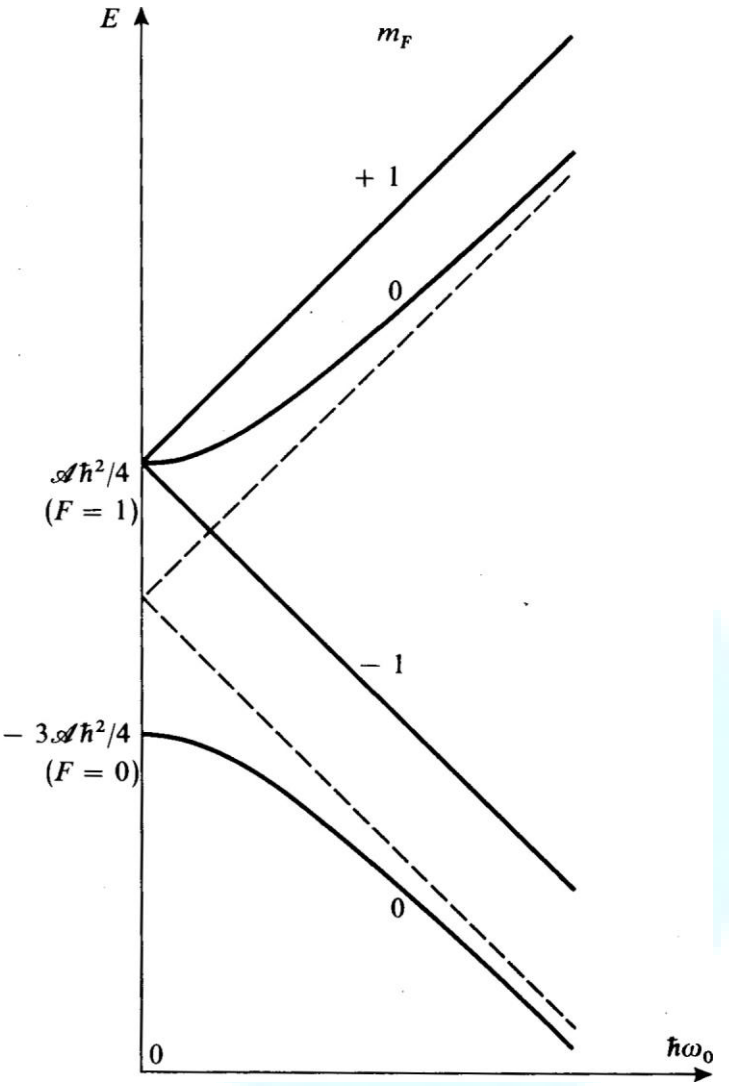


FIGURE 9

The Zeeman diagram (for an arbitrary field) of the Is ground state of the hydrogen atom : m_F remains a good quantum number for any value of the field. We obtain two straight lines, of opposite slopes, corresponding to the values + I and — I of RIF, as well as a hyperbola whose two branches are associated with the two = 0 levels. Figures 5 and 7 give, respectively, the tangents at the origin and the asymptotes of the levels shown in this diagram.

D. THE HYPERFINE STRUCTURE OF THE $n = 1$ LEVEL

We see that the energy depends only on n and J, and not on l.

If we make a limited expansion of formula (C-27) in powers of cc, we obtain :

$$= \text{nt c2} — \frac{1}{2} m_e c^2 \alpha^2 \frac{1}{n^2} - \frac{m_e c^2}{2n^4}\left(\frac{n}{J + 1/2} - \frac{3}{4}\right)\alpha^4 + \ldots \qquad \text{(C-28)}$$

The first term is the rest-mass-energy of the electron. The second term follows from the theory of chapter VII. The third term gives the correction to first order in wf calculated in this chapter.

(iv) Even in the absence of an external field and incident photons, a fluctuating electromagnetic field must be considered to exist in space (cf. complement KY, 3-d-ö). This phenomenon is related to the quantum mechanical nature of the electromagnetic field, which we have not taken into consideration here. The coupling of the atom with these fluctuations of the electromagnetic field removes the degeneracy between the 2s1/2 and 2P1/2 levels. The 2s1/2 level is raised with respect to the 2P112 level by a quantity called the "Lamb shift " which is of the order of I MHz (fig. 4, page 1231).

