings among librational states occur. Couplings due to core effects are so large that the librational state energies are almost F independent. Simultaneously the doublet structure in the rotational part has never been resolved and additional lines arising from the even states of the diamagnetic manifold have never been observed.

When B increases, the librational states are first modified: the alternate odd and even states progressively group into doublets. This situation, somewhat similar to that of hydrogen, is obvious in Fig. 1 obtained for $B = 3.11$ T. In this new experimental situation, the pronounced hydrogenic character of librational states is responsible for the small values of the anticrossing widths occurring when the electric field increases. Simultaneously the doublet structure typical of a nonhydrogenic behavior persists for rotational states.

The structure of the $n=30$, $M=0$ manifold of lithium obtained by a diagonalization calculation disregarding intermanifold couplings $H_d(n,n')$ and $\Delta V(n,n')$ for $B = 3.11$ T is presented in Fig. 2(c).

This discussion emphasizes the importance in the lithium atom of the non-Coulombic interaction $\Delta V(n)$, which is responsible for the appearance in the higher part of the multiplet of a doublet structure which persists over a large range of B strength, extending from $B \sim B_{n_0 p}$ up to $B > B^c_{n_0 s}$.

E. Inter-n-mixing effects in the diamagnetic manifold of lithium

Intermanifold couplings due to non-Coulombic interaction are expressed[14]

$$\Delta V(n,n') = \sum_n \sum_{n'(\neq n)} \sum_l \left[|nlM\rangle \frac{\delta_l}{(nn')^{3/2}} \langle n'lM| + |n'lM\rangle \frac{\delta_l}{(nn')^{3/2}} \langle nlM| \right] , \tag{15}$$

which is similar to the expression for $\Delta V(n)$ [Eq. (9)].

The strength of the coupling $\Delta V(n, n\pm 1)$ does not differ significantly from $\Delta V(n)$. In the presence of a sufficiently large magnetic field strength, diamagnetic manifolds widen, and states of two adjacent manifolds overlap. The key result of this analysis can be summarized as follows: when intermanifold couplings due to the magnetic field $H_d(n,n')$ cannot be disregarded and when core effects $V(n)$ within a manifold are important, it is necessary to take explicitly into account the intermanifold coupling term $\Delta V(n,n')$. Then $\mathcal{H}_0$ reads

$$\mathcal{H}_0 = H_0 + H_d(n) + \Delta V(n) + H_d(n,n') + \Delta V(n,n') \ .$$

The spectrum obtained by a diagonalization is presented in Fig. 2(d). Comparison between Figs. 2(b) and 2(d) shows that nonhydrogenic effects are especially important on the even upper energy states. In particular, the introduction of $H_d(n,n')$ leads to inversion of components in the upper doublet: the more excited component of the manifold is then an odd-parity state. Furthermore, n-mixing effects [see Figs. 2(c) and 2(d)] contribute to decrease the splitting in low-energy dou-

blets, i.e., to increase the hydrogenic character in low-lying states of the manifold.

The two classes of states in the diamagnetic manifold behave differently with respect to n-mixing effects arising from $\Delta V(n,n')$: when $\Delta V(n,n')$ is introduced in the diagonalization, the amplitude $B_{l=0}^{n_0 k}$ of the $l=0$ component in the wave function increases in the high-energy part of the multiplet but decreases in the low-energy part. This behavior can be understood from simple considerations. The $n_0 s$ state lies between the n_0 and n_0-1 incomplete manifolds. Therefore a diagonalization calculation restricted to the states with the same n_0 quantum number overestimates (or underestimates) the coupling between the $n_0 s$ state and the low-lying (or high-lying) states of the incomplete n_0 diamagnetic manifold. When intermanifold couplings are introduced, the $n_0 s$ state is strongly coupled to the upper states of the n_0-1 incomplete diamagnetic manifold, which lie very close in energy; consequently its mixing with the lowest states of the incomplete n_0 manifold decreases.

For low-lying states of the manifold, the comparison between Figs. 2(a) and 2(d), and the analysis of the $B_{l=0}^{n_0 k}$ quantities for hydrogen in the inter-l-mixing regime and for lithium in the inter-n-mixing regime, demonstrate that for sufficiently high B strengths the non-Coulombic interaction partially cancels intermanifold coupling effects.

