

# Experimental determinations of the hyperfine structure in the alkali atoms

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The measurements of the hyperfine structure of free, naturally occurring, alkali atoms are reviewed. The experimental methods are discussed, as are the relationships between hyperfine structure data and other atomic constants.

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## I. INTRODUCTION

Within the last few years, a considerable evolution has been observed in the experimental investigations of atomic hyperfine splittings (henceforth abbreviated as hfs). Several new techniques have been developed and the range of atomic states whose hfs have been investigated has expanded enormously; this is particularly true for alkali atoms: owing to their one-electron configurations, it is only natural that new techniques are first tested with them.

In addition, a considerable amount of research work has been carried out on the theoretical side of this same problem, in connection with both the calculation of hfs and with a more thorough understanding of the hyperfine interaction in its finer details.

We have therefore deemed it useful to summarize in a single article all the experimental data that are presently available (and reliable), in order to offer to the experimentalist a review of the state of the art, and to the theoretician a set of values that can conveniently be used in further calculations and theoretical consistency checks.

The most recent review paper, of which we are aware, covering the hyperfine structure investigations of all kinds of atoms, is by Fuller and Cohen (1969); although references to more recent literature can be found in the compilation by Hagan and Martin (1972). We have limited our investigation to the neutral, naturally occurring, alkali isotopes. With this restriction more recent compilations of data exist, by Rosén and Lindgren (1972) and by Happer (1975). Both compilations, however, are included in those works in order to discuss a theoretical behavior, and not to compare the results of different experiments. This is what we have attempted to do in this paper.

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After a brief theoretical introduction where we summarize the most standard formulas and we mention the problems that are open, without attempting to be complete or critical, we discuss the various experimental techniques that have been used in the investigation of the hfs of the naturally occurring alkali isotopes. After this, all recent accurate works on hfs existing to our knowledge are listed for each atomic state. Owing to the tight relationship between hfs measurements and gyromagnetic ratios measurements, a section is also devoted to gyromagnetic ratios. On the contrary, since the relationship between nuclear quadrupole moments and measured values of the hyperfine coupling constants relies on a theoretical knowledge of some finer details in the electronic wave functions, we did not attempt to evaluate critically the various nuclear quadrupole values quoted in the literature. We leave this problem to the theoretician, once a reliable set of experimental coupling constants is given (something we attempt to give at the end of this article).

Hyperfine structure anomalies have been computed as well from the experimental data. A review of such anomalies for all atoms has been written by Fuller and Cohen (1970). Our table updates this work for the naturally occurring alkali isotopes.

## II. THEORETICAL BACKGROUND

### A. hfs Hamiltonian

Several authoritative reviews on the theory of hyperfine interactions have been presented by different authors. Let us remember first the book by Kopfermann (1958) where the development of the hyperfine interaction theory for the one- and two-electron spectra is fully described. More recent treatments, mainly for the many-electron spectra, have been reported in detail in a book by Armstrong (1971). Fully relativistic calculations and comparisons between theoretical and experimental results have been thoroughly discussed in a recent review by Lindgren and Rosén (1974a). So we will limit ourselves here to the basic considerations showing how the theoretical relations are used to fit the experimental results. Moreover, apart from a few cases, hyperfine interactions in alkali atoms have been measured in states with a single electron in an unclosed shell. Thus the theoretical considerations presented here will be related to systems whose configuration is composed of several closed shells and one electron in the state  $nl$ ,  $n$  being the principal quantum number and  $l$  the orbital angular momentum quantum number. Finally, an extension to the quartet metastable autoionizing states, experimentally investigated, will be considered.

The Hamiltonian for the interaction between the nucleus and the atomic electrons can be written in the form

$$\mathcal{H}_{\text{hfs}} = \sum_k \mathbf{T}^{(k)} \cdot \mathbf{M}^{(k)}, \quad (2.1)$$

where  $\mathbf{T}^{(k)}$  and  $\mathbf{M}^{(k)}$  are spherical tensor operators of rank  $k$ , representing the electronic and nuclear part of the interaction. Terms with even  $k$  represent the electric interactions, those with odd  $k$  the magnetic inter-

actions. The lowest  $k=0$  order represents the electric interaction of the electron with the spherical part of the nuclear charge distribution. This term has the same effect on all levels of a given configuration, due to the spherical symmetry; hence it is not considered in the hyperfine-splitting Hamiltonian.

The  $k=1$  term describes the magnetic dipole coupling of the nuclear magnetic moment with the magnetic field created by the electron at the nucleus position. Then for a nuclear angular momentum  $\mathbf{I}$  we write

$$\mathbf{M}^{(1)} = \mu_I = -g_I \mu_B \mathbf{I}, \quad (2.2)$$

with  $\mu_B$  the Bohr magneton, and with the convention that the sign of the  $g$  factor is taken opposite to the sign of the associated magnetic moment.  $\mathbf{T}^{(1)}$  is the opposite of the electronic magnetic field created by a single electron at the nucleus position in the origin of the coordinate and calculated in a nonrelativistic treatment it results (Armstrong, 1971)

$$\mathbf{T}^{(1)} = 2 \frac{\mu_0}{4\pi} \mu_B \left\{ \frac{\mathbf{L}}{r^3} - \frac{1}{r^3} \left[ \mathbf{S} - 3 \frac{\mathbf{S} \cdot \mathbf{r}}{r^2} \mathbf{r} \right] + \frac{2}{3} \frac{\delta(r)}{r^2} \mathbf{S} \right\}, \quad (2.3)$$

with  $\mu_0$  the vacuum susceptibility. Here  $\mathbf{L}$  and  $\mathbf{S}$  are the operators of the orbital angular momentum and spin and  $\mathbf{r}$  the vector position of the electron. The first term in  $\mathbf{T}^{(1)}$  comes from the magnetic field produced at the nucleus position by the orbital motion. The second one is connected to the magnetic field created, in the dipolar interaction, by the intrinsic angular momentum of the electron. The last term is called the contact interaction and originates from the magnetic field created by the part of electronic magnetization present at the nucleus position. Through the  $\delta(r)$  dependence this interaction involves the electronic wavefunction at the origin of the coordinates and in a nonrelativistic treatment is different from zero only for  $s$  electrons. Let us introduce the tensor operator  $\mathbf{C}^{(k)}$  of rank  $k$  through its  $q$ th components

$$C_q^{(k)} = \left( \frac{4\pi}{2k+1} \right)^{1/2} Y_q^{(k)}, \quad (2.4)$$

with  $Y_q^{(k)}$  a normalized spherical harmonic. It is convenient to write the dipolar part in the magnetic field interaction through the rank-one irreducible tensor operator in the tensor product of  $\mathbf{S}$  and  $\mathbf{C}^{(2)}$

$$\mathcal{H}_{\text{dip}} = -2 \frac{\mu_0}{4\pi} \mu_B \frac{1}{r^3} (10)^{1/2} (\mathbf{S} \cdot \mathbf{C}^{(2)})^{(1)} \cdot \mu_I. \quad (2.5)$$

The second order term in the hyperfine interaction is the electric quadrupole part with

$$\mathbf{T}^{(2)} = -\frac{e}{4\pi\epsilon_0} \frac{1}{r^3} \mathbf{C}^{(2)} \quad (2.6a)$$

$$\mathbf{M}^{(2)} = \frac{e}{2} \frac{(6)^{1/2} Q}{I(2I-1)} (\mathbf{I} \cdot \mathbf{I})^{(2)}, \quad (2.6b)$$

where  $(\mathbf{I} \cdot \mathbf{I})^{(2)}$  represents the rank-two irreducible tensor operator formed by the nuclear angular momentum operator. The scalar quantity  $Q$  is conventionally taken as a measure of the nuclear quadrupole moment. The higher-order terms on the hyperfine interaction have not been measured in any alkali state; however, magnetic octupole and electric hexadecapole interactions

have been described by Lindgren and Rosén (1974a).

The hyperfine structure of an atom is usually defined over the  $\{J, I, F, m_F\}$  eigenstates, where  $F$  is the quantum number of the total angular momentum  $\mathbf{F} = \mathbf{I} + \mathbf{J}$ . The nuclear angular momentum  $I$  is always a good quantum number, as very large energies are involved in the transitions between nuclear states. In the first approximation  $J$  is also considered as a good quantum number; that is, matrix elements of  $\mathcal{H}_{\text{hfs}}$  over states with different  $J$  are neglected. In this approximation the hyperfine energy  $W_F$  of the magnetic dipole and electric quadrupole interactions is written

$$W_F = \frac{1}{2} h A K + h B \frac{\frac{3}{2} K(K+1) - 2I(I+1)J(J+1)}{2I(2I-1)2J(2J-1)}, \quad (2.7)$$

where  $K = F(F+1) - I(I+1) - J(J+1)$ . The electronic quadrupole interaction is present only for  $I, J \geq 1$  and in general the  $k$ th order in the hfs Hamiltonian (2.1) requires  $k \leq 2I$  and  $k \leq 2J$ .

The orbital and dipolar interactions in (2.3) contribute to the magnetic dipole constant  $A$  for an electron in a state with  $l > 0$ . This results in

$$A = -\frac{1}{h} \frac{\mu_0}{4\pi} \mu_B^2 \frac{2l(l+1)}{J(J+1)} g_I \langle r^{-3} \rangle_{nl} \quad (2.8a)$$

where  $\langle r^{-3} \rangle_{nl}$  is the average over the wavefunction of the electronic state  $nl$ . For an electron in a state  $s$  with orbital angular momentum equal to zero, only the contact interaction is different from zero

$$A = -\frac{1}{h} \frac{16\pi}{3} \frac{\mu_0}{4\pi} \mu_B^2 g_I |\Psi_s(0)|^2 \quad (2.8b)$$

with  $\Psi_s(0)$  the value of the Schrödinger wavefunction at the nucleus position.<sup>1</sup> For the electric quadrupole constant we obtain

$$B = \frac{1}{h} \frac{e^2}{4\pi\epsilon_0} \frac{2J-1}{2J+2} \langle r^{-3} \rangle_{nl} Q. \quad (2.9)$$

In a relativistic treatment the electronic operators are calculated using the wavefunction solutions of the Dirac equation. However, for a comparison with the experimental results it is more convenient to consider the effective operator formalism for the relativistic hyperfine structure calculations, as developed by Sandars and Beck (1965). The idea of this treatment is to define an effective hfs Hamiltonian for which the matrix elements between the electronic nonrelativistic  $\mathbf{LS}$  coupled states of a given configuration are equal to the matrix elements of the true hfs Hamiltonian between the relativistic states. If the effective Hamiltonian is expressed in terms of the electronic and nuclear spherical tensor operators, as in relation (2.1), the effective electronic operators of the magnetic dipole and electric quadrupole interactions are (Armstrong, 1971)

<sup>1</sup>Let us note that the minus sign in front of the expressions (2.8a) and (2.8b) for the dipolar coupling constant derives from the adopted convention for the nuclear  $g$  factor. The  $A$  constant has the same sign as the nuclear magnetic moment.

$$\mathbf{T}_{\text{eff}}^{(1)} = 2(\mu_0/4\pi)\mu_B \{ \mathbf{L} \langle 1/r^3 \rangle_{01} - (10)^{1/2} (\mathbf{S} \cdot \mathbf{C}^{(2)})^{(1)} \langle 1/r^3 \rangle_{12} + \frac{2}{3} \mathbf{S} \langle 1/r^3 \rangle_{10} \}, \quad (2.10)$$

$$\mathbf{T}_{\text{eff}}^{(2)} = -\frac{e}{4\pi\epsilon_0} \{ \mathbf{C}^{(2)} \langle 1/r^3 \rangle_{02} - (\mathbf{S} \cdot \mathbf{L})^{(2)} \langle 1/r^3 \rangle_{11} + (\mathbf{S} \cdot (\mathbf{C}^{(4)} \cdot \mathbf{L})^{(3)})^{(2)} \langle 1/r^3 \rangle_{13} \},$$

where the radial averages are radial integrals over the relativistic wavefunctions defined, for instance, by Armstrong (1971) or by Lindgren and Rosén (1974a). In the nonrelativistic limit the operators  $\mathbf{T}^{(1)}$  and  $\mathbf{T}^{(2)}$  are obtained. Thus the radial integrals  $\langle 1/r^3 \rangle_{01}$ ,  $\langle 1/r^3 \rangle_{12}$  and  $\langle 1/r^3 \rangle_{02}$  go over into  $\langle 1/r^3 \rangle_{nl}$ . The integrals  $\langle 1/r^3 \rangle_{11}$  and  $\langle 1/r^3 \rangle_{13}$ , purely relativistic in nature, vanish. The integral  $\langle 1/r^3 \rangle_{10}$  in the nonrelativistic limit is different from zero only for  $s$  electrons and becomes  $8\pi |\Psi_s(0)|^2$ . The main difference between nonrelativistic and relativistic calculations is that in the former case only one radial parameter  $\langle 1/r^3 \rangle_{nl}$  appears in the dipole and quadrupole coupling. Instead in the relativistic effective operators several different radial parameters are necessary to properly describe the experimental results. In particular three different terms are involved in the quadrupole coupling, whereas only one appears in the nonrelativistic interaction. However, relativistic effects are generally small and the appearance of two supplementary terms in the quadrupole coupling usually cannot be tested experimentally. Then in the following we will consider only the first term, also included in the nonrelativistic treatment. The radial parameters in the effective Hamiltonian are usually indicated by a letter, to distinguish their origin, with the following notation:

$$\langle 1/r^3 \rangle_o = \langle 1/r^3 \rangle_{01}; \quad \langle 1/r^3 \rangle_d = \langle 1/r^3 \rangle_{12}; \quad \langle 1/r^3 \rangle_q = \langle 1/r^3 \rangle_{02}.$$

Moreover it is convenient to define the coupling constants  $a_o$ ,  $a_d$ ,  $a_c$ , and  $b_q$  to represent the different contributions to the dipolar and quadrupolar splitting:

$$\begin{aligned} a_{o,d} &= -2 \frac{\mu_0}{4\pi} \frac{1}{h} \mu_B^2 g_I \langle 1/r^3 \rangle_{o,d}, \\ a_c &= -\frac{\mu_0}{3\pi} \frac{1}{h} \mu_B^2 g_I \langle 1/r^3 \rangle_{10}, \\ b_q &= \frac{e^2}{4\pi\epsilon_0} \frac{Q}{h} \langle 1/r^3 \rangle_q. \end{aligned} \quad (2.11)$$

The previous expressions for the hfs Hamiltonian are based on a central-field model with the closed shells exactly spherical, hence not exhibiting any interaction with the nucleus. In this description the hyperfine interaction is entirely due to the single external electron. A more precise model must include the polarization effects associated with the interaction of the valence electron with the closed-shell electrons in the core. For instance, the electrons in core states, with their spin parallel to the valence electron, experience a weaker exchange interaction than those in the core states with an antiparallel spin. This leads to a distortion of the electron orbitals, so that closed shells are no longer spherically symmetric and contribute to the hyperfine interaction. This core polarization effect, called "ex-

change polarization", influences both the magnetic dipole and the electric quadrupole coupling constants. In the direct polarization effect a quadrupole hyperfine interaction arises because an unfilled shell of electrons with  $l > 0$  is not spherical and creates a nonspherical potential in which all the other electrons move. In the language of perturbation theory the polarization effects are described by a wavefunction correction containing states in which some electron from the core is moved into all of the many energy levels outside the core. This "virtual excitation" of the core electrons comes about through the interaction with the valence electron. Then in the lowest-order perturbation the polarization contribution to the hfs is the matrix element of the hyperfine interaction between the zeroth-order central field wavefunction and those first-order, polarized core, wavefunctions. Distortion of closed  $s$  shells, or single excitation of an  $s$  electron, leads to a net spin density at the nucleus position and hence to a contact interaction in the hyperfine Hamiltonian. This particular effect will be referred to as spin polarization, and is of particular importance when the valence electron has no contact hyperfine interaction. Another deviation from the central field model is created by the correlation among electrons, involving the mutual polarization of the closed- and vacant-shell electrons. The electrons do not move independently of each other but are correlated in their motion. In the language of virtual transitions the correlation effects are described by the contemporary excitations of two electrons.

The calculations of polarization and correlation contributions to the hfs involve a knowledge of radial integrals in the Coulomb interaction between the electrons. The contributions to the hfs Hamiltonian in the lowest order of perturbation have been fully described by Armstrong (1971). For an analysis of the experimental results it is important to observe that in a nonrelativistic treatment the admixture of other configurations may be taken into account in the hfs electronic operators of Eq. (2.10) through a modification in the radial integrals (Lindgren, 1975b). Thus the nonrelativistic hfs Hamiltonian in presence of configuration interaction has the same form as for the single electron in the valence shell. The additivity of polarization and correlation effects to the relativistic hfs Hamiltonian has been investigated by Feneuille and Armstrong (1973), and new terms in the effective operators are included to correct for the nonadditivity. Moreover for comparison with the experimental results, we will limit our consideration to the  $a_o$ ,  $a_d$ ,  $a_c$ , and  $b_q$  as effective independent parameters, allowing contributions from relativistic, core polarization and correlation effects.

With the effective operators defined in Eq. (2.10) the hyperfine energy for an unfilled shell containing an  $s$  electron is given by

$$W^{\text{eff}} = \hbar a_c \mathbf{I} \cdot \mathbf{S} \quad (2.12)$$

As long as  $J$  is considered as a good quantum number, for the states with  $J = l \pm 1/2$ , the dipole and quadrupole contributions to the hyperfine energies are written

$$W^{\text{eff}} = \hbar A \mathbf{I} \cdot \mathbf{J} + \hbar B \frac{6(\mathbf{I} \cdot \mathbf{J})^2 + 3(\mathbf{I} \cdot \mathbf{J}) - 2I(I+1)J(J+1)}{2I(2I-1)2J(2J-1)}, \quad (2.13)$$

where

$$A = \left(1 \mp \frac{1}{2l+1}\right) a_o \pm \frac{1}{2l+1} a_c + 3 \left[ \frac{5(2J+1)(2l+1)l(l+1)}{J(J+1)(2l+3)(2l-1)} \right]^{1/2} \left\{ \begin{array}{ccc} \frac{1}{2} & \frac{1}{2} & 1 \\ l & l & 2 \\ J & J & 1 \end{array} \right\} a_d, \quad (2.14a)$$

$$B = \frac{2J-1}{2J+2} b_q. \quad (2.14b)$$

The explicit expression for the  $9-j$  symbol, the quantity in braces, has been given by Lindgren and Rosén (1974a). The effective parameter Hamiltonian has been extensively applied to the many-electron systems where it is possible to determine separately all the orbital, spin-dipolar, and contact contributions by measuring experimentally the hyperfine constants in several eigenstates of  $\mathbf{J}$ . For the alkali atoms two dipolar constants are measured for a term of fine structure. Then the three effective parameters in the dipolar coupling cannot be completely derived from the experimental results, unless some assumptions are used; for instance, Lunell (1973) has derived the dipolar parameters for the  $4p$  state of  ${}^7\text{Li}$  using an assumption about the scaling of these parameters in the  $p$  states. Additional information may be obtained by measuring the matrix elements of the effective hfs Hamiltonian between states with a different  $J$  value, as will be discussed in a subsequent paragraph.

Several methods for accurate many-body calculations have been developed and most of them have been applied to calculations of the hyperfine interactions (for reviews see Lindgren, 1974b and 1975a, b). The hyperfine structure of the ground and excited  $S$  states of the alkali atoms have been considered in complete calculations. As an estimate of the different contributions to the hfs splitting, let us report the results of calculations for the  $3^2S_{1/2}$  to  $10^2S_{1/2}$  states of sodium (Mahanti *et al.*, 1974). It has been found that for the sodium ground state the core polarization contribution is of the order of 20% of the contact term of the valence electron, and that this ratio remains constant as excited states are considered. For the ground state the correlation effect contribution is approximately 20% and decreases in excited states, whereas relativistic effects for the contact contribution of the valence electron are less than 1%. Both these contributions get smaller and smaller as one gets up to the excited states which are farther from the nucleus. Relativistic effects instead get larger as the hyperfine structure in heavier alkali atoms is considered. A detailed comparison between experimental results and theoretical values for hyperfine structure in the  $S$  states of alkali atoms has been carried on by Gupta *et al.* (1973) and these authors conclude that "although many creditable attempts have been made to calculate the  $S$ -state hfs intervals of alkali atoms, no really precise theory seems to exist yet." For the other states let us remember that the  $2p$  states of lithium have been considered by several authors, for instance Lyons *et al.* (1969), Nesbet (1970), Larsson (1970) and Hameed and Foley (1972); complete calculations for the  $2p$ ,  $3p$  and

4*p* states of Li and the 3*p* state of Na have been carried on by Garpman *et al.* (1975), and the hyperfine structure in the *d* states of Rb has been investigated by Lindgren (1975a).

### B. Semiempirical formulas

As complete calculations of the hyperfine coupling constants have been carried on only recently, several approaches have been combined to compare the experimental values, employing nonrelativistic relations and experimental data from fine-structure or binding energies of the states under investigation. An extensive description of these relations is reported in the book by Kopfermann (1958). Thus we limit ourselves to the main formulas, while we discuss more recent considerations on the hfs contributions. The simplest approach is to use in the nonrelativistic expressions for the dipolar and quadrupolar coupling the  $\langle r^{-3} \rangle_{nl}$  parameter obtained in the theory of hydrogenic atoms:

$$\langle r^{-3} \rangle_{nl} = \frac{Z^3}{a_0^3 n^3 (l + \frac{1}{2}) l (l + 1)}, \quad l \neq 0, \quad (2.15)$$

where  $Z$  is the atomic number and  $a_0$  the Bohr radius. The dipolar coupling constant for all the  $l=0$  and  $l>0$  quantum numbers may be written

$$A = \frac{-R\alpha^2 Z^3 g_I}{n^3 (l + \frac{1}{2}) J(J + 1)}, \quad (2.16)$$

with  $\alpha$  the fine structure constant and  $R$  the Rydberg constant expressed in frequency units.

A better agreement with the experimental results is obtained in the classical penetrating-orbit picture. Then in the previous formula  $Z^3$  has to be replaced by  $Z_i Z_0^2$ , where  $Z_0$  is net charge of the ion around which the single electron moves and  $Z_i$  an effective nuclear charge in the inner region where the orbit penetrates. The quantum number  $n^3$  is replaced by  $n^{*3}$ , with  $n^*$  the effective principal quantum number. The difference  $n - n^* = \sigma(n)$  is the quantum defect or Rydberg correction. For a series in the alkali optical spectrum the electronic binding of the states is represented by

$$E_b = hR Z_0^2 / n^{*2}. \quad (2.17)$$

Thus the dipolar coupling constant, depending on  $1/n^{*3}$ , is proportional to  $E_b^{3/2}$ , as very well verified by the experimentally measured dipole constants in the *S* states on the alkalis (Gupta *et al.*, 1973) and in the  $^2P_{1/2}$  and  $^2P_{3/2}$  states of  $^{39}\text{K}$  (Belin *et al.*, 1975b). For the *S* states the Schrödinger wavefunction at the nucleus position may be expressed through the effective nuclear charge and the effective quantum number, and the Fermi-Segré formula for the dipolar constant is obtained

$$A_s = -\frac{8}{3} R g_I \alpha^2 \frac{Z_i Z_0^2}{n^{*3}} \left(1 - \frac{d\sigma}{dn}\right). \quad (2.18)$$

The relativistic effects may be included in this expression by introducing a relativistic correction factor  $F_{r,J}(n, l, Z)$  near unity for light atoms and significantly different from unity for large  $Z$ . Other correction factors are included:  $1 - \delta$  for the change in the electronic wave function for distributions of the nuclear charge over the nuclear volume and  $1 - \epsilon$  for the change in the electron-nuclear interaction by the distribution of the

magnetic moment. Thus the dipolar constant is written

$$A_s = -\frac{8}{3} R g_I \alpha^2 \frac{Z_i Z_0^2}{n^{*3}} \left(1 - \frac{d\sigma}{dn}\right) F_{r,1/2} (1 - \delta)(1 - \epsilon). \quad (2.19)$$

For electronic states with  $l>0$  the fine-structure splitting  $\delta W$  (in frequency units) is given by

$$\delta W = \frac{1}{h} 2 \frac{\mu_0}{4\pi} \mu_B^2 \left(l + \frac{1}{2}\right) \langle r^{-3} \rangle_{nl} Z_i H_r, \quad (2.20)$$

where a relativistic correction factor  $H_r(l, Z)$  has been included. As a final result the dipolar hyperfine constant is expressed as a function of the fine-structure splitting and the correction factors

$$A(J) = \frac{-\delta W}{(l + \frac{1}{2}) Z_i H_r} g_I \frac{l(l+1)}{J(J+1)} F_{r,J} (1 - \delta)(1 - \epsilon). \quad (2.21)$$

The effective nuclear charge  $Z_i$  has been found empirically to be approximately equal to  $Z$  for *s* electrons,  $Z - 4$  for *p* electrons, and  $Z - 11$  for *d* electrons; exact  $Z_i$  values have been calculated by Sternheimer and Peierls (1971) and Rosén and Lindgren (1972), where a dependence on the  $n$  quantum number has been found. The  $F_{r,J}$  correction factors are tabulated in the book by Kopfermann (1958), but more precise calculations of these factors have been reported by Rosén and Lindgren (1972, 1973). A significant dependence on the  $n$  and  $l$  quantum numbers has been pointed out by those authors. The values of the relativistic corrections  $H_r$  have been compiled by Kopfermann (1958), while the calculations of the corrections  $\delta$  and  $\epsilon$  for the finite size of the nucleus have been fully discussed in the book by Armstrong (1971).

In the hyperfine structure of a doublet term the contact contribution of the core polarization is of equal size and opposite sign in the  $J = l + \frac{1}{2}$  and  $J = l - \frac{1}{2}$  states [see Eq. (2.14a)]. The dipolar constants are written

$$\begin{aligned} A(l + \frac{1}{2}) &= a_{l+1/2} + \bar{a}_c, \\ A(l - \frac{1}{2}) &= a_{l-1/2} - \bar{a}_c, \end{aligned} \quad (2.22)$$

where  $\bar{a}_c$  represents the contact term and  $a_{l+1/2}$  and  $a_{l-1/2}$  include the orbital and dipolar contributions. In the analysis of the experimental results it is a usual approximation to correct these last interactions only for the relativistic effects, because the core polarization is expected to give the largest contribution to the contact term through the distortion of closed *s* shells. Thus from expression (2.21) one obtains

$$\frac{a_{l-1/2}}{a_{l+1/2}} = \frac{2l+3}{2l-1} \frac{F_{r,l-1/2}(nl, Z)}{F_{r,l+1/2}(nl, Z)} \quad (2.23)$$

so that the  $\langle r^{-3} \rangle_{nl}$  parameter may be derived from the measured dipolar constants for the states of the doublet. In the measurements on the  $^2P$  terms of alkali atoms good agreement is found between the radial parameters obtained through the approximate approach and those derived from the fine-structure separation (e.g., Belin and Svanberg, 1971; Feiertag and zu Putlitz, 1973).

In the heavier alkali atoms because of the matrix elements of the spin-orbit interaction connecting different terms of the  $^2P$  series, the radial part of the electronic wavefunctions is altered. This effect changes the rela-

tive strength of the components in the higher-order doublets  ${}^2P - {}^2S$ , as first explained by Fermi (1930a). Fischer (1970) has calculated the first-order correction to the  $A$  factor by that spin-orbit perturbation. In the analysis of the dipolar hyperfine structure in the  ${}^2P$  terms of Rb (Feiertag and zu Putlitz, 1973) and in the  $6{}^2P$  term of Cs (Abele, 1975b) this spin-orbit correction to the hyperfine splitting has been considered, deriving the amount of perturbation from the fine-structure measurements.

For the quadrupolar coupling constant  $B$  an approximate expression is obtained introducing a relativistic correction factor  $R_r(l, J, Z_i)$  in the nonrelativistic relation (2.9):

$$B = \frac{e^2}{4\pi\epsilon_0} \frac{2J-1}{2J+2} \langle r^{-3} \rangle_n Q R_r. \quad (2.24)$$

This correction factor has been evaluated in the book by Kopfermann (1958) and recalculated by Rosén and Lindgren (1972, 1973). However a more substantial correction has to be applied to the  $\langle r^{-3} \rangle$  parameter for the core polarization. This correction, called the Sternheimer effect, is due to the fact that the electrons of the closed shells are deformed by the quadrupolar gradient to which they are subjected, and therefore also contribute to the field gradient at the nucleus. This effect is represented in the  $B$  quadrupole constant by multiplying the  $\langle r^{-3} \rangle$  parameter by a factor  $(1-R)$ . A positive  $R$  factor is a reduction of the total quadrupole coupling and is caused by a shield of the nuclear quadrupole by the angular redistribution of the electronic charge in the closed shells. A negative  $R$  factor is an increase of the quadrupole interaction by the antishielding effect of the radial distribution of the electronic charge (Sternheimer, 1950, 1951). In the standard procedure for evaluating the nuclear quadrupole moment from the experimental results the radial  $\langle r^{-3} \rangle$  parameter is derived from the magnetic dipole constant. In order to consider the contribution of the core polarization, the contact part is separated through the measurement of the magnetic hyperfine coupling in both the states of the doublet, as presented before. The radial parameter is derived from the orbital and dipolar contribution considering the relativistic effects and supposing the contribution of the core polarization to be negligible. With this  $\langle r^{-3} \rangle$  value and the measured  $B$  constant, an effective nuclear quadrupole moment  $Q_{\text{hfs}}$  is derived from expression (2.24). The Sternheimer correction factor is applied to obtain the true nuclear quadrupole moment  $Q$

$$Q = (1-R)^{-1} Q_{\text{hfs}}. \quad (2.25)$$

The most recent theoretical values of the  $R$  factors for the first three excited  $nP$  states of each of the five alkali atoms have been reported in Sternheimer and Peierls (1971), while for the lowest three excited  $nD$  states they have been derived by Sternheimer (1974). It has been recently observed (Lindgren, 1974b, 1975a) that the entire procedure of extracting the  $\langle r^{-3} \rangle$  value from the dipolar constant and applying the  $R$  correction factor to the quadrupolar constant, must be handled very carefully. In effect the Sternheimer correction contains only the polarization contribution to the quadrupole interaction and neglects the correlation effects. Moreover,

polarization and correlation effects may be important for the orbital and dipolar parts of the magnetic dipole coupling.