The theoretical and experimental study of this phenomenon, which was discovered in 1949, has been the object of a great deal of research, leading to the development of modern quantum electrodynamics.

D.THE HYPERFINE STRUCTURE OF THE n = 1 LEVEL

It would now seem logical to study the effect of Whf inside the fine structure levels 2s1/2, 2P1/2 and 2P3/2, in order to see if the interactions related to the proton spin I cause a hyperfine structure to appear in each of these levels. However, since wf does not remove the degeneracy of the ground state Is, it is simpler to study the effect of Whf on this state. The results obtained in this special case can easily be generalized to the 2s1/2, 2P1/2 and 2P3/2 levels.

1.Statement of the problem

a. THE DEGENERACY OF THE Is LEVEL

For the Is level, there is no orbital degeneracy (l = O). On the other hand, the Sz and Iz components of S and I can still take on two values: ms = + 1/2 and tnl = + 1/2. The degeneracy of the Is level is therefore equal to 4, and a possible basis in this level is given by the vectors :

$$\left\{ \left| n = 1 ; l = 0 ; m_L = 0 ; m_S = \pm \frac{1}{2} ; m_I = \pm \frac{1}{2} \right\rangle \right\}$$

b. THE Is LEVEL HAS NO FINE STRUCTURE

We shall show that the wf term does not remove the degeneracy of the Is level.

The Wmv and WD terms do not act on ms and ml, and are represented in the Is subspace by multiples of the unit matrix. We find (cf. complement BXII) :

$$\frac{5}{mec\,\alpha}\,mv\,Is$$

$$s = \frac{1}{72\,mec\,\alpha}$$

Finally, calculation of the matrix elements of the Wso term involves the " angular " matrix elements < I = 0, ntL = O I Lx y z I = O, ml, = 0 which are obviously zero (l = 0); therefore :

SO Is —

In conclusion, Wf merely shifts the Is level as a whole by a quantity equal to :

$$-\frac{5}{-}+\frac{1}{-}\quad\quad 1$$

$$-\,mec\,a = --\,8\,mec\,oc$$

without splitting the level. This result could have been foreseen : since I 0 and s =1/2, J can take on only one value, J = 1/2, and the Is level therefore gives rise to only one fine structure level, ISI/2.

Since the Hamiltonian WI does not split the Is level, we can now consider the effect of the Wkf term. To do so, we must first calculate the matrix which represents Wkf in the Is level.

2. Matrix representation of Wkf in the Is level

a. TERMS OTHER THAN THE CONTACT TERM

Let us show that the first two terms of Whf [formula (B-20)] make no contribution.

Calculation of the contribution from the first term, — go q ^{3} L . MI, leads 47t meR to the "angular" matrix elements < I = 0, n1L = O I L I I = 0, ml, = 0 which are obviously zero (l = 0).

Similarly, it can be shown (cf. complement BXI, 3) that the matrix elements of the second term (the dipole-dipole interaction) are zero because of the spherical symmetry of the Is state.

b. THE CONTACT TERM

The matrix elements of the last term of (B-20), that is, of the contact term, are of the form :

〈n =1 ; I = 0 ; ntL = 0 ; ms ; ml

$$-\frac{2\mu_0}{3}\mathbf{M}_S \cdot \mathbf{M}_I\, \delta(\mathbf{R}) \,|\, n = 1\,;\, l = 0\,;\, m_L = 0\,;\, m_S\,;\, m_I \,\rangle$$

If we go into the { I r > } representation, we can separate the orbital and spin parts of this matrix element and put it in the form :

$\mathscr{A}$ < m's; m'l I . S ms; ml >

where is a number given by :

$$\mathscr{A} = \frac{q^2}{3\varepsilon_0 c^2}\frac{g_p}{m_e M_p} \langle n = 1; l =$$

$$= \frac{q^2}{3\varepsilon_0 c^2}\frac{g_p}{m_e M_p}\frac{1}{4\pi}|R_{10}(0)|^2 \quad O; \qquad -0\ 1^{\delta(\mathbf{R})} \mid n = 1; l = 0; m_L = 0 \rangle$$

4 me m 1 g_p mec2a4 1 + _

We have used the expressions relating Ms and Ml to S and I [cf. (B-18)], as well as the expression for the radial function RIO(r) given in SC-4-c of chapter VIl*.