III. THREE-STATE ANTICROSSING BETWEEN THE $n=29$ AND 30 DIAMAGNETIC MANIFOLD OF LITHIUM ATOM IN THE PRESENCE OF AN ADDITIONAL ELECTRIC FIELD (F‖B)

A. Experimental results

The evolution of the structure of the diamagnetic multiplet $n=30$, $M=0$, $B=3.11$ T in the lithium atom has been studied in great detail when an additional electric field **F** is applied in **B** direction. The experimental setup has been described elsewhere;[10,3] we only recall here its main features. The atoms of an atomic beam of lithium are excited in a one-step process by a pulsed tunable laser propagating perpendicularly to the atomic beam direction. A magnetic field and an electric field both parallel to the atomic beam are applied in the interaction region. By using π-polarized light atoms are excited in $M=0$ states and are then detected by field ionization.

In the present experiment $B=3.11$ T ($\gamma^2 n^7 \sim 3.83$), and the $n=30$ and 29 manifolds begin to nearly overlap. An additional weak **F** field is sufficient to lead to penetration of the lowest state of the $n=30$ manifold into the upper part of the $n=29$ manifold. As shown in Fig. 1 the first anticrossing appears at $F \sim 25$ V/cm. For such a low **F** value, H_f can be treated as a perturbation with respect to core effects ΔV and to the diamagnetic interaction H_d. Furthermore, because H_f couples states with opposite parity, the Stark effect provides a probe for analyzing the properties of the upper states in the even-parity diamagnetic manifold of lithium.

A series of systematic recordings obtained by increasing the **F** field in steps has allowed us to follow the evolution of both energy and intensity of the lines corresponding to the excitation of the lowest $n=30$ state and of the most excited $n=29$ doublet. The corresponding spectra are reported in Fig. 3. For the outermost **F** values only two components are observed, but in the intermediate **F** range both the resolution and the excitation rate are sufficient for the three components to be observed. Indeed the anticrossing effects remove the degeneracy in the $n=29$ doublet, and the parity mixing due to **F** allows the observation of the two corresponding lines. Consequently the present spectra provide the first experimental confirmation for the existence of doublets of states with a small energy spacing in the upper part of the $M=0$ diamagnetic manifold of lithium.

Figure 4 presents the electric field dependence for the energies of the three states involved in the anticrossing. These experimental data agree with the ones calculated from the diagonalization method. The manifestation of anticrossing effects is strongly localized: the three-component structure appears only in a very narrow range of electric field strength ($\Delta F=4$ V/cm) and the total energy separation W between the components is minimum for $F_0^{\text{expt}}=27.5$ V/cm where $W_{\text{expt}}=0.163$ cm^{-1}. The intensity of the most intense line does not change significantly, and simultaneously the energy of this state is not modified by the anticrossing effect. The energies of the outer two components vary with increasing F and these lines interchange their intensity at a field strength a little smaller than F_0^{expt}. After the anticrossing the energies of the two lines regain their initial electric field dependence.

Figure 4 clearly shows that when the electric field increases, the lowest component of the $n=30$, $M=0$, $B=3.11$ T diamagnetic manifold, named 30-St according to its linear Stark behavior, does not interact significantly with the uppermost state of the $n=29$ manifold. This latter state which is weakly perturbed by H_f, and which corresponds to an odd-parity state in the absence of F field, is named 29-o. In the same range of electric field strength the 30-St state undergoes a noticeable anticrossing with the lower component of the uppermost doublet, named 29-e according to its even parity in the limit of vanishing electric field.

B. Qualitative analysis

The observed spectra are quantitatively reproducible—with respect to intensity and position—by a diagonalization calculation. However, in such a process no information is obtained on the relative importance of the non-Coulombic interaction and of intermanifold couplings induced by the magnetic field. To quantitatively disentangle relative contributions of the different physical effects, more simple models are discussed below.