### C. Hyperfine structure in a magnetic field

In the presence of an applied static magnetic field  $\mathbf{H}$  the Hamiltonian contains the Zeeman interaction of the orbital and spin magnetic moments for the electrons and the nucleus of the atom. The Hamiltonian may be expressed through the interaction of the valence electron and the nucleus with the static magnetic field. Neglecting the diamagnetic terms dependent on the square of the static field intensity, this Zeeman Hamiltonian results:

$$\mathcal{H}_Z = -(\boldsymbol{\mu}_L + \boldsymbol{\mu}_s + \boldsymbol{\mu}_I) \cdot \mathbf{H} = (g_L L_z + g_S S_z + g_I I_z) \mu_B H, \quad (2.26)$$

where  $L_z$ ,  $S_z$ , and  $I_z$  are the projections of the angular momentum operators along the static magnetic field direction.  $g_L$ ,  $g_S$ , and  $g_I$  are the respective  $g$  factors expressed in units of the Bohr magneton  $\mu_B$ . Also in the Zeeman Hamiltonian we have followed the convention that the signs on the  $g$  factors are opposite to the signs of the associated magnetic moments. The nuclear  $g$  factor contains the atomic diamagnetism corrections. In the lowest order of approximation the  $g$  factors for the orbital and spin angular momentum of the electron are respectively one and two. The higher-order contributions, arising also from the terms in the Zeeman Hamiltonian for the total atom, are expressed through corrections of these  $g$  factors.

The most important correction, one part in a thousand, comes from the virtual radiative contributions to the  $g$  factor of the electron spin, the so-called quantum electrodynamics Schwinger correction. In the more accurate calculations (Levine, 1971) the  $g_S$  factor for the free electron is

$$g_S = 2(1+a) \quad (2.27)$$

$$a = \frac{1}{2} \frac{\alpha}{\pi} - 0.32848 \left( \frac{\alpha}{\pi} \right)^2 + (1.49 \pm 0.2) \left( \frac{\alpha}{\pi} \right)^3$$

in very good agreement with the present experimental determination as discussed by Hughes (1973). The next important corrections, that influence both the electronic  $g$  factors, are due to relativistic and diamagnetic effects, and are approximately one part in a thousand (Hughes, 1959). The relativistic effect correction depends on the electronic kinetic energy and is a direct consequence of considering the magnetic field interaction in the Dirac-Breit equation for the atom. The diamagnetic effect is caused by the modifications in the interactions between the valence electron and the core, because of the Larmor precession of the core electrons in the external magnetic field. Core polarization affects the electronic  $g$  factors only at the second-order perturbation on the atomic wavefunction, through the combined effect of configuration electrostatic interaction and mixing by the spin-orbit coupling (Phillips, 1952). The core polarization fractional changes are estimated to pass from one part in a million for Na to 70 parts in a million for Cs. Because of the nuclear motion the  $g_L$  factor deviates from unity by a quantity that depends on

the ratio between the electronic and nuclear masses (Phillips, 1949), while the  $g_s$  correction depends on  $(Z\alpha)^2$  times the ratio of the electronic to the nuclear mass (Grotch and Hegstrom, 1971). For a comparison with the experimental values, reasonable agreement was found by Perl (1953) (revised by Hughes, 1959) between the calculated relativistic and diamagnetic corrections and earlier results of atomic beam measurements in the ground state. The lack of more recent comparisons is ascribed to the imperfect knowledge about the atomic wavefunctions, as compared to the very accurate experimental values.

The eigenvalues of the hyperfine structure in an external static magnetic field have been discussed in several standard books (Kopfermann, 1958; Ramsey, 1956) and will be presented here only very briefly. For a Zeeman interaction that is small as compared to the fine structure the eigenstates have a well defined angular momentum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  and the Zeeman interaction is written

$$\mathcal{H}_Z = (g_J J_z + g_I I_z) \mu_B H, \quad (2.28)$$

where the  $g_J$  factor is expressed as a function of  $J, L, S$ , and  $g_S$  through the well-known Landé formula. Then the expression (2.13) for the hyperfine interaction in a state with defined  $J$  is used and the eigenvalues of all the Zeeman sublevels are obtained from the diagonalization of the matrix of  $H_Z + H_{hfs}$ . For the case of  $J = \frac{1}{2}$  the eigenenergies are expressed by means of the Breit-Rabi formula and are represented in Fig. 1 for the ground state of Na ( $I = \frac{3}{2}$ ). Each level is labeled by the total angular momentum  $\mathbf{F} = \mathbf{J} + \mathbf{I}$  corresponding to the zero-field hyperfine state from which the level is derived, while the longitudinal magnetic quantum number  $m_F$  is a good quantum number for any value of the static field. The eigenvalues are represented as functions of  $x = (g_J - g_I) \mu_B H / \delta W_0$ , a dimensionless parameter measuring the field strength relative to the hyperfine splitting at zero static field  $\delta W_0 = A/I(2I + 1)$ . For higher values of  $J$  computer solutions are used to derive the

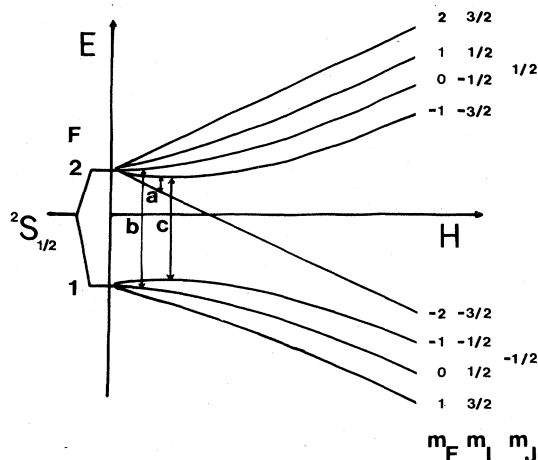


FIG. 1. Energy level diagram in a  $^2S_{1/2}$  state of an atom with nuclear spin 3/2, in the presence of a magnetic field. Reference to the transitions marked a, b, c is made in the text (Sec. III.E.1).

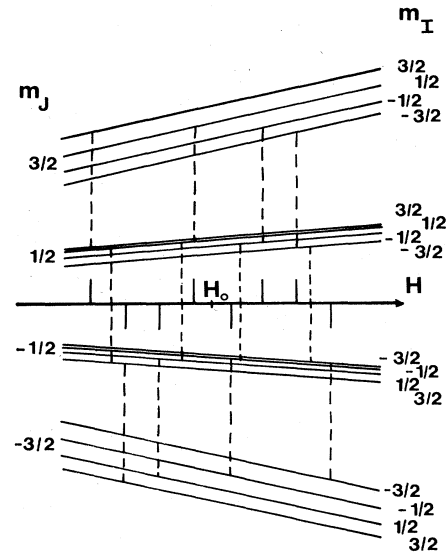


FIG. 2. Energy level diagram in a state with  $J = 3/2$  for an atom with nuclear spin 3/2, in the presence of a strong magnetic field. The resonance fields for the electronic magnetic resonance transitions and the overall center of gravity  $H_0$  are marked.

eigenvalues and to predict the transition frequencies. In general at weak fields, when the Zeeman splitting is small as compared to the hyperfine splitting, each hyperfine state is composed of a set of equally spaced Zeeman levels, with energy separation  $g_F \mu_B H$ , where  $g_F$  is expressed by a Landé formula as a function of  $g_J$  and  $g_I$ . At strong fields, in the Back-Goudsmit region where the Zeeman interaction is larger than the hfs interaction,  $\mathbf{I}$  and  $\mathbf{J}$  are decoupled and  $F$  is no longer a good quantum number. Thus the eigenvalues of the states  $3^2P_{3/2}$  of Na ( $I = \frac{3}{2}$ ) given in Fig. 2 as functions of the static field  $H$  are labeled by the  $m_J$  and  $m_I$  longitudinal quantum numbers. Two groups of transitions lying in different frequency regions can be observed between these levels: the nuclear transitions  $\Delta m_I = \pm 1$  for a fixed longitudinal electronic angular momentum and the electronic  $\Delta m_I = 0, \Delta m_J = \pm 1$  transitions (shown in Fig. 2). The former transitions have been observed in atomic beam magnetic resonance experiments in order to determine the nuclear  $g_I$  factor with high accuracy (e.g., Beckmann *et al.*, 1974); from the latter electronic intense transitions the electronic  $g$  factors and the hyperfine constants can be derived. For  $J = \frac{1}{2}$  where quadrupole hfs interaction is absent,  $2I + 1$  electronic transitions ( $m_I = -I, \dots, +I$ ) with equal width and amplitude are observed. As a function of the static magnetic field they are symmetrically spread around a center of gravity depending upon the  $g_J$  value, with spacing depending upon  $A$ . For an electronic angular momentum larger than  $\frac{1}{2}$  the electric quadrupolar interaction is included in the hyperfine structure. Still the overall center of gravity depends on the electronic  $g$  factor only. The electronic transitions between the levels with the same  $m_I$  have a frequency separation depending upon  $B$  only and their center of gravity has a distance  $\hbar A / \mu_B g_J$  from the center of gravity of another group of transitions. If the dipolar constant  $A$  is larger than the quad-



rupolar constant  $B$  (as it occurs in most experiments, e.g., in Fig. 2) it may be easily derived from the spacing between different groups.

If the magnetic field is strong enough to produce an incipient decoupling of  $\mathbf{L}$  and  $\mathbf{S}$  a slight admixture with nearby states of the fine structure has to be taken into account. The effect on the energy eigenvalues is to add a term depending on the inverse of the fine-structure splitting. Measurements of hyperfine structure in this intermediate coupling region have been carried on by Dodd and Kinnear (1960) and by Ackermann (1966) on the  $3^2P_{3/2}$  state of sodium.

#### D. Off-diagonal hyperfine constants

The dipolar and quadrupolar hfs Hamiltonians, involving the interaction of spin and orbital angular momenta with the nuclear moments, have matrix elements, diagonal over  $F$  and  $m_F$ , but connecting states with different  $J$  values (Childs, 1973). These matrix elements, the so-called off-diagonal hyperfine constants, produce a mixing of the eigenstates and a shift of the energies. Whenever the levels with a different  $J$  value are far apart in energy, the influence of the off-diagonal interaction on the hyperfine splitting can be described through a perturbation treatment. For the alkali atoms the off-diagonal constant perturbation is due to the matrix elements of the hfs Hamiltonian between the states inside a fine-structure doublet and mainly in the Back-Goudsmit and Paschen-Back regions, where the Zeeman interaction mixes the states of the hyperfine and fine structure, respectively. The energies of the doublet states, in presence of an off-diagonal hyperfine interaction and calculated in a perturbative scheme, keeping terms of order  $1/\delta W$  ( $\delta W$  the fine-structure splitting) have been reported by Clendenin (1954) and Harvey (1965). A numerical calculation for the energies in the  $2^2P$  term of Li from zero-field to the strong-field region has been discussed by Lyons and Das (1970). The dipolar coupling part of the off-diagonal hyperfine interaction is usually expressed in terms of the following constant:

$$A_{J,J-1} = \frac{1}{I(J^2 - M_J^2)^{1/2}} \langle J, I, M_J, I | \mathbf{T}^{(1)} \cdot \mathbf{M}^{(1)} | J-1, I, M_J, I \rangle \quad (2.29)$$

defined over the  $\{JIM_JM_I\}$  representation as the measurements of the off-diagonal constants are performed at magnetic fields strong enough to decouple  $\mathbf{J}$  and  $\mathbf{I}$ . As a function of the  $a_i$  parameters in the hfs effective Hamiltonian, the off-diagonal hyperfine constant between the states of a doublet results

$$A_{l+1/2, l-1/2} = \frac{1}{(2l+1)} (a_o - \frac{1}{2}a_d - a_c). \quad (2.30)$$

This off-diagonal constant has been derived from the experimental results in the recent very accurate magnetic resonance experiments in the  $2^2P$  doublet of  $^6\text{Li}$  and  $^7\text{Li}$  (Orth *et al.*, 1974, 1975). Combining the measurement of diagonal  $A_{1/2}$ ,  $A_{3/2}$  and off-diagonal  $A_{3/2, 1/2}$  constants all three effective parameters  $a_o$ ,  $a_d$ ,  $a_c$ , have been determined.

Information on the off-diagonal elements may be obtained also by investigating the structure of the fine and

hyperfine states at static magnetic fields high enough to create crossing and anticrossing phenomena between different fine levels. In the crossing, the states with different quantum number  $m_F$  have the same energy. An anticrossing occurs because the states with the same  $m_F$  value cannot cross (Von Neumann and Wigner, 1929). Owing to the small interaction between them, determined mainly by the hyperfine interaction, the two levels repel each other. The quantities of interest at the anticrossing are the field intervals between the anticrossings as well as the interaction matrix element which causes the anticrossing. For the state  $2P$  of Li these quantities have been related to the  $a_i$  values by Lyons and Das (1970), so that combining the experimental measurement of the anticrossing with the magnetic resonance experiments the off-diagonal constant has been measured with better precision (Orth *et al.*, 1974, 1975). Expressions for the magnetic fields at the centers of the anticrossing points in the  $D$  states of Rb have been reported by Liao *et al.* (1974).

#### E. Quartet autoionizing states

Among the states involving filled shell excitations in the alkali atoms, only the metastable autoionizing quartet terms have been investigated. The states formed by the excitation of a single electron from the outermost filled shell have been described by Feldman and Novick (1967) and have energies greater than the first ionization energy of the atom. They are metastable for radiative decay and autoionization, with a lifetime of the order of  $10^{-5}$  sec. For instance, in lithium the states  $1s2s2p^4P_J$  with  $J = \frac{5}{2}, \frac{3}{2}$ , and  $\frac{1}{2}$  have been investigated by Feldman *et al.* (1968); in potassium the states  $3p^54s3d^4F_{9/2}$  and  $3p^54s4p^4D_{7/2}$  have been investigated by Sprott and Novick (1968). Gaupp *et al.* (1976) have instead examined the hyperfine structure in the term  $1s2p^2^4P$  of Li where two electrons are excited. In a configuration  $nl$  with a single unfilled shell containing  $N$  equivalent electrons, the magnetic dipole hfs Hamiltonian is written

$$\mathcal{H}_{\text{hfs}}^{(N)} = \sum_{i=1}^N [a_o \mathbf{l}_i - (10)^{1/2} a_d (\mathbf{s} \cdot \mathbf{C}^{(2)})_i^{(1)} + a_c \mathbf{s}_i] \cdot \mathbf{I}, \quad (2.31)$$

with  $\mathbf{l}_i$  and  $\mathbf{s}_i$  the orbital and spin angular momentum operator for each electron. The  $a$ 's are considered as independent parameters describing the relativistic and many-body effect contributions for all the equivalent electrons. If there are several unfilled shells, a set of "a" parameters is introduced by a Hamiltonian  $\mathcal{H}_{\text{hfs}}^{(N)}$  for each shell.

From the matrix elements of the hfs Hamiltonian over the eigenstates, the magnetic dipole constants are derived for the comparison with the experimental values (Childs, 1973). However for the alkali atom experiments, there are not enough measured dipolar hyperfine constants to determine all the parameters and it is usual to restrict the analysis to the "a" parameters that give a larger contribution to the hyperfine splitting. This means the core polarization contributions are neglected. Then, for instance, in the study of the  $3p^5 4s 3d^4F_{9/2}$  state of K (Sprott and Novick, 1968) a single constant is used to describe the contribution of each shell to the hfs: a contact part for the 4s electron,



and orbital and dipolar parts for each of the  $3p$  and  $3d$  shells. In that paper a few relations are reported to express the dipole coupling constant  $A$  in terms of the contribution from the individual shells.

A similar treatment may be applied to determine the quadrupolar coupling constant  $B$  as a function of the contributions from the different shells.

### F. Hyperfine anomalies

As long as the nucleus is represented by a point charge, the electronic wavefunction depends only on the nuclear charge and is equal for different isotopes of the same element. Then from expression (2.21) we find that the ratio between the dipole interaction constants of two isotopes is equal to the ratio of their gyromagnetic nuclear factor. This relation, known as the Fermi rule (Fermi, 1930b), has been applied in the first hyperfine measurements to obtain a good estimate of unknown hyperfine constants or to check the consistency of several measurements. However owing to the finite size of the nucleus this relation is not exactly satisfied by the experimental results. As a measure of the finite structure influence on the dipole constants of isotopes 1 and 2, hyperfine anomaly  $\Delta_{12}$  has been introduced through the following definition:

$$\Delta_{12} = (A_1/A_2)(g_2/g_1) - 1, \quad (2.32)$$

where  $A_1, g_1$  are the dipole interaction constant and the nuclear  $g$  factor of isotope 1, and so on. The first correction to the dipole interaction constants results when the reduced mass is introduced in the electronic wavefunction and in the electronic orbital  $g$  factor. However, all these reduced mass corrections are important only for the higher elements. It was first pointed out by Rosenthal and Breit (1932) that the potential felt by the electron deviates from the Coulomb potential inside the nuclear volume, which is different for the isotopes of the same elements. The effect contributes only of order  $10^{-4}$  to the hyperfine anomaly of isotopes in most nuclei, and is consequently small compared to the corrections resulting from the distribution of the magnetization inside the finite volume of the nucleus (Bohr and Weisskopf, 1950).

Obviously the structure effects of the nuclear magnetization are felt by an electron only when there is a large probability that the electron will be found near the nucleus, i.e., only in  $s$  orbitals. Then hyperfine anomaly effects are important for  $S_{1/2}$  states and, by relativity effects may become appreciable for  $P_{1/2}$  states. For these states the small components of the relativistic wavefunction have the character of  $s$ -wavefunctions and determine the electronic density at the center. The value of the hyperfine anomaly will therefore be of the order of  $(Z\alpha)^2$  of that for a  $S_{1/2}$  state. Through the core polarization  $s$  electron density can be produced in any state, and a hyperfine anomaly can be expected in the contact contribution to the dipolar hyperfine constant. A review of the theoretical status of hyperfine anomalies has been published by Foley (1969).

### III. EXPERIMENTAL TECHNIQUES

In this section we shall summarize briefly the methods that have been used to investigate the hyperfine struc-

ture of alkali atoms. Some of them are rather "classical" and well known, others have been developed in the last few years and will require a more complete description. Rather than concentrating on the various experimental arrangements (something that would require an excessive amount of space) we shall devote some attention to the most important aspects of each method and on the main causes of inaccuracy. This will be necessary in order to compare the results obtained with different techniques.

#### A. Optical spectroscopy

A transition between two levels, each of them a hyperfine multiplet, consists of several lines whose spacing and intensities depend upon the hyperfine splittings in both states and upon the  $I, J, F$  values. It is therefore possible, with the customary techniques of optical spectroscopy, to get information on the hfs. Working in absorption at low densities, the intensities of the individual lines of the array allow us to assign to each of them the proper values of  $F$  in the lower and upper level (by means of the White-Eliason tables), thus offering a very straightforward data analysis; with this method one obtains a complete information on the hfs, including the sign of the coupling constants, something that is not determined with most other methods.

The strongest limitation of this method is its imprecision: the width of the optical lines is of the same order of magnitude as, or larger than, the hfs, so that in most cases the optical methods have been completely superseded by other methods. However, with the development of techniques of high resolution spectroscopy, and mainly of atomic beam sources, in some cases there are recent optical measurements that are of comparable (or even better) accuracy than those obtained with other more sophisticated methods. This is obviously more likely if the hfs is fairly large. Many books describe the optical methods; the most recent of them is probably the one by Thorne (1974). A very good example of these techniques can be found in the work by Beacham and Andrews (1971). With the recent progress in narrow-band tunable dye lasers, the classical methods of optical spectroscopy in absorption or fluorescence can be extended to high resolution spectroscopy, limited only by the natural width. Several reviews of such techniques exist, and we may quote those by Stroke (1972), Demtröder (1973), Lange *et al.* (1974), Jacquinet (1975), and Walther (1976). To achieve such a high resolution, the Doppler width must be sufficiently reduced (we do not consider here Doppler-free two-photon spectroscopy which will be discussed in Sec. III.I). This is usually obtained with the use of very well collimated atomic beams. A series of experiments has been carried out on Na in order to resolve the hfs of the  $D_1$  (Hartig and Walther, 1973) and  $D_2$  (Hartig and Walther, 1973; Schuda *et al.*, 1973; Lange *et al.*, 1973) lines. In the  $D_1$  experiment the residual Doppler width and the laser spectral width are both about 2 MHz, whereas the natural width is about 10 MHz. In Fig. 3 the hyperfine structure of the  $D_2$  line of  $^{23}\text{Na}$  is shown completely resolved. The results are consistent with those (more accurate) obtained with double resonance or level-crossing in-

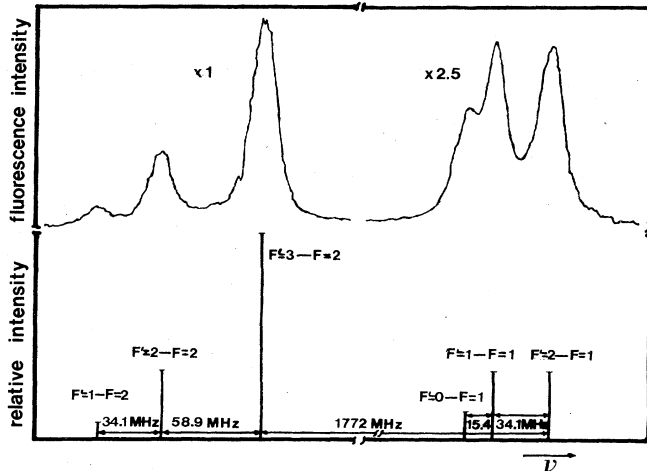


FIG. 3. Hyperfine structure of the  $D_2$  line of  $^{23}\text{Na}$ , investigated by means of a tunable laser in an atomic beam.  $F'$  and  $F$  denote the hyperfine levels of the  $3^2P_{3/2}$  and  $3^2S_{1/2}$  states, respectively. The frequency scale is interrupted (from Walther, 1973).

vestigations. We can nevertheless recall the fact that such techniques have proved to be very useful when studying isotopic shifts, or elements that cannot be studied as readily as alkali atoms: for instance, Broadhurst *et al.* (1974) obtained results for Yb that improve on previous determinations by an order of magnitude.

One of the most important problems connected with this kind of experiment is the calibration of the laser wavelength within the tuning range. This can be achieved by means of interferometric techniques (e.g., a confocal Fabry-Perot interferometer; Biraben *et al.*, 1974b). In order to have an accuracy comparable with the linewidth however, very long interferometric paths would be required, thus limiting the accuracy by thermal fluctuations. An elegant solution has been described by Walther (1974): one makes use of two lasers, each of them locked to the two different hyperfine components connecting the two levels whose spacing one wants to measure. The energy difference can then be measured by observing the beats between the two lasers. Clearly this technique can be used only for well resolved resonances. In another version, one laser is locked to one transition, the second one to the first, through beating signals. By changing the beating frequency one obtains a wavelength sweep of the second laser. A two-channel Michelson interferometer with a fixed path difference has been introduced by Juncar and Pinard (1975) to realize high-precision measurements of the wavenumber of the laser radiation and to stabilize or pilot the laser frequency.

When one wishes to study states that are not connected to the ground state with an electric dipole transition (i.e., all non- $P$  states) one can reach them by stepwise excitation. First the atom absorbs a resonance photon reaching a  $P$  state, then another photon reaching an  $S$  or  $D$  state. This technique was used by Kastler (1936), for example, in the study of mercury atoms. More recently this excitation technique has been widely used, not in optical investigations, but rather in double resonance or level-crossing experiments, and will be more

fully described later. A purely optical experiment has been carried out by Duong *et al.* (1974a) exciting an atomic beam of Na by means of two tunable lasers first to the  $3^2P_{1/2}$  and successively to the  $5^2S_{1/2}$  state; by observing the fluorescence from the  $5^2S_{1/2}$  state as a function of the tuning of the laser, they were able to measure the hfs of this state.

## B. Optical pumping

The main disadvantage of the optical spectroscopic technique is that it is necessary to evaluate a small quantity (a hfs) as a difference of two large quantities (the optical frequencies). Several techniques have been developed to investigate the hfs with direct transitions between the hyperfine levels, i.e., magnetic-dipole radiofrequency transitions. Since no such transition can be detected, unless in the sample of atoms under investigation the two hyperfine levels involved in the transition have appreciably different occupation numbers, and since this does not occur under thermodynamic equilibrium conditions (the hfs is always  $\ll kT$ ), several methods have been devised to alter these occupation numbers. Among these methods, one of the most important and simple is the optical pumping. It was first proposed by Kastler in 1950 and has since then been developed by many authors and has many applications, both scientific and technological. There are many review papers and books on this subject, the most recent of which have been written by Happer (1972) and by Balling (1975). Here we shall only describe the optical pumping process in the particular case of an hfs investigation.

In Fig. 4 an example of a hyperfine multiplet is shown. If the atoms are submitted to resonance radiation whose intensity is frequency independent over the spectral region of absorption ("white" radiation) the ratio of the probability of absorption to that of spontaneous emission is exactly the same for all hyperfine components of the multiplet, and thus the ground-state sublevels (initially equally populated) continue to be equally populated. But if the incoming radiation is not white, and its intensity on the hyperfine components connecting one hyperfine state  $|a\rangle$  of the ground state to the upper state is lower than the intensity on the other components connecting the other state  $|b\rangle$ , the state  $|b\rangle$  will be depleted at a larger rate than it is refilled, whereas the opposite occurs to the state  $|a\rangle$ . One can thus alter the Boltzmann distribution of the atoms in the ground state. If one destroys this population difference with a radiofrequency transition between the two hyperfine sublevels, the occupation number of the less absorbing level  $|a\rangle$  decreases, whereas that of the more absorbing level  $|b\rangle$  increases by the same amount; thus the transmitted light decreases. A schematic experimental arrangement is shown in Fig. 5. The lamp creates the difference between the occupation numbers of the hyperfine sublevels. The photomultiplier tube detects a signal when the frequency of the applied radio frequency field is in resonance with the energy difference between the two hyperfine sublevels, and a standard servo system can lock the radio frequency to the atomic transition.

In order to have a light source having different intensities on the hyperfine components, one can use a

filter (hyperfine filters have been developed for Na by Moretti and Strumia, 1971; for Rb by Bender *et al.*, 1958; and for Cs by Ernst *et al.*, 1967; Bernabeu *et al.*, 1969; and Beverini and Strumia, 1970) or a very narrow tunable source (laser), but this is not strictly necessary since ordinary spectral lamps always have a nonuniform spectral distribution over a hyperfine multiplet. Even though it is not essential, some kind of hyperfine filtering is useful, however, since it increases the signal-to-noise ratio. In addition, if—with suitable filtering—it is possible to populate sufficiently the upper hyperfine sublevel, maser action can start. Such a device has been developed by Davidovits and Novick (1966) in  $^{87}\text{Rb}$  and by Vanier *et al.* (1970) in  $^{85}\text{Rb}$ . The magnetic resonance between the hyperfine levels consists of a set of Zeeman components, each of them being displaced by the static magnetic field. Since it is impossible to measure the static field intensity with an accuracy comparable to the hfs measurements, it is convenient to use the  $|F=I+\frac{1}{2}, M_F=0\rangle \leftrightarrow |F=I-\frac{1}{2}, M_F=0\rangle$  transition, since in this case the linear term of the field dependence of the two states is zero and there is only a small quadratic term. The magnitude of the static field will be chosen in such a way as to separate the  $0 \leftrightarrow 0$  transition from all other transitions, to avoid overlapping. In these circumstances the field is still rather low, and the error introduced by the uncertainty in the field calibration is negligible.

The causes of broadening of the magnetic resonance in an optical pumping experiment can be summarized as follows:

(a) *"Natural" width.* The width connected with the spontaneous transitions between the two hyperfine sublevels is obviously negligible. However, since relaxation occurs, some broadening is produced which is proportional to the relaxation rate. That is one reason (besides having a good signal-to-noise ratio) for attempting to minimize the relaxation rate. Normally this can be achieved either by coating the cell walls with a suitable substance (a technique first introduced by Robinson *et al.*, 1958) or by introducing a buffer gas to slow down the rate of collisions of pumped atoms with the walls. This method, introduced by Brossel *et al.* (1955) is very effective in preventing relaxation if the collisions with the buffer gas do not appreciably induce hyperfine transitions. Relaxation rates of the order of a few  $\text{s}^{-1}$  can easily be achieved.

(b) *Light broadening.* The pumping light and the rf field cause an atom to stay for a limited amount of time in a defined state. The average rate of absorption of the incoming photons thus affects the width of the resonance. The investigation of this problem is strictly related to the light shift that will be mentioned below.

(c) *Doppler width.* Dicke (1953) has shown that the collisions of an emitting atom, distributing among two or more partners the recoil momentum of the photon, quite effectively reduce the Doppler effect. The presence of a buffer gas at a suitable pressure, in addition to increasing the relaxation rate, reduces the Doppler width as well by a factor of as much as 300 (Bender *et al.*, 1958).

(d) *Instrumental broadening.* Some broadening can also be ascribed to instrumental factors, like inhomogeneities of the applied static field, of the rf field, and so on. Some investigation of this sort of problem has been carried out by Arditì (1958c). The main sources of noise are the instability of the pumping lamp and the photomultiplier noise. Other sources, like fluctuations of the applied fields, are usually negligible.

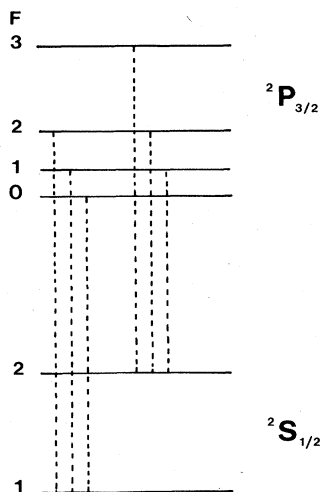


FIG. 4. Hyperfine multiplet corresponding to a  $D_2$  transition.

The magnetic resonance lines can be shifted by the static field (something that has already been discussed), by the collisions with buffer gas molecules, and by the pumping light itself:

(a) The hyperfine pressure shift has been investigated by many authors (Arditi and Carver, 1958a, b, 1961; Arditì, 1958c; Beaty *et al.*, 1958; Bender *et al.*, 1958; Bloom and Carr, 1960; Ramsey and Anderson, 1965; Bernheim and Kohuth, 1969; Wright *et al.*, 1969; Beer, 1970; Morgan, 1971; Aleksandrov *et al.*, 1973; Dorenburg *et al.*, 1974; Bava *et al.*, 1975; Batygin, 1975; Beer and Bernheim, 1976; and Strumia *et al.*, 1976). The whole problem has been discussed in detail by Balling (1975). The shift is proportional to the buffer gas density, and depends upon the cell temperature. It has been found that, as in the case of optical transitions, light buffer atoms give positive shifts (i.e., towards higher frequencies) whereas the opposite is true for heavy buffer atoms. An accurate measurement of the shift coefficient (shift per unit density) is difficult because one cannot measure accurately the buffer gas pressure. Nevertheless, it is possible to carry out several magnetic resonance measurements at different

geneties of the applied static field, of the rf field, and so on. Some investigation of this sort of problem has been carried out by Arditì (1958c). The main sources of noise are the instability of the pumping lamp and the photomultiplier noise. Other sources, like fluctuations of the applied fields, are usually negligible.

