Atomic Diamagnetism and Diamagnetically Induced Configuration Mixing in Laser-Excited Barium

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The diamagnetic Zeeman effect has been isolated by observing energy shifts of the $6s6p\ ^1P_1^\circ$-$6sns\ ^1S_0$ Rydberg series in laser-excited Ba in magnetic fields of 20–40 kG. Perturbation of this series by the $5d7d\ ^1S_0$ level reduces the shift below the hydrogenic value for $n = 18$. Magnetically induced mixing between the $6sns\ ^1S_0$ and $6snd\ ^1D_2$ series causes both an enhancement in intensity of the higher members of the $^1S_0$ series and deviations of the shifts from the hydrogenic values.

The diamagnetic Zeeman effect results in a net upward energy-level shift which is in addition to any other Zeeman or Paschen-Back effects present.[1] This shift depends only on the orbital motion of the electrons and is usually important only for large electron orbits and strong magnetic fields. With the assumption of hydrogenic wave functions and high effective quantum number n^* for an atom in a Rydberg state, the shift is given by

$$\Delta\sigma_H = 4.98\times10^{-15}(n^*)^4B^2\ \mathrm{cm}^{-1} \qquad (1)$$

when the excited electron has $l=0$. While the electron behavior at small radial distances is dominated by interactions with the core, the diamagnetic potential ($V_D \sim r^2B^2\sin^2\theta$, where θ is the polar angle) prevails at large r and imposes cylindrical symmetry on the orbital motion, leaving only m_l and parity as strict invariants. When $\Delta\sigma_H$ is comparable to the separation between states, the orbital angular momentum of the excited electron is no longer conserved and mixing occurs between states with l differing by $\Delta l = 0$ or ±2.[2] At higher excitation, mixing of states with different principal quantum number n also occurs. Early experiments[3] on the principal series of the alkalis confirmed the basic nature of this effect, and later both l mixing and n mixing have been observed at high resolution in the principal series of Ba I.[4]

We have studied the behavior of highly excited even-parity states of neutral barium in a strong magnetic field ($B \geq 20$ kG) by absorption spectroscopy out of a laser-populated lower level. The diamagnetic Zeeman shift has been isolated for levels with $n \leq 30$ in the $6sns\ ^1S_0$ Rydberg series, which have no linear or residual quadratic Zeeman shifts due to the paramagnetic term in the Hamiltonian. The shifts depart noticeably from the hydrogenic result [Eq. (1)] in regions where interactions with states of the $5d7d$ configuration are strong. In addition to deviations of the shifts from the hydrogenic values and the appearance of satellite lines, diamagnetically induced l mixing is clearly demonstrated by the transfer of oscillator strength from the $6s6p\ ^1P_1^\circ$-$6snd\ ^1D_2$ series to the $6s6p\ ^1P_1^\circ$-$6sns\ ^1S_0$ series. This results in an intensity enhancement of the $^1S_0$ series for $n > 20$, allowing levels with $n > 30$ to be detected even though they are too weak to be seen without the applied field.

Our experimental technique was similar to that described by Rubbmark, Borstrom, and Bockasten.[5] A nitrogen-laser–pumped dye laser, polarized parallel to the transverse magnetic field, was used to pump the $6s^2\ ^1S_0(M=0)$-$6s6p\ ^1P_1^\circ(M=0)$ transition in a column of Ba vapor. A separate dye cell was pumped with the same nitrogen laser to produce unpolarized continuum light, which was used as a background to observe (absorption) transitions out of the excited state to the $6sns\ ^1S_0$, $6snd\ ^1D_2$, and other highly excited states. A resistively heated cylindrical oven, producing a Ba vapor pressure of $P_{\mathrm{Ba}} \sim 0.2$ Torr

at $T = 760°C$, was placed in the core of a superconducting dipole magnet capable of producing a transverse field of up to 40 kG. Neon was used as a buffer gas with $P_{Ne} = 5$ Torr. Spectra were recorded with the Argonne National Laboratory 30-ft Paschen-Runge spectrograph. A Wollaston prism in front of the slit separated the π and σ polarizations. The shifts of the $6sns\ ^1S_0$ states were determined directly on each plate, and the estimated uncertainties of the measurements were usually less than ± 0.015 cm^{-1}. For the field strengths used, the diamagnetic shift of the $M = 0$ sublevel of the $6s6p\ ^1P_1^\circ$ state is well below this uncertainty and any line shifts detected are due solely to movement of the upper states.

