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Diamagnetic shift and singlet-triplet mixing of $6snp$ Yb Rydberg states with large radial extent

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The diamagnetic shifts of the $m_J=0$ and $m_J=\pm1$ components of $6snp\ ^1P_1$ ($n=40,55,70,85,100$) and $6s55p\ ^3P_{0,1}$ Rydberg states of ^{172,174}Yb have been measured in external magnetic fields up to $\cong 3$ kG by high-resolution three-photon spectroscopy. The diamagnetic shifts have been analyzed to yield the singlet-triplet mixing due to spin-orbit interaction. At $n=40$, the singlet-triplet mixing derived from diamagnetic shifts and hyperfine-structure data are in excellent agreement.

There is much current interest in the study of diamagnetism of atomic Rydberg states.[1] For ground states or low-lying levels, diamagnetic shifts produced by laboratory magnetic fields are negligible and the Zeeman term accounts for the observed splittings. However, the diamagnetic energy becomes dominant at high principal quantum numbers, since it is proportional to r^2 and hence n^{*4}, n^* being the effective principal quantum number. The motion of the Rydberg electron is profoundly modified at magnetic field strengths, for which the diamagnetic energy is comparable to its Coulomb binding energy.[1] On the contrary in this Rapid Communication we report on the diamagnetism of Rydberg states of two-electron systems in a low-field regime. The diamagnetic shifts of $6snp\ ^{1,3}P_1$ Rydberg states of ^{172,174}Yb with principal quantum numbers up to $n=100$ have been measured for sufficiently low magnetic field strengths to avoid l mixing and n mixing.[1] Although the operator describing the diamagnetic energy does not depend on the spin variables explicitly, nevertheless, diamagnetic shifts of singlet and triplet states are different due to spin-orbit interaction. Contrary to low-lying atomic levels, for Rydberg states with large radial extent, diamagnetic shifts are pronounced even at magnetic fields low enough not to cause Paschen-Back effects, and, hence, m_J rather than m_L is a constant of the motion. Up to now diamagnetic shifts of Rydberg states of two-electron systems have not been measured with sufficient precision to notice their dependence on the singlet-triplet character. Here, we exploit for the first time diamagnetic shifts to derive singlet-triplet mixing of Rydberg states with high principal quantum numbers. Singlet-triplet mixing provides[2,3] valuable experimental information necessary for a description of Rydberg series of two-electron systems by multichannel quantum-defect theory (MQDT).[4]

Our experiment [cf. Fig. 1(a)] employs three-photon excitation of the Rydberg states, following a procedure described previously in some detail.[5] Two photons are absorbed coherently from the first laser beam ($\lambda_1=582.23$ nm), when inducing the two-photon resonance $6s^2\ ^1S_0 \rightarrow 6s7s\ ^1S_0$. Scanning the second cw dye laser across the upper atomic transition $6s7s\ ^1S_0 \rightarrow 6snp\ ^{1,3}P$, high-resolution spectra were obtained due to two-photon absorption line narrowing. Excitation of the Rydberg states was monitored with the use of thermionic detection. Twelve tungsten wires in an annular arrangement[6] served as cathode of the diode. To enhance its sensitivity, besides ytterbium, a small amount of barium was added to the diode, heated to 550–600 °C. Barium is known to lower the work function of tungsten dramatically, thus facilitating the formation of the electron cloud. The magnetic field, produced by a stabilized 4-in. (Varian) electromagnet, was calibrated, measuring the Zeeman splitting of the $6s6p\ ^3P_1$ level, the g_J factor of which is known with high precision ($g_J=1.492\,82$). Figure 1(b) displays a typical spectrum obtained for the $6s100p\ ^1P_1$ state at $B=278(1)$ G. The polarization of the second laser beam was chosen perpendicularly to the magnetic field. The spectrum clearly reveals the diamagnetic shifts of the $m_J=\pm1$ components for the most abundant isotopes ^{172,174}Yb. The diamagnetic shifts were measured relative to the signal of ^{174}Yb at zero magnetic field.