The orbital variables have therefore completely disappeared, and we are left with a problem of two spin 1/2's, I and S, coupled by an interaction of the form :

$$J\,\mathbf{l}\cdot\mathbf{s}$$

where is a constant.

c. EIGENSTATES AND EIGENVALUES OF THE CONTACT TERM

To represent the operator UI . S, we have thus far considered only the basis :

$$\left\{ \left| s = \frac{1}{2}; I = \frac{1}{2} \right.\right. ; \text{ms; ml} > \qquad \text{(D-10)}$$

formed by the eigenvectors common to S^2, $\mathbf{I}^2$, S_z, I_z. We can also, by introducing the total angular momentum:

$$\mathbf{F} = \mathbf{S} + \mathbf{l}$$

use the basis: i

$$-5' \quad = \frac{1}{2}; F; m_F > \Big\} \qquad \text{(D-12)}$$

formed by the eigenstates common to S^2, 1^2, F^2, Fz. Since s 1/2, F can take on only the two values F = 0 and F = l. We can easily pass from one basis to the other by means of (B-22) and (B-23) of chapter X.

* The factor (l + me/MP) ^{3} in (D-8) arises from the fact that it is the reduced mass which enters into R 10(0). It so happens that, for the contact term, it is correct to take the nuclear finite mass effect into account in this way.

** The total angular momentum is actually F = L + S + I, that is, F = J + I. However, for the ground state, the orbital angular momentum is zero, so F reduces to (D-l l).

The { [F, ntF > } basis is better adapted than the { I ms, ml > } basis to the study of the operator JI . S, as this operator is represented in the { I F, mp > }

basis by a diagonal matrix (for the sake of simplicity, we do not explicitly write s = 1/2 and I = 1/2). This is true, since we obtain, from (D-l l) :

Ml. s (F ^{2} - 1 ^{2} - S ^{2})
2

It follows that the states I F, > are eigenstates of MI . S:

$$\mathscr{A}\mathbf{I}\cdot\mathbf{S}\,|\,F, m_F\rangle = \frac{\mathscr{A}\hbar^2}{2}[F(F+1) - I(I+1) - S(S+1)]\,|\,F, \qquad \text{(D-14)}$$

We see from (D-14) that the eigenvalues depend only on F, and not on "-IF. They are equal to :

$$\frac{\mathscr{A}\hbar^2}{2}\left[2 - \frac{3}{4} - \frac{3}{4}\right] = \frac{\mathscr{A}\hbar^2}{4} \qquad \text{(D-15)}$$

for F = 1, and:

3 3
___ 0_ _ _(D-16) 2 4

for F = O.

The four-fold degeneracy of the Is level is therefore partially removed by Wkf. We obtain a three-fold degenerate F = I level and a non-degenerate F = O level. The (2F + l)-fold degeneracy of the F = I level is essential and is related to the invariance of Wkf under a rotation of the total system.