The strongly localized character of the recorded phenomenon suggests an analysis in the three-state model (30-St, 29-o, 29-e). Owing to the very small value of the electric field, H_f can be treated as a perturbation. Then the 29-o and 29-e states can be studied independently and the three-state model reduces to two independent two-state models (30-St, 29-o) and (30-St, 29-e), respectively.

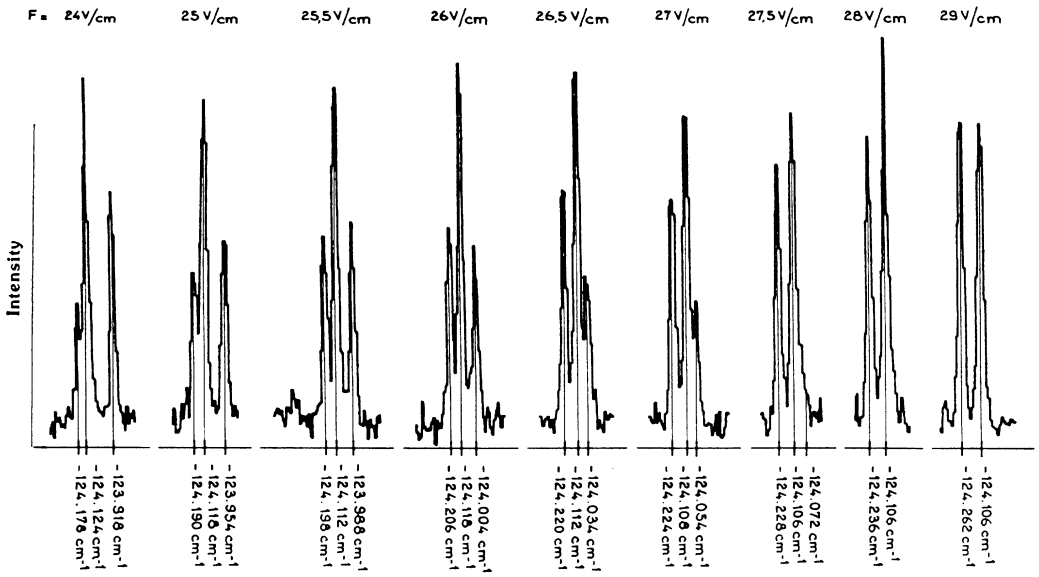

FIG. 3. Experimental $M=0$ spectra recorded for the lithium atom in the presence of a magnetic field $B=3.11$ T and an electric field **F** parallel to the **B** field. The **F** field strength is gradually changed. In the studied energy range, the lowest state of the $n=30$ manifold undergoes anticrossing with the more excited doublet of states in the $n=29$ manifold, which results in the observation of three components in the spectrum. The energies are given to the zero-field ionization limit.

However, in order to account for the Stark character of the 30-St state, it is necessary to form the corresponding wave function as a linear combination with an equal weight of the wave functions of the lowest two states of the $n=30$ manifold which have respectively the even and odd parity.

In a calculation to first order of perturbation theory the physical interactions responsible for the anticrossing width in a two-state model are tightly connected to the approximations used to determine the zeroth-order wave functions. Indeed when the Hamiltonian H of the system is split into $H=\mathcal{H}_0+H_1$, zeroth-order wave functions are eigenstates of $\mathcal{H}_0$, and the anticrossing width between two degenerate eigenstates of $\mathcal{H}_0$, ψ_0 and ψ_0', is equal to