In the following paragraph we calculate to first order the diamagnetic shifts of the $m_J=0$ and $m_J=\pm1$ components for $6snp\ ^{1,3}P_1$ Rydberg states. The Hamiltonian $\mathcal{H}_d$ describing the diamagnetic contribution to the total energy is given by[1]

$$\mathcal{H}_d=(e^2B^2/8m_ec^2)r^2\sin^2\theta \ . \tag{1}$$

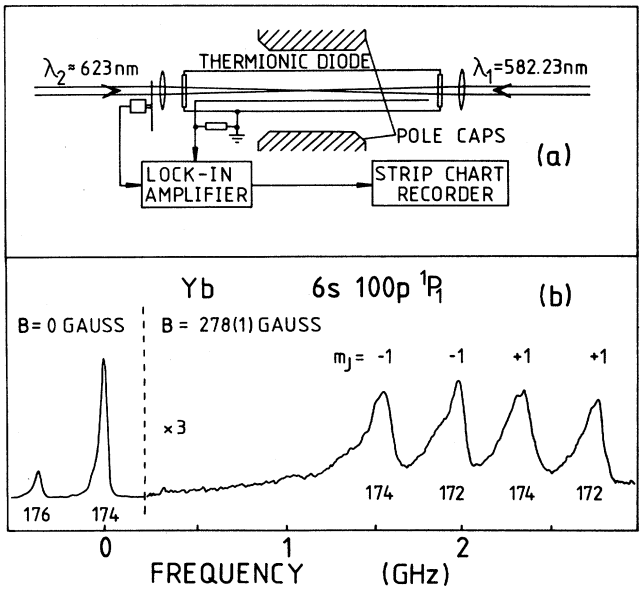

FIG. 1. (a) Experimental setup; (b) high-resolution three-photon excitation spectrum of the $6s100p\ ^1P_1$ ^{172,174,176}Yb Rydberg state at $B=0$ and 278 G.

The z axis has been taken along the magnetic field and r and θ refer to the Rydberg electron. For our purposes the wave functions $|6snp\ ^1P_1\rangle$ of the Rydberg states can be written as

$$|^1P_1\rangle = \Lambda|^1P_1\rangle_{SL} + \Omega|^3P_1\rangle_{SL} \ , \tag{2}$$

where $|6snp\ ^1P_1\rangle_{SL}$ and $|6snp\ ^3P_1\rangle_{SL}$ correspond to pure configuration, exactly SL-coupled basis vectors. An analogous equation holds for the corresponding $^3P_1$ states. The wave function given in Eq. (2) can be used to calculate the diamagnetic shifts for Rydberg states of pure $6snp$ character ($\Lambda^2+\Omega^2=1$) as well as for those perturbed by the admixture of doubly excited configurations ($\Lambda^2+\Omega^2<1$). The contribution of such configurations can be neglected because of the small radial extent of both excited electons.[7] Hence, configuration mixing influences the diamagnetic shifts only indirectly by reducing the Rydberg character. Employing angular momentum algebra, the diamagnetic shift is calculated to first order to be

$$\langle {}^1P_1, m_J|\mathscr{H}_d|{}^1P_1, m_J\rangle = CB^2[(\Lambda^2+\Omega^2)(1+m_J^2) + \Omega^2(1-3m_J^2/2)] \ , \tag{3}$$

where C is given by

$$C = e^2\langle 6snp|r^2|6snp\rangle/(20m_ec^2) \ . \tag{4}$$

Whereas the experimentally observed shifts $E_{\pm1}$ of the $m_J=\pm1$ components contain the linear Zeeman effect, the average $(E_{+1}+E_{-1})/2$ depends on the diagmagnetic interaction only. From Eq. (3) it follows immediately that the ratio $R=(E_{+1}+E_{-1})/2E_0$ of this average and the shift E_0 of the $m_J=0$ component is given by

$$R = [2-\tfrac{1}{2}\Omega^2(\Lambda^2+\Omega^2)^{-1}]/[1+\Omega^2(\Lambda^2+\Omega^2)^{-1}] \ . \tag{5}$$

For $\Lambda^2+\Omega^2=1$ the ratio R varies between 0.75 and 2 for pure $^3P_1$ ($\Omega^2=1$) and pure $^1P_1$($\Omega^2=0$) states, respectively, and, hence, can be exploited to probe singlet-triplet mixing of Rydberg states of two-electron systems.

In Fig. 2 the diamagnetic shift E_0 and the average $(E_{+1}+E_{-1})/2$ have been plotted for the $6s85p\ ^1P_1$ Rydberg state versus the square of the external magnetic field strength. The data were derived from the shifts measured for the most abundant isotopes ^{172,174}Yb and corrected for the isotope shift in zero magnetic field. Within our error limits, E_0 and $(E_{+1}+E_{-1})/2$ depend quadratically on the magnetic field strength. The slope of both straight lines differ by a factor of about 2 [$R=1.85(3)$]. This immediately proves the state under discussion to be of predominant