3. The hyperfine structure of the Is level

a. POSITIONS OF THE LEVELS

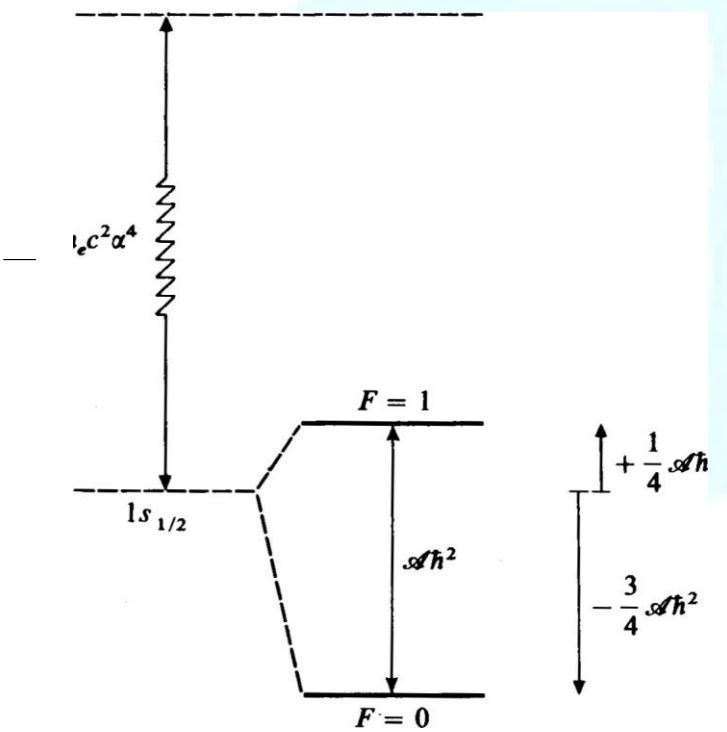
Under the effect of Wf, the energy of the Is level is lowered by a quantity $mec^2a^4/8$ with respect to the value — gc^2 0c $^2/2$ calculated in chapter VIl. Wkf then splits the ISI/2 level into Jwo hyperfine levels, separated by an energy d h ^{2} (fig. 3).

Mh^2 is often called the " hyperfine structure of the ground state ".

COMMENT:

It could be found, similarly, that Whf splits each of the fine structure levels 2.s1/2, 2P1/2 and 2P3/2 into a series of hyperfine levels, corresponding to all the values of F separated by one unit and included between J + I and IJ — Il. For the 2s1/2 and 2P1/2 levels, we have J = 1/2. Therefore, F takes on the two values F = I and F = 0. For the 2P3/2 level, J = 3/2, and, consequently, we have F = 2 and F = I (cf. fig. 4).

D.



Is FIGURE 3

The hyperfine structure of the n = 1 level of the hydrogen atom. Under the effect of WI, the n I level undergoes a global shift equal to

1— mec^2 0t $^4/8$;

—mc a

8J can take on only one value, J = 1/2. When the hyperfine coupling Wkf is taken into account, the ISI/2 level splits into two hyperfinelevels, F = I and F = 0. T'he hyperfine tran2 sition

$$F = 1 \longleftrightarrow F = 0$$

(the 21 cm line studied in radioastronomy) has a frequency which is known experimentally to twelve significant figurß (thanks to the hydrogen maser).

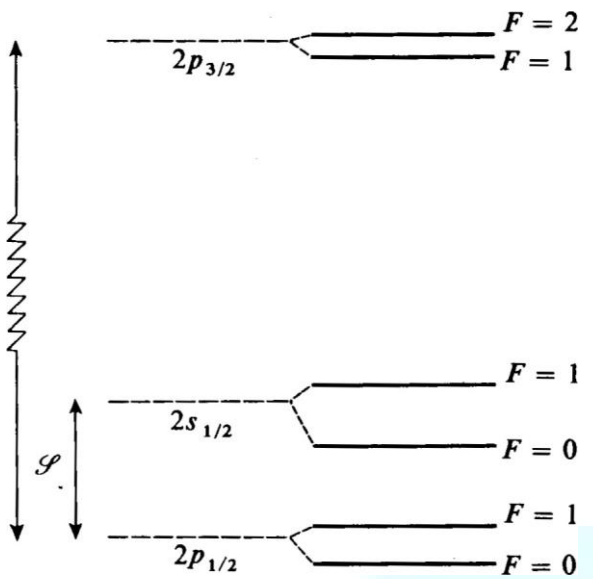


FIGURE 4

ne hyperfine structure of the n = 2 level of the hydrogen atom. The separation S^P between the two levels 2s1/2 and 2P1/2 is the Lamb shift, which is about ten times smaller than the fine structure splitting AE separating the two levels 2P1/2 and 2P3/2 (9^0 1 057.8 MHz; ZE 10 969.1 MHz). When the hyperfine coupling Wkf is taken into account, each level splits into two hyperfine sublevels (the corresponding value of the quantum number F is indicated on the right-hand side of the figure). The hyperfine splittings are equal to 23.7 MHz for the 2P3/2 level, 177.56 MHz for the 2s1/2 level and 59.19 MHz for the 2P1/2 level (for the sake of clarity, the figure is not drawn to scale).