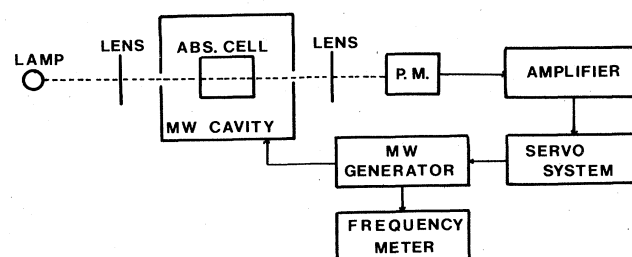


FIG. 5. A typical and simplified experimental apparatus used to investigate hyperfine structures with optical pumping techniques.

buffer gas pressures and to extrapolate to zero pressure. Obviously this shift does not occur if one does not use a buffer gas. This can happen if the sample of atoms is an atomic beam [as in the work of Arditi and Cerez (1972a, b)]. In a cell the Dicke effect is so important that the use of a buffer gas can be avoided only if the normal Doppler width is smaller than the other sources of broadening [as in the work of White *et al.* (1968)]. However this is not the case in the hfs studies of the ground state of the alkali atoms.

(b) The influence of the pumping light on the optical pumping cycle has been investigated theoretically by Barrat and Cohen-Tannoudji (1961) and Cohen-Tannoudji (1962) in the presence of an rf field causing magnetic transitions in the ground state. They found theoretical expressions for light shift, due to both real and virtual transitions, that have been later checked in several experiments. The light shift was first observed by Cohen-Tannoudji (1961) and, in the hfs of alkali atoms, by Arditi and Carver (1961). The work by Barrat and Cohen-Tannoudji also includes investigation of the effect of the pumping light on the width of the magnetic resonance. The light shifts in the particular case of the hfs of the alkali atoms have been investigated theoretically by Happer and Mathur (1967) and experimentally by Mathur *et al.* (1968). A review of such shifts can be found in the works of Happer (1970, 1972); further investigations are those by Busca *et al.* (1973a, b) concerning the  $^{87}\text{Rb}$  maser and Arditi and Picqué (1975b) concerning the 0-0 hyperfine transition in  $^{133}\text{Cs}$ . A technique using pulsed illumination in order to reduce the light shifts has been introduced by Arditi and Carver (1964) and has recently been discussed theoretically by Yakobson (1973).

(c) Other types of shifts, like wall shift and spin-exchange shift, that have been found to be important in the hydrogen maser, do not play a significant role in the alkali atoms. The effect of wall collisions on alkali atoms was investigated by Goldenberg *et al.* (1961).

The optical pumping technique has been extended by Pavlovic and Laloë (1970) to the investigation of the excited states. However this has never been done with the alkali atoms. The peculiar problems arising in the optical pumping cycle when the pumping source is a laser have been reviewed by Cohen-Tannoudji (1975).

### C. Cascade decoupling

In recent years a new technique (Chang *et al.*, 1971) has been developed affording the possibility of measuring the hfs in states that are not directly accessible from the ground state, namely *S* or *D* states that are reached by spontaneous decay from an upper *P* state. A detailed description of the method has been published by Gupta *et al.* (1972b). We shall summarize here its essential features. Resonance light incoming on atoms in their ground state  $|g\rangle$  (see Fig. 6) takes them to the excited state  $|e\rangle$  (a high-lying state). State  $|b\rangle$  (an *S* or *D* state) under investigation is reached by spontaneous decay from  $|e\rangle$ . Using polarized exciting light and observing the fluorescent light in the decay from  $|b\rangle$  to  $|f\rangle$  it is possible to investigate the hfs of  $|b\rangle$ .

If the exciting light has a polarization  $\hat{e}$ , during the

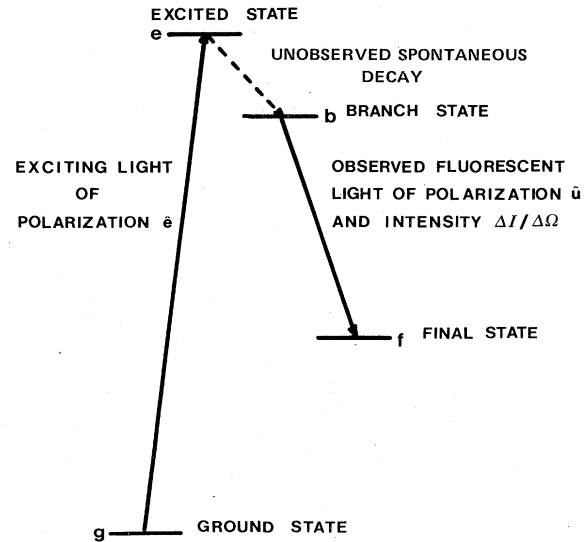


FIG. 6. The atomic states involved in a cascade fluorescence experiment (from Gupta *et al.*, 1972b).

process  $|g\rangle \rightarrow |e\rangle \rightarrow |b\rangle$  a part of the polarization of the incoming photons is transferred to the state  $|b\rangle$ . As a consequence, the light emitted in the decay  $|b\rangle \rightarrow |f\rangle$  is partly polarized as well. If the fluorescent light is observed with a suitable analyzer, as a function of the intensity of an applied static magnetic field  $H$ , one observes that the amount of polarized fluorescent radiation increases with  $H$ . This effect is not new: in the thirties Ellett and Heydenburg (1934) and Larrick (1934) applied it in the study of resonance radiation from Cs and Na.

The polarization of the fluorescent light depends upon  $\langle J_z \rangle$  in  $|b\rangle$ . In this state the coupling between  $\mathbf{J}$ ,  $\mathbf{I}$ , and  $\mathbf{H}$  can be described by a Hamiltonian that is the sum of Eq. (2.13) and Eq. (2.28). Owing to the hyperfine interaction, part of the electronic orientation  $\langle J_z \rangle$  is transferred to the nucleus,  $\langle I_z \rangle$ , and this transfer is more intense if the hyperfine coupling is stronger. With increasing  $\mathbf{H}$ ,  $\mathbf{I}$  and  $\mathbf{J}$  decouple progressively, thus there is less transfer of orientation, and the fluorescent light gets more polarized. All this qualitative reasoning can be put in quantitative terms, and one can compute the dependence of the light polarization upon the magnetic field intensity  $H$ , using the hyperfine coupling constants as parameters; thus fitting the experimental results to this dependence one obtains the best values of the coupling constants. The complete theory has been developed by Gupta *et al.* (1972b). In particular one can show that the intensity  $\Delta I$  of the fluorescent light with polarization  $\hat{u}$  emitted in a small solid angle  $\Delta\Omega$  is given by (Tai *et al.*, 1975):

$$\frac{\Delta I}{\Delta\Omega} = \sum_{\substack{m, n \\ j, k \\ \mu, \nu}} C_{mn, \mu} \langle j | \mathbf{p} | m \rangle \langle n | \mathbf{p} | k \rangle \langle k | \hat{u} \cdot \mathbf{p} | \nu \rangle \\ \times \langle \nu | \hat{u}^* \cdot \mathbf{p} | j \rangle \langle m | \hat{e} \cdot \mathbf{p} | \mu \rangle \langle \mu | \hat{e}^* \cdot \mathbf{p} | n \rangle \\ \times (\Gamma_e + i\omega_{mn})^{-1} (\Gamma_b + i\omega_{jk})^{-1}, \quad (3.1)$$

where the subscripts  $m$  and  $n$  refer to substates of  $|e\rangle$ ,

$j$  and  $k$  of  $|b\rangle$ ,  $\mu$  of  $|g\rangle$ , and  $\nu$  of  $|f\rangle$ ;  $\mathbf{p}$  is the atomic dipole moment operator,  $\Gamma_e$  and  $\Gamma_b$  are the widths of the states  $|e\rangle$  and  $|b\rangle$ , and  $\hbar\omega$  is the energy difference between two specified substates. The factor  $C_{mn,\mu}$  is independent of  $m$ ,  $n$ , and  $\mu$  for "white" excitation (i.e., with spectral width much larger than the hyperfine multiplet in absorption), and can then be easily calculated. Expression for  $C$  can also be obtained in the case of nonwhite excitation (Tai *et al.*, 1975).

Since in many cases the lifetimes of  $S$  and  $D$  states have not been measured directly, it is customary to use computed values (Bates and Damgaard, 1949; Heavens, 1961) that have been found to be in good agreement with experimental values when the latter are available.

The accuracy of this method is not very high (5 to 10%) and thus it is not sufficient to determine the  $B$  value of  $D$  states; in the fitting procedure  $B$  is thus taken to be zero.

The method, however, is sensitive to the sign of  $A$ , since the fitting curves have different shapes for different signs. The curves are sensitive to both the hfs of the  $|b\rangle$  and  $|e\rangle$  states; since however the two hfs are appreciably different, they affect the shape of the experimental curve in different regions and thus the two effects can be distinguished easily in the data reduction process (Gupta *et al.*, 1973).

This technique has been applied to the investigation of the hfs of the second and third excited  $S$  states of  $^{39}\text{K}$ ,  $^{41}\text{K}$ ,  $^{85}\text{Rb}$ ,  $^{87}\text{Rb}$ ,  $^{133}\text{Cs}$  (Gupta *et al.*, 1972b) and of a few  $D$  states in  $^{85}\text{Rb}$ ,  $^{87}\text{Rb}$ , and  $\text{Cs}$  (Chang *et al.*, 1972; Tai *et al.*, 1975). In order to show an example of application of this method, in Fig. 7 we reproduce the energy levels diagram and a schematic drawing of the apparatus used in the study of the  $7S_{1/2}$  state of  $^{87}\text{Rb}$ . The third (ultraviolet) resonance line of a Rb lamp is used to excite the  $7P$  term. Part of the atoms (about 25%) decay to the  $7S_{1/2}$  state with a lifetime of about 100 ns. The fluorescent light emitted at 7408 Å in the transition from the  $7S_{1/2}$  state to the  $5P$  term is observed.

It is necessary to resolve the fine structure of this line since the intensity of the polarized fluorescent light to the  $P_{3/2}$  state is proportional to (Gupta *et al.*, 1972b)

$$I_{3/2} \propto \left[ \frac{1}{2} + \langle J_z \rangle \right] \Delta\Omega \quad (3.2a)$$

and to the  $P_{1/2}$  it is

$$I_{1/2} \propto \left[ \frac{1}{2} - \langle J_z \rangle \right] \Delta\Omega. \quad (3.2b)$$

The sum of the two lines is therefore independent of  $\langle J_z \rangle$ . This fact can be explained more intuitively as follows: if the fine structure is unresolved, the spin-orbit coupling can be considered as weak and  $S_z$  and  $L_z$  are separately good quantum numbers; then  $\Delta\langle S_z \rangle$  must be zero in the transition, and therefore the whole orientation of  $|b\rangle$  (an  $S$  state!) is transferred to  $|f\rangle$ , leaving no trace in the fluorescent light. It is then clear that the method is not very convenient in the lighter alkalis where the LS coupling is weaker.

In excitation, it is not necessary to resolve the fine structure. At any rate the cascade process through the  $7P_{3/2}$  state is strongly favored, because the hfs of the

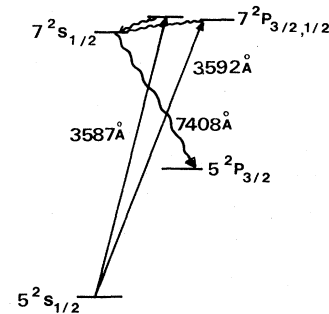
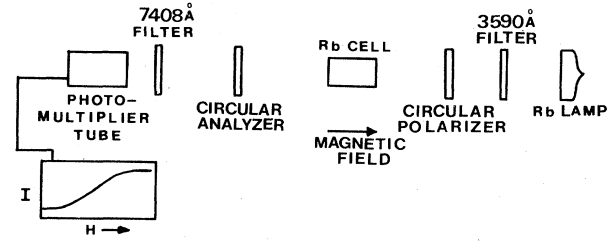


FIG. 7. Experimental apparatus (above) used to investigate the hyperfine structure of the  $7^2S_{1/2}$  state of  $^{87}\text{Rb}$  with the method of cascade decoupling. The relevant energy levels and transitions are shown below (from Gupta *et al.* 1972b).

$P_{3/2}$  is smaller than that of the  $P_{1/2}$ . Thus  $I$  and  $J$  decouple in the  $P_{3/2}$  at lower  $H$  values than in the  $P_{1/2}$ , thus the  $P_{3/2}$  state transfers the polarization better to the  $7S_{1/2}$  state. Gupta *et al.* (1972b) have computed the depolarization curve according to whether the  $|e\rangle$  state is the  $7P_{1/2}$  or  $7P_{3/2}$  state. The experimental results support the assumption that the  $P_{3/2}$  state is favored (see Fig. 8).

The most important causes of error are: magnetic scanning of the absorption lines, and nonwhite excitation (something that it is possible to take partially into account in the reduction of the experimental data) and depolarization by collisions in the  $|b\rangle$  state. The latter effect introduces systematic errors that it is difficult to control.

With the cascade technique it is practically possible to populate only relatively low-lying  $S$  and  $D$  states. For higher  $P$  states the transition strength diminishes rapidly and the resonance radiation is further displaced in the ultraviolet. In addition this technique has not been applied to the lowest excited  $S$  states, since it would be necessary to observe the fluorescent light emitted from this state to the lowest  $P$  state, a radiation that generally occurs in a spectral region (infrared) where the most sensitive detectors cannot be used.

## D. Optical double resonance

### 1. Principle of the method

Optical double resonance (ODR) investigations of excited atomic states began with the experiment of Brossel and Bitter (1952) on the  $6s6p\ ^3P_1$  state of mercury. The purpose of the method is to produce a non-uniform distribution of the populations in the states under investigation and to detect the magnetic resonance

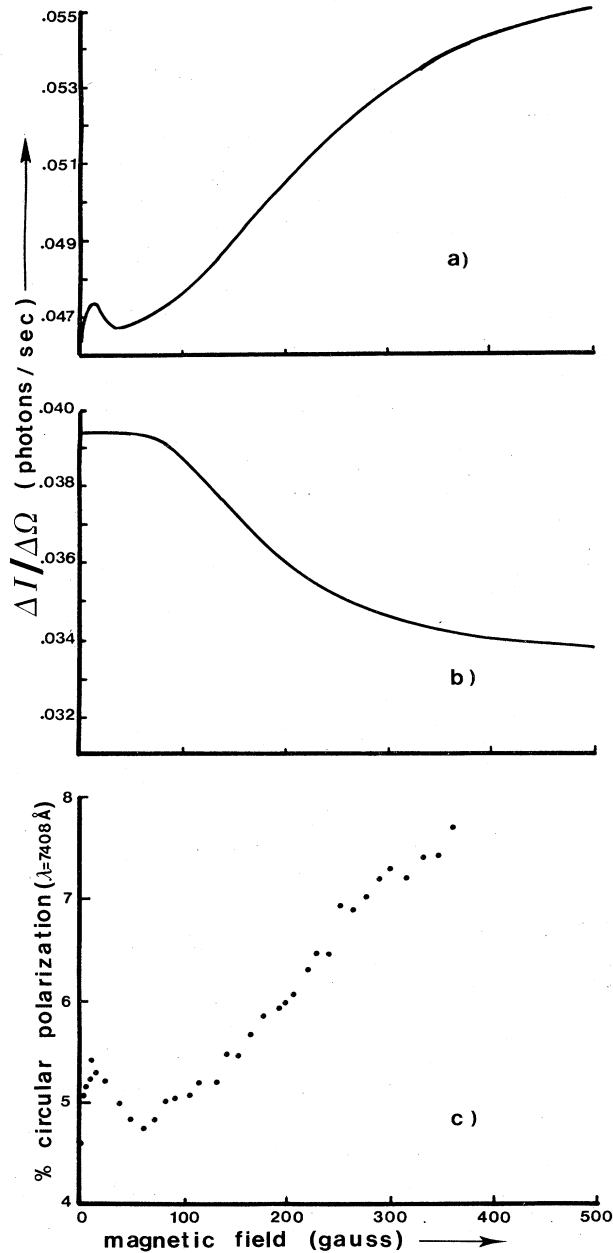


FIG. 8. The graphs (a) and (b) show the behavior of the fluorescent light  $\Delta I$  in a solid angle  $\Delta\Omega$  observed in the cascade decoupling investigation of the  $7^2S_{1/2}$  state of  $^{87}\text{Rb}$ , computed with the assumptions that the upper state of the cascade be either the  $7^2P_{3/2}$  state [as in (a)] or the  $7^2P_{1/2}$  state [as in (b)]. The experimental results, shown in (c), clearly support the first assumption (from Gupta *et al.*, 1972b, redrawn).

in the excited state through the changes in the polarization or the intensity of the fluorescent light. The most recent reviews of this type of experiment can be found in the works of Budick (1967) and zu Putlitz (1969); whereas detailed accounts of the experimental arrangements and the signal intensity are given in the reviews by Series (1959) and zu Putlitz (1965b).

The combination of polarizations for the exciting and fluorescent light has to be chosen in relation with the

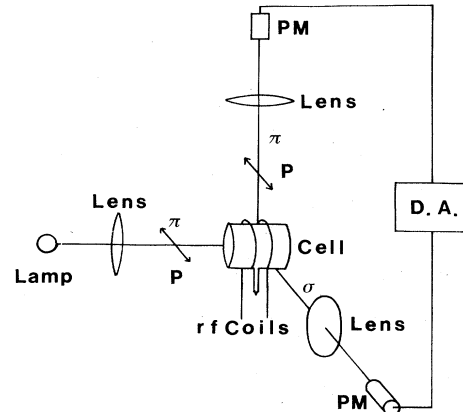


FIG. 9. A typical apparatus for double-resonance experiments in  $P_{3/2}$  states. The settings of the polarizers P can be varied in the individual experiments. Using a differential amplifier (D.A.) the resonance signal coming from each photomultiplier tube (PM) is increased, and the noise due to lamp fluctuations is reduced. The light is assumed to be properly filtered.

levels to be investigated. As an example let's consider an ODR experiment in a strong magnetic field on the  $^2P_{3/2}$  and  $^2P_{1/2}$  levels, as for instance in the recent measurements on the  $6^2P_{3/2}$  of  $\text{Cs}^{133}$  (Abele 1975a). A schematic diagram of an experimental apparatus is shown in Fig. 9 for the investigation in a  $P_{3/2}$  state, whereas the method may be illustrated in the schematic diagram of Fig. 10. Here only the  $m_J$  electronic quantum number has been reported and in the strong field regime only the  $\Delta m_I = 0$  transitions have to be considered. Light from the source is polarized with the electric vector parallel to the static magnetic field ( $\pi$  polarization). The atoms are transferred from the ground to the excited state with the  $\Delta m_J = 0$  selection rule and the  $m_J = \pm 1/2$  Zeeman sublevels of the  $^2P_{3/2}$  are populated. By an rf field applied in a direction orthogonal to the static one,  $\Delta m_J = \pm 1$  transitions are induced. The atoms are transferred to other magnetic sublevels: the transitions  $m_J = \pm 1/2 \leftrightarrow m_J = \pm 3/2$  ( $m_J = +I, \dots, -I$ ) could be detected by a decrease of the  $\pi$  component intensity or by an increase of the  $\sigma = (\sigma^+ + \sigma^-)$  component intensity in the fluorescent light, observed through an appropriate

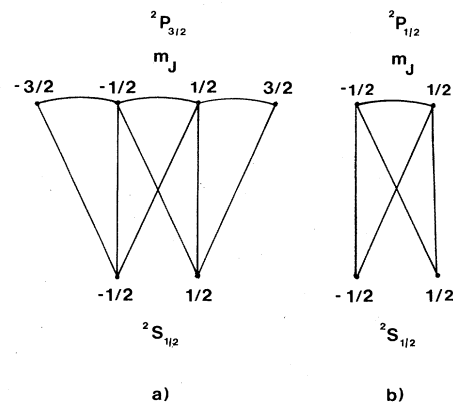


FIG. 10. Heisenberg diagrams of the  $D_2$  and  $D_1$  transitions, without considering the nuclear spin.

analyzer by a photomultiplier. The transitions between the levels  $m_J = +1/2 \leftrightarrow m_J = -1/2$  do not change the intensity of the  $\pi$  or  $\sigma$  components of the fluorescent light, and thus cannot be detected by this experimental arrangement. Observing at the same time through a differential amplifier the decrease in the  $\pi$  light and the increase in the  $\sigma$  light, the ODR signal is doubled and the fluctuations in the light source are compensated. The signal-to-noise ratio may be increased by amplitude modulation of the rf field intensity or of the static magnetic field, combined with a phase detection.

The excitation with  $\pi$  light is ineffective in detecting the resonance in the  ${}^2P_{1/2}$  states as it appears in Fig. 10(b). This level may be studied by means of  $\sigma^-$  light in excitation and  $\sigma^+$  or  $\pi$  in fluorescent decay (Abele, 1975b).

A large number of hyperfine splitting measurements have been carried on in ODR experiments at zero magnetic field, where the axis of quantization is conveniently defined with reference to the polarization of the exciting light. As the rf field frequency is swept,  $\Delta m_F = \pm 1$  transitions are induced between the hyperfine multiplets and intensity changes in the fluorescent light are detected. A complete analysis of the ODR zero-field experiments has been reported by zu Putlitz (1965b). Making use of the self-absorption phenomena zero-field ODR signals have been observed in the  ${}^7P_{1/2}$  state of cesium by Bucka (1956, 1958) by the change in the intensity of the light transmitted through the vapor. A nonuniform distribution of the population in the excited states is realized by the different intensities of the two resolved hyperfine components in the  $6^2S_{1/2}$ - $7^2P_{1/2}$  exciting light. The redistribution of the population occurring in the rf resonance conditions and the transfer to the less absorbing levels produce an increase in the total light emerging from the absorbing vapor.

ODR resonance has been applied also to fine-structure transitions, as between the Zeeman split  $2^2P_{1/2}$  and  $2^2P_{3/2}$  levels of  ${}^7\text{Li}$  (Orth *et al.*, 1975) to determine with high precision dipolar and quadrupolar coupling constants, including off-diagonal terms.

## 2. Indirect excitation schemes

The ODR spectroscopy has been extended to highly excited states, not directly connected by optical transitions to the ground level, through the cascade or two-step excitations. In the cascade rf spectroscopy the levels to be investigated are populated by spontaneous decay of highly excited states. The method of excitation is the same as in the cascade decoupling experiments (see the lower part of Fig. 7 in the case of the  $7^2S_{1/2}$  state of Rb). By circularly polarized uv exciting light an electronic polarization is created in the  $7P$  states. By successive spontaneous decays the polarization is partially carried over, first to the  $7^2S_{1/2}$  state and thereafter to the lower states. By the magnetic resonance in the  $7^2S_{1/2}$  the electronic polarization is decreased and the change can be observed as a decrease in the circular polarization of the fluorescent light superposed to the typical behavior of the cascade decoupling signal versus the intensity of the static field (see Sec. III.C). Figure 11 shows the results of an ex-

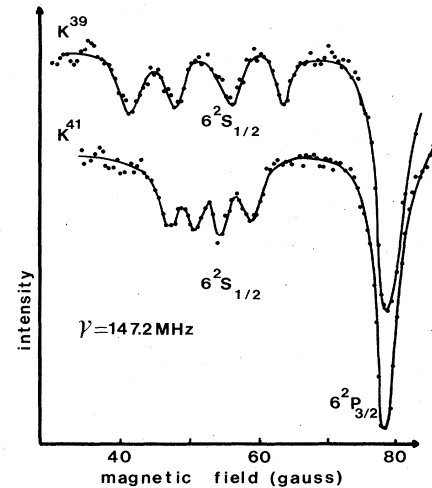


FIG. 11. Cascade radiofrequency signal for rf transitions in  $6^2S_{1/2}$  states and unresolved resonances in the  $6^2P_{3/2}$  states of  ${}^{39}\text{K}$  and  ${}^{41}\text{K}$  (from Gupta *et al.*, 1973).

periment in the  $6^2S_{1/2}$  state of  ${}^{39}\text{K}$  and  ${}^{41}\text{K}$  (Gupta *et al.*, 1973). The light emitted in the spontaneous decay of the levels under investigation may lie in a spectral region inconvenient for detection by conventional photomultipliers. Then the changes in the circular polarization can be observed in the following steps of the cascade process, although the magnitude of the signal is degraded by the additional steps in the cascade. This method has been applied to hyperfine structure measurements in several  $D$  levels (Gupta *et al.*, 1972a; Tai *et al.*, 1975) and excited  $S$  states including the lowest one (Gupta *et al.*, 1973; Liao *et al.*, 1973). In the experimental arrangement the electronic polarization is created and detected by circularly polarized light beams propagating along the static magnetic field direction. In the investigation of magnetic resonances in the  $S$  states, the problem of filtering the fine structure components is precisely the same as was discussed in the case of cascade decoupling. Amplitude modulation of the fluorescent light and of the rf power, combined with phase detection and signal averaging techniques are used to improve the signal-to-noise ratio.

A comparison between ODR after cascade (or "cascade radiofrequency") and cascade decoupling experiments shows that the former are usually more accurate by as much as an order of magnitude. In addition, states that can be reached after two steps in cascade can still be investigated with ODR, whereas this is almost impossible with cascade decoupling. However, since ODR experiments cannot determine the sign of the coupling constants, whereas this is possible with cascade decoupling, it is customary to combine both techniques to get an accurate measurement *and* the sign of the coupling constants. It should also be noted that for atoms with a high nuclear spin a cascade decoupling experiment is more convenient (there is a larger exchange of orientation between nucleus and electrons) and a radiofrequency experiment is less convenient (the number of Zeeman sublevels gets larger).

In the recent cascade radiofrequency experiment on



the  $6D_{3/2}$  of  $^{133}\text{Cs}$  (Tai *et al.*, 1975; Happer, 1975) the sign of the dipolar constant  $A$  has been determined relatively to the sign of the hyperfine constant in the  $8P_{1/2}$  feeder state, by comparing the relative amplitudes of the magnetic resonance transitions in these two states. In the high field region, where the experiment has been performed,  $2I+1$  resonances are observed corresponding to the different values of  $m_I$ . The relative amplitude of these resonances is determined by the population distribution in the Zeeman sublevels. As the nuclear polarization is not changed in the spontaneous decay at high field, the same population distribution is obtained in the feeder and fluorescent states. Then the component with the same relative position on the frequency scale will or will not have the same amplitude, whether the hyperfine dipolar constant has or has not the same sign in the two states.

In the two-step excitation the states are populated via an intermediate state through two successive absorptions of photons with different wavelength. Because of the short lifetime of the intermediate state, the success of this technique relies upon the efficiency of the optical excitations. ODR investigations of several excited  $S$  and  $D$  levels have been carried on using tunable lasers (e.g., Svanberg and Tsekeris, 1975b). In the first step the strong  $D_1$  and  $D_2$  lines from an rf lamp transfer atoms from the ground state to the first excited  $P$  states. In the second step radiation from a cw dye laser, multimode operating, excites atoms from one of the  $P$  levels to  $S$  and  $D$  levels. From these states  $P$  and  $F$  levels are also populated by cascade decay.

ODR experiments have been carried on in highly excited states of Na and Cs, populated by collisions with slow electrons (Archambault *et al.*, 1960). This method is not very accurate because the distribution of the population over the Zeeman sublevels is not precisely known. In effect by this method only rough values for the hyperfine coupling constants have been derived.

### 3. Broadening and shift of the resonance lines

In optical double resonance, as in the other experiments involving the radiofrequency field  $H_1$  as a probe, the precision of the measurements is affected by the electromagnetic field itself. Uncertainty and systematic errors in the resonance maximum position are connected to the broadening and shift produced by the radiofrequency field. The resonance has a natural linewidth from the radiative lifetime  $\tau$  of the participating levels, and as in general the investigated alkali levels are connected by intense optical lines the natural linewidth is in the megahertz range. The radio frequency field produces an additional broadening of the ODR signal and the measured full linewidth  $\Delta\nu$  is

$$\Delta\nu = (\pi\tau)^{-1} [1 + K(\mu_B g_J H_1 \tau / \hbar)^2]^{1/2}, \quad (3.3)$$

where  $K$  is a constant involving the matrix elements of the operators  $J_{\pm}$  between the investigated levels. Additional contributions to the linewidth  $\Delta\nu$  arise from multiple-quantum transitions but are usually negligible. The broadening produced by the radiofrequency field is comparable to the natural one, as a detectable ODR signal is obtained for an amplitude of the radiofre-

quency field of the order of magnitude of the inverse of the lifetime:  $\mu_B g_J H_1 / \hbar \sim 1/\tau$  (Series, 1970). The eigenenergies of the atomic levels are perturbed by the electromagnetic field, so that their energy separation  $\Delta E$  depends on the amplitude of the rf field. Thus the transition frequency  $\nu = \Delta E/\hbar$  has a shift  $\delta\nu$  or, for magnetic field scanning at a fixed frequency, the resonance field  $H_0$  has a shift  $\delta H_0 = -(dH_0/d\nu)\delta\nu$ . For a spin  $\frac{1}{2}$  system in a magnetic field a shift occurs because of the influence of that rotating component of the radiofrequency field which is out of resonance; this is the well-known Bloch-Siegert shift (Bloch and Siegert, 1940). For a multilevel system, additional and larger shifts result because of the presence of nearby quasi-resonant levels. The displacement of the transitions between the hyperfine levels of an alkali has been derived first by Salwen (1956) through a second-order perturbation approach. In this approximation a shift of the resonances proportional to  $H_1^2$  is predicted by the theory. Since in most cases the absolute amplitude of the applied rf field is known with poor precision, it is customary to plot the position of the resonance peak against the radiofrequency power and obtain the unperturbed position by a linear extrapolation to vanishing rf field. If the magnitude of the rf interaction is comparable to or larger than the hyperfine interaction dipole or quadrupole constants, the approximation on which this procedure is based breaks down. Through a refined perturbation treatment (Pegg, 1969a) the displacement of the resonance has been shown proportional to  $H_1$ , not  $H_1^2$ .