We restrict our discussion to transitions out of the $6s6p\ ^1P_1^\circ (M = 0)$ sublevel with the selection rule $\Delta M = 0$ (π polarization) which insures that there are no linear Zeeman or Paschen-Back effects present. Since only transitions between singlet states are considered, there are no quadratic Zeeman effects due to the paramagnetic term in the Hamiltonian.

The shifts of the $^1S_0$ states versus $(n^*)^4$ are plotted in Fig. 1 for five field strengths. The position of the very weak $6s6p\ ^1P_1^\circ$-$6s28s\ ^1S_0$ line was measured only when it was clearly resolved from a nearby stronger line. The general agreement of the data with the straight lines given by Eq. (1) is evident, but noticeable deviations from the hydrogenic values occur near $n = 18$ and 28. To obtain an understanding of these deviations,

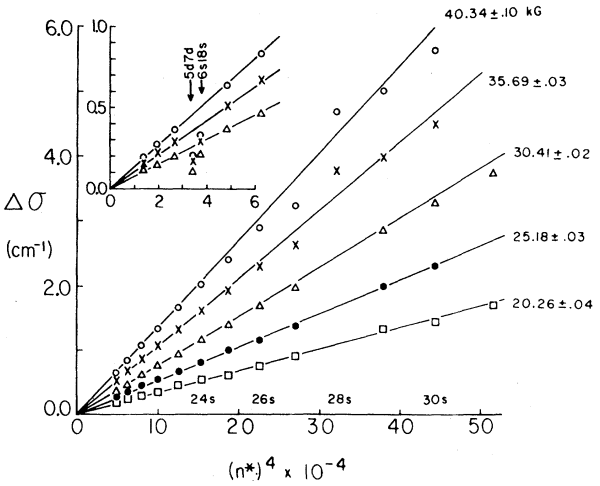

FIG. 1. Diamagnetic shift $\Delta\sigma$ vs $(n^*)^4$ for the $^1S_0$ levels. Solid lines are the hydrogenic values given by Eq. (1), which does not include the influence of l mixing. The values of B are given next to the solid lines.

a multichannel quantum-defect plot[6] for the even-parity states of Ba I at zero field is given in Fig. 2(a). The differences between the measured shift, $\Delta\sigma$, and the hydrogenic value, $\Delta\sigma_H$, for the $^1S_0$ series with $B = 35.7$ kG is plotted against n_2^* and placed below the quantum-defect plot for comparison.

Figure 2(a) was constructed with data taken from Ref. 5, except for the points in the $6s18s\ ^1S_0$ region. The quantum-defect plot indicates that the levels labeled $6s26d\ ^1D_2$ and $6s26\ ^3D_2$ in Ref. 5 should instead have their assignments exchanged. The $6s18s$ line of Ref. 5 splits in the π polarization when $B \neq 0$ and hence is incorrectly assigned. We have identified two $^1S_0$ levels in this region. Because of its small electronic orbits, the doubly excited $5d7d\ ^1S_0$ level has a negligible diamagnetic shift, and we assign the $^1S_0$ line with the smaller shift to this $5d7d\ ^1S_0$ term, while the line with the larger shift, which is given the label

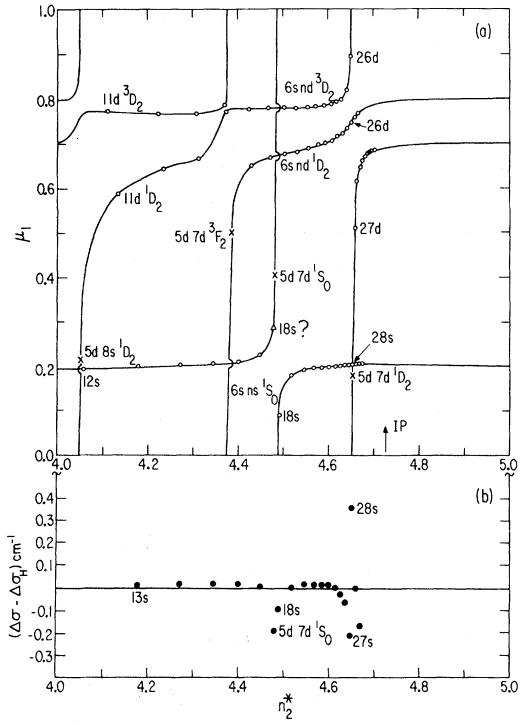

FIG. 2. (a) Multichannel quantum-defect plot of even-parity states of Ba I, using the data from Ref. 5. μ_1 is the quantum defect with respect to the $6s\ ^2S_{1/2}$ ionization threshold, while n_2^* is the effective quantum number with respect to the $5d\ ^2D_{3/2}$ threshold. The $18s$ datum point with a question mark is from Ref. 5. (b) Deviations of measured shifts of the $6sns\ ^1S_0$ series and its perturber from the values given by Eq. (1) for $B = 35.69 \pm 0.03$ kG.