b. IMPORTANCE OF THE HYPERFINE STRUCTURE OF THE Is LEVEL

The hyperfine structure of the ground state of the hydrogen atom is currently the physical quantity which is known experimentally to the highest number of significant figures. Expressed in Hz, it is equal to* •

$$\frac{}{27t} = 1\,420\,405\,751.768 \pm 0.001 \text{ Hz}$$

Such a high degree of experimental accuracy was made possible by the development of the " hydrogen maser" in 1963. The principle of such a device is, very schematically, the following: hydrogen atoms, previously sorted (by a magnetic selection of the Stern-Gerlach type) so as to choose those in the upper hyperfine level F = l, are stored in a glass cell (the arrangement is similar to the one shown in figure 6 of complement Fl). This constitutes an amplifying medium for the hyperfine frequency $\frac{E(F=1) - E(F=0)}{h}$. If the cell is placed in a cavity tuned to the hyperfine frequency, and if the losses of the cavity are small enough for the gain to be greater than the losses, the system becomes unstable and can oscillate : we obtain an " atomic oscillator" (a maser). The frequency of the oscillator is very

stable and of great spectral purity. Its measurement gives directly the value of the hyperfine splitting, expressed in Hz.

Note, finally, that hydrogen atoms in interstellar space are detected in radioastronomy by the radiation they emit spontaneously when they fall from the F = I hyperfine level to the F = 0 hyperfine level of the ground state (this transition corresponds to a wave length of 21 cm). Most of the information we possess about interstellar hydrogen clouds is supplied by the study of this 21 cm line.

E. THE ZEEMAN EFFECT OF THE Is GROUND STATE HYPERFINE STRUCTURE

1. Statement of the problem

a. THE ZEEMAN HAMILTONIAN wz

We now assume the atom to be placed in a static uniform magnetic field B

o

*parallel to Oz. This field interacts with the various magnetic moments present in q the atom : the orbital and spin magnetic moments of the electron, ML = — L and

2me q

= — P I [cf. expres— S, and the magnetic moment of the nucleus, Ml

2MP

sion (B-i8)].

* The calculations presented in this chapter are obviously completely incapable of predicting all these significant figures. Moreover, even the most advanced theories cannot, at the present time, explain more than the first five or six figures of (D-17).

The Zeeman Hamiltonian Wz which describes the interaction energy of the atom with the field Bo can then be written :

$$-\mathbf{B}_0 \cdot (\mathbf{M}_L + \mathbf{M}_S + \mathbf{M}_I)$$

=OO(Lz + msZ) + OnIz

where oo (the Larmor angular frequency in the field Bo) and on are defined by:

$$\begin{cases} \omega_0 = -\dfrac{q}{2m_e} B_0 \\ \omega_n = \dfrac{q}{2M_p} g_p B_0 \end{cases}$$

Since M > me, we clearly have :

1001 > . lonl

COMMENT :

Rigorously, Wz contains another term, which is quadratic in Bo (the diamagnetic term). This term does not act on the electronic and nuclear spin variables and merely shifts the Is level as a whole, without modifying its Zeeman diagram, which we shall study later. Moreover, it is much smaller than (E-l). Recall that a detailed study of the effect of the diamagnetic term is presented in complement DVll•

b. THE PERTURBATION "SEEN" BY THE Is LEVEL

In this section, we propose to study the effect of Wz on the Is ground state of the hydrogen atom (the case of the n = 2 level is slightly more complicated since, in a zero magnetic field, this level possesses both a fine and a hyperfine structure, while the n I level has only a hyperfine structure; the principle of the calculation is nevertheless the same). Even with the strongest magnetic fields that can be produced in the *laboratory, Wz is much smaller than the distance between the Is level and the other levels; consequently, its effect can be treated by perturbation theory.

The effect of a magnetic field on an atomic energy level is called the " Zeeman effect ". When Bo is plotted on the x-axis and the energies of the various sublevels it creates are plotted on the y-axis, a Zeeman diagram is obtained.

If Bo is sufficiently strong, the Zeeman Hamiltonian Wz can be of the same order of magnitude as the hyperfine Hamiltonian Whf*, or even larger. On the other hand, if Bo is very weak, Wz < Whf. Therefore, in general it is not possible to establish the relative importance of Wz and Whf. To obtain the energies of the various sublevels, (Wz + Whf) must be diagonalized inside the n I level.