In order to present the main features of different ODR arrangements, we will consider the most usual cases:

(a) *Zero-field hyperfine transitions.* Magnetic resonance curves for transitions with  $\Delta F = \pm 1$  are observed by varying the frequency while keeping the amplitude of the rf field fixed. From the measured hyperfine frequency, the dipole and quadrupole constants are derived. Shifts of these resonances are originated through virtual transitions from the two hyperfine multiplets involved in the transitions to other hyperfine levels. The perturbation of the energy levels by the rf field can be calculated in a second-order perturbation theory with the axis of quantization along the direction of the rf field. With  $\hbar V$  the Hamiltonian for the interaction between the atom and the rf field of frequency  $\nu$ , the change in energy  $\Delta\omega_i$  (in frequency units) of the level  $i$  is given by (Senitzky and Rabi, 1956; Serber, 1969)

$$\Delta\omega_i = - \sum_l \left[ \frac{|V_{il}|^2}{\omega_{ii} - \nu} + \frac{|V_{il}|^2}{\omega_{ii} + \nu} \right], \quad (3.4)$$

where  $\omega_{ii}$  is the Bohr frequency between levels  $i$  and  $l$ , and the summation is to be carried out over all the levels with the same  $m_F$ , omitting the terms with vanishing denominators. In a zero static field experiment, the Zeeman components of a transition are degenerate for zero rf field intensity, so that the shifts given by the previous expression have to be calculated for each  $m_F$  state. It turns out that different Zeeman components have different corrections and that components with the largest shifts also have the greatest weights. Then the overall position of the maximum is derived

adding together the different shifts with a weight proportional to the intensity of the corresponding Zeeman component of the line. This laborious analysis has been applied in only a few cases, where a long time after the experiment the experimental data have been reexamined. For instance Pegg (1969a) has reanalyzed the zero-field experiment of Ritter and Series (1957) on the  $5^2P_{3/2}$  state of  $^{89}\text{K}$ ; and Arimondo and Kraifiska (1975) have derived new hyperfine constants from Schüssler's (1965) measurements on the  $5^2P_{3/2}$  state of  $^{85}\text{Rb}$ . A complete theoretical treatment and a careful experimental analysis of the shift in zero-field optical double resonance experiments have been given by Faist *et al.* (1964) for the 7 and  $8^2P_{3/2}$  states of  $^{133}\text{Cs}$ .

(b) *Weak and intermediate fields.* For this range of static field the  $\Delta m_F = 1$  Zeeman or hyperfine transitions are usually observed in the ODR spectra. The hyperfine constants and the gyromagnetic ratios  $g_J$  and  $g_I$  can be determined as well. The resonance lines are produced by one of the two rotating components of the applied rf field but the shift has contributions from both the rotating components of the radiofrequency field. Theoretically the radiative displacement of each level is represented by the expression (3.4), where those levels which are involved in the summation are now determined by the selection rules for the rf field polarization. As it appears from that expression, a significant shift of a resonance line may occur only when the energy separation between the two levels investigated is not very different from that of some other neighboring allowed transition. When the  $F = I + \frac{1}{2}$ ,  $m_F = -(I - \frac{1}{2}) \leftrightarrow m_F = -(I + \frac{1}{2})$  transition is investigated at intermediate field strengths, its energy separation is large as compared to all the other ones. Then negligible shifts result for this resonance, as, for instance, in the recent cascade experiments of the Columbia group (e.g. Gupta *et al.*, 1973).

(c) *High field.* In this case the electronic and nuclear angular momenta are decoupled and the electronic transitions for a fixed nuclear angular momentum ( $\Delta m_I = 0$ ) are usually observed. In a state with electronic angular momentum  $J = \frac{1}{2}$ , for each  $m_I$  component the  $m_J = -\frac{1}{2} \leftrightarrow m_J = +\frac{1}{2}$  transition represents a two level system. A displacement of the resonance peak occurs only by the Bloch-Siegert effect through the action of the component of the rf field rotating out of resonance (Bloch and Siegert, 1940). This shift, inversely proportional to the static field intensity, is very small for the rf field intensities applied in most experiments. In a state with  $J > \frac{1}{2}$  the Bloch-Siegert shift displaces the overall center of gravity of the resonance pattern, that depends upon the  $g_J$  value of the state: this shift is negligible as well. The  $2J + 1$  electronic levels with the same  $m_I$  value constitute an isolated group, not interacting with levels of different  $m_I$ . The center of gravity of this group of levels is independent of the quadrupolar coupling constant  $B$ . The spacing between the center of gravity of different groups depends on the dipolar coupling constant  $A$  only and is not altered by the rf interaction. Then the rf perturbation does not affect the value of  $A$  derived from that spacing (Pegg, 1969b). Inside a group with defined  $m_I$  the intervals between the electronic levels would be equal if the quadrupole hyperfine con-

stant were zero. Thus for a  $B$  constant smaller than the natural linewidth of the levels or for rf field interaction larger than the quadrupolar coupling, the very intense multiple-quantum transitions in a system with quasiequally spaced levels have to be considered. The resonance curve may be described as a set of poorly resolved multiple-quantum resonances. For a large quadrupole interaction the electronic transitions between the levels with the same  $m_I$  are well resolved and have a frequency spacing of the order of  $B$  and independent of  $A$ . It has been shown by Pegg (1969b) that the action of the applied rf field changes the spacing by  $(K^2 B^2 + (\mu_B g_J H_1)^2 / 2)^{1/2} - KB$ , where  $K$  is a constant depending on  $m_I$  and  $m_J$ . For small rf fields the quadratic dependence on  $H_1$  results for the radiative shift, as obtained in a perturbative approach; whereas at large rf power the shift depends linearly on  $H_1$ . The analysis by Pegg has been applied to solve the discrepancy between the ODR measurements of Ritter and Series (1957) and later level crossing investigations (Schmieder *et al.*, 1968; Ney, 1969) on the  $5^2P_{3/2}$  state of  $^{89}\text{K}$ . An accurate computation of the line shape for that ODR experiment has been carried on by Hartmann (1970b) in good agreement with the experimental spectrum.

The source of systematic errors in ODR experiments will be mentioned only briefly here, since their physical origins are the same as in atomic beam magnetic resonance and optical pumping experiments, where they are more fully discussed since such experiments are usually much more accurate.

(a) Calibration of the static field with optical pumping techniques is usually applied to have enough accuracy. For the rf field it is usual to measure only the relative intensities of the applied rf power and to get rid of radiative shifts by making an extrapolation to zero power. If numerical evaluation of the radiative corrections are intended, the rf field intensity can be derived from the observed power broadening, with low precision if several transitions are blended. A precise measurement is obtained observing the nutation frequency in the transient phenomena at the application of the rf field (e.g., Cagnac, 1961).

(b) Inhomogeneous static field broadening is not important for the excited state resonances; whereas the inhomogeneous distribution of the rf field may produce alterations in the line shape.

(c) Owing to the sweep of the static magnetic field over a large interval a background signal may appear below the ODR signal. Contributions to the background come from level crossing and anticrossing and from the decoupling of the I and J angular momenta. In the cascade radiofrequency experiments decoupling signals occur from the feeder state and from the states involved in the cascade (see Sec. III.C). This background leads to a small shift in the peak of the experimental resonance curve, to be eliminated by an accurate data reduction.

(d) If the hyperfine interaction is comparable to or smaller than the linewidth, the rf spectrum is an unresolved superposition of several overlapping resonance transitions. A curve-fitting procedure may be used to ana-

lyze the data, adding together resonance lines of different relative heights, widths, and positions and comparing the resulting curve with the rf spectrum. An accurate comparison between the theoretical and experimental line shapes has been carried on by Hartmann (1975) for an experiment in a strong magnetic field on the  $7^2P_{3/2}$  state of  $^{133}\text{Cs}$ . Good agreement has been obtained between the experimental curves and the line profiles numerically derived in a semiclassical treatment. In several ODR measurements in highly excited states as in the 8, 9, and  $10^2D_{5/2}$  levels of  $^{133}\text{Cs}$  at strong magnetic field (Svanberg and Tsekeris, 1975), an unresolved signal structure is observed because of the small magnetic dipole hyperfine constant  $A$ . The observed linewidth is the convolution of  $2I+1$  resonance transitions, corresponding to the different values of  $m_I$ , with spacing equal to the constant  $A$ . From the measured signal structure half-width extrapolated to zero rf power, and from the theoretically calculated lifetime of the state, the dipole hyperfine constant can be inferred, with poor accuracy. In the cascade rf experiments, the rf resonances in the feeder states and in other states involved in the cascade are observed at the same time as the signal in the investigated level (Gupta *et al.*, 1973). Moreover the intensities of the various resonances can be modified in the cascade process, due to the recoupling of the electronic and nuclear angular momenta in the successive stages. Distortions of the resonance line shape caused by these phenomena have to be considered in the analysis of the experimental data, but they are not significant in the experiments performed up to now.

## E. Atomic beam magnetic resonance

### 1. Ground states

Besides optical spectroscopy, the oldest technique that has been used to investigate the hfs is the Atomic Beam Deflection Method, first proposed by Breit and Rabi in 1931.

The Atomic Beam Magnetic Resonance (ABMR) method that was developed thereafter mainly by Rabi and his associates in the thirties is still today one of the most accurate measurement techniques in all of Physics.

It is most frequently used in the study of the ground states, with a purpose (obtaining nonstatistical distribution of the atoms, and detecting a resonance) quite similar to that described for optical pumping. Even though it has such a large historical and metrological importance, it is described only at this stage, in this paper, because of its strong ties with the methods just described, namely optical pumping and double resonance.

The method has been described in detail in many review papers and books, among others those by Ramsey (1956) and by Kusch and Hughes (1959). A survey of more recent work can be found in English and Zorn (1974).

A schematic diagram of a typical ABMR apparatus is given in Fig. 12. The purpose of the A and B magnets is to deflect the beam of atoms originating from the source S, this deflection being caused by the force acting on a magnetic dipole by a nonuniform magnetic field. The

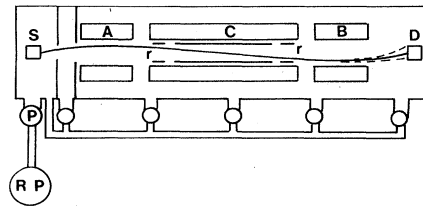


FIG. 12. A typical ABMR apparatus. S: atomic source; A, B, C: magnets; D: detector; P: ionic or diffusion pumps (only one is labeled); RP: mechanical pump; r: radio frequency coils used with Ramsey's method.

atoms in different  $|J_z\rangle$  states are therefore deflected in a different way. If, in the region of the C magnet, a radio frequency transition between two such states occurs, the trajectory will be different than in the case of no transition, and the atom will impinge on the detector (D) plane at a different point. It is thus possible, by properly selecting the nonuniform fields of the A and B magnets and the position of the detector of atoms, to find out whether a transition is occurring in the C region or not. If the C magnet delivers a uniform field of known intensity, the energy difference between two states in that field can thus be measured in a resonant way. When such energy differences are known, it is easy to compute such atomic constants as gyromagnetic factors and zero-field hyperfine splittings.

A very large number of experimental variations have been developed on this basic idea; a discussion of them is well beyond the scope of this paper, and the reader is referred to specialized works. We shall only discuss a few cases in order to make clear what sort of constants can be measured.

(a) *Weak fields.* The A and B fields must always be rather strong, in order to have a considerable deflection and thus a narrow resonance at the detector. I and J are thus decoupled during the deflection, so that only transitions with  $\Delta m_J \neq 0$  can be observed. If the C field is low enough to have a small Zeeman splitting as compared to the hfs, a transition connecting two states with a different  $m_J$  value in high fields can be observed, like the transition "a" shown in Fig. 1. Its frequency gives us information mainly on  $g_F$  (as defined in Sec. II.C), since the field dependence is almost linear in the low field region. Several other transitions are possible connecting states with different  $F$  values, like the "b" transition shown in Fig. 1. Once the  $g_F$  value is known, the frequency of such a transition gives us information on the zero-field hfs.

(b) *Intermediate fields.* In this case the C field is such that the Zeeman splitting is comparable with the hfs. In this case the interpretation of the raw data is less straightforward; using the Breit-Rabi formula, however, it is possible to compute the frequency of each transition for each field value as a function of the hfs and the gyromagnetic ratios  $g_J$  and  $g_I$ . This method is particularly accurate if transitions are used (as the "c" transition in Fig. 1) whose frequency passes through an extremum as a function of the applied field.

(c) *Strong fields.* If the C field is large enough to decouple I and J, the spacing between the various transitions (with  $\Delta m_J = \pm 1$ ;  $\Delta m_I = 0$ ) gives us the same kind of

information as in the corresponding case of a double-resonance experiment.

With ABMR experiments it is usually not possible to obtain information on the sign of the splitting constants. King and Jaccarino (1954), using a suitable stop in the B region and studying  $\Delta F=0$  transitions, were able to determine the sign of  $A$  in the ground state of the bromine isotopes. This technique has been employed by other authors as well, but never—to our knowledge—in the study of alkali atoms.

The main causes of broadening of the resonance are the following:

(a) Since the atoms spend a limited amount of time in the C region where radio frequency is applied, the resonance width is proportional to the reciprocal of this time. With atomic velocities in the beam following a Maxwellian distribution [ $\rho(v) \propto v^3 e^{-v^2/\alpha^2}$ ] the width is  $\Delta\nu = 0.95 \bar{v}/L$ , where  $\bar{v}$  is the average velocity and  $L$  is the length of the region exposed to the rf field.

(b) The geometrical characteristics of the beam (cross section, collimation, deflection angles, length) and the detector also determine to some extent a broadening of the resonances. It is possible, however, to design the apparatus in such a way as to have this broadening smaller than the previous one.

(c) If the C field is to some extent inhomogeneous, the resonance frequency is not exactly the same throughout the C region, with a resulting broadening of the observed resonance.

It is fairly obvious that the effects of the phenomena (a) and (c) above are to some extent complementary: one can reduce the width by increasing the length of the radiofrequency region, but in this way it is more difficult to have a homogeneous field over a larger area; and vice versa. A method to control these two causes of broadening at the same time has been described by Ramsey in 1950: two coherent oscillating fields are placed at the beginning and at the end of the C region; between them there is only the static C field. A careful analysis has been carried out including the effect of phase shifts between the two oscillators (Ramsey and Silsbee, 1951). It has been demonstrated that in this case, taking into account the velocity distribution in the beam, the line shape is as shown in Fig. 13, with the central peak having a width about 40% less than the width with a single oscillating field (with the same length of the C region). And, what is more important, the area where the atoms can absorb radio frequency is much smaller than in the single oscillating field case; thus the requirements on the field homogeneity are much less stringent. The major disadvantage of Ramsey's method is that, owing to the complicated line shape, the interpretation of the results is much more difficult if one has a spectrum with several closely spaced or overlapping resonances.

In order to determine with high accuracy the position of the center of the resonance line, it is necessary to have a high signal-to-noise ratio. The main sources of noise are:

(a) The beam intensity can fluctuate according to fluctuations in the vapor pressure in the source (an oven,

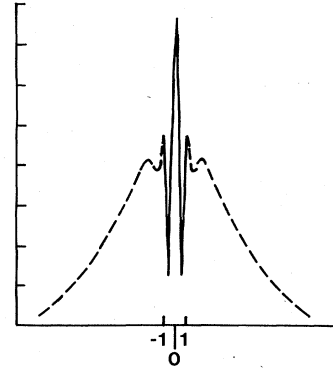


FIG. 13. Signal obtained with Ramsey's method (theoretical computation): the central peak is very narrow and can thus be easily identified. The width of a normal resonance (without Ramsey's technique) under the same circumstances is shown at the bottom.

for alkali atoms), thus it is necessary to control carefully the oven temperature.

(b) The most convenient kind of detector is a Langmuir-Taylor detector, whose efficiency is very high for alkali atoms and drastically lower for residual gas molecules. This kind of detector is most sensitive and, in the case of low-intensity beams, can be integrated by mass spectrometry and cryopumping reaching a sensitivity of 100 particles/sec.

(c) Short-term fluctuations of the C field intensity and of the rf field intensity and/or frequency also manifest themselves as overall noise. Their effect can, however, be kept very low with conventional electronic techniques.

As for systematic errors, these can be divided into two main categories: calibration uncertainties and experimental shifts:

(a) Since the overall accuracy of this kind of experiment is very high, a very good knowledge of the applied field intensity is required. In low-field experiments (transitions like "b" in Fig. 1) the effect of the field on the measured frequency is not very important (and this is especially true for the  $|F=I+\frac{1}{2}, m_F=0\rangle \rightarrow |F=I-\frac{1}{2}, m_F=0\rangle$  transition), and calibration with standard techniques is acceptable. In high field experiments, a more accurate calibration is usually necessary. In some cases this has been achieved by splitting the atomic beam in two: one beam of the atoms under investigation, and one beam of an atom whose hfs is already well known. The two beams pass exactly in the same resonance area at the same time, so one can continuously monitor the applied field.

(b) No problems arise from uncertainty in the frequency measurements, since electronic counters give all the required accuracy. By the way, we recall that the present standard of frequency is precisely that of an atomic beam apparatus working on the hfs of an alkali atom.

(c) Bloch-Siegert type shifts can be induced by the applied radio frequency field. They have been discussed in detail in Sec. III.D, which is devoted to double resonance experiments.

(d) The inhomogeneities of the static C field and of the rf field can cause deformations of the line shape and thus affect the determination of the line center (Böklen, 1974).

(e) If the resonance is scanned by changing the rf frequency, some dependence of the rf field intensity on the frequency is almost inevitable owing to small mistuning of the high quality resonators. Such an effect manifests itself in a shift of the line center.

It is very difficult to assess in general the relative importance of all these causes of systematic errors; this must be done carefully for each experiment. A very good example of such an analysis can be found in a recent paper by Beckmann *et al.* (1974).

## 2. Excited states

The techniques mentioned above have been designed to study the hfs of an atom in its ground state. In order to study the hfs in an excited state, some modifications are required. The problem has been investigated in detail by Perl *et al.* (1955). Since the lifetime of an excited alkali state is typically  $10^{-8}$  sec, i.e., much less than the transit time in an atomic beam apparatus, it is necessary to excite the atom and submit it to an rf field at the same location, i.e., the C region. In the excited state the same kind of transitions occur, as we have seen for the ground state, thus with a change of  $m_j$ . Upon decaying to the ground state, the probability of reaching a ground state sublevel with a given  $m_j$  is different, whether the rf transition in the upper state has occurred or not. With the same detection techniques of a conventional ABMR experiment it is thus possible to investigate the excited state as well.

The case of an excited state is however quite different if one considers the sources of uncertainty:

(a) Each atom stays in the upper state only for a time of the order of  $10^{-8}$  sec, much less than the time spent by a ground-state atom in the C region of a conventional ABMR experiment. The width of the resonance is therefore much larger; in addition, Ramsey's method obviously cannot be used. An advantage, however, is that field inhomogeneities are negligible.

(b) The number of atoms undergoing a transition is much less than in the ground-state case; thus the signal-to-noise ratio is much lower.

(c) In order to have a high transition probability in the small area ( $\sim 10^{-3}$  cm) where the atom stays in the upper state, the rf field intensity must be larger than in the ground-state case, thereby increasing broadening and Bloch-Siegert shifts of the resonance.

The overall accuracy of the excited-state experiments is thus much lower than that of the ground-state experiments.

Bucka (1966a) proposed the use of optical pumping techniques (excitation by means of circularly polarized light) in order to polarize the ground state (thus using only the B magnet for analysis, and not the A magnet) and monitoring the resonance in the excited state by observing the change in the ground-state polarization induced through the pumping cycle. This technique was used by Zimmermann (1969) to study the hfs in excited K atoms.

## F. Other atomic beam deflection methods

In addition to ABMR, several other techniques have been developed that use beam deflection as a monitor of

the resonance, but use optical rather than magnetic resonance.

### 1. Magnetic deflection

In an apparatus similar to an ABMR apparatus, the transfer between Zeeman states in the C region can be accomplished by Zeeman optical pumping instead of an applied rf field. The effects of the pumping radiation on an atomic beam had already been investigated by Perl *et al.* (1955). Duong *et al.* (1973b) investigated with this technique a beam of sodium irradiated by a narrow-band tunable laser, thus detecting the resonance by the beam deflection, and obtained values of the hfs that are consistent with those obtained with more accurate techniques. Another technique has been developed by Duong and Vialle (1974a). A sodium beam passes through a hexapole focusing the atoms in a  $m_j = +\frac{1}{2}$  state. Before entering the hexapole the atoms are irradiated by a tunable dye laser; when the laser is in resonance there is hyperfine optical pumping. Passing from the outer to the inner parts of the hexapole, the atoms pass adiabatically from a low field region to a high field region. All atoms in the  $F=1$  level have  $m_j = -\frac{1}{2}$  in strong field (see Fig. 1) and are therefore not focused by the magnet. One has therefore an increase of the signal whenever the laser is in resonance with a transition starting from the  $F=1$  level of the ground state, and vice versa. With this technique the hfs of the sodium  $D_1$  line has been completely resolved. There is the advantage that the atomic beam does not need to be as collimated as in an usual apparatus with A and B magnets; on the other side the lesser collimation leads to broader resonance curves and thus to a lower accuracy.

### 2. Stark coincidence

Another method was first proposed by Marrus and McColm (1965) in order to study the isotopic shifts, and later used by Marrus *et al.* (1967) to measure hfs. The basic idea of this method is to observe optical coincidences by shifting the optical lines by means of an electric (instead of a magnetic) static field applied in the C region. A schematic diagram of such an apparatus is shown in Fig. 14. The lamp emits narrow lines that are slightly off resonance (the lamp contains a different isotope than the atomic beam). By applying an electric

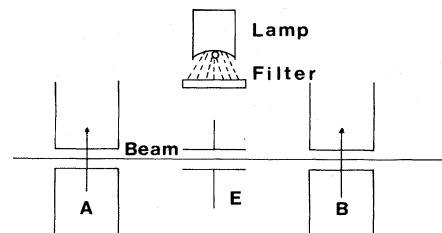


FIG. 14. Schematic diagram of an apparatus for the investigation of the hyperfine structure with the technique of Stark coincidences. The purpose of the A and B magnets is the same as in an ABMR experiment. Resonance occurs (and the atoms change state by means of optical pumping) when the electric field  $E$  displaces the absorption lines in resonance with the lamp.

field in the C region, the absorption lines of the beam are Stark shifted until they coincide with one of the lines emitted by the lamp. When such a coincidence occurs, some atoms change their  $m_J$  value by means of a transition first to the excited state and then back to the ground state by spontaneous decay. The detector thus "sees" a resonance. The apparatus can be calibrated by observing first the hyperfine splitting in the ground state, which is already well known. The excited state hfs can thus be measured.

### 3. Deflection by light

In another set of methods, the beam is deflected directly by the exciting light by means of exchange of momentum between the photons and the atoms. The deflection of a collimated beam of sodium atoms, transversely irradiated with a spectral lamp, was first observed by Frisch (1933). About forty years later the experiment has been repeated, with higher sensitivity, by Picqué and Vialle (1972). The deflection is higher for lighter than for heavier atoms, since the deflection angle  $\alpha$  is given by  $\alpha = p/mv$ , where  $p = \lambda/c$  is the photon momentum,  $m$  the atomic mass and  $v$  the atomic velocity.  $\alpha$  can be increased if the same atom absorbs several photons consecutively. This can be achieved with a laser as a pumping source, and by increasing the time spent by each atom under the pumping light. The first experiment of beam deflection by light using a laser was carried out by Schieder *et al.* (1972) on sodium, with an average of 60 excitations per atom. Since the laser line can be very narrow, and the beam is well collimated, it is possible to resolve the hyperfine components of the resonance line. The technique can thus be applied to spectroscopic investigations of the hfs. Jacquinet *et al.* (1973) resolved the hfs of the sodium  $D$  lines. In Fig. 15 the completely resolved hyperfine structure of the  $D_1$  line is shown. In this case, however, it is not possible to have a high number of successive excitations of the same atom, since, because of the hyperfine pumping after having absorbed one (or a few) photon the atom passes to the other hyperfine sublevel and cannot thus absorb any more single-frequency radiation. The recording shown in Fig. 15 has been obtained with a continuous scanning of 2 GHz of the dye laser frequency.

This technique is particularly suitable for the study of radioactive atoms (thus achieving a higher detection sensitivity) or for atoms with a diamagnetic ground state, thus avoiding hyperfine pumping effects.

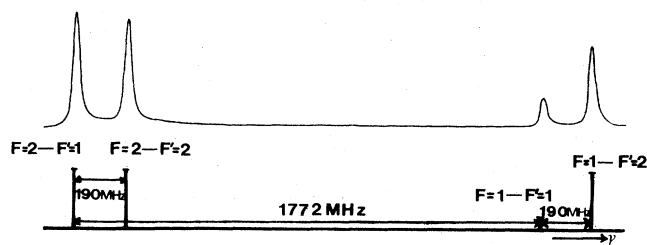


FIG. 15. Detection of optical resonance using atomic beam deflection by light. Hyperfine structure of the Na  $D_1$  line.  $F$  and  $F'$  denote the hyperfine levels of the  $3^2S_{1/2}$  and  $3^2P_{1/2}$  states, respectively (from Jacquinet *et al.*, 1973).

### 4. Photoionization

Still another technique for monitoring the absorption of resonant radiation is to use, instead of the fluorescence from the upper state under investigation, the further absorption by that state of photons leading to an ionized state. The first step must be carried out with as narrow (in order to have high resolution) and as intense (in order to obtain a high probability of absorption in the upper state) a light beam as can be delivered by a single-mode continuously tunable laser. The second step can be carried out with a broad band lamp. Monitoring the produced ions (deflected by an electric field) one observes resonance of the laser radiation with the atomic absorption lines.

Duong *et al.* (1973b) carried out such an experiment on a sodium beam. First they excited the transition to the  $3^2P_{1/2}$  state ( $D_1$  line) with a dye laser. The atoms in the  $3^2P_{1/2}$  state, submitted to the radiation from a high pressure mercury lamp, absorb the radiation, reaching an ionized state (the photoionization threshold for the  $3P_{1/2}$  state is  $\lambda = 4082 \text{ \AA}$ ). The light of much shorter wavelength ( $\lambda \leq 2500 \text{ \AA}$ ) might induce photoionization directly from the ground state, but it is absorbed by the optical system that has been used. Thus there is production of ions along the atomic beam only if the laser radiation is in resonance.

Brinkmann *et al.* (1974) have used this technique with a narrow source (a second laser) also as an ionization source, in a Ca beam; in this way the transition reaches an autoionizing state, thus increasing appreciably the overall ionization probability.

### 5. Zeeman quenching

When different states of the same multiplet have much different lifetimes (as in the case of autoionizing multiplets), the application of a magnetic field couples the various states together and modifies the lifetimes accordingly. A metastable state can thus be quenched by the application of the magnetic field. By observing this quenching in an atomic beam it is possible to infer the energy separation between the two states.

This technique was described by Feldman and Novick (1967) and used by Feldman *et al.* (1968) in the study of the fine and hyperfine structure of the  $1s2s2p^4P$  multiplet of lithium. Sprott and Novick (1968) have used a similar magnetic quenching effect in an ABMR experiment to obtain state selection by quenching instead of by interaction with external fields.

### G. Level crossing

#### 1. Principle of the method and experimental arrangements

The level-crossing method does not use a magnetic resonance to investigate the hfs, but rather its purpose is to determine under which circumstances the sublevels of an excited level have the same energy.

All Zeeman sublevels corresponding to the same  $F$  value have the same energy when there are no applied static fields. This particular kind of level crossing is known as the "Hanle effect" and was investigated experimentally in the twenties and a semiclassical inter-

pretation of it was given (Hanle, 1924). A complete theoretical investigation in the general case of any kind of degenerate levels was carried out by Breit (1933).

It is not, however, until the late fifties that an improved technology allowed the observation of level-crossing in a nonzero field (Colegrove *et al.*, 1959). A detailed interpretation of the effect has been given by Rose and Carovillano (1961) and by Franken (1961) (a mistake in Franken's paper has been pointed out by Stroke *et al.*, 1968). Only level crossings in nonzero field are usable to investigate the hfs.

Even though the level-crossing method has been very widely used, there is not, to our knowledge, any review work dealing exclusively with it. Nevertheless, some general description of the method is included in the works of zu Putlitz (1965), Budick (1967), and Series (1970). A very detailed description of a level-crossing experiment, including theory and data reduction, can be found, e.g., in the work of Schmieder (1969).

The basic idea underlying the method is that two states can be excited coherently when they are degenerate (and when the selection rules allow it); then they interfere and radiate coherently, with a spatial distribution of the fluorescence that is affected by the interference between the two states. If the two states are not degenerate, the excitation is incoherent, there is no interference, and the fluorescence is distributed in a different way. The outgoing light can thus be described as the sum of two terms: an incoherent term that is unaffected by the level crossing, i.e., by whether the two levels are degenerate or not, and a coherent, resonant term, that occurs only when the two levels cross. The latter term has the form

$$W_{\text{coh}} = \frac{\Gamma_{12}\alpha_{12}}{\Gamma_{12}^2 + E_{12}^2} - \beta_{12} \frac{E_{12}}{\Gamma_{12}^2 + E_{12}^2}, \quad (3.5)$$

where  $\Gamma_{12}$  is the average width of the two levels,  $E_{12}$  is the energy difference between the two levels, and  $\alpha_{12}$  and  $\beta_{12}$  are proportional to the real and imaginary part, respectively, of

$$\langle c | \mathcal{K}_g^+ | b_1 \rangle \langle c | \mathcal{K}_g^+ | b_2 \rangle^* \langle b_1 | \mathcal{K}_f | a \rangle \langle b_2 | \mathcal{K}_f | a \rangle^*, \quad (3.6)$$

where  $|b_1\rangle$  and  $|b_2\rangle$  are the crossing states.  $|a\rangle$  and  $|c\rangle$  are lower states that are radiatively connected with them.  $\mathcal{K}_f$  is the operator for absorption of a photon whose frequency, direction, and polarization are specified by  $\mathbf{f}$ ; and  $\mathcal{K}_g^+$  is the corresponding operator for emission of a photon  $\mathbf{g}$ . It is usually possible to choose the geometry in such a way that  $\alpha_{12} \neq 0, \beta_{12} = 0$ , or  $\alpha_{12} = 0, \beta_{12} \neq 0$ . In such cases the crossing signal has, respectively, a Lorentzian or a dispersive shape.

A very simple experimental setup for studying the hfs with this technique is shown in Fig. 16. The light emitted by the lamp is polarized and then absorbed by the vapor, and the fluorescent light (of suitable polarization) is monitored by photomultipliers. By changing the intensity of the applied magnetic field, two levels pass through a crossing; and a resonant signal is observed by the photomultiplier. It is thus possible to find out exactly for which value of the applied field the two levels have the same energy. The schematic apparatus shown in Fig. 16 is extremely simplified; several experimental techniques have been used in order to im-

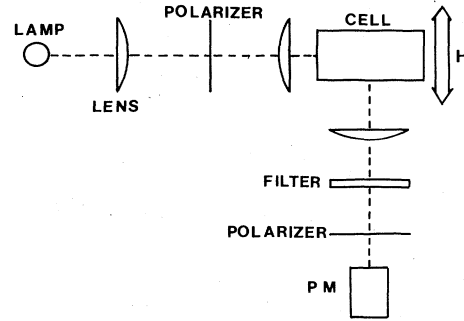


FIG. 16. A very schematic level-crossing apparatus. The arrow  $H$  shows the direction of the magnetic field. The geometry can slightly vary from one experiment to another.

prove the signal-to-noise ratio and thus the accuracy in determining the crossing point. A technique consists in modulating the applied field and observing the derivative of the signal (Bucka, 1966b; Schönberner and Zimmerman, 1968; Svanberg and Rydberg, 1969; Isler *et al.*, 1969a, b). The instrumental corrections that must be applied in this case were discussed by Isler (1969c). Modulation of the incoming light polarization and differential monitoring of the fluorescent light to get rid of the incoherent signal were used by Violino (1969).