$5d7d\,^1S_0$ in Ref. 5, is assigned to the $6s18s\,^1S_0$ term. The quantum-defect plot indicates strong mixing between the $5d7d$ and $6s18s$ configurations due to electron-core correlation, which qualitatively accounts for both lines having shifts that are nonzero and less than the hydrogenic value.

The departure of the shifts around $n = 28$ from the hydrogenic values of Eq. (1) are evident only for the higher field strengths in Fig. 1. Diagmagnetic l mixing between the $6sns$ and $6snd$ series is of increasing importance in this region as the magnetic interaction energy, $\Delta\sigma_H$, becomes comparable to the separation between states. Although the $6sns\,^1S_0$ series is relatively unperturbed in this region when $B = 0$, the $6snd\,^1D_2$ is strongly mixed with the $6snd\,^3D_2$ series and the $5d7d\,^1D_2$ perturber [see Fig. 2(a)]. These perturbations on the $6snd\,^1D_2$ series are reflected in the anomalous shifts of the $6sns\,^1S_0$ series [see Fig. 2(b)] as these two series mix diamagnetically. In Fig. 2(b), the rapid variation of $\Delta\sigma - \Delta\sigma_H$ as n^* increases contrasts sharply with the monotonic $(n^*)^{11}$ behavior of these deviations in the one-electron spectra for the l-mixing regime.[2] Detailed calculations of the diamagnetic shifts in Ba I require a complete multichannel quantum-defect analysis[7] of the zero-field spectrum and will be reported in a separate publication.

Diamagnetic configuration mixing is even more dramatically demonstrated in Fig. 3, which presents microdensitometer tracings for $B = 0$ and 36 kG for states lying near the ionization limit. When $B = 0$, the $6sns\,^1S_0$ series, which has a relatively constant quantum defect for $n > 20$, is observed up to $n \approx 30$ as the intensities decrease with the hydrogenic $(n^*)^{-3}$ dependence. However, the zero-field intensity distribution of the $6snd\,^1D_2$ series is perturbed by configuration interaction with the $5d7d\,^1D_2$ level such that the higher members of the $6snd\,^1D_2$ series are detected up to $n \approx 45$. In the presence of a strong magnetic field, the breakdown of the orbital angular momentum invariance causes a redistribution of the oscillator strengths among series of equal parity and equal M. To a first approximation, the weaker $6s6p\,^1P_1^\circ(M=0)$-$6sns\,^1S_0$ series mixes only with the stronger $6s6p\,^1P_1^\circ(M=0)$-$6snd\,^1D_2(M=0)$ series and obtains added oscillator strength, which results in significant intensity enhancement of the $^1S_0$ series for $n > 20$ when $B \gtrsim 20$ kG. For $n > 30$, the shifted $^1S_0$ states appear near their expected positions even though these transitions were too weak to be seen when $B = 0$. In the same energy region, the $^1D_2$ series shows a drastic decrease