$$\Delta W=2|\langle\psi_0|H_1|\psi_0'\rangle| \ . \tag{16}$$

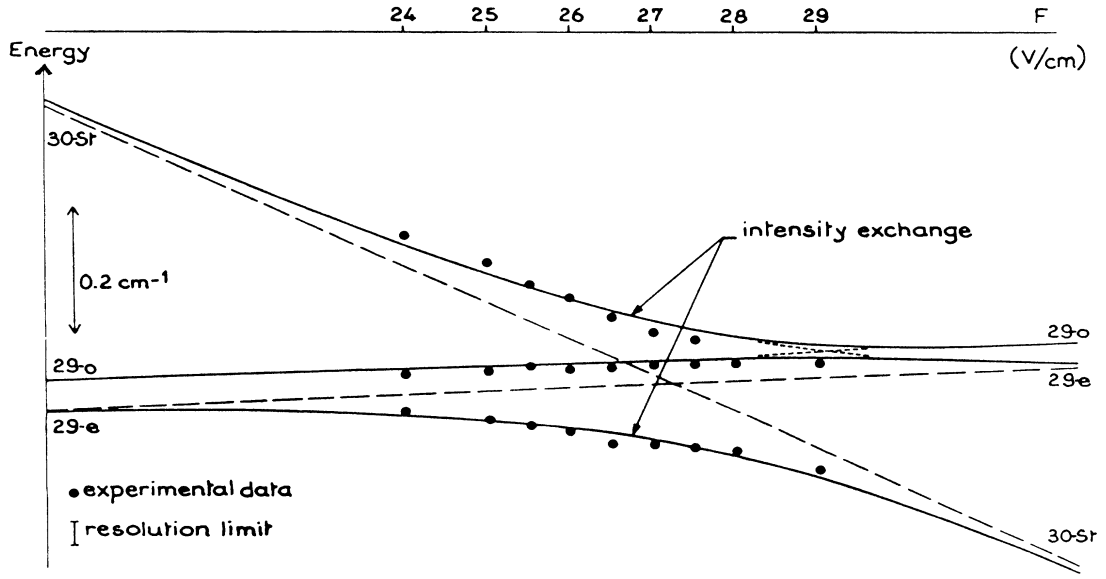

FIG. 4. Energies of the three states involved in the anticrossing as a function of the electric field strength. 30-St: lowest state of the $n=30$ manifold possessing a librational symmetry. 29-o and 29-e: components of the highest excited doublet in the $n=29$ manifold, possessing a rotational symmetry. The 29-o (or 29-e) state is adiabatically connected to an odd- (or even-) parity state for vanishing electric field.

Because of the large magnetic field strength, $H_d(n)$ is necessarily introduced in the zeroth-order Hamiltonian $\mathcal{H}_0$. The other terms $H_d(n,n')$, $\Delta V(n)$, and $\Delta V(n,n')$ may be included or not in $\mathcal{H}_0$ depending on the chosen approximation. Four different models have been successively analyzed. They correspond, respectively, to the following choices of $\mathcal{H}_0$.

(a) *Diamagnetic interaction in an isolated manifold of hydrogen:*

$$\mathcal{H}_0 = H_0 + H_d(n) ,$$

$$H_1 = H_d(n,n') + \Delta V(n) + \Delta V(n,n') + H_f(n) + H_f(n,n') .$$

(b) *Diamagnetic interaction in hydrogen including intermanifold couplings:*

$$\mathcal{H}_0 = H_0 + H_d(n) + H_d(n,n') ,$$

$$H_1 = \Delta V(n) + \Delta V(n,n') + H_f(n) + H_f(n,n') .$$

(c) *Diamagnetic interaction in an isolated manifold of lithium:*

$$\mathcal{H}_0 = H_0 + H_d(n) + \Delta V(n) ,$$

$$H_1 = H_d(n,n') + \Delta V(n,n') + H_f(n) + H_f(n,n') .$$

(d) *Diamagnetic interaction in lithium including intermanifold couplings:*

$$\mathcal{H}_0 = H_0 + H_d(n) + \Delta V(n) + H_d(n,n')\Delta V(n,n') ,$$

$$H_1 = H_f(n) + H_f(n,n') .$$

In the four models the zeroth-order wave functions for the three studied states $\psi^0_{30\text{-St}}$, $\psi^0_{29\text{-e}}$, and $\psi^0_{29\text{-o}}$ are expanded in a spherical basis. For each state, the expansion is characterized by the angular coefficients a_{nl} [Eq. (5)] and B_l [Eq. (7)]. The contribution to the anticrossing width arising from the non-Coulombic interactions ΔV [Eqs. (9) and (15)] and for the two studied two-state systems are

$$2\langle \psi^0_{30\text{-St}} | \Delta V | \psi^0_{29\text{-}x} \rangle = \sum_l \delta_l B_l^{30\text{-St}} B_l^{29\text{-}x} \quad (x = \text{o or e}) .$$

The contributions arising from H_d and H_f are explicitly determined by calculating the matrix elements of the operators ρ^2 and z.