As clearly shown by Eq. (3.5), the width of a resonance is related to the width of the levels (in fact, the zero-field level crossing is a widely used technique for investigating lifetimes). It has been shown, however, that by suitably choosing the time interval of observation after the excitation it is possible to reduce considerably the width of the resonance beyond the natural width. This effect was first observed by Ma *et al.* (1967, 1968) in double-resonance experiments and was accurately described for level-crossing experiments by Copley *et al.* (1968). The theoretical aspects of time-resolved spectroscopy have recently been reviewed by Stenholm (1975). Accurate level-crossing measurements of the hfs of the alkalis have been carried out with this technique by Deech *et al.* (1974) and Figger and Walther (1974).

## 2. Data analysis

Since the relationship linking the energy of the state to the magnetic field through the hyperfine coupling constants and the gyromagnetic factors is well known, the observation of two or more crossing points allows a determination of  $A$  and  $B$  if  $g_J$  and  $g_I$  are known, and of  $g_J$  if  $A$ ,  $B$ , and  $g_I$  are known. If one neglects the very small influence of  $g_I$ , the effect of a change of  $A$  and  $B$  on the crossing points is exactly the same as a change of  $1/g_J$ . It is thus not possible to measure  $A$ ,  $B$ , and  $g_J$  simultaneously in a level-crossing experiment. In most cases a level-crossing experiment is used to measure  $A$  and  $B$  using either a  $g_J$  value measured in double resonance experiments, or a theoretical  $g_J$  value. In other cases, however, a comparison of the  $A$  and  $B$  values, measured in a double resonance work, with the results of a level-crossing experiment is used to evaluate  $g_J$  (the importance of taking into account  $g_I$  in such evaluations has been stressed by Violino, 1970). In this



paper this sort of comparison will be made in Sec. IV. A few authors have finally used the  $A$  value from a double resonance experiment and the  $B/A$  value from a level-crossing experiment to find  $B$  with better accuracy than by measuring it directly in a double resonance experiment. In the present work we have re-analyzed those experiments as far as possible to obtain information on  $A$  or  $g_J$  as well. This will be presented at appropriate locations in Sec. V. The problem of computing the relationship between the level-crossing points and the atomic constants has been discussed analytically (Kapelewski and Rosiński, 1965; Tudorache *et al.*, 1971a), graphically (Schönberner and Zimmermann, 1968) and numerically (Violino, 1972). Many authors do not even attempt to find the precise crossing positions, but fit their overall data directly to the sum of several crossing curves in order to find  $A$  and  $B$ . In those cases when modulation is used, other characteristic features of the experimental curves can be used to find  $A$  and  $B$ , like the maxima of the first derivative of the crossing signal.

### 3. Sources of uncertainties

The main sources of systematic errors in level-crossing experiments are:

(a) *Calibration of the applied field.* Since the overall accuracy of these experiments can be rather good, it is necessary to measure the applied field very well, since in most cases a 1% accuracy is not sufficient. Therefore calibration with optical pumping techniques is most often useful.

(b) *Magnetic scanning.* Since the exciting radiation is not "white", some nonresonant change of the absorption is always present as a function of the applied field owing to the Zeeman effect in the absorption cell. Thus the

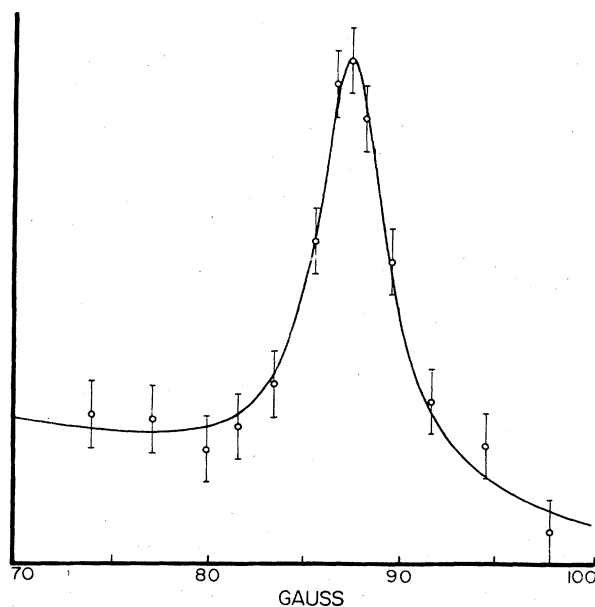


FIG. 17. A typical level-crossing signal in cesium: experimental points fitted to a Lorentzian curve plus a straight line to take into account magnetic scanning effects (from Violino, 1969).

incoherent signal is not field-independent, and the crossing point does not exactly correspond to the maximum of the resonance (see Fig. 17). With an accurate data reduction it is possible to minimize the error introduced by this effect.

(c) *Overlapping of several crossings.* When two crossing points are nearer than the width of a resonance, a careful data reduction is again required to properly individuate the crossing points. The problem is particularly severe for overlapping of a nonzero-field crossing with the Hanle effect (zero-field crossing point) whose intensity is always much larger than that of all nonzero-field level crossings. For this reason the accuracy is much lower when the hfs is comparable to or smaller than the level width.

(d) *Other sources of instrumental errors.* It is possible to take care of other sources of instrumental errors (like inhomogeneity of the field and the effect of the changing field on the multiplication factor of the photomultipliers) with standard techniques. The resonant collisions have been investigated by Gallagher and Lewis (1974) as a cause of broadening of level-crossing curves; in hfs experiments, however, this is not a source of trouble.

### 4. Other level-crossing schemes

A few extensions of the level-crossing technique that have been proposed will be briefly mentioned here.

Level crossings in the presence of an electric, instead of a magnetic, field were first investigated by Khadjavi *et al.* (1968), and the use of both electric and magnetic fields together was introduced by Volikova *et al.* (1971) in order to investigate the electric polarizabilities. A review of the work carried out by the Leningrad group can be found in a paper by Kalitejewski and Tschaika (1975) where a result for hfs is also given. A similar technique was also used by Hogervorst and Svanberg (1975) in order to determine the sign of the coupling constants in highly excited states where the hfs is so narrow that there is no way to find out the sign with optical or cascade techniques. The Stark effect in the hfs of alkali atoms was investigated theoretically by Manakov *et al.* (1975).

If the level whose sublevels cross is not excited directly (from the ground state or by means of multiple excitation) but in cascade, in order to observe a signal the coherence must be conserved in passing from the state that is directly excited to the state under investigation. Since this does not usually occur, it is not possible to observe such an effect except under very special circumstances since otherwise the signal-to-noise ratio is too poor. The problem has been investigated theoretically by Gupta *et al.* (1973), Bhaskar and Lurio (1976), and Bulos *et al.* (1976b). Nonzero-field level crossings after cascade have been observed experimentally in alkali atoms by Tai *et al.* (1975) using the well-known accidental coincidence of the 3888 Å line of helium to strongly excite the  $8P_{1/2}$  level of cesium and then observing the level crossing in cascade in the  $6^2D_{3/2}$ . The effect is doubtless very interesting; but from the point of view of measuring hfs "it is not a very promising technique in general because of the poor signal-to-noise ratio," as the authors themselves state. No particular

problems arise, on the contrary, with stepwise excitation, the coherence in the state under investigation being introduced only by the last step.

Some effects that closely resemble level crossing have also been discussed for the ground state (Series, 1970; Happer, 1972). Nevertheless an investigation of the hfs with such techniques is presently out of the question.

## 5. Anticrossing

In some instances the hfs is too narrow to be investigated directly with a level-crossing technique, but it is possible to observe the crossing of states that belong to two different fine (instead of hyperfine) levels. This can be done practically in the lowest terms of lithium (in the other alkalis, fine structure crossings in the low-lying terms occur at too high field values) or in higher  $P$  or  $D$  terms. Owing to the presence of hyperfine structure, each of the crossing levels consists of several states. As an example, in Fig. 18 an "enlarged" view of the 915 G level crossing in  ${}^6\text{Li}$  is reported. The crossing levels are those labeled by  $3^2P_{1/2}$ ,  $m_J = +\frac{1}{2}$  and  $3^2P_{3/2}$ ,  $m_J = -\frac{3}{2}$ . Since  ${}^6\text{Li}$  has nuclear spin 1, each level is split into three states that cross with each other. However, as it has been mentioned in Sec. II.D, at a point where two states with the same  $m_F$  value ( $-\frac{1}{2}$  in this case) should cross, we have instead an anticrossing. Owing to the small interaction between them, the two levels repel each other, and in this area the two wavefunctions change very rapidly, the general behavior of the two levels remaining unchanged when their energy separations is larger than the interaction between them. The phenomenon was first described (and christened) by Eck *et al.* (1963), and while some preliminary comments on its meaning were first given by Series (1963, 1964), Lassila (1964), and Eck (1967), a complete interpretation of it was given by Wieder and Eck (1967). It turns out that, in addition to a term that is analogous to the level-crossing case (due to the proximity of the two levels) there are other terms that are related to the coherence in only the excitation or the detection part of the experiment, and a term (the "pure anticrossing" signal) that does not require coherence and vanishes when the interaction between the crossing states is zero.

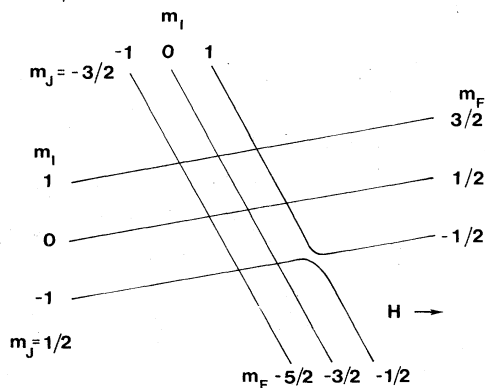


FIG. 18. A very "enlarged" view of the 915 G anticrossing in  ${}^6\text{Li}$ . The two states with the same value of  $m_F$  ( $-\frac{1}{2}$ ) cannot cross and repel each other.

This analysis has two important consequences: first, the shape of the resonance curve is different from the normal level-crossing case; and, second and most important, it is possible to observe anticrossings in cascade, because coherence in the intermediate state is not essential. This cascade anticrossing effect has been observed by Liao *et al.* (1974) and used to investigate the hfs in the  $4^2D$  term of rubidium.

As pointed out by Khvostenko (1969), a similar anticrossing effect can be observed in the presence of an electric field that couples the crossing states. Measurements of this kind have been performed on cesium (Khvostenko *et al.*, 1974).

## H. Quantum beats

### 1. Normal states

In the quantum beats spectroscopy the atomic states to be investigated are coherently excited by an optical pulse; and the fluorescent light following the excitation of the atom is examined. The emitted light presents the spontaneous decay damping and an amplitude modulation at the frequencies of the energy separations in the excited state. This phenomenon is a direct consequence of the fact that each level coherently excited has a different time evolution. The phenomenon was studied originally for Zeeman structures by means of conventional light sources, but has been developed as a powerful tool with the advent of tunable lasers as a light source with short pulses and high power. In the experiments the duration of the optical pulse is short compared with the excited state lifetime and with the modulation periods, in order to instantaneously excite the atoms. A degradation of the amplitude modulation occurs if the coherent excitation is not uniformly distributed over the excited levels. Thus an exciting light spectrum broad compared with the hyperfine separation is required, but such a condition is satisfied by the applied short optical pulses. With these assumptions and ignoring the stimulated emission, the expression for the time-dependent emitted light intensity results

$$I(t) = k \sum_{a,c} \frac{\langle c | \mathcal{J}_z^+ | b_1 \rangle \langle c | \mathcal{J}_z^+ | b_2 \rangle^* \langle b_1 | \mathcal{J}_z | a \rangle \langle b_2 | \mathcal{J}_z | a \rangle^*}{\Gamma_{12} - iE_{12}} \times \exp[(iE_{12} - \Gamma_{12})t/\hbar],$$

with  $k$  a constant,  $|a\rangle$  and  $|c\rangle$  the ground-state levels,  $|b_1\rangle$  and  $|b_2\rangle$  the investigated excited levels, and all other notations as defined in Sec. III.G.1. The nonuniformity of the exciting light spectrum and the finite duration of the optical pulse have been considered by Deech *et al.* (1974). There is a close analogy between the expression (3.5) for the coherent part of the fluorescent light in a level-crossing experiment and the above expression for the light intensity in the quantum beats, apart from the time dependence with the excited state lifetime and the Bohr-frequency modulations. In effect both phenomena rely on the coherent excitation from lower levels to a set of excited states to be investigated.

In the first application to alkali atoms the hfs in the  $7^2P_{3/2}$  state of  ${}^{133}\text{Cs}$  has been investigated by Haroche *et al.* (1973). More recently the 8, 9, and  $10^2D_{3/2}$  states of  ${}^{133}\text{Cs}$  have been investigated by stepwise excitation

(Deech *et al.*, 1975). A conventional cesium lamp has been used for the first step from the ground state to the  $6^2P$  term and a pulsed laser for the second step. In this experiment the fluorescent light was observed through an analyzer. It was observed that the intensity of the modulation depends upon the relative orientation of the analyzer with reference to the direction of the electric vector of the incident light, and for an angle of  $54^\circ$  the modulation is suppressed. A more recent experiment has been reported by Schenck and Pilloff (1975a, b) to investigate the hfs in the  $4^2D$  levels of  $^{23}\text{Na}$ . After step-wise excitation by two tunable lasers, the fluorescence emitted after two or three lifetimes has been detected. Thus the small dipolar hfs of the  $4^2D_{3/2}$  level was resolved [ $|A| = 0.507(68)$  MHz].

The accuracy in the quantum beats measurements of the hfs performed up to the present time is limited to about one percent, comparable or superior to what can be obtained in the level-crossing experiments on the same states. Very large splittings cannot be resolved because they require too short optical pulses. Such an investigational technique is a good and reliable method to investigate hfs in the highly excited states. The main advantage of this type of investigation is that the atomic spectrum is detected in the absence of any external electromagnetic fields.

## 2. Beam-foil spectroscopy

The application of heavy ion accelerators in the MeV range to the study of atomic structure was first proposed, independently, by Kay (1963) and by Bashkin (1964). It basically consists in accelerating ions to relativistic velocities and then (sometime after recombination into neutral atoms) letting them impinge on a thin solid foil, thus exciting them to highly excited states or ionizing them further. The observation of the light emitted after the excitation can give information on such excited states. In particular, since the excitation occurs in a very short time, quantum beats occur, thus giving information on the spacing of nearby levels. This technique is suited to the study of ionic states or highly excited states of atoms with a high ionization potential: Thus this technique is not convenient for studying the hfs of neutral alkali atoms, except in autoionizing states. A recent review of the method, including a discussion of the problems connected with hfs measurements, has been published by Martinson and Gaupp (1974). More detailed descriptions of quantum-beats effects in beam-foil spectroscopy can be found in the works of Bashkin (1971) and Andr a (1975). So far, the only application of this technique to hfs measurements of neutral alkali atoms has been carried out by Gaupp *et al.* (1976).

### 1. Doppler-free laser spectroscopy

#### 1. Saturated absorption spectroscopy

One of the first applications of the frequency selectivity of lasers to high resolution spectroscopy was based on the saturated absorption spectroscopy. This method has been applied by H ansch *et al.* in 1971 to investigate the hfs in the  $D$  lines of sodium. Two laser beams at the same frequency propagate in opposite di-

rections through an absorption cell containing Na vapor. The first beam, more intense (about 50 mW), saturates the transition line for a bunch of atoms with velocity component  $v$  along the propagation direction of the light. The weaker second beam (about 0.5 mW) probes the atoms with a velocity component  $-v$ . When the laser frequency is tuned over the Doppler line, the second beam probes atoms saturated by the first one only if  $v$  is zero. This appears as a change in the absorption of the probe beam. As only the atoms with zero velocity component along the light propagation direction are detected, the Doppler effect is nearly eliminated, and the width of the saturated absorption peak is determined by the natural linewidth. The 40 MHz line broadening observed by H ansch *et al.* (1971) for the  $D_1$  line has been ascribed to the laser bandwidth and the residual Doppler broadening by the finite crossing angle of the two beams. In that experiment only the  $D_1$  line hfs was resolved.

Reviews of the saturated absorption technique can be found in the works of Bord e and Hall (1974) and H ansch (1973). Other Doppler-free laser spectroscopy techniques, closely related to saturated absorption, have been proposed by Bord e *et al.* (1973) and by Wieman and H ansch (1976). However, they have not been used in the hfs investigations of interest in this work.

#### 2. Two-photon spectroscopy

The excited  $S$  and  $D$  states of the alkali atoms cannot be attained by an electric dipole optical transition from the ground state with absorption of one photon. The selection rule  $\Delta l = 0, \pm 2$  may be satisfied instead by the contemporary absorption of two photons. Transitions involving several quanta of the electromagnetic field were considered theoretically for the first time by G oppert-Mayer in 1931. The absorption of two photons has a transition probability that depends on the square of the light intensity. The probability of this process is greatly enhanced by the presence of a quasisonant intermediate level, as it depends inversely on the mismatch between the virtual intermediate level and the real ones.

It has been only recently with the development of lasers that enough power has been available in a narrow band of frequencies to allow the detection of many-quantum transitions on atomic vapors. The first experiment of two-photon spectroscopy was carried out by Abella in 1962 with a ruby laser on the  $6^2S_{1/2} - 9^2D_{3/2}$  transition in Cs, matching the laser over the 6935.5   wavelength by thermal tuning of the ruby line. The appearance of the tunable dye lasers has produced significant development in the two-photon investigations. In the meantime an experimental technique has been developed to eliminate the Doppler broadening of the optical two-photon transitions, without a loss in the number of the atoms participating to the absorption. The basic idea of this method, first proposed by Vasilenko *et al.* (1970) and developed by Cagnac *et al.* (1973), is presented in Fig. 19. The absorbing atomic system is irradiated by two laser beams of angular frequency  $\omega$ , propagating in opposite directions and tuned in resonance with the frequency  $\omega_{eg} = (E_e - E_g)/2\hbar$  to produce a two-photon transition between the ground state of energy  $E_g$  and an excited state with energy  $E_e$ . Let  $v$  be the velocity com-

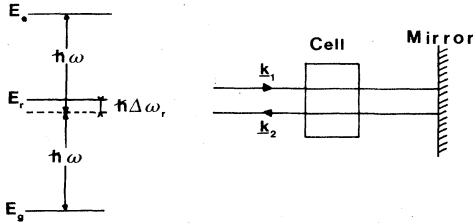


FIG. 19. Schematic energy diagram and experimental arrangement for the two-photon spectroscopy experiments.

ponent of an absorbing atom along the propagation direction of the lasers and let  $\hbar\mathbf{k}_1$  and  $\hbar\mathbf{k}_2$  denote the momenta of the photons in the two counter-propagating beams. The total momentum transferred from the electromagnetic field to the absorbing system in each transition is zero:

$$\hbar \sum_i \mathbf{k}_i = 0.$$

When relativistic terms in  $v^2/c^2$  are neglected in the energy balance, the recoil energy is zero whatever the velocity  $v$  may be and the energy of the photons is entirely utilized as a change in the internal energy of the absorbing atom. Thus all the atoms have the resonance for  $\omega = \omega_{eg}$ . From the point of view of the reference frame of the atom, the photons of the two lasers have frequencies  $\omega(1 - v/c)$  and  $\omega(1 + v/c)$ , and the resonance condition is

$$E_e - E_g = 2\hbar\omega_{eg} = \hbar\omega \left(1 - \frac{v}{c}\right) + \hbar\omega \left(1 + \frac{v}{c}\right) = 2\hbar\omega$$

whatever the velocity  $v$  may be.

The transition probability for a two-photon absorption has been derived by Cagnac *et al.* (1973) in a second-order perturbation treatment. If  $\mathcal{H}_1$  and  $\mathcal{H}_2$  are the Hamiltonians for the interaction with photons of the first and second laser beams,  $\delta\omega$  is the frequency distance from the resonance condition, and  $\Gamma_e$  the spontaneous decay rate for the excited state, the transition probability for absorption of one photon from each beam is given by

$$P_{12}(\delta\omega) = \left| \sum_r \frac{\langle e|\mathcal{H}_1|r\rangle\langle r|\mathcal{H}_2|g\rangle + \langle e|\mathcal{H}_2|r\rangle\langle r|\mathcal{H}_1|g\rangle}{\Delta\omega_r} \right|^2 \times \frac{\Gamma_e}{4\delta\omega^2 + \Gamma_e^2/4}. \quad (3.7)$$

The sum is extended over all the intermediate levels with energy  $E_r$  and frequency mismatch  $\Delta\omega_r = \omega - (E_r - E_g)/\hbar$ . The probability for a transition with absorption of two photons from a single beam is given by

$$P_{ii}(\delta\omega) = \left| \sum_r \frac{\langle e|\mathcal{H}_i|r\rangle\langle r|\mathcal{H}_i|g\rangle}{\Delta\omega_r} \right|^2 \frac{\Gamma_e}{4(\delta\omega \pm kv)^2 + \Gamma_e^2/4}, \quad i=1, 2, \quad (3.8)$$

with  $k$  the momentum of the photon.

Because of the Doppler broadening  $P_{11}$  and  $P_{22}$  have a Gaussian profile while  $P_{12}$  conserves a Lorentzian shape with a linewidth  $\Gamma_e/2$ . For equal optical intensities in

the two beams the maximum value of  $P_{12}$  is four times larger than the maximum value of  $P_{11}$  or  $P_{22}$ . The two-photon resonance line without Doppler broadening is represented by a high and narrow Lorentzian line over a weak and broad band absorption. If the polarizations of the two counter-propagating beams are chosen in such a way that  $\langle e|\mathcal{H}_1|r\rangle$  and  $\langle r|\mathcal{H}_2|g\rangle$  both equal zero, the Doppler broadened profile is eliminated as the two-photon transition may occur only by the absorption of one photon from each light beam.

The first applications of this method were reported in 1974: Pritchard *et al.* (1974) have investigated the fine structure in the  $4D$  term of sodium; Biraben *et al.* (1974a) and Levenson and Bloembergen (1974b) have measured the hyperfine structure in the transition  $3^2S_{1/2} - 5^2S_{1/2}$  of sodium. Levenson and Salour (1974a) have investigated the transition  $3^2S_{1/2} - 6^2S_{1/2}$ . After these experiments with pulsed tunable dye lasers, a better signal-to-noise ratio was obtained utilizing a continuous dye laser, as by Biraben *et al.* (1974b) for the  $3^2S_{1/2} - 5^2S_{1/2}$  transition in Na. All these experiments have been performed on sodium atoms because the intermediate  $3^2P$  level has a very small frequency mismatch  $\Delta\omega_r/\omega \sim 1/50$ , the first transition  $3^2S - 3^2P$  has an oscillator strength near unity, and because the wavelengths for these two-photon experiments in sodium lie in the spectral region of the best efficiency for the Rhodamine 6G dye. A complete description of the different investigations with Doppler-free two-photon spectroscopy has been given by Cagnac (1975a, b). Let us mention here the experiment of Hänsch *et al.* (1975) on the  $1^2S_{1/2} - 2^2S_{1/2}$  transition in hydrogen without near-resonance intermediate states and where the frequency for the two-photon transition was in the ultraviolet (2430.7 Å). Other experiments have been performed on neon (Biraben *et al.*, 1975), on potassium highly excited  $S$  and  $D$  states (Levenson *et al.*, 1975) and on rubidium  $D$  states with principal quantum number from 11 to 30 (Kato and Stoicheff 1975, 1976).

In Fig. 20 the experimental apparatus for the investigation of the two-photon  $3^2S_{1/2} - 5^2S_{1/2}$  in sodium is schematized. The beam from the dye laser is focused in the absorption cell and the transmitted light is refocused in the cell by a spherical mirror. The small diameter of the focalization spots inside the cell, less than 0.1 mm, requires a careful alignment of the reflecting mirror. To prevent the reflected beam from returning to the laser cavity, an optical isolator based on the Faraday effect is sometimes used (Cagnac, 1975a). The detection of the two-photon transition is based on the collection of photons emitted in the spontaneous decay at a wavelength different from the laser excitation.

The main sources of errors are: (a) the width of the two-photon peaks because of the jitter in the laser and (b) the nonlinearity in the sweep of the laser frequency. The total error in this type of experiment amounts to about 6–7%.

A phenomenon intrinsic to the two-photon absorption is the presence of light shifts, because of virtual transitions from both the ground  $|g\rangle$  and excited  $|e\rangle$  levels to the intermediate  $|r\rangle$  states. Large light shifts have been observed by Liao and Bjorkholm (1975) on the two-photon transitions from the  $3S$  to the  $4D$  states of

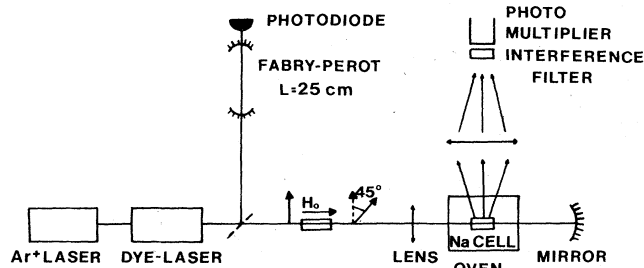


FIG. 20. Experimental apparatus for the investigation of two-photon absorption in the  $3^2S_{1/2} - 5^2S_{1/2}$  transition in sodium (from Cagnac, 1975a).

sodium. In this experiment the absorption occurred by photons of two different laser beams, the first laser tuned near resonance with the  $3S-3P$  transition, the second one near resonance with the  $3P-4D$  transition. Broadening and asymmetry of the absorption line have been observed in that experiment: the different atomic velocity groups experience different level shifts since the light beams have a different frequency in the reference frame of each velocity group. The light shifts in two-photon spectroscopy have been discussed by Cagnac *et al.* (1973), Kelley *et al.* (1974), and Bjorkholm and Liao (1975). The broadening phenomenon has been considered by Bjorkholm and Liao (1974), while the effect of a resonant intermediate state in the Doppler-free two-photon transitions has been theoretically investigated by Salomaa and Stenholm (1975). It has been observed by Cagnac (1975a) that in the experiments with two identical counterpropagating beams (same intensity and frequency) if the matrix elements  $\langle g|\mathcal{H}_1|r\rangle$  and  $\langle r|\mathcal{H}_2|e\rangle$  are of the same order of magnitude, the light shifts are inferior to the present overall accuracy of the method.

In Fig. 21 a typical result of a two-photon absorption in the  $3S-5S$  transition in sodium (Cagnac, 1975a) is reported. For the transition between S states the selec-

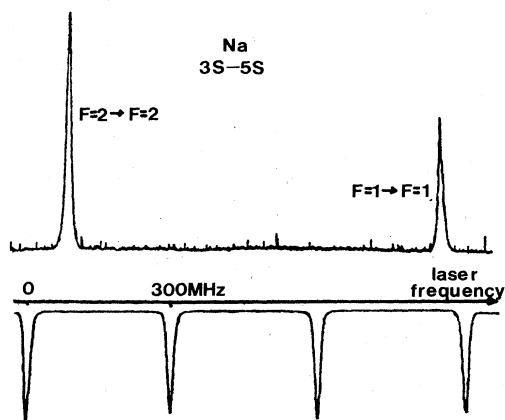


FIG. 21. Signal observed in the two-photon absorption on the  $3^2S_{1/2} - 5^2S_{1/2}$  transition in sodium. The photomultiplier output is plotted versus the laser frequency, whereas in the lower part the signal of the Fabry-Perot interferometer allows to determine the frequency scale (from Cagnac, 1975a).

tion rules are  $\Delta F=0, \Delta m_F=0$ , whence only two resonance lines are observed and the Doppler broadened background is eliminated by using two circularly polarized light beams. The accuracy of this experiment is comparable to that obtained by Duong *et al.* (1974a) using laser two-step excitation on an atomic beam.

## IV. GYROMAGNETIC FACTORS

### A. $g_J$ values (direct measurements)

Since the value of  $g_J$  is important in obtaining  $A$  and  $B$  values from level-crossing experiments and from strong-field double-resonance experiments, and conversely it is possible to get information on  $g_J$  from the comparison between low-field double-resonance and level-crossing experiments, in this section we shall shortly review the existing  $g_J$  values. Only the most accurate measurements will be considered.

#### 1. Ground states

Many atomic beam experiments give ratios of  $g_J$  values related to different atoms or isotopes. Since the best known of these ratios involve Rb, the absolute values involve the knowledge of  $g_J(\text{Rb})/g(e)$ . The ratio  $g_J(^{85}\text{Rb})/g_J(^{87}\text{Rb})$  has been found to differ from 1 by less than a few ppb (White *et al.*, 1968). The best available value of  $g(e)$  is that obtained by Wesley and Rich (1971):  $g(e)=2.002\,319\,315\,4(70)$ . This experiment has been re-analyzed by Granger and Ford (1972), together with the work by Wilkinson and Crane (1963), obtaining a final value of  $2.002\,319\,313\,4(70)$ . This value is recommended by Cohen and Taylor (1973). Using the latter value, one can list the following  $g_J$  values:

*Rubidium*: Since  $g_J(\text{Rb})/g(e)=1.000\,005\,90(10)$  (Tiedemann and Robinson, 1972), we have  $g_J(\text{Rb})=2.002\,331\,13(20)$ .

*Cesium*: White *et al.* (1973) give  $g_J(\text{Cs})/g_J(\text{Rb})=1.000\,104\,473\,7(44)$ . Therefore  $g_J(\text{Cs})=2.002\,540\,32(20)$ .

*Potassium*: From  $g_J(\text{Rb})/g_J(\text{K})=1.000\,018\,44(5)$  (Beahn and Bedard, 1972) we get  $g_J(\text{K})=2.002\,294\,21(24)$ .

*Lithium*: Böklen *et al.* (1967) measured  $g_J(\text{Li})/g_J(\text{K})=1.000\,003\,4(3)$ ; therefore  $g_J(\text{Li})=2.002\,301\,0(7)$ .

*Sodium*: There are two measurements of  $g_J(\text{Na})/g_J(\text{K})$  of comparable precision and reliability, by Böklen *et al.* (1967) and Vanden Bout *et al.* (1968) whose weighted average is  $1.000\,000\,9(4)$ . Therefore  $g_J(\text{Na})=2.002\,296\,0(7)$ .