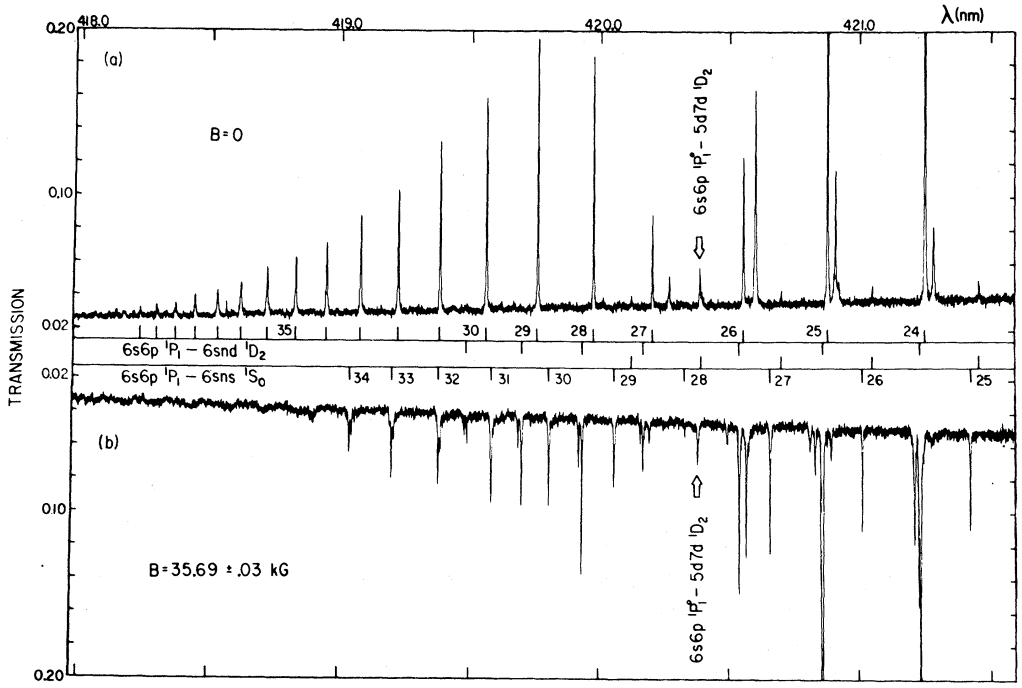

FIG. 3. Microdensitometer recording of the plate transmission in the region of the ionization limit. (a) $B = 0$, (b) $B = 35.69 \pm 0.03$ kG (π polarization). The upper panel (a) is inverted to facilitate comparison with the lower panel (b).

in its intensity due to mixing not only with the weaker $^1S_0$ levels, but also with the $6sng\,^1G_4$ series, which is not optically connected to the lower $6s6p\,^1P_1^\circ$ level. At the higher n values observed, further mixing with additional even-parity series is evidenced by the appearance of satellite lines and a rapid drop in oscillator strength as n increases.

In addition to the case of the $6s18s\,^1S_0$ level discussed earlier, the utility of the diamagnetic shift in differentiating between Rydberg states and doubly excited states is demonstrated by noting that the $6s6p\,^1P_1^\circ$-$5s7d\,^1D_2$ line in Fig. 3 exhibits a shift that is appreciably less than that of nearby $^1D_2$ Rydberg levels.

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Deflection of High-Rydberg Atoms in Collisions at Thermal Energy

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Lithium atoms in high Rydberg states, excited in an atomic beam by pulsed electron impact, are passed through a target gas and detected following electric-field state selection. Cross sections obtained from time-of-flight spectra are virtually independent of the principal quantum number and in numerical agreement with calculations for deflection of the core ion alone. This deflection has also been observed directly. These results suggest a new method for very-low-energy ion-atom scattering experiments.

Recent interest in the collisional interactions of high Rydberg states has been directed toward l-changing processes[1-3] and detachment of the outer electron by ions[4] and by polar and electronegative molecules.[5,6] When ionization takes place in collisions with molecules, the outer electron appears to behave as a free particle, independent of the core ion to which it is weakly bound. When Rydberg atoms are deflected by neutral atoms or molecules, it is conversely possible that the core ion is scattered as an electron-independent system.

Ion-atom and ion-molecule interactions have traditionally been studied by ion-beam scattering above about 1 eV and by drift-tube techniques at lower energies. The important thermal energy region has not been fully explored,[7] as slow ion beams have proved difficult to produce and maintain, while drift experiments measure ion transport properties rather than differential cross sections. This work considers the possibility that free-ion scattering can be observed at thermal energies in the deflection of high-Rydberg atoms by neutral gaseous targets. In the experiments to be described, a lithium atomic beam containing high Rydberg states (Li*) is scattered by a gas at low density.

The experimental geometry has been discussed previously.[8] Lithium atoms from a 500°C oven are excited by a transverse beam of electrons from a heated cathode. The electron accelerating potential is pulsed with a repetition rate of 850 Hz, a pulse width of 10 μsec, and an amplitude of 10 V. A 1.5-kG magnetic field, parallel to the electron beam, is applied to the excitation region to remove ions and electrons from the atomic beam and to focus the bombarding electrons.

Near the end of its 35-cm flight path, the Li beam passes through a pair of parallel electric field plates and a grounded aperture of 0.5-cm radius before entering an excited-atom detector.