The calculated values for the anticrossing full widths at half maximum $\frac{1}{2}\Delta W$ in the two two-state systems (30-St, 29-e) and (30-St, 29-o) for the four above defined models are shown in Table I.

Models (a) and (b) lead to calculated anticrossing widths twice as great as the experimentally observed total width W^0_{expt}. The result of model (d) agrees nicely with the experimental value. This demonstrates that the studied anticrossings which involve several strong interactions can be treated as two independent two-state systems when the zeroth-order wave functions are suitably chosen.

In model (c), the width calculated for the anticrossing (30-St, 29-e) is significantly too large. This confirms the statement developed in Sec. II E: when the magnetic field strength is sufficiently important to induce significant intermanifold couplings $H_d(n,n')$ and when core effects within a manifold $\Delta V(n)$ cannot be treated as a perturbation, then intermanifold couplings $\Delta V(n,n')$ induced by core effects, which are of the same order of magnitude as $\Delta V(n)$, have to be introduced in the zeroth-order Hamiltonian.

In models (a) and (b), hydrogenic wave functions are used to describe the diamagnetism either in the inter-l-mixing regime or in the inter-n-mixing regime. The operators H_d and H_f lead to completely negligible contributions to the anticrossing widths between states belonging to adjacent n manifolds. This indicates that the approximate constant of the motion for the problem of hydrogen in parallel **B** and **F** fields in the inter-l-mixing regime remains valid for higher field strengths corresponding to the inter-n-mixing regime.[15]

In models (a) and (b), the anticrossing widths result only from the non-Coulombic interaction. For the two-state system (30-St, 29-e) or (30-St, 29-o) these widths are directly related to the quantum defects δ_s or δ_p. For the (30-St, 29-o) system, this anticrossing width is of the same order of magnitude as the widths previously measured for anticrossings between odd magnetic states of lithium.[4] Although the n-mixing effects are important in the upper part of the diamagnetic manifold (see Sec. II B), the results obtained in models (a) and (b) are very similar, which confirms that the intermanifold coupling $H_d(n,n')$ does not modify the l distribution B_l in the wave functions.

TABLE I. Partial contributions (in 10^{-3} cm^{-1}) to the anticrossing half width $\frac{1}{2}\Delta W$ arising from core effects ΔV, diamagnetic interaction H_d, or Stark interaction H_f. The two-state systems (20-St–29-e) and (30-St–29-o) are studied independently. The zeroth-order wave functions are eigenstates of $\mathcal{H}_0$, couplings between states result from H_1 specified in the text. The magnetic field strength is $B = 3.11$ T, the electric field strength is $F = 27.5$ V/cm. Experimental total half width for the three-state system $\frac{1}{2}W^0_{\text{expt}} = 80\times10^{-3}$cm^{-1}.

		Two-state system 30-St–29-e				Two-state system 30-St–29-o			
Model	$\mathcal{H}_0$	ΔV	H_d	H_f	$\frac{1}{2}\Delta W$	ΔV	H_d	H_f	$\frac{1}{2}\Delta W$
(a)	$H_0 + H_d(n)$	229	1×10^{-5}	9×10^{-7}	229	20	-2×10^{-5}	9×10^{-7}	20
(b)	$H_0 + H_d(n) + H_d(n,n')$	248		1×10^{-5}	248	21		-2.1×10^{-5}	21
(c)	$H_0 + H_d(n) + \Delta V(n)$	198	278	6	482	-9	-12	28	7
(d)	$H_0 + H_d(n) + \Delta V(n)$ $+ H_d(n,n') + \Delta V(n,n')$			110	110			10	10

In model (d), the anticrossing widths result only from the Stark interaction. For the two-state system (30-St, 29-o) the calculated width is rather small. The quantum defect δ_p being almost negligible, the wave function of the 29-o diamagnetic state of lithium does not significantly differ from the corresponding one in hydrogen. Because of parity arguments, only the even-parity components in the wave function of the 30-St state contribute to the matrix element $\langle \psi^0_{30\text{-St}}|z|\psi^0_{29\text{-e}}\rangle$. As this matrix element cancels for hydrogenic wave functions [see models (a) and (b)], the very small value obtained in model (d) demonstrates that the $\psi^0_{30\text{-St}}$ wave function in lithium does not strongly differ from the hydrogenic one. This confirms that for a sufficiently high B strength inter-n-mixing effects partially cancel core effects.