#### 2. Excited states

The methods used for directly measuring the  $g_J$  factor in excited states are only those of double resonance and optical spectroscopy. The indirect method of comparing double-resonance and level-crossing results will be considered later. The most recent and accurate direct measurements are listed in Table I. When the original data are referred to the individual isotopes of the same atom, only an average of them is given here. It is worth noting that in one case only (i.e., the auto-ionizing  $^1F_{3/2}$  state of K) is the experimental value not coincident with the Russel-Saunders value within the stated errors.

TABLE I. Direct measurements of the electronic gyromagnetic factors in the excited states. All states are doublet states unless otherwise indicated.

Atom	State	$g_J$	Reference	
Li	$2P_{1/2}$	0.6668(20)	Ritter, 1965	
	$2P_{3/2}$	1.335(10)	Ritter, 1965	
Na	$3P_{1/2}$	0.66581(12)	Hartmann, 1970a	
	$3P_{3/2}$	1.3344(4)	Ackermann, 1967	
		1.3341(3)	Dodd <i>et al.</i> , 1960	
K	$5P_{3/2}$	1.34(2)	Ritter <i>et al.</i> , 1957	
	$5D_{3/2}$	0.7997(7)	Belin <i>et al.</i> , 1975a	
	$5D_{5/2}$	1.2004(10)	Belin <i>et al.</i> , 1975a	
	$6P_{1/2}$	0.6663(4)	Belin <i>et al.</i> , 1975a	
	$6P_{3/2}$	1.3337(8)	Belin <i>et al.</i> , 1975a	
	$6D_{3/2}$	0.7999(14)	Belin <i>et al.</i> , 1975a	
	$6D_{5/2}$	1.2013(20)	Belin <i>et al.</i> , 1975a	
	$7S_{1/2}$	2.0020(10)	Belin <i>et al.</i> , 1975a	
	$7P_{1/2}$	0.6659(6)	Belin <i>et al.</i> , 1975a	
	$7P_{3/2}$	1.3336(8)	Belin <i>et al.</i> , 1975a	
	$8S_{1/2}$	2.0028(12)	Belin <i>et al.</i> , 1975a	
	$3p^5 4s4d \ ^4D_{7/2}$	1.42945(13)	Sprott <i>et al.</i> , 1968	
	$3p^5 4s3d \ ^4F_{9/2}$	1.33395(7)	Sprott <i>et al.</i> , 1968	
	Rb	$6P_{1/2}$	0.6659(3)	Feiertag <i>et al.</i> , 1973
			0.671(20)	Anisimova <i>et al.</i> , 1968
$6P_{3/2}$			1.334(1)	Schüssler, 1965
			1.337(4)	Anisimova <i>et al.</i> , 1968
		1.3337(10)	Feiertag <i>et al.</i> , 1973	
$7P_{1/2}$		0.6655(5)	Feiertag <i>et al.</i> , 1973	
$8D_{5/2}$		1.1998(15)	Belin <i>et al.</i> , 1976a	
$9P_{3/2}$		1.3335(15)	Belin <i>et al.</i> , 1974a	
$9D_{5/2}$		1.1995(15)	Belin <i>et al.</i> , 1976a	
$10P_{3/2}$		1.3332(20)	Belin <i>et al.</i> , 1976a	
Cs	$6P_{1/2}$	0.66590(9)	Abele, 1975a	
	$6P_{3/2}$	1.3340(3)	Abele <i>et al.</i> , 1975a,c	
	$7P_{1/2}$	0.667(1)	Feiertag <i>et al.</i> , 1972	
	$7P_{3/2}$	1.33410(15)	Baumann <i>et al.</i> , 1972	
	$8P_{3/2}$	1.3342(2)	Abele <i>et al.</i> , 1975a,c	
	$11P_{3/2}$	1.3337(10)	Belin <i>et al.</i> , 1974a	
	$11D_{5/2}$	1.1994(10)	Svanberg <i>et al.</i> , 1974	
	$12P_{3/2}$	1.3340(15)	Belin <i>et al.</i> , 1974a	
	$12D_{3/2}$	0.8001(10)	Svanberg <i>et al.</i> , 1974	
	$12D_{5/2}$	1.1996(10)	Svanberg <i>et al.</i> , 1974	
	$13P_{3/2}$	1.3337(20)	Belin <i>et al.</i> , 1976b	
	$13D_{5/2}$	1.1998(10)	Svanberg <i>et al.</i> , 1974	

## B. Nuclear $g$ factors

Nuclear gyromagnetic factors are useful since they are a measure of the nuclear magnetic moment, thus entering in the definition of the coupling constant  $A$ , and since they are needed in the interpretation of high precision experiments using an external magnetic field, as level-crossing, double-resonance or ABMR experiments. Beckmann *et al.* (1974) have accurately measured  $g_I/g_J$  in the ground state of Li, Na, K (except  $^{40}\text{K}$ ). For rubidium there are measurements by White *et al.* (1968), for cesium by White *et al.* (1973). For  $^{40}\text{K}$  Eisinger *et al.* (1952) have measured  $g_I(^{40}\text{K})/g_I(^{39}\text{K})$ . From these ratios and the given values of the electronic  $g_J$  factors, one can obtain the values listed in Table II.

## C. $g_J$ values from level-crossing experiments

When the zero-field hyperfine frequencies are known from low-field double-resonance experiments, and

TABLE II. Nuclear gyromagnetic ratios of the alkali isotopes.

Isotope	$g_I$
$^6\text{Li}$	-0.0004476540(3)
$^7\text{Li}$	-0.0011822130(6)
$^{23}\text{Na}$	-0.0008046108(8)
$^{39}\text{K}$	-0.00014193489(12)
$^{40}\text{K}$	+0.000176490(34)
$^{41}\text{K}$	-0.00007790600(8)
$^{85}\text{Rb}$	-0.0002936400(6)
$^{87}\text{Rb}$	-0.0009951414(10)
$^{133}\text{Cs}$	-0.00039885395(52)

level-crossing experiments are available quoting the level-crossing positions (and not just the resulting  $A$  and  $B$  values) it is possible with standard techniques (e.g., Violino, 1970, 1972) to obtain the  $g_J$  value by a comparison of the two data sets. Such "indirect" estimates are generally less accurate than direct measurements, but they are useful when no direct measurement exists.

We have therefore computed the  $g_J$  value for all states where zero-field hfs and the level-crossing positions are known. A weighted average has been computed when several such measurements exist. All such results are summarized in Table III. The values thus obtained for Na and Cs agree both with the theoretical value and with the direct measurements. For Rb, there are direct measurements only for the  $6P_{3/2}$  level, where the agreement is not very good. The other values thus obtained for Rb are in significant disagreement with the theoretical values. In both cases the level-crossing data have been taken from a work by Belin and Svanberg (1971), whereas the hfs data are taken from Schüssler (1965) (corrected for rf shift) and Bucka *et al.* (1968), respectively, for the  $5P_{3/2}$  and  $7P_{3/2}$  levels. We feel that a further set of measurements on these levels would be highly desirable.

## V. REVIEW OF THE EXISTING EXPERIMENTAL DATA

### A. General remarks

In this section we list and briefly discuss, state by state, the relevant hfs experimental data for the stable isotopes of the alkali elements. We have not taken into account the older and definitely less accurate measurements that can be found in other compilations (e.g., Fuller and Cohen, 1969). For all states where there are several measurements, we mention here the techniques and the results of each of them; and we discuss

TABLE III.  $g_J$  values from double-resonance and level-crossing experiments.

Atom	State	$g_J$
Na	$3P_{3/2}$	1.354(92)
Rb	$5P_{3/2}$	1.3362(13)
Rb	$6P_{3/2}$	1.3353(12)
Rb	$7P_{3/2}$	1.3365(16)
Cs	$6P_{3/2}$	1.3362(50)
Cs	$7P_{3/2}$	1.3340(9)
Cs	$8P_{3/2}$	1.331(7)

the agreement or the causes of disagreement. Sometimes some results have been corrected, either for instrumental shifts that had not been taken into account by the authors, or by using more recent values of fundamental constants. A set of recommended values will be found in Sec. VI. The experimental errors are quoted in parenthesis and refer to the last digits; they are normalized to one standard deviation wherever possible. The states are listed in the following order for each isotope: first the normal states (they are all doublet states and the label "doublet" is omitted), then the anomalous autoionizing states; within each group, first those with the lowest value of the principal quantum number; among them those with the lowest  $L$  value; among them that with the lower  $j$  value. Information on off-diagonal coupling constants, when available, is listed after the last state of the term to which they refer. We have not attempted to evaluate the nuclear quadrupole moment from the  $B$  values. Nevertheless, when the authors of the cited experiments give also  $Q$  values (or the experimental values have been later re-analyzed) the most recent of them are reported. The values of  $Q$  are expressed in millibarns ( $1 \text{ mb} = 10^{-31} \text{ m}^2$ ). We also do not list values of the contributions of coupling constants of the single terms of the Hamiltonian, e.g., of contact, dipolar and orbital terms. In fact, these are not experimental values, but rather they arise from a theoretical interpretation of the experimental data and we prefer—as we stated in Sec. I—to leave this job to the theoreticians. We list contact and orbital terms only in the case of a few autoionizing terms, where no direct measurement of  $A$  and  $B$  are available.

As discussed in Sec. III, only a few experimental techniques allow a direct determination of the sign of the coupling constants, essentially only optical spectroscopy and cascade decoupling. When there are no measurements with such techniques, some information on the sign can be obtained indirectly. With level-crossing or double resonance experiments, if one observes three (or more) well-resolved crossings or resonances, the attribution of them to the proper quantum numbers is very easy since only one attribution gives a reasonable confidence in the  $\chi^2$  test. The relative sign of  $A$  and  $B$  can thus be determined leaving uncertainty only in one sign (for example, one can ascertain that either  $A$  and  $B$  are both positive or both negative, but one can rule out that  $A$  is positive and  $B$  negative). In addition, if one has information on the sign of the constants for the same state in another isotope of the same atom, or in a state of the same isotope with higher and lower principal quantum number, or of the individual contact, dipolar and orbital parts of states in the same multiplet, one can—using the known relations existing among such parameters—find out the sign of either  $A$  or  $B$ , and thus (if a resolved level-crossing or double-resonance experiment exists) of both; even though such relations are only approximate, they are quite sufficient to find out the sign. In practice, we can safely state that the sign can be determined with certainty in all  $S$  and  $P$  states. Owing to the smaller amount of information available, the case of  $D$  and  $F$  states is sometimes still open, and we have thus reported the

sign only when a direct measurement of it exists. In some cases, however, the indirect considerations mentioned above can already suggest the sign in the case of  $D$  states too, as we shall briefly discuss in Sec. VII. We have omitted here all states where a single measurement of the coupling constants exists, without additional information and without a need for emphasizing the technical details of the experiment. All such results will be listed in Sec. VI.

We cannot refrain here from mentioning that many experimental works would be more useful, and the work of the reviewers would be a lot easier, if the authors would conform—in writing their papers—to the recommendations of many authorities on the subject of data presentation (e.g., Eisenhart, 1968, or CODATA, 1974). It sometimes happens that only the final values issuing from the data reduction process are listed, without a detailed indication of the experimental and theoretical elements that have led to the determination of the final values and the listed errors. In this way a lot of useful information gets lost. In many cases we have attempted to extract the missing information from various sources (like the intensity of the radio frequency field from the width of the resonances as can be seen in figures, or the value of  $g_J$  used in obtaining  $A$  and  $B$  in a level-crossing experiment from the crossing positions, and so on) but in a few cases we have been unable to explain some discrepancies.

## B. Lithium

It has two stable isotopes, of masses 6 and 7. Lithium 6 has nuclear spin 1, lithium 7 spin  $3/2$ . Working with lithium is a rather difficult job with most techniques owing to its extreme chemical reactivity with transparent materials at the temperatures where it has a reasonable vapor density (400–450 °C). For this reason some special techniques have been developed for building lamps and resonance cells (for instance by Minguzzi *et al.*, 1966, 1969, and by Slabinski and Smith, 1971), and the amount of experimental data is not as large as it is for other elements.

### 1. ${}^6\text{Li}$

$2S_{1/2}$  (ground state). The most recent and accurate measurements with the atomic beam magnetic resonance method are those of Schlecht and McColm (1966), Huq *et al.* (1973), and Beckmann *et al.* (1974), yielding for the separation between the  $F=1/2^-$  and  $F=3/2^-$  states values of 228.205 28(8), 228.205 261(3), and 228.205 259(3) MHz respectively, with a very good consistency. There are also measurements with an optical pumping technique (Balling *et al.*, 1969; Wright *et al.*, 1969) where the difficulty of obtaining an intense source of lithium resonance light has been overcome by pumping lithium by spin exchange with optically pumped rubidium. The value of the hyperfine separation obtained with this technique is 228.205 261(12) MHz, in very good agreement with the ABMR measurements.

$2P_{1/2}$ . There are two double-resonance measurements in atomic beams by Ritter (1965) and Orth *et al.* (1974). Ritter compares the results with  ${}^6\text{Li}$  with those with  ${}^7\text{Li}$  using the known ratio of the nuclear



gyromagnetic factors and obtains  $A = 17.48(15)$  MHz. Orth *et al.* (1974) use a strong field and obtain  $A = 17.375(18)$  MHz. The agreement is satisfactory.

$2P_{3/2}$ . There is only an atomic-beam double-resonance measurement by Orth *et al.* (1974) yielding  $A = -1.155(8)$ ;  $B = -0.010(14)$  MHz. The off-diagonal constant  $A_{3/2,1/2}$  has been evaluated by the same authors to be  $4.72(33)$  MHz.

$3P_{3/2}$ . There is a fine-structure level-crossing experiment by Isler *et al.* (1969a); by considering the distance between the crossing points they estimate  $A = -0.40(2)$  MHz.

$1s2s2p^4P^o$ . Feldman *et al.* (1968) have investigated this autoionizing multiplet with the Zeeman quenching technique. For the dipolar interaction they use a theoretical value and obtain  $a_c = 65.16(21)$  mK =  $1953.4(63)$  MHz for the Fermi contact constant.

$1s2p^2^4P$ . Gaupp *et al.* (1976) have used the observation of quantum beats after beam-foil excitation in order to study the fine and hyperfine structure of this multiplet. They use nonantisymmetrized wavefunctions and neglect all quadrupole interaction, assuming that the ratio of the Fermi contact interactions scales in the two lithium isotopes in the same way as the nuclear gyromagnetic ratios. In separating the contribution to the overall hyperfine structure for each electronic orbital, they obtain  $a_c = 5.58(9)$  GHz for the  $1s$  electron (a value that is rather larger than the fine structure between the  $J = 5/2$  and  $J = 1/2$  levels). For the  $p$  electrons  $a_o = 23(16)$  MHz and  $a_d = 0$  within experimental accuracy. The signs are obtained by the interpretation by Levitt and Feldmann (1969) of the optical results of Herzberg and Moore (1959).

## 2. $^7\text{Li}$

$2S_{1/2}$  (ground state). There are ABMR measurements by Schlecht and McColm (1966) and Beckmann *et al.* (1974) yielding a separation between the levels with  $F = 1$  and  $F = 2$  of  $803.504\,04(48)$  and  $803.504\,086\,6(10)$  MHz, respectively. Wright *et al.* (1969) have used the same technique described for  $^6\text{Li}$  obtaining  $803.504\,094(25)$  MHz. All measurements are in excellent agreement with each other.

$2P_{1/2}$ . Double-resonance investigations by Ritter (1965) and Orth *et al.* (1975) give, respectively,  $A = 46.17(35)$  and  $45.914(25)$  MHz. The slight disagreement is attributed by Orth *et al.* to a mixing in Ritter's experiment owing to the high field intensity that simulates a higher  $A_{1/2}$  parameter via the off-diagonal  $A_{1/2,3/2}$  parameter.

$2P_{3/2}$ . There is a level-crossing investigation by Brog *et al.* (1967) on the fine structure where some information is also obtained [using the data of Ritter (1965) on the  $2P_{1/2}$  state] on the hfs. Later Lyons and Das (1970) have given a new interpretation of this experiment with a set of results for  $A$  ranging between  $-3.24(13)$  and  $-3.03(13)$  MHz according to the approximations that are used in the computation. The value of  $B$  is  $-0.18(12)$  MHz. Di Lavore (1967) measured (again with a level-crossing technique)  $B$  directly obtaining  $-0.14(10)$  MHz. Recently Orth *et al.* (1975) have carried out a double-resonance experiment as in the case of the  $2P_{1/2}$  state, obtaining  $A = -3.055(14)$  and  $B$

$= -0.221(29)$  MHz. In the  $2P$  term, the off-diagonal constant  $A_{1/2,3/2}$  has been evaluated by Orth *et al.* (1975) either by using their experimental results and those of Brog *et al.* (1967), or by using the orbital, dipolar and contact constants computed by Lyons and Das (1970) by means of the experimental results of Ritter (1965) and Brog *et al.* (1967). The values are, respectively,  $A_{1/2,3/2} = 11.823(81)$  and  $11.739(126)$  MHz. A discussion of the  $Q$  values can be found in Orth *et al.* (1975). They obtain  $Q = 41(6)$  mb both using  $\langle r^{-3} \rangle_a$  obtained theoretically by Garpman *et al.* (1975) or using  $\langle r^{-3} \rangle_o$  and  $\langle r^{-3} \rangle_d$  with the Sternheimer correction factor  $R = 0.1166$ .

$3P_{1/2}$ . There is a fine-structure level-crossing experiment by Budick *et al.* (1966). Observing from a comparison with the analysis carried out by Wieder (1964) for the  $2P$  term, that the ratio of the crossing positions in the  $2P$  and  $3P$  states is very closely equal to the ratio of the fine-structure intervals, they assume a positive  $A$  constant and use Ritter's (1965) value for the  $2P_{1/2}$  hfs to derive a scaled contact constant. The final result is  $A = 13.5(2)$  MHz.

$3P_{3/2}$ . Isler *et al.* (1969a) have carried out a low-field level-crossing experiment and succeeded in obtaining well-resolved crossings with a result of  $A = -0.965(20)$  and  $B = -0.019(22)$  MHz. Budick *et al.* (1966) obtain, as in the case of the  $3P_{1/2}$  state,  $A = -0.96(13)$  MHz.

$4P_{3/2}$ . In a fine-structure level-crossing experiment, Isler *et al.* (1969a) estimate  $A$  to be  $-0.41(2)$  MHz.

$1s2s2p^4P^o$ . As for the same multiplet in  $^6\text{Li}$ ,  $a_c = 172.09(56)$  mK =  $5.159\,1(17)$  GHz.

$1s2p^2^4P$ . This state was investigated with optical spectroscopy by Herzberg and Moore (1959) and their data analyzed by Levitt and Feldman (1969). More recently Gaupp *et al.* (1976) studied it with the same technique as for the same state in  $^6\text{Li}$ . By handling together the data of  $^6\text{Li}$  and  $^7\text{Li}$ , they obtain  $a_c = 14.90(25)$  GHz;  $a_o = 60(40)$  MHz, and  $a_d = 0$  within experimental accuracy.

## C. Sodium

It has only one stable isotope of mass 23 and spin  $3/2$ .

$3S_{1/2}$  (ground state). The most recent ABMR measurements are those of Kusch and Taub (1949) [giving for the  $F = 1$  and  $F = 2$  separation a value of  $1771.61(3)$  MHz] and of Chan *et al.* (1970) and Beckmann *et al.* (1974) both giving  $1771.626\,128\,8(10)$  MHz. There are as well several measurements with optical pumping techniques, namely those of Arditì (1958c) [ $\Delta\nu = 1771.626\,20(10)$ ], Ramsey and Anderson (1965) [ $\Delta\nu = 1771.626\,15(25)$  MHz], and Martenson and Stigmark (1967) [ $\Delta\nu = 1771.626\,150(50)$  MHz]. Among these, the paper that seems to consider most carefully the hyperfine pressure shift is the one by Ramsey and Anderson (1965).

$3P_{1/2}$ . There is an ABMR experiment by Perl *et al.* (1955) with an exciting lamp in the C region giving  $A = 94.45(50)$  MHz. A more recent double resonance experiment in the strong field by Hartmann (1970a) yields  $A = 94.3(1)$  MHz, with a very good agreement between the two measurements.

$3P_{3/2}$ . There are many measurements which are summarized in Table IV. Among them, those quoting a

TABLE IV. Experimental values of  $A$  and  $B$  for the  $3^2P_{3/2}$  state of  $^{23}\text{Na}$ .

$A$ (MHz)	$B$ (MHz)	Method <sup>a</sup>	Reference
18.5(6)	2.25(40)	ODR	Dodd <i>et al.</i> , 1960
18.5(4)	3.0(6)	TRLC	Copley <i>et al.</i> , 1968
18.5(4.5)	3.2(5)	ODR	Baumann <i>et al.</i> , 1966
18.62(8)	3.04(19)	TRLC	Figger <i>et al.</i> , 1974
18.65(10)	2.82(30)	LC	Schönberner <i>et al.</i> , 1968
18.7(1)	3.0(2)	TRLC	Deech <i>et al.</i> , 1974
18.7(4)	3.4(4)	ODR	Ackermann, 1966, 1967
18.80(15)	2.9(3)	LC	Baumann, 1968, 1969
18.90(15)	2.40(15)	LC	Schmieder <i>et al.</i> , 1970
18.92(40)	2.4(4)	LC	Tudorache <i>et al.</i> , 1971b, 1974
19.06(36)	2.58(30)	ABMR	Perl <i>et al.</i> , 1955
19.1(4)	2.5(4)	LC	Baylis, 1967
19.5(6)	2.4(14)	ODR	Sagalyn <i>et al.</i> , 1954
19.74(5)	3.34(4)	LC	Mashinskii, 1970a

<sup>a</sup>In Tables IV through VIII the symbols have the following meaning: ABMR: atomic beam magnetic resonance with resonance light in the C region; LC: level crossing; ODR: optical double resonance; QB: quantum beats; TRLC: time resolved level crossing.

better accuracy are those by Baumann (1968), Deech *et al.* (1974), Figger and Walther (1974), Mashinskii (1970a), Schmieder *et al.* (1970), and Schönberner and Zimmermann (1968). Four of them (Baumann, Deech, Figger, Schönberner) exhibit an excellent agreement with each other, while the results of Schmieder *et al.* are still in acceptable agreement for  $A$  but not for  $B$ , and that of Mashinskii for  $A$  is in complete disagreement with all other five. It must be pointed out, however, that the error quoted by Mashinskii contains only the uncertainty in the field calibration, with no discussion of the other causes of error; and that later the same author (Mashinskii and Chaika, 1970b) measured one further level crossing whose position is in disagreement with his values quoted for  $A$  and  $B$ . It seems therefore that such results are not entirely reliable. On the contrary, we have no explanation for the discrepancy between the  $B$  values of Schmieder *et al.* on one side and those of Figger *et al.* and Deech *et al.* on the other. The discrepancy, however, is not very large (less than twice the sum of the standard deviations). In the level-crossing experiments, Schönberner *et al.* use  $g_J = 1.334$ , and Schmieder *et al.*,  $g_J = 4/3$ . A comment on the work of Perl *et al.* was made by Series (1967). The quadrupole moment has been derived by Garpman *et al.* (1975) from the experimental quadrupole coupling constant of Figger and Walther based on a theoretical value for  $\langle r^{-3} \rangle_e$  and based on the measured average of the orbital and spin-dipole  $\langle r^{-3} \rangle$  parameters using the Sternheimer's correction factor. The results are respectively 120(8) and 116(8) mb.

$4P_{3/2}$ . There are two level-crossing measurements by Schmieder *et al.* (1970) and Schönberner and Zimmermann (1968) yielding respectively for  $A$  6.2(1) and 6.006(30) MHz, and for  $B$  1.00(5) and 0.86(9) MHz. There is also a less accurate double-resonance experiment by Krüger and Scheffler (1958) yielding  $A = 6.2(12)$ ;  $B = 1.0(3)$  MHz. The agreement is good in all cases except between the  $B$  values of Schmieder and Schönberner, where it is nevertheless satisfactory. From the

quadrupole constant of Schönberner and Zimmermann, Sternheimer and Peierls (1971) obtain a corrected quadrupole moment  $Q = 100(11)$  mb, while Schmieder *et al.* give an average value obtained from the experimental data of the  $3P_{3/2}$  and  $4P_{3/2}$  states, without Sternheimer's correction,  $Q = 95(20)$  mb.

$4D_{5/2}$ . A preliminary investigation has been reported by Schenk and Pilloff (1975b); no value of  $A$  has yet been given.

$5S_{1/2}$ . There are two two-photon measurements by Biraben *et al.* (1974a) (with a cw laser) and by Levenson and Bloembergen (1974b) (with a pulsed laser) giving respectively  $A = 75(5)$  and  $78(5)$  MHz (Bloembergen *et al.*, 1974). There is also a two-step excitation (with two cw lasers passing through the  $3^2P_{1/2}$  level) optical measurement by Duong *et al.* (1974a) yielding  $\Delta\nu_{12} = 159(6)$  MHz, i.e.,  $A = 79.5(30)$  MHz. Tsekeris *et al.* (1976b) by means of optical double resonance after two-step excitation have obtained  $A = 77.6(2)$  MHz.

$5D_{5/2}$ . There is only an order-of-magnitude estimate by Archambault *et al.* (1960) with rf transition in the state that has been populated by electron excitation. The result is  $|A| < 0.33$  MHz.

## D. Potassium

It has three naturally occurring isotopes, of masses 39, 40, 41 and nuclear spins  $3/2, 4, 3/2$ .  $^{40}\text{K}$  is radioactive, but has a lifetime in excess of a billion years; its relative abundance is only 0.012%, and therefore there are not many measurements concerning it.

### 1. $^{39}\text{K}$

$4S_{1/2}$  (ground state). In the last 20 years there have been four ABMR measurements by McDermott and Gould (1959), Dahmen and Penselin (1967), Chan *et al.* (1970), and Beckmann *et al.* (1974). All of them are in excellent agreement with each other. The most accurate are the last two, giving, respectively,  $\Delta\nu = 461, 719\,720\,1(6)$  and  $461, 719\,720\,2(14)$  MHz. There is also an optical pumping measurement by Bloom and Carr (1960) giving  $\Delta\nu = 461, 719\,690(30)$  MHz, thus in agreement with the more accurate results using the ABMR method.

$4P_{3/2}$ . The existing data are summarized in Table V. All measurements are in reasonable agreement with each other. Those with the highest quoted accuracy are those of Ney (1969) and Schmieder *et al.* (1968b). Svanberg (1971) has derived the quadrupole moment using a quadrupole constant  $B = 2.77(10)$  MHz, on the basis of  $\langle 1/r^3 \rangle$  that is a mean value of the parameters derived

TABLE V. Experimental results for the  $4^2P_{3/2}$  state of  $^{39}\text{K}$ .

$A$ (MHz)	$B$ (MHz)	Method <sup>a</sup>	Reference
5.70(27)	2.8(8)	ABMR	Buck <i>et al.</i> , 1957
6.00(5)	2.9(1)	LC	Schmieder <i>et al.</i> , 1968
6.10(25)	1.8(12)	ABMR	Zimmermann, 1969
6.13(5)	2.72(12)	LC	Ney, 1969
6.16(15)	2.7(6)	ABMR	Boroske <i>et al.</i> , 1971
6.4(4)	3.0(12)	LC	Baylis, 1967

<sup>a</sup>The symbols have the same meaning as in Table IV.

from the hyperfine structures (corrected for core polarization) and the fine structures, and applying the appropriate Sternheimer correction factor (Sternheimer and Peierls, 1971). The result is  $Q = 58.8$  mb.

$5P_{1/2}$ . There are two double-resonance experiments by Ritter and Series (1957) and Fox and Series (1961) yielding  $A = 9.3(5)$  and  $8.99(15)$  MHz, respectively. The agreement is good.

$5P_{3/2}$ . There are three level-crossing measurements by Schmieder *et al.* (1968b), Ney (1969), Svanberg (1971) with the following respective results:  $A = 1.950(25)$ ;  $1.97(2)$ ;  $1.973(12)$  MHz;  $B = 0.92(5)$ ;  $0.85(3)$ ;  $0.870(18)$  MHz. The agreement between these experiments is good. The uncertainty quoted by Svanberg (1971) is three times the standard deviation plus allowance for systematic errors. There is also a double-resonance experiment by Ritter and Series (1957) quoting  $A = 1.97(10)$  and  $B = 1.54(15)$  MHz. The large discrepancy between the  $B$  value of this experiment and those of the level-crossing experiments has been attributed by Pegg (1969b) to an excessive intensity of the rf field. With appropriate corrections Pegg (1969b) gives the following values using the experimental data by Ritter and Series (1957):  $A = 1.97(10)$  and  $B = 0.9(2)$  MHz, in agreement with the level-crossing measurements. Svanberg (1971) has derived the quadrupole moment by the same procedure as in the  $4P_{3/2}$  state; with  $B = 0.866(15)$  MHz he has obtained  $Q = 59.6$  mb.

$6P_{3/2}$ . A level-crossing experiment has been carried out by Svanberg (1971) obtaining  $A = 0.886(8)$  and  $B = 0.370(15)$  MHz. The uncertainty is three times the standard deviation plus allowance for systematic errors. Later Belin *et al.* (1975a), with cascade after two-step excitation, have obtained  $A = 0.89(5)$  MHz and no information about  $B$ . The agreement is a check of consistency of the latter procedure. Svanberg (1971) has derived the quadrupole moment by the same procedure as in the  $4P_{3/2}$  state, obtaining  $Q = 57$  mb. A weighted average of the three determinations in the 4, 5, and  $6P_{3/2}$  states yields  $Q = 59(6)$  mb.

## 2. $^{40}\text{K}$

$4S_{1/2}$  (ground state). There are only ABMR measurements; the most recent are those by Zacharias (1942), Davis *et al.* (1949) and Eisinger *et al.* (1952) yielding respectively  $|\Delta\nu|$  ( $F = 7/2$ ;  $F = 9/2$ ) =  $1285.7(1)$ ;  $1285.73(5)$ ;  $1285.790(7)$  MHz. The agreement between the last two values is not very good, but is nevertheless acceptable.

$4P_{3/2}$ . There is a level-crossing measurement by Ney *et al.* (1968), yielding  $A = -7.59(6)$ ;  $B = -3.5(5)$  MHz. Sternheimer and Peierls (1971) have obtained with the appropriate correction factor  $Q = -81(12)$  mb.

$5P_{3/2}$ . Bucka (1962) has carried out a double-resonance experiment with the result:  $A = -2.450(46)$ ;  $B = -1.31(33)$  MHz. Later Ney *et al.* (1968) with a level-crossing experiment has obtained  $A = -2.45(2)$ ;  $B = -1.1(2)$  MHz. The agreement is very good. Sternheimer and Peierls (1971) have obtained from the value of Ney *et al.* a quadrupole moment  $Q = -79(14)$  mb. Svanberg (1971) reports that deriving the  $\langle 1/r^3 \rangle$  parameter as for the  $4^2P_{3/2}$  state of  $^{39}\text{K}$ , from the experimen-

tal results of Ney *et al.* the corrected and averaged quadrupole moment of  $^{40}\text{K}$  is found to be  $Q = -75(11)$  mb.