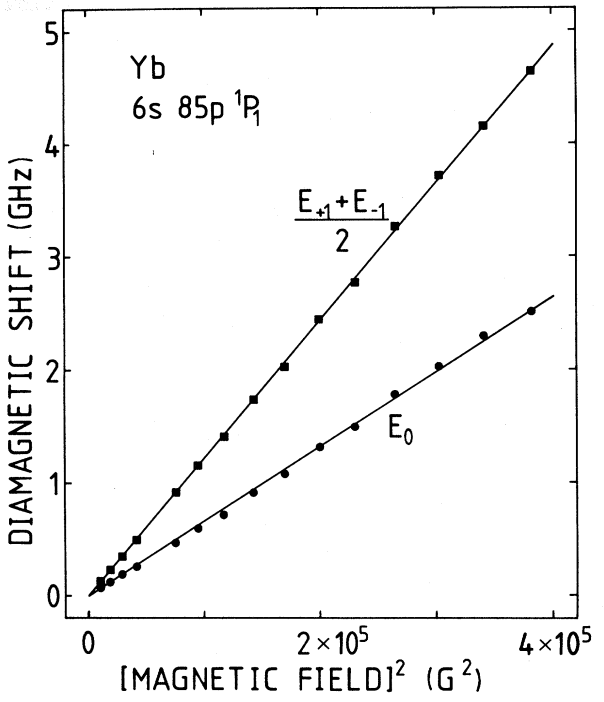

FIG. 2. Diamagnetic shifts E_{m_J} of the $6s85p\ ^1P_1$ Yb Rydberg state. Experimental uncertainties are indicated by the size of the symbols.

singlet character. From measured term values[8] of $6snp\ ^1P_1$ ($25\leq n\leq 120$) and $6snp\ ^3P_1$ ($25\leq n\leq 75$) states we conclude that the Rydberg character of these levels exceeds $\Lambda^2+\Omega^2\geq 0.98$, in agreement with a MQDT analysis[9] based on a limited data set. Using Eq. (5), the triplet character is found to be $\Omega^2(6s85p\ ^1P_1)=0.06(1)$.

The analysis outlined in the preceding paragraph neglects higher-order contributions. As is well known, an energy shift proportional to B^2 is caused by the diamagnetic part ($\mathscr{H}_d$) in first order and by the paramagnetic term [$\mathscr{H}_p=\mu_B(L_z+2S_z)B$] of the Hamiltonian in second order. In this Rapid Communication we refer to the second-order contribution of $\mathscr{H}_p$ as quadratic Zeeman effect. For example, the $6s55p\ ^3P_1$ and $6s55p\ ^3P_0$ fine-structure components are separated by about 1 GHz only. Hence, for magnetic fields in the order of 1 kG, the Zeeman energy μ_BB becomes comparable to the fine-structure splitting, resulting in a partial Paschen-Back effect. This is illustrated in Fig. 3,

TABLE I. Relative diamagnetic shifts $R=(E_{+1}+E_{-1})/2E_0$, slopes C [cf. Eq. (4)], and singlet-triplet mixing parameters Ω^2 of $6snp\ ^1P_1$ Rydberg states. (*) The results given in the last line refer to the $55p\ ^3P_1$ state.

n	Energy (cm^{-1})	R	C (MHz/G^2)	Ω^2;(*)Λ^2 (%)
40	50358.6	1.84(2)	$2.45(5)\times10^{-4}$	6.4(0.8)
55	50400.9	1.81(3)	$9.85(15)\times10^{-4}$	7.6(1.2)
70	50417.9	1.88(4)	$2.81(9)\times10^{-3}$	4.8(1.6)
85	50426.3	1.85(3)	$6.24(25)\times10^{-3}$	6.0(1.2)
100	50431.1	1.91(1)	$1.28(2)\times10^{-2}$	3.6(0.4)
55*	50399.8	0.79(1)	$9.67(20)\times10^{-4}$	6.5(1.6)

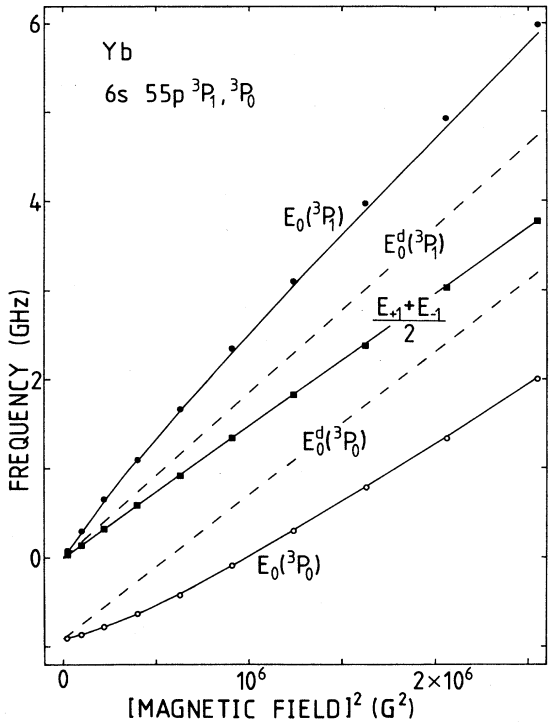

FIG. 3. Diamagnetic shifts and Paschen-Back effect of the $6s55p\ ^3P_0$ and $^3P_1$ Rydberg states. Correcting for the Paschen-Back effect, $E_0^d(^3P_0)$ and $E_0^d(^3P_1)$ were obtained.