The experimentally observed three-state anticrossing has been analyzed in detail in terms of two independent anticrossings, each involving two states belonging to different n manifolds. Important results have been deduced from this investigation; they are summarized below.

(i) If hydrogenic wave functions are used, the peculiar symmetry of the Coulomb potential results in the existence of an approximate constant of motion and intermanifold coupling $H_d(n,n')$ can be disregarded. The anticrossing widths are then to be ascribed to core effects and they are large only for states having a large even-parity component in their wave functions. The anticrossing width for the two-state system (29-o, 30-St) is so small that it is possible to consider that the 29-o state nearly crosses the 30-St state. Furthermore, because of the localization of the wave functions of rotational states 29-o and 29-e near the $z=0$ plane, the strength of the electric-field-induced coupling $H_f(n)$ between these states is negligible. Consequently, the 29-o state is nearly uncoupled from the mutually interacting states (29-e+30-St) which exhibit a noticeable anticrossing effect. In Fig. 4, the three states involved in the anticrossing are connected adiabatically when F increases; then there is a small avoided crossing between the 29-o state and the upper state of the anticrossing (29-e+30-St). There are two confirmations for the existence of the nearly exact crossing 29-o—(29-e+30-St). First, in the experiment the energy and intensity of the most intense line, which corresponds to the excitation of the 29-o state, does not change during the anticrossing. Second, the diagonalization calculation confirms that on both sides of the anticrossing region the more excited component in the upper $n=29$ doublet corresponds to an odd-parity state.

(ii) If wave functions typical of lithium are used, then for relatively large values of the studied B strength, the introduction of only intermanifold coupling $H_d(n,n')$ is insufficient: we have to introduce also $\Delta V(n,n')$. The anticrossing widths are to be ascribed to the Stark interaction. The small width for the anticrossing 30-St–29-o confirms the nearly hydrogenic behavior for the lowest state of the diamagnetic manifold at $B=3.11$ T. Another confirmation of the nearly hydrogenic behavior of low-lying states of the $n\simeq 30$, $M=0$ manifolds of lithium at $B=3.11$ T is manifested in Fig. 1: when the electric field parallel to the magnetic field is increased, the low-lying librational states undergo narrow avoided crossings [in hydrogen, librational states cross by pair with increasing **F** (Refs. 3 and 9)]. Figure 1 is to be compared with Figs. 3 and 5 of Ref. 12, which represent the evolution with increasing **F** of the structure of the $n=30$, $M=0$ diamagnetic manifold of lithium at $B=2.33$ T: large core effects, which are not canceled by inter-n-mixing interactions, result in large avoided crossings, leading to energies which are nearly electric field independent for librational states.

IV. CONCLUSION

In lithium, due to the importance of core effects arising from the large value of δ_s, the diamagnetic structure of a multiplet differs drastically from that of hydrogen and depends on the field strength. More particularly pairs of quasidegenerate states are present in the upper part of the manifold. However, this doublet structure had not been observed previously because of the opposite parity of its two components. For a sufficiently high B strength, the addition of a relatively small electric field parallel to the magnetic field is sufficient to reveal the existence of these pairs of nearly degenerate states through the appearance at the anticrossing of three resolved components. The detailed analysis of the different behavior of both states in the uppermost pair of a manifold at the anticrossing with the lowest state of the multiplet lying immediately above confirms that, in the diamagnetic manifold of hydrogen, states with an opposite symmetry behave differently with respect to inter-n-mixing effects or to non-Coulombic effects. It can be inferred that for a sufficiently high B strength these two effects cancel in the low-energy part of the manifold resulting in states with a nearly hydrogenic character. Simultaneously, strong non-Coulombic effects persist in the even-parity high-energy part of the manifold.

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