## 3. $^{41}\text{K}$

$4S_{1/2}$  (ground state). The most recent and accurate ABMR measurements are those by Chan *et al.* (1970) and Beckmann *et al.* (1974), giving  $\Delta\nu_{21} = 254.013\,870(1)$  and  $254.013\,872(2)$  MHz, respectively. In addition, there is an optical pumping experiment by Bloom and Carr (1960), giving  $\Delta\nu = 254.013\,870(35)$  MHz. The agreement between all three measurements is excellent.

$4P_{3/2}$ . There is a level-crossing measurement by Ney (1969) yielding  $A = 3.40(8)$ ;  $B = 3.34(24)$  MHz. The uncorrected quadrupole moment is reported as  $Q = 76.1(36)$  mb. In addition, a less accurate but consistent measurement has been carried out by means of a modified ABMR experiment (with optical-pumping orientation) by Boroske and Zimmermann (1971) obtaining  $A = 3.6(3)$ ;  $B = 2.8(8)$  MHz;  $Q_{\text{unc}} = 63(18)$  mb.

## E. Rubidium

It has two naturally occurring isotopes of masses 85 and 87 and nuclear spins  $5/2$  and  $3/2$ .  $^{87}\text{Rb}$  is radioactive, but has a lifetime much longer than the life of the Earth, and its relative abundance is over 27%.

### 1. $^{85}\text{Rb}$

$4D_{3/2}$ . A radiofrequency cascade spectroscopy experiment has been carried out by Liao *et al.* (1974), obtaining only the  $A$  value [ $7.3(5)$  MHz] since the  $B$  value is too small to be measured in low-field experiments. An investigation of this level has also been carried out by the same authors with the cascade anticrossing technique; they do not publish an  $A$  value, but it seems to be possible to obtain from their data  $A = 7.26(58)$  MHz.

$4D_{5/2}$ . The method is the same as for  $4D_{3/2}$ ;  $A = -5.2(3)$  MHz with radiofrequency;  $A = -5.03(34)$  MHz with anticrossing. Liao *et al.* (1974) do not give the value of the off-diagonal constant in the  $4D$  term but it can be evaluated using Eq. (2.30) and their results, obtaining  $A_{5/2, 3/2} = 7.14(24)$  MHz.

$5S_{1/2}$  (ground state). In addition to a recent optical measurement by Beacham and Andrews (1971) (whose accuracy is obviously low in a ground state) there are three accurate ABMR measurements by Bederson and Jaccarino (1952), Braslau *et al.* (1961) and Penselin *et al.* (1962), whose results are, respectively,  $\Delta\nu(F = 2 - F = 3) = 3035.735(2)$ ;  $3035.7327(7)$ ;  $3035.732\,439(5)$  MHz. The agreement is satisfactory, and this is especially true between the two most accurate measurements. Penselin *et al.* (1962) have also carried out a measurement of  $g_I/g_J$ , that has been found to be in considerable disagreement with later measurements by White *et al.* (1968) and by Ehlers *et al.* (1968). Nevertheless, the hfs measurement by Penselin *et al.* (1962) seems to be reliable. It is in complete agreement with the measurement by Vanier *et al.* (1974), carried out by extrapolation to zero buffer gas pressure in an optical pumping experiment [this result is  $3035.732\,440(10)$  MHz].

$5P_{1/2}$ . There is an ABMR experiment by Senitzky and

Rabi (1956) with a resonance light source in the C region, giving  $A = 120.7(10)$  MHz. Nevertheless, the measurement with an optical method by Beacham and Andrews (1971) has succeeded in this case in obtaining a better accuracy:  $A = 120.72(25)$  MHz. The agreement is excellent.

$5P_{3/2}$ . The hfs has been measured by Schüssler (1965) with a double-resonance experiment, obtaining the results:  $A = 25.029(16)$ ;  $B = 26.032(70)$  MHz. Later a level-crossing experiment by Arimondo and Kraińska (1975) has yielded  $A = 24.99(1)$ ;  $B = 25.88(3)$  MHz, in appreciable disagreement with those of Schüssler. The discrepancy has been explained by Arimondo and Kraińska (1975) showing that Schüssler neglected to consider some radiofrequency shifts. After a proper correction for these shifts, the results by Schüssler become  $A = 25.010(22)$ ;  $B = 25.89(10)$  MHz, in very good agreement with the level-crossing results. An optical measurement has also been carried out by Beacham and Andrews (1971), with the results:  $\Delta\nu(4, 3) = 119.92(30)$ ;  $\Delta\nu(3, 2) = 67.5(11)$ ;  $\Delta\nu(2, 1) = 42.9(15)$  MHz. These results [corresponding to  $A = 26.19(20)$ ;  $B = 18.9(10)$  MHz] are in very strong and surprising disagreement with the previous ones. A consistency check on Beacham's results gives only a reliability of 4.5% in the  $\chi^2$  test. An older ABMR measurement by Senitzky and Rabi (1956) seems to be strongly affected by rf shifts, and cannot be used for comparison. From the experimental results of Schüssler, the quadrupole moment is derived by Feiertag and zu Putlitz (1973) with corrections for core polarization, Sternheimer factor, and spin-orbit perturbation yielding  $Q = 275(2)$  mb.

$5D_{3/2}$ . A set of measurements has been carried out by the Columbia group [first by Gupta *et al.* (1972a), then by Tai *et al.* (1975)] with the cascade radiofrequency method, supplemented by the cascade decoupling method to obtain information about the sign of the coupling constant. The most recent results are:  $A = 4.18(20)$  MHz,  $|B| < 5$  MHz. The error on  $A$  includes three times the standard deviation plus allowance for systematic errors.

$6P_{3/2}$ . There are three double-resonance experiments by Meyer-Berkhout (1955), Schüssler (1965), and Bucka *et al.* (1961). The results of the former two are, respectively:  $A = 8.16(6)$ ;  $8.25(10)$ ;  $B = 8.40(40)$ ;  $8.16(20)$  MHz. Bucka *et al.* find  $\Delta\nu_{43} = 39.275(48)$ ;  $\Delta\nu_{32} = 20.812(61)$ ;  $\Delta\nu_{21} = 9.824(44)$  MHz; a least-squares fit of these data gives  $A = 8.179(12)$ ;  $B = 8.190(49)$  MHz with a 44% confidence. In addition, there is a level-crossing measurement by Bucka *et al.* (1966b) that, using the theoretical  $g_J$  value of 1.3341, gives  $A = 8.163(4)$ ,  $B = 8.191(27)$  MHz, and a level-crossing experiment with electric and magnetic fields quoted by Kalitejewski and Tschaika (1975) (using  $g_J = 1.334(1)$ , as stated by Grigoreva *et al.*, 1973) giving  $A = 8.16(2)$ ;  $B = 8.20(20)$  MHz. The agreement is generally good. For a comment on Bucka's results, see the same state of  $^{87}\text{Rb}$ . In the same way as for the  $5P_{3/2}$  state, Feiertag and zu Putlitz (1973) report  $Q = 273(2)$  mb.

$6D_{3/2}$ . Hogervorst and Svanberg (1975) measured the sign of  $A$  by a Stark-effect level-crossing experiment, finding it to be probably (but not certainly) positive. Since no absolute measurement is available, the value

of  $A = (+)2.28(6)$  MHz has been published by scaling the corresponding value for  $^{87}\text{Rb}$ .

$6D_{5/2}$ . By means of a Stark-effect level-crossing experiment, Hogervorst and Svanberg (1975) obtain  $A = -0.95(20)$  MHz. About  $B$ , it can only be said that  $|B| < |A|$  and that "a preference for positive  $B$  factors is found".

$7S_{1/2}$ . The hfs has been measured by the Columbia group in several cascade decoupling and cascade radio frequency experiments. There is an appreciable but not large spread between the measurements with and without radio frequency. The most recent result is  $A = 94.00(64)$  MHz by Gupta *et al.* (1973).

$7P_{1/2}$ . An earlier double-resonance experiment by Feiertag and zu Putlitz (1968) has been superseded (owing to an underestimation of the errors) by Feiertag and zu Putlitz (1973) who repeated the experiment obtaining  $A = 17.68(8)$  MHz.

$7P_{3/2}$ . Bucka *et al.* (1968) carried out a double-resonance experiment with extrapolation to zero rf field intensity and were able to measure only one transition  $\Delta\nu(F=4 - F=3) = 17.78(4)$  MHz.  $A$  and  $B$  are estimated using the ratio of the nuclear gyromagnetic ratios of  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$ , measured by Blumberg *et al.* (1961) and the  $A$  and  $B$  values for  $^{87}\text{Rb}$  (see below). They obtain  $A = 3.71(1)$ ;  $B = 3.68(8)$  MHz. In the same way as for the state  $5P_{3/2}$ , Feiertag and zu Putlitz (1973) derive the quadrupole moment:  $Q = 272(6)$  mb.

$7D_{3/2}$ . The method is the same as for  $6D_{3/2}$  but in this case the sign is certain;  $A = +1.34(1)$  MHz.

$8S_{1/2}$ . There are two cascade measurements, one by Gupta *et al.* (1972b) with cascade decoupling obtaining  $A = 45(5)$  MHz, and one by Gupta *et al.* (1973) with cascade radiofrequency obtaining  $A = 45.2(20)$  MHz.

$8P_{3/2}$ . There is only a double-resonance experiment carried out by zu Putlitz and Venkataramu (1968) where only one resonance (between  $F=4$  and  $F=3$ ) has been resolved. After extrapolation to zero rf field intensity, the result is  $\Delta\nu_{43} = 9.55(6)$  MHz. Using a similar result for  $^{87}\text{Rb}$  and the ratios of the nuclear gyromagnetic ratios (Blumberg *et al.*, 1961) and of the nuclear quadrupole moments (as obtained by Trischka and Braunstein, 1954, in a RbCl beam experiment) they deduce the following values:  $A = 1.99(2)$ ;  $B = 1.98(12)$  MHz. The quadrupole moment is derived using the  $\langle r^{-3} \rangle$  value from the fine-structure splitting (zu Putlitz, 1967) and with the Sternheimer correction it results  $Q = 270(17)$  mb.

$8D_{3/2}$ . The method is the same as for  $7D_{3/2}$ ;  $A = +0.84(1)$  MHz.

## 2. $^{87}\text{Rb}$

$4D_{3/2}$ . A radiofrequency cascade spectroscopy experiment has been carried out by Liao *et al.* (1974) obtaining only the  $A$  value [25.1(9) MHz] since the  $B$  value is too small to be measured in low-field experiments. The same authors also carried out a cascade anticrossing experiment. They do not publish a value for  $A$ , nevertheless from the data they do publish it seems possible to extract  $A = 24.6(19)$  MHz.

$4D_{5/2}$ . The method is the same as for  $4D_{3/2}$ ;  $A = -16.9(6)$  MHz with radiofrequency,  $A = -17.0(12)$  with anticrossing. The off-diagonal coupling constant of the  $4D$  term can be obtained by scaling the corresponding

value for  $^{85}\text{Rb}$ :  $A_{5/2,3/2} = 24.18(83)$  MHz.

$5S_{1/2}$  (ground state). In addition to a recent optical investigation by Beacham and Andrews (1971), there are several ABMR measurements; the most accurate are those by Essen *et al.* (1961), and Penselin *et al.* (1962) giving, respectively,  $\Delta\nu_{12} = 6834.682\,614\,0(10)$  and  $6834.682\,614(3)$  MHz. There are also two optical pumping experiments by Bender *et al.* (1958) and by Arditì and Cerez (1972a,b) giving, respectively,  $6834.682\,608(7)$  and  $6834.682\,612\,8(2)$  MHz. The agreement among all four measurements is quite satisfactory.

$5P_{1/2}$ . There are two atomic beam investigations by Senitzky and Rabi (1956) and Duong *et al.* (1968). While the former is an usual ABMR experiment with resonance light in the C region, the latter is a rather modified experiment, where in the C region there is an electric field and the light is slightly off-resonance, coming from a  $^{85}\text{Rb}$  lamp. The resonances are thus obtained by Stark-shifting the absorption of the  $^{87}\text{Rb}$  atoms. The results obtained for  $A$  are  $409(4)$  MHz by Senitzky and Rabi (1956) and  $406(7)$  MHz by Duong *et al.* (1968). There is in addition a direct optical measurement by Beacham and Andrews (1971) that is in agreement with, and more accurate than, the two atomic beam experiments, yielding  $A = 406.2(8)$  MHz.

$5P_{3/2}$ . There is a relatively old ABMR experiment by Senitzky and Rabi (1956) yielding  $A = 85.8(7)$ ;  $B = 11.8(6)$  MHz. A more recent double-resonance experiment was described first by Bucka *et al.* (1963b) and then more completely by Schüssler (1965), with the result:  $A = 84.852(30)$ ;  $B = 12.611(70)$  MHz. The radio-frequency shift that has been mentioned in connection with the same state for  $^{85}\text{Rb}$  is in this case rather small and can be almost neglected [the corrected values are  $84.845(55)$  and  $12.61(13)$  MHz, respectively]. A level-crossing measurement of  $B/A$  has been carried out by Belin and Svanberg (1971), who, using the  $A$  value by Schüssler, obtain  $B = 12.510(57)$ . Since these authors give the values of the level-crossing positions, we have reanalyzed their results in order to obtain both  $A$  and  $B$  using for  $g_J$  its Russel-Saunders value:  $g_J = 1.334\,11(48)$ , the uncertainty being the standard deviation from the Russel-Saunders value of all directly measured  $g$  values in alkali  $P_{3/2}$  states. The results are:  $A = 84.689(51)$ ;  $B = 12.49(7)$  MHz. The agreement between this  $A$  value and that of Schüssler is not good, and might imply a significant deviation of  $g_J$  from the Russel-Saunders value for this state, as Belin and Svanberg explicitly state. An optical measurement by Beacham and Andrews (1971) is in agreement with, but less accurate than, both previous measurements. Their results [ $\Delta\nu_{32} = 8.88(6)$ ;  $\Delta\nu_{21} = 5.23(6)$ ;  $\Delta\nu_{10} = 2.35(11)$  mK] correspond to  $A = 84.55(58)$  and  $B = 12.6(14)$  MHz. Belin and Svanberg (1971) derive the quadrupole moment from their measured  $B$  value, using a radial parameter which is the average of the values from fine-structure splitting and magnetic dipole coupling constant corrected for core polarization. The quadrupole moment results, applying the Sternheimer correction,  $Q = 131$  mb.

$5D_{3/2}$ . Several results have been published by the Columbia group. The most recent are those by Tai *et al.* (1975) using the cascade radiofrequency method

TABLE VI. Quoted values of  $A$  and  $B$  for the  $6^2P_{3/2}$  state of  $^{87}\text{Rb}$ .

$A$ (MHz)	$B$ (MHz)	Method <sup>a</sup>	Reference
27.612(49)	3.91(11)	LC	Bucka <i>et al.</i> , 1966b
27.63(10)	4.06(20)	ODR	Meyer-Berkhout, 1955
27.70(2)	3.94(4)	ODR	zu Putlitz <i>et al.</i> , 1965a
27.707(15)	4.000(39)	ODR	Bucka <i>et al.</i> , 1961
27.96(35)	3.95(10)	ODR	Schüssler, 1965
	3.947(13)	LC	Belin <i>et al.</i> , 1971

<sup>a</sup>The symbols have the same meaning as in Table IV.

(and the cascade decoupling method for finding the sign) obtaining  $A = 14.43(23)$  MHz, the error including three standard deviations plus an allowance for systematic errors. It has been possible to determine only an upper limit for  $B: |B| < 3.5$  MHz.

$6P_{3/2}$ . The results are summarized in Table VI. The results quoted as "Bucka *et al.*, 1966b" have been calculated from their data using for  $g_J$  the experimental value  $1.3339(11)$  (that is a weighted average of the values listed in Table I). The  $B$  value quoted by Belin and Svanberg (1971) has been evaluated from their measurement of  $B/A$  and the  $A$  value of zu Putlitz and Schenck (1965a) (using  $g_J = 1.3347$ ). The results quoted by Schüssler (1965) are actually not experimental data, but rather evaluations using the corresponding results for  $^{85}\text{Rb}$  and the ratio between the corresponding constants for  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$  in the  $5P_{3/2}$  state. We have reanalyzed the results of Belin and Svanberg as in the case of the  $5P_{3/2}$  state, but using the experimental  $g_J$  value, obtaining  $A = 27.674(28)$ ;  $B = 3.945(19)$  MHz. There is a reasonably good agreement among all such determinations, with the possible exception of the  $A$  values measured by Bucka *et al.* (1966b) with a level-crossing experiment on one side, and by Bucka *et al.* (1961) and zu Putlitz and Schenck (1965a) on the other with double-resonance experiments. Bucka *et al.* do not explain this discrepancy. It is worth noting, however, that the values we have obtained analyzing the level-crossing experiment by Belin and Svanberg agree with all other values, although they have a good precision. Belin and Svanberg and Bucka disagree on the positions of two crossing points; this may possibly be because Bucka used a modulated magnetic field, whereas the instrumental shift for this kind of experiment (Isler, 1969c) is not explicitly taken into account. Belin and Svanberg (1971) have derived the quadrupole moment from their  $B$  value, with Sternheimer correction and  $\langle r^{-3} \rangle$  calculated as for the  $5^2P_{3/2}$  state, obtaining  $Q = 133$  mb.

$6D_{3/2}$ . The absolute values of  $A$  and  $B$  have been measured with two-step excitation by Svanberg *et al.* (1973) and later by Svanberg and Tsekeris (1975b) with a level-crossing experiment and using the theoretical  $g_J = 0.7995$ ; the latest results are  $A = 7.84(5)$ ;  $B = 0.53(6)$  MHz. The signs of  $A$  and  $B$  have been determined by Hogervorst and Svanberg (1975) with a Stark-effect experiment. For the strongly perturbed  $D$  state of rubidium the Sternheimer corrections are hardly applied, as discussed by Lindgren (1975a). This author has derived the quadrupole moment calculating the  $\langle r^{-3} \rangle_q$  parameter, obtaining  $Q = 210$  mb, and applying appropriate

corrections to the  $\langle r^{-3} \rangle_c$  parameter on the basis of the experimental magnetic hfs, obtaining  $Q = 170$  mb.

$6D_{5/2}$ . Svanberg and Tsekeris (1975b) in a double-resonance experiment after two-step excitation obtain  $|A| = 3.6(7)$  MHz, but no information on  $B$ . The sign of  $A$  has been found to be negative with a Stark-effect level-crossing experiment by Hogervorst and Svanberg (1975) on  $^{85}\text{Rb}$ .

$7P_{3/2}$ . There is a double-resonance experiment by Bucka *et al.* (1968) where the splittings have been extrapolated to zero rf field intensity, with the results:  $A = 12.57(1)$ ;  $B = 1.71(3)$  MHz. The  $B/A$  ratio has been later measured in a level-crossing experiment by Belin and Svanberg (1971) who, using the  $A$  value quoted above, report  $B = 1.768(8)$  MHz. With the same technique described for the  $5P_{3/2}$  state, we have reanalyzed this level-crossing experiment obtaining  $A = 12.549(7)$ ;  $B = 1.765(10)$  MHz. The disagreement between level-crossing and double-resonance results is, in this case, less pronounced than for the  $5P_{3/2}$  state, but is still remarkable. In this case the disagreement exists also between the  $B$  value obtained with ODR and in the level-crossing experiment by considering the  $B/A$  ratio and the  $A$  value from the ODR experiment, and cannot therefore be ascribed to a significant deviation of  $g_J$  from the Russell-Saunders value. Belin and Svanberg (1971) have derived the quadrupole moment from their  $B$  value using the Sternheimer correction and the  $\langle r^{-3} \rangle$  as for the  $5^2P_{3/2}$  state obtaining  $Q = 133$  mb.

$7D_{3/2}$ . The method is the same as for  $6D_{3/2}$ ;  $A = 4.53(3)$ ;  $B = 0.26(4)$  MHz. With the same analysis as in the  $6D_{3/2}$  state the following values are obtained:  $Q = 180$  mb and  $Q = 150$  mb, respectively.

$7D_{5/2}$ . The method is the same as for  $6D_{5/2}$ ; Svanberg and Tsekeris (1975b) give  $|A| = 2.2(5)$  MHz.

$8S_{1/2}$ . There is a cascade decoupling measurement by Gupta *et al.* (1972b) as well as a cascade radio frequency experiment (Gupta *et al.*, 1973) yielding, respectively,  $\Delta\nu = 290(20)$  MHz [ $A = 145(10)$  MHz] and  $A = 158.3(30)$  MHz. In addition, a modified double-resonance experiment after two-step excitation has been carried out by Tsekeris *et al.* (1975a) improving on the accuracy of the cascade experiments, and giving  $A = 159.2(15)$  MHz.

$8P_{3/2}$ . zu Putlitz and Venkataramu (1968) have carried out a double-resonance experiment resolving only one resonance and obtaining  $\Delta\nu_{32} = 21.20(4)$  MHz after extrapolation to zero rf field intensity. Using the same procedure as in the same state of  $^{85}\text{Rb}$  they obtain the following values for the coupling constants:  $A = 6.75(3)$ ;  $B = 0.96(6)$  MHz. In addition, there is a level-crossing experiment carried out by Belin and Svanberg (1971) where, assuming  $g_J$  to be 1.336, they get  $A = 6.747(14)$ ;  $B = 0.933(20)$  MHz. These authors have derived the quadrupole moment as in the previous  $P_{3/2}$  states obtaining  $Q = 131$  mb. Estimating the uncertainties in the  $\langle r^{-3} \rangle$  determination and in the Sternheimer correction factors they report an averaged quadrupole moment for the measurements in the  $P_{3/2}$  states:  $Q(^{85}\text{Rb}) = 132(9)$  mb.

$8D_{5/2}$ . An unresolved double-resonance experiment after two-step excitation has been carried out by Svanberg and Belin (1974), obtaining  $|A| = 1.2(2)$  MHz and no indication about  $B$ . The error has been further reduced by the same authors (Belin *et al.*, 1976a) to 0.15 MHz.

Hogervorst and Svanberg (1975) with an experiment on  $^{85}\text{Rb}$  determined the sign of  $A$  to be negative.

$9P_{3/2}$ . A double-resonance experiment after two-step excitation has been carried out by Belin and Svanberg (1974a) yielding only the  $A$  value [4.05(10) MHz]. The experiment has been repeated by the same authors (Belin *et al.*, 1975a) obtaining  $A = 4.04(3)$  MHz; in addition, Svanberg (1975c) and coworkers have found  $B = 0.55(3)$  MHz.

## F. Cesium

It has only one stable isotope, of mass 133 and spin  $7/2$ .

$5F_{5/2}$ . After a two-step excitation and cascade an unresolved optical resonance is attempted, yielding only a "rough upper limit" (Svanberg *et al.*, 1973a):  $|A| < 0.7$  MHz.

$6S_{1/2}$  (ground state). By international agreement, the frequency of the transition between the hyperfine sublevels of this state is taken to be equal to exactly 9192.631 770 MHz. The primary standard is an ABMR source, but some work has also been carried out with optical pumping techniques on Cs cells (Bava *et al.*, 1975), and the possibility is being investigated of building a Cs maser (Strumia, 1970, 1975) and a new optically pumped primary frequency standard (Arditi and Picqué, 1975a). A recent review paper on atomic frequency standards has been written by Hellwig (1975).

$6P_{1/2}$ . There is a double-resonance measurement by Abele (1975b) yielding  $A = 291.90(12)$  MHz. In addition, there are three fairly recent optical measurements, by Kleiman (1962), Eriksson *et al.* (1965), and Hühnermann and Wagner (1968), giving respectively  $A = 293.0(37)$ ;  $304.3(105)$ ;  $292.09(33)$  MHz. The agreement between all these measurements is quite acceptable.

$6P_{3/2}$ . The results are summarized in Table VII. The values of  $A$  and  $B$  quoted by Buck *et al.* (1956) and listed in the table are not entirely consistent with their experimental data, owing to an obvious computational mistake. The correct values are (Violino, 1969)  $A = 50.60(12)$ ;  $B = -0.53(75)$  MHz. In the case of Kallas *et al.* (1965), the experimental results for the level-crossing positions are not in agreement with the theory, predicting a relationship between the positions of the three level crossing which are connected to only two constants, as it can easily be shown with the method suggested by Schönberner and Zimmermann (1968). It seems therefore fair to assume that the errors quoted by Kallas *et al.* (1965) are somewhat underestimated. Of the two double-resonance investigations, one (Svanberg and Belin, 1972) has been carried out in zero-field with extrapolation to zero rf power, while the other one (Abele *et al.*, 1975a, c) in a strong field, and its main purpose was measuring the  $g_J$  factor. The agreement among all measurements is reasonable, except for the level-crossing measurement by Svanberg and Rydberg (1969). The effect of instrumental shifts on this experiment (Violino, 1970) has been found to be negligible (Rydberg, 1970). The reason for this discrepancy can be found in the value that has been used for  $g_J(1.345)$  that is very far from both the theoretical (1.3341) and the experimental [1.3340(3), (Abele, 1975a)] values. After this



TABLE VII. Experimental results for the  $6^2P_{3/2}$  state of  $^{133}\text{Cs}$ .

A (MHz)	B (MHz)	Method <sup>a</sup>	Reference
50.02(25)		ODR	Abele, 1975a
50.31(5)	-0.30(33)	ODR	Svanberg <i>et al.</i> , 1972
50.45(8)	-0.66(72)	LC	Violino, 1969
50.67(11)	-0.46(53)	ABMR	Buck <i>et al.</i> , 1956
50.72(3)	-0.38(18)	LC	Svanberg <i>et al.</i> , 1969
50.9(5)	-0.9(6)	LC	Kallas <i>et al.</i> , 1965

<sup>a</sup>The symbols have the same meaning as in Table IV.

correction is applied (using the experimental  $g_J$ ), the  $A$  value of Svanberg and Rydberg (1969) becomes 50.31(4) MHz, and reasonable agreement exists among all measurements. An additional level-crossing experiment has been carried out by Minemoto *et al.* (1974) with a different purpose and only the first crossing point was measured. Rydberg and Svanberg (1972) have derived the quadrupole moment  $Q = -2.8$  mb from their measured  $B$  constant, applying the Stenheimer correction factor, the spin-orbit interaction correction and using a  $\langle r^{-3} \rangle$  value, mean value of the radial parameter obtained from the fine structure and from the dipole constants, corrected for core polarization.

$6D_{3/2}$ . Tai *et al.* (1975) have measured  $A$  with three cascade methods (namely decoupling, radiofrequency, and level-crossing) using the 3888.65 Å line of He for excitation through the  $8P_{1/2}$  state. The best result is  $A = 16.30(15)$  MHz. Only an upper limit was obtained for  $B$ , with the cascade radiofrequency method, namely  $|B| < 8$  MHz.

$7P_{1/2}$ . There are two double-resonance experiments by Bucka (1956 and 1958) and by Feiertag *et al.* (1972), yielding  $A = 100.20(25)$  and  $94.35(4)$  MHz, respectively. In both cases there should be no appreciable Bloch-Siegert shift, so we cannot find a clear-cut explanation for the discrepancy. The method used by Bucka is a rather modified version of a double-resonance experiment, using the self-absorption as a means for analysis.

$7P_{3/2}$ . The results are summarized in Table VIII. The experiment by Baumann *et al.* (1972) is in a strong field. Bucka *et al.* (1959) consider corrections for rf shifts, that are found to be small. There is in addition a double-resonance measurement of  $\Delta\nu_{32} = 49.81(3)$  MHz by Faist *et al.* (1964) and a level-crossing experiment by Minemoto *et al.* (1974), not quoting any  $A$  or  $B$  value. The agreement between all measurements is good. Svanberg and Rydberg (1969) use, in the data analysis of their level-crossing experiment, the value  $g_J = 1.3349$ . If instead they used the experimental  $g_J = 1.33410(5)$ , their  $A$  would be  $16.600(7)$  MHz. For the quadrupole moment Sternheimer and Peierls (1971) have applied a correction factor  $C = 1/(1-R) = 0.829$  to the experimental results of Bucka *et al.* (1959), yielding  $Q = -3.0(11)$  mb. Rydberg and Svanberg (1972) have derived the quadrupole moment  $Q = -3.3(10)$  mb with the same correction as for the  $6P_{3/2}$  state.

$7D_{3/2}$ . A level-crossing investigation after two-step excitation has been carried out by Belin *et al.*, 1976b, obtaining  $|A| = 7.4(2)$  MHz, and no information on  $B$ . The second and third crossings are unresolved.

TABLE VIII. Experimental results for the  $7^2P_{3/2}$  state of  $^{133}\text{Cs}$ .

A (MHz)	B (MHz)	Method <sup>a</sup>	Reference
16.58(40)		QB	Haroche <i>et al.</i> , 1973
16.591(25)		ODR	Baumann <i>et al.</i> , 1972
16.6(1)	-0.14(7)	LC	Kallas <i>et al.</i> , 1965
16.60(1)	-0.11(8)	ODR	Althoff <i>et al.</i> , 1954, 1955
16.609(5)	-0.16(6)	ODR	Bucka <i>et al.</i> , 1959
16.610(6)	-0.15(3)	LC	Svanberg <i>et al.</i> , 1969

<sup>a</sup>The symbols have the same meaning as in Table IV.

$8S_{1/2}$ . Several cascade experiments have been carried out by the Columbia group. The most recent one (Gupta *et al.*, 1973) is with cascade radio frequency and supersedes the older cascade decoupling experiments where the magnetic field was insufficient to decouple  $I$  and  $J$ ; the result is  $A = 218.9(16)$  MHz. Radiofrequency shifts, if considered, would give a slightly higher result. In addition there is an optical study by Kleiman (1962), yielding  $A = 228(15)$  MHz, in good agreement with the cascade experiment.

$8P_{3/2}$ . There are four double-resonance investigations by Barbey and Geneux (1962), Bucka and von Oppen (1963a), Faist *et al.* (1964) and Abele *et al.* (1975a, c). The last one is in a strong field. Faist *et al.* (1964) take into account rf shifts (something the earlier authors did not), but resolve only two transitions while Abele includes the effect of rf shifts in the errors. Their results are respectively:  $A = 7.55(5); 7.626(5); 7.58(1); 7.644(25)$  MHz and  $B = +0.63(35); -0.049(42); -0.14(5)$  MHz (Abele gives no  $B$  value). The agreement among these measurements is rather poor. The reason for this disagreement is largely due to rf shifts in the earlier experiments, but it is not fully understood. A discussion can be found in the paper by Faist *et al.* (1964). Svanberg and Rydberg (1969) carried out a level-crossing experiment, but measured only the position of the first crossing. Bucka and von Oppen (1963a) report an uncorrected quadrupole moment  $Q = -2.4(20)$  mb.