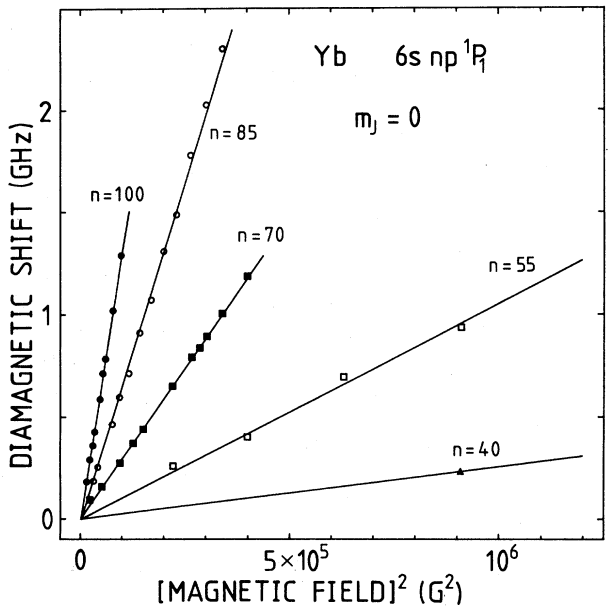

FIG. 4. Diamagnetic shifts of $6snp\ ^1P_1$ Rydberg states.

where the shifts $E_0(^3P_0)$, $E_0(^3P_1)$, and $(E_{+1}+E_{-1})/2$ have been plotted versus the square of the magnetic field strength. The Paschen-Back effect leads to a mutual repulsion of both $m_J=0$ components which no longer depend quadratically on the external field. This mixing can be taken into account quantitatively by solving a corresponding 2×2 secular equation, resulting in the solid lines in Fig. 3. The dashed straight lines (Fig. 3) correspond to the diamagnetic shifts $E_0^d(^3P_0)$ and $E_0^d(^3P_1)$ corrected for the Paschen-Back effect. As expected for a state of predominant triplet character, the slope of the dashed straight line $E_0^d(^3P_1)$ exceeds that of the average $(E_{+1}+E_{-1})/2$. The corresponding singlet character $\Lambda^2=0.065(16)$ is given in Table I, together with the triplet character obtained for the $6snp\ ^1P_1$ Rydberg states with external magnetic fields applied up to 3.2, 1.6, 0.6, 0.6, 0.3 kG at $n=40$, 55, 70, 85, and 100, respectively. Within our error limits the triplet character and the singlet character, admixed into the $6s55p\ ^1P_1$ and $6s55p\ ^3P_1$ Rydberg states, respectively, are the same. With increasing principal quantum number the singlet-triplet mixing is seen to decrease slightly. At $n=40$, our result is in excellent agreement with the triplet character $\Omega^2(6s40p\ ^1P_1)=0.064(3)$ derived from hyperfine-structure (hfs) data of ^{171,173}Yb.[8] Because of the strong hyperfine coupling of the $6s$ electron, above $n=45$ the determination of the singlet-triplet character from hfs measurements is strongly hampered by hyperfine-induced singlet-triplet mixing[10] and n mixing.[6] Within our error limits the quantities C [cf. Eq. (4)] scale with n^{*4}. This clearly rules out shifts caused by motional Stark effect which, in our case, should increase proportional to n^{*7}. Figure 4 compares diamagnetic shifts of $6snp\ ^1P_1$ Rydberg states with different principal quantum numbers.

To summarize, we have exploited diamagnetic shifts of Yb Rydberg states with large radial extent to determine their singlet-triplet character. In contrast, at high principal quantum numbers, experimental g_J factors are less suited for this purpose because the Zeeman energy amounts to a minor fraction of the total magnetic energy only. Likewise, at high n, hyperfine structure is dominated by hyperfine-induced singlet-triplet mixing[10] and n mixing,[6] obscuring the effect of spin-orbit interaction. In general, our results show the effect of electronic spin on atomic diamagnetism of two-electron systems not to be negligible.

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