$8D_{3/2}$ . A measurement of the absolute value of  $A$  has been carried out by Svanberg and Tsekeris (1975b) by means of a level-crossing experiment after two-step excitation. The sign has been determined further by Hogervorst and Svanberg (1975) with the Stark effect, with the result:  $A = +3.98(12)$  MHz (the listed error being quoted more recently by Tsekeris, 1976a). Another measurement with the quantum beats method has been performed by Deech *et al.* (1975), yielding  $A = 3.92(7)$  MHz. No information on  $B$  is available;  $B$  is explicitly set equal to zero by Hogervorst and Svanberg (1975) in their data reduction, owing to the small quadrupole moment of Cs.

$8D_{5/2}$ . There is a double-resonance experiment after two-step excitation by Svanberg and Tsekeris (1975b) obtaining  $|A| = 0.9(4)$  MHz, and a level-crossing experiment with an electric field by Hogervorst and Svanberg (1975) obtaining  $A = -0.8(3)$  MHz.

$9S_{1/2}$ . Two cascade measurements have been carried out by the Columbia group, one without radiofrequency (Gupta *et al.*, 1972b) yielding  $A = +101.1(75)$  MHz, and one with radiofrequency (Gupta *et al.*, 1973) yielding



TABLE IX. Recommended  $A$  and  $B$  values. For each isotope, the states are listed in order of increasing  $n$ , then of increasing  $L$ , then of increasing  $J$ . All states are doublet states unless otherwise noted; quartet states are listed at the end of the corresponding isotope.

Isotope	State	$A$ (MHz) <sup>a</sup>	$B$ (MHz) <sup>a</sup>	Technique <sup>b</sup>	Reference
<sup>6</sup> Li	2S <sub>1/2</sub>	152.136 840 7(20)		ABMR	Huq <i>et al.</i> , 1973 and Beckmann <i>et al.</i> , 1974
	2P <sub>1/2</sub>	17.375(18)		ODR	Orth <i>et al.</i> , 1974
	2P <sub>3/2</sub>	-1.155(8)	-0.10(14)	ODR	Orth <i>et al.</i> , 1974
	3P <sub>3/2</sub>	-0.40(2)		LC	Isler <i>et al.</i> , 1969a
<sup>7</sup> Li	2S <sub>1/2</sub>	401.752 043 3(5)		ABMR	Beckmann <i>et al.</i> , 1974
	2P <sub>1/2</sub>	45.914(25)		ODR	Orth <i>et al.</i> , 1975
	2P <sub>3/2</sub>	-3.055(14)	-0.221(29)	ODR	Orth <i>et al.</i> , 1975
	3P <sub>1/2</sub>	13.5(2)		LC	Budick <i>et al.</i> , 1966
	3P <sub>3/2</sub>	-0.965(20)	-0.019(22)	LC	Isler <i>et al.</i> , 1969a
	4P <sub>3/2</sub>	-0.41(2)		LC	Isler <i>et al.</i> , 1969a
<sup>23</sup> Na	3S <sub>1/2</sub>	885.813 064 4(5)		ABMR	Chan <i>et al.</i> , 1970 and Beckmann <i>et al.</i> , 1974
	3P <sub>1/2</sub>	94.3(1)		ODR	Hartmann, 1970a
	3P <sub>3/2</sub>	18.69(9)	2.90(21)	LC	Schönberner <i>et al.</i> , 1968; Baumann, 1969; Schmieder <i>et al.</i> , 1970; Figger <i>et al.</i> , 1974; and Deech <i>et al.</i> , 1974
	4S <sub>1/2</sub>	202(3)		CR	Liao <i>et al.</i> , 1973
	4P <sub>3/2</sub>	6.022(61)	0.97(6)	LC	Schönberner <i>et al.</i> , 1968 and Schmieder <i>et al.</i> , 1970
	4D <sub>3/2</sub>	± 0.507(68)		QB	Schenck <i>et al.</i> , 1975a
	5S <sub>1/2</sub>	77.6(2)		2S	Tsekeris <i>et al.</i> , 1976b
	5D <sub>5/2</sub>	<± 0.33		EE	Achambault <i>et al.</i> , 1960
	6S <sub>1/2</sub>	39(3)		2P	Levenson <i>et al.</i> , 1974
	<sup>39</sup> K	4S <sub>1/2</sub>	230.859 860 1(3)		ABMR
4P <sub>1/2</sub>		28.85(30)		ABMR	Buck <i>et al.</i> , 1957
4P <sub>3/2</sub>		6.06(8)	2.83(13)	LC	Schmieder <i>et al.</i> , 1968 and Ney, 1969
5S <sub>1/2</sub>		55.50(60)		CR	Gupta <i>et al.</i> , 1973
5P <sub>1/2</sub>		9.02(17)		ODR	Ritter <i>et al.</i> , 1957 and Fox <i>et al.</i> , 1961
5P <sub>3/2</sub>		1.969(13)	0.870(22)	LC	Schmieder <i>et al.</i> , 1968; Ney, 1969; and Svanberg <i>et al.</i> , 1971
5D <sub>3/2</sub>		± 0.44(10)		2S	Belin <i>et al.</i> , 1975b
5D <sub>5/2</sub>		± 0.24(7)		2S	Belin <i>et al.</i> , 1975b
6S <sub>1/2</sub>		21.81(18)		CR	Gupta <i>et al.</i> , 1973
6P <sub>1/2</sub>		± 4.05(7)		2S	Belin <i>et al.</i> , 1975b
6P <sub>3/2</sub>		0.886(8)	0.370(15)	LC	Svanberg, 1971
6D <sub>3/2</sub>		± 0.2(2)		2S	Belin <i>et al.</i> , 1975b
6D <sub>5/2</sub>		± 0.10(10)		2S	Belin <i>et al.</i> , 1975b
7S <sub>1/2</sub>		10.79(5)		2S	Tsekeris <i>et al.</i> , 1974 and Belin <i>et al.</i> , 1975b
7P <sub>1/2</sub>		± 2.18(5)		2S	Belin <i>et al.</i> , 1975b
7P <sub>3/2</sub>		± 0.49(4)		2S	Belin <i>et al.</i> , 1975b
8S <sub>1/2</sub>		5.99(8)		2S	Belin <i>et al.</i> , 1975b
10S <sub>1/2</sub>		2.41(5)		2S	Belin <i>et al.</i> , 1975b
3p <sup>5</sup> 4s3d <sup>4</sup> F <sub>3/2</sub>		103.56(9)	-78.86(80)	ABMR	Sprott <i>et al.</i> , 1968
3p <sup>5</sup> 4s4p <sup>4</sup> D <sub>1/2</sub>		150.03(90)	-78.5(32)	ABMR	Sprott <i>et al.</i> , 1968
<sup>40</sup> K	4S <sub>1/2</sub>	-285.7308(24)		ABMR	Davis <i>et al.</i> , 1949 and Eisinger <i>et al.</i> , 1952
	4P <sub>3/2</sub>	-7.59(6)	-3.5(5)	LC	Ney <i>et al.</i> , 1968
	5P <sub>3/2</sub>	-2.45(2)	-1.16(22)	VR	Bucka <i>et al.</i> , 1962 and Ney <i>et al.</i> , 1968
<sup>41</sup> K	4S <sub>1/2</sub>	127.006 935 2(6)		ABMR	Chan <i>et al.</i> , 1970 and Beckmann <i>et al.</i> , 1974
	4P <sub>3/2</sub>	3.40(8)	3.34(24)	LC	Ney, 1969
	5S <sub>1/2</sub>	30.75(75)		CR	Gupta <i>et al.</i> , 1973
	5P <sub>3/2</sub>	1.08(2)	1.06(4)	LC	Ney, 1969
	6S <sub>1/2</sub>	12.03(40)		CR	Gupta <i>et al.</i> , 1973
<sup>85</sup> Rb	4D <sub>3/2</sub>	7.3(5)		CR	Liao <i>et al.</i> , 1974
	4D <sub>5/2</sub>	-5.2(3)		CR	Liao <i>et al.</i> , 1974
	5S <sub>1/2</sub>	1011.910 813(2)		VR	Penselin <i>et al.</i> , 1962 and Vanier <i>et al.</i> , 1974
	5P <sub>1/2</sub>	120.72(25)		OPT	Beacham <i>et al.</i> , 1971

TABLE IX. (Continued).

Isotope	State	A (MHz) <sup>a</sup>	B (MHz) <sup>a</sup>	Technique <sup>b</sup>	Reference	
<sup>85</sup> Rb	5P <sub>3/2</sub>	25.009(22)	25.88(3)	VR	Schüssler, 1965 and Arimondo <i>et al.</i> , 1975	
	5D <sub>3/2</sub>	4.18(20)	<±5	CR	Tai <i>et al.</i> , 1975	
	5D <sub>5/2</sub>	-2.12(20)		CR	Tai <i>et al.</i> , 1975	
	6S <sub>1/2</sub>	239.3(12)		CR	Gupta <i>et al.</i> , 1973	
	6P <sub>1/2</sub>	39.11(3)		ODR	Feiertag <i>et al.</i> , 1973	
	6P <sub>3/2</sub>	8.179(12)	8.190(49)	ODR	Bucka <i>et al.</i> , 1961	
	6D <sub>5/2</sub>	-0.95(20)		LC	Hogervorst <i>et al.</i> , 1975	
	7S <sub>1/2</sub>	94.00(64)		CR	Gupta <i>et al.</i> , 1973	
	7P <sub>1/2</sub>	17.68(8)		ODR	Feiertag <i>et al.</i> , 1973	
	7P <sub>3/2</sub>	3.71(1)	3.68(8)	ODR	Bucka <i>et al.</i> , 1968	
	7D <sub>5/2</sub>	-0.55(10)		LC	Hogervorst <i>et al.</i> , 1975	
	8S <sub>1/2</sub>	45.2(20)		CR	Gupta <i>et al.</i> , 1973	
	8P <sub>3/2</sub>	1.99(2)	1.98(12)	ODR	zu Putlitz <i>et al.</i> , 1968	
	8D <sub>5/2</sub>	-0.35(7)		LC	Hogervorst <i>et al.</i> , 1975	
	<sup>87</sup> Rb	4D <sub>3/2</sub>	25.1(9)		CR	Liao <i>et al.</i> , 1974
		4D <sub>5/2</sub>	-16.9(6)		CR	Liao <i>et al.</i> , 1974
5S <sub>1/2</sub>		3417.341 306 42(15)		ABMR	Essen <i>et al.</i> , 1961 and Arditì <i>et al.</i> , 1972a,b	
5P <sub>1/2</sub>		406.2(8)		OPT	Beacham <i>et al.</i> , 1971	
5P <sub>3/2</sub>		84.845(55)	12.52(9)	VR	Schüssler, 1965 and Belin <i>et al.</i> , 1971	
5D <sub>3/2</sub>		14.43(23)	<±3.5	CR	Tai <i>et al.</i> , 1975	
5D <sub>5/2</sub>		-7.44(10)	<±5	CR	Tai <i>et al.</i> , 1975	
6S <sub>1/2</sub>		809.1(50)		CR	Gupta <i>et al.</i> , 1973	
6P <sub>1/2</sub>		132.56(3)		ODR	Feiertag <i>et al.</i> , 1973	
6P <sub>3/2</sub>		27.700(17)	3.953(24)	VR	Bucka <i>et al.</i> , 1961; zu Putlitz <i>et al.</i> , 1965 and Belin <i>et al.</i> , 1971	
6D <sub>3/2</sub>		7.84(5)	0.53(6)	LC	Svanberg <i>et al.</i> , 1975	
6D <sub>5/2</sub>		-3.4(5)		LC	Hogervorst <i>et al.</i> , 1975	
7S <sub>1/2</sub>		318.1(32)		CR	Gupta <i>et al.</i> , 1973	
7P <sub>1/2</sub>		59.92(9)		ODR	Feiertag <i>et al.</i> , 1973	
7P <sub>3/2</sub>		12.57(1)	1.762(16)	VR	Bucka <i>et al.</i> , 1968 and Belin <i>et al.</i> , 1971	
7D <sub>3/2</sub>		4.53(3)	0.26(4)	LC	Svanberg <i>et al.</i> , 1975	
7D <sub>5/2</sub>		-2.0(3)		LC	Hogervorst <i>et al.</i> , 1975	
8S <sub>1/2</sub>		159.2(15)		2S	Tsekeris <i>et al.</i> , 1975	
8P <sub>1/2</sub>		32.12(11)		2S	Tsekeris <i>et al.</i> , 1975	
8P <sub>3/2</sub>		6.739(15)	0.935(22)	VR	zu Putlitz <i>et al.</i> , 1968 and Belin <i>et al.</i> , 1971	
8D <sub>3/2</sub>		±2.840(15)	±0.17(2)	LC	Belin <i>et al.</i> , 1976a	
8D <sub>5/2</sub>		-1.20(15)		2S	Belin <i>et al.</i> , 1976a	
9S <sub>1/2</sub>		90.9(8)		2S	Tsekeris <i>et al.</i> , 1975a	
9P <sub>3/2</sub>		4.05(3)	0.55(3)	2S	Belin <i>et al.</i> , 1976a	
9D <sub>3/2</sub>		1.90(1)	0.11(3)	LC	Belin <i>et al.</i> , 1976a	
9D <sub>5/2</sub>		±0.80(15)		2S	Belin <i>et al.</i> , 1976a	
10S <sub>1/2</sub>		56.27(12)		2S	Tsekeris, 1976a	
10P <sub>3/2</sub>		2.60(8)		CR	Belin <i>et al.</i> , 1976a	
11S <sub>1/2</sub>		37.4(3)			Gupta, 1976	
<sup>133</sup> Cs		5D <sub>5/2</sub>	±22.2(5)			Lam, 1975
		5F <sub>5/2</sub>	<±0.7		CR	Svanberg <i>et al.</i> , 1973
		5F <sub>7/2</sub>	<±1.0		CR	Svanberg <i>et al.</i> , 1973
	6S <sub>1/2</sub>	2298.157 942 5				
	6P <sub>1/2</sub>	291.90(13)		VR	Hühnermann <i>et al.</i> , 1968 and Abele, 1975b	
	6P <sub>3/2</sub>	50.34(6)	-0.38(18)	VR	Buck <i>et al.</i> , 1956; Svanberg <i>et al.</i> , 1969; Violino, 1969; and Svanberg <i>et al.</i> , 1972	
	6D <sub>3/2</sub>	16.30(15)	<±8	CR	Tai <i>et al.</i> , 1975	
	6D <sub>5/2</sub>	-3.6(10)		CD	Tai <i>et al.</i> , 1975	
	6F <sub>5/2</sub>	<±1.0		2S	Svanberg, 1975a	
	6F <sub>7/2</sub>	<±1.0		2S	Svanberg, 1975a	
	7S <sub>1/2</sub>	546.3(30)		CR	Gupta <i>et al.</i> , 1973	
	7P <sub>1/2</sub>	94.35(4)		ODR	Feiertag <i>et al.</i> , 1972	
	7P <sub>3/2</sub>	16.605(6)	-0.15(3)	VR	Althoff, 1955; Bucka <i>et al.</i> , 1959; Svanberg <i>et al.</i> , 1969	
	7D <sub>3/2</sub>	±7.4(2)		LC	Belin <i>et al.</i> , 1976b	
	7D <sub>5/2</sub>	-1.7(2)		2S	Bulos <i>et al.</i> , 1976a	
	8S <sub>1/2</sub>	218.9(16)		CR	Gupta <i>et al.</i> , 1973	
	8P <sub>1/2</sub>	42.97(10)		CD	Tai <i>et al.</i> , 1973	
	8P <sub>3/2</sub>	7.58(1)	-0.14(5)	ODR	Faist <i>et al.</i> , 1964	

TABLE IX. (Continued)

Isotope	State	A (MHz) <sup>a</sup>	B (MHz) <sup>a</sup>	Technique <sup>b</sup>	Reference
<sup>133</sup> Cs	8D <sub>3/2</sub>	3.94(8)		VR	Svanberg <i>et al.</i> , 1975b and Deech <i>et al.</i> , 1975
	8D <sub>5/2</sub>	-0.85(20)		VR	Svanberg <i>et al.</i> , 1975b and Hogervorst <i>et al.</i> , 1975
	9S <sub>1/2</sub>	110.1(5)		2S	Tsekeris, 1976a
	9P <sub>1/2</sub>	23.19(15)		2S	Tsekeris <i>et al.</i> , 1975b
	9P <sub>3/2</sub>	4.123(3)	-0.051(25)	LC	Rydberg <i>et al.</i> , 1972
	9D <sub>3/2</sub>	2.35(4)		VR	Svanberg <i>et al.</i> , 1975b and Deech <i>et al.</i> , 1975
	9D <sub>5/2</sub>	-0.45(10)		VR	Svanberg <i>et al.</i> , 1975b and Hogervorst <i>et al.</i> , 1975
	10S <sub>1/2</sub>	63.2		2S	Tsekeris <i>et al.</i> , 1974
	10P <sub>3/2</sub>	2.481(9)		LC	Rydberg <i>et al.</i> , 1972
	10D <sub>3/2</sub>	1.51(2)		VR	Svanberg <i>et al.</i> , 1975b and Deech <i>et al.</i> , 1975
	10D <sub>5/2</sub>	-0.35(10)		VR	Svanberg <i>et al.</i> , 1975b and Hogervorst <i>et al.</i> , 1975
	11S <sub>1/2</sub>	39.4(2)		2S	Tsekeris <i>et al.</i> , 1974
	11P <sub>3/2</sub>	1.600(15)		2S	Belin <i>et al.</i> , 1974a
	11D <sub>3/2</sub>	± 1.055(15)		LC	Svanberg <i>et al.</i> , 1974
	11D <sub>5/2</sub>	± 0.24(6)		2S	Svanberg <i>et al.</i> , 1974
	12S <sub>1/2</sub>	26.31(10)		2S	Tsekeris <i>et al.</i> , 1975a
	12P <sub>3/2</sub>	1.10(3)		2S	Belin <i>et al.</i> , 1976b
	12D <sub>3/2</sub>	± 0.758(12)			Svanberg <i>et al.</i> , 1974
	12D <sub>5/2</sub>	± 0.19(5)		2S	Svanberg <i>et al.</i> , 1974
	13S <sub>1/2</sub>	18.40(11)		2S	Tsekeris, 1976a
	13P <sub>3/2</sub>	0.77(5)		2S	Belin <i>et al.</i> , 1976b
	13D <sub>3/2</sub>	± 0.556(8)		LC	Svanberg <i>et al.</i> , 1974
	13D <sub>5/2</sub>	± 0.14(4)		2S	Svanberg <i>et al.</i> , 1974
	14S <sub>1/2</sub>	13.41(12)		2S	Tsekeris, 1976a
	14D <sub>3/2</sub>	± 0.425(7)		LC	Belin <i>et al.</i> , 1976b
	15D <sub>3/2</sub>	± 0.325(8)		LC	Belin <i>et al.</i> , 1976b
	16D <sub>3/2</sub>	± 0.255(12)		LC	Belin <i>et al.</i> , 1976b
	17D <sub>3/2</sub>	± 0.190(12)		LC	Belin <i>et al.</i> , 1976b
18D <sub>3/2</sub>	± 0.160(10)		LC	Belin <i>et al.</i> , 1976b	

<sup>a</sup>The symbol ± in front of a value means that the sign has not been determined experimentally. The symbol < means that there is only an estimate of the upper limit. Uncertainties are given in brackets and refer to the last digits.

<sup>b</sup>The symbols have the following meaning: ABMR atomic beam experiments, CD cascade decoupling, CR cascade radiofrequency, EE rf transition after electron excitation, LC level crossing, in any of its variations, ODR optical double resonance in its basic version, OPT optical spectroscopy, QB quantum beats, VR average of measurements taken with several unlike techniques (further details can be found in Sec. V), 2P two-photon transition, 2S rf transition after multistep excitation.

A = 109.5(20) MHz. Later Tsekeris (1976a) improved on the accuracy of this measurement by means of double-resonance after two-step excitation.

9P<sub>1/2</sub>. Tsekeris *et al.* (1975b) carried out a modified double-resonance experiment, after a multistep excitation by means of a dye laser. Their result is A = 23.19(15) MHz, the quoted uncertainty being two standard deviations plus allowance for possible systematic errors.

9P<sub>3/2</sub>. A level-crossing experiment has been carried out by Rydberg and Svanberg (1972); using the value  $g_I = 1.336(2)$ , the results are A = 4.129(7); B = -0.051(25) MHz.

9D<sub>3/2</sub>. The method is the same as for 8D<sub>3/2</sub>; Svanberg and Tsekeris (1975b) and Hogervorst and Svanberg (1975) give A = 2.37(3) MHz; Deech *et al.* (1975) give A = 2.32(4) MHz.

9D<sub>5/2</sub>. The method is the same as for 8D<sub>5/2</sub>; Svanberg

and Tsekeris (1975b) give |A| = 0.5(2) MHz and Hogervorst and Svanberg (1975) give A = -0.40(15) MHz. In addition there was an older estimate by Archambault *et al.* (1960) with a double-resonance method after electronic excitation, of 0.195 < |A| < 0.45 MHz.

10D<sub>3/2</sub>. The method is the same as for 8D<sub>3/2</sub>; Svanberg and Tsekeris (1975b) and Hogervorst and Svanberg (1975) give A = 1.52(3) MHz; Deech *et al.* (1975) give A = 1.51(2) MHz.

10D<sub>5/2</sub>. The method is the same as for 8D<sub>5/2</sub>; Svanberg and Tsekeris (1975b) give |A| = 0.4(2) MHz and Hogervorst and Svanberg (1975) give A = -0.30(10) MHz.

12D<sub>3/2</sub>. Svanberg and Belin (1974) studied this state by means of level crossing and by double resonance after two-step excitation. They do not state whether the result given [|A| = 0.758(12) MHz] is from level crossing, double resonance or some average of the two methods.

## VI. RECOMMENDED DATA SET

### A. Coupling constants

In Table IX we have summarized the results for each state where an experimental determination of  $A$  and  $B$  exists. The states are ordered in the same way as in Sec. V. For each state:

- (i) If only one measurement exists, we list the corresponding values.
- (ii) If several measurements exist, but some of them are definitely less accurate than others ("definitely" means that their uncertainty is at least four times larger than the most accurate one), we consider only the most accurate one(s), provided a general agreement exists among all measurements, or an explanation for a disagreement has been found.
- (iii) If several measurements of comparable accuracy exist, and there is a general agreement between them, we list a weighted average of them.
- (iv) If several measurements exist, but there is a substantial and unexplained disagreement among them, we quote the result obtained with the most usual technique, where it is most difficult to imagine unidentified sources of error. If several measurements have been consecutively published by the same authors with the same or similar technique, only the most recent one is considered.

In Table IX only diagonal  $A$  and  $B$  values are listed. When measurements of other quantities are only available without a possibility of computing  $A$  or  $B$ , the reader is referred to Sec. V. In the references to Table IX, no mention is made of works that give the sign of the coupling constants but whose accuracy on the measurement of their absolute value is definitely less than the accuracy in other works.

When in Sec. V we have reanalyzed and corrected some experimental works, the corrected results have been used in the compilation of Table IX.

When the data listed in Sec. V arise *only* from scaling considerations and not from some direct measurements of the absolute value of the coupling constants, the corresponding value is omitted in Table IX.

### B. Hyperfine anomalies

Using the data presented in Table IX, and the definition of the hyperfine anomaly given in equation (2.31), it is possible to compute the value of the hyperfine anomalies between  ${}^6\text{Li}$  and  ${}^7\text{Li}$ ,  ${}^{85}\text{Rb}$  and  ${}^{87}\text{Rb}$ , and any two of the three K isotopes, for a number of states. Since the un-

TABLE X. Hyperfine anomalies (computed from the values in Table IX).

Isotopes		State	Anomaly
1st	2nd		
${}^6\text{Li}$	${}^7\text{Li}$	$2^2S_{1/2}$	+0.000 068 06(63)
${}^6\text{Li}$	${}^7\text{Li}$	$3^2P_{3/2}$	+0.095(71)
${}^{39}\text{K}$	${}^{40}\text{K}$	$4^2S_{1/2}$	+0.004 67(20)
${}^{39}\text{K}$	${}^{41}\text{K}$	$4^2S_{1/2}$	-0.002 293 6(19)
${}^{40}\text{K}$	${}^{41}\text{K}$	$4^2S_{1/2}$	-0.006 928(93)
${}^{85}\text{Rb}$	${}^{87}\text{Rb}$	$5^2S_{1/2}$	+0.003 514 2(30)
${}^{85}\text{Rb}$	${}^{87}\text{Rb}$	$5^2P_{1/2}$	+0.0072(40)

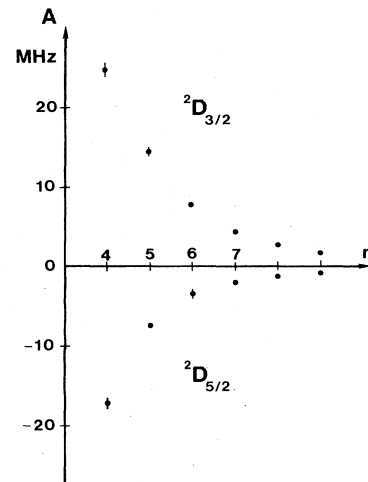


FIG. 22. Magnetic hyperfine coupling constants for the  ${}^2D_{3/2}$  and  ${}^2D_{5/2}$  states of  ${}^{87}\text{Rb}$ , as functions of the principal quantum number. Even though the signs for the  $8^2D_{3/2}$  and  $9^2D_{5/2}$  states have not been determined, we have assumed them to be positive and negative, respectively.

certainty is the sum of the uncertainties on the  $A$  and  $g_I$  values for both isotopes, the accuracy is not very high, and in most cases the result is zero within experimental accuracy. All results whose value differs from zero more than its uncertainty are listed in Table X.

The most surprising result is in the  $3P_{3/2}$  state of Li, where the anomaly appears to be excessively large, and might be ascribed to a slight underestimate of the errors in the original experiment (Isler *et al.*, 1969a).

It must be pointed out that a few of the listed values may appear to be appreciably different from the corresponding values listed by Fuller and Cohen (1970). The reason for this apparent discrepancy is that these authors use a definition of the anomaly that is not the same as the one we use [Eq. (2.39)] and is most commonly used (e.g., Foley 1969, Stroke 1969). If allowance for this different definition is made, our values

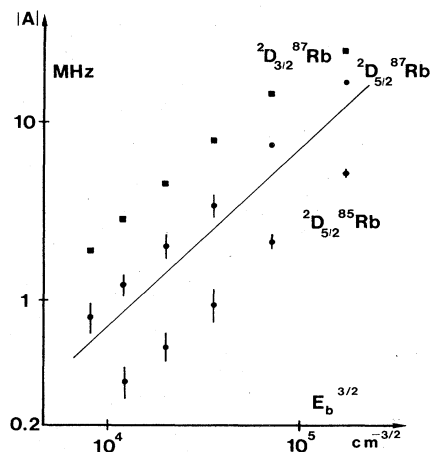


FIG. 23. Absolute values of the magnetic coupling constants for the  ${}^2D_{5/2}$  states in  ${}^{85}\text{Rb}$  and  ${}^{87}\text{Rb}$  (circles) as well as  ${}^2D_{3/2}$  states in  ${}^{87}\text{Rb}$  (squares), plotted versus  $E_b^{3/2}$ ,  $E_b$  being the binding energy of the state. The theoretical slope is shown as a straight line.

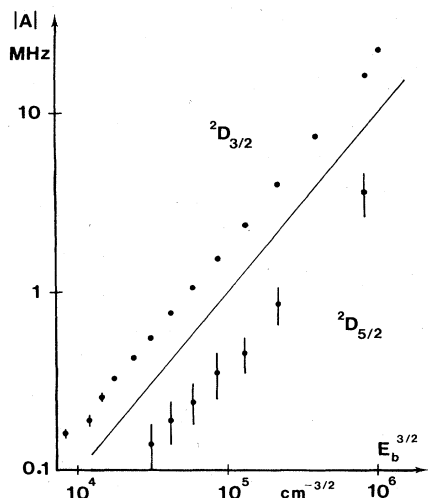


FIG. 24. Absolute values of the magnetic coupling constants for the  ${}^2D$  states of  ${}^{133}\text{Cs}$  versus  $E_b^{3/2}$ ,  $E_b$  being the binding energy. The theoretical slope is shown as a straight line.

agree with those by Fuller and Cohen (1970). For the same reason there is an apparent discrepancy between our value for the  $2S_{1/2}$  state of lithium and that by Schlecht and McColm (1966), quoted by Stroke (1969).

## VII. CONCLUSIONS

The analysis of the previously reported values for the hyperfine constants requires a theoretical investigation that is beyond the scope of this work. Moreover the different orbital dipolar and contact contributions to the dipolar hyperfine constant have been completely determined only in the cases where a third piece of information on the hyperfine structure could be derived from the experiments: the  $2P$  term of Li and the  $4D$  term of Rb. In both terms the fine-structure interval is small and the off-diagonal constant is important in determining the resonance frequencies or the anticrossing points. In both cases the  $a_c$  constant is negative; in the  $4D$  term the  $a_d$  constant is also negative. For all the other states only a semiempirical analysis could be used to derive the different contributions; and significant contributions due to the core polarization have been found in the contact term for  $P$  states, but this analysis requires some theoretical assumptions on the orbital and dipolar terms. Only very recently a preliminary analysis has been carried on for the  $D$  states (Lee *et al.*, 1975). Thus it may be interesting to choose these states to show the regular behavior of the hyperfine structure constants. The dipolar hyperfine constants may be plotted as functions of the principal quantum number  $n$ , as in Fig. 22 for the hyperfine constants in the  ${}^2D_{3/2}$  and  ${}^2D_{5/2}$  states of  ${}^{87}\text{Rb}$ . It results from the regular behavior that the dipolar hyperfine constant for the  ${}^2D_{3/2}$  states is always positive, while for the  ${}^2D_{5/2}$  state is always negative. Then for several states of  ${}^{87}\text{Rb}$  and  ${}^{133}\text{Cs}$  where the sign of the constant is unknown, it may be assigned through this regularity.

Another check of the general behavior for the dipolar hyperfine constant is provided by the linear dependence as a function of  $E_b^{3/2}$ , with  $E_b$  the binding energy, as

found in the semiempirical analysis of Sec. II.B. In Figs. 23 and 24 the dipolar hyperfine constants for  $D$  states of Rb and Cs have been plotted versus  $E_b^{3/2}$ . It results that the experimental values fall along straight lines with the linear theoretical slope, except for the  $4{}^2D_{3/2}$  state of  ${}^{87}\text{Rb}$ .

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