* Recall that Wf shifts the Is level as a whole; it therefore also shifts the Zeeman diagram as a whole.

We showed in D-2 that the restriction of Wkf to the n — I level could be put in the form 31 . S. Using expression (E-l) for Wz, we see that we must also calculate matrix elements of the form :

$$\langle n = 1 ; I = 0; mL = 0; m's; m; I \; oo(Lz + 2Sz) + onlz \; | \; n = 1 ; l = 0 ; m_L = 0 ; m_S ; m_I \rangle$$

The contribution of ooLz is zero, since I and are zero. Since 200Sz + onlz acts only on the spin variables, we can, for this term, separate the orbital part of the matrix element :

$$\langle n = l ; 1 = 0; = O \; l \; n = 1 ; l = 0 ; m_L = 0 \rangle \text{ - } l$$

from the spin part.

In conclusion, therefore, we must, ignoring the quantum numbers n, l, ntL, diagonalize the operator :

$\mathscr{A}$ I. S + 200sz + $\omega_n I_z$

which acts only on the spin degrees of freedom. To do so, we can use either the { | ms, ml > } basis or the { I F, mp > } basis.

According to (E-4), the last term of (E-7) is much smaller than the second one. To simplify the discussion, we shall neglect the term onlz from now on (it would be possible, however, to take it into account*). The perturbation " seen " by the Is level can therefore be written, finally :

$\mathscr{A}$ I. S + 200sz

c. DIFFERENT DOMAINS OF FIELD STRENGTH

By varying Bo, we can continuously modify the magnitude of the Zeeman term 200Sz. We shall consider three different field strengths, determined by the respective orders of magnitude of the hyperfine term and the Zeeman term :

(i) hoo < J h ^{2} : weak fields
(ii) hoo > edh ^{2} : strong fields
(iii) hoo d h ^{2} : intermediate fields

We shall later see that it is possible to diagonalize operator (E-8) exactly. However, in order to give a particularly simple example of perturbation theory, we shall use a slightly different method in cases (i) and (ii). In case (i), we shall treat 200Sz like a perturbation with respect to . S. On the other hand, in case (ii), we shall treat MI . S like a perturbation with respect to 200Sz. The exact diagonalization of the set of two operators, indispensable in case (iii), will allow us to check the preceding . results.

2. The weak-field Zeeman effect

The eigenstates and eigenvalues of M I . S have already been determined (S D-2). We therefore obtain two different levels : the three-fold degenerate level,

$$\{ | F = 1 ; m_F = -1, 0, +1 \rangle \},$$

★ This is what we do in complement Cx„, in which we study the hydrogen-like systems (muonium, positronium) for which it is not possible to neglect the magnetic moment of one of the two particles.

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of energy dh ^{2}/4, and the non-degenerate level, { I F = 0; = 0 > }, of energy _ 3Mh ^{2}/4. Since we are treating 200Sz like a perturbation with respect to d I . S, we must now separately diagonalize the two matrices representing 200Sz in the two levels, F = I and F = 0, corresponding to two distinct eigenvalues of I . S.

a. MATRIX REPRESENTATION OF IN THE { IF. } BASIS

Since we shall need it later, we shall begin by writing the matrix which represents Sz in the { I F, ntF) } basis (for the problem which concerns us here, it would suffice to write the two submatrices corresponding to the F = I and F = 0 subspaces).

By using formulas (B-22) and (B-23) of chapter X, we easily obtain:

$$\begin{cases} S_z | F = 1 ; m_F = 1 \rangle = \dfrac{\hbar}{2} | F = 1 ; m_F = 1 \rangle \\ S_z | F = 1 ; m_F = 0 \rangle = \dfrac{\hbar}{2} | F = 0 ; m_F = 0 \rangle \\ S_z | F = 1 ; m_F = -1 \rangle = -\dfrac{\hbar}{2} | F = 1 ; m_F = \\ S_z | F = 0 ; m_F = 0 \rangle = \dfrac{\hbar}{2} | F = 1 ; m_F = 0 \rangle \end{cases}$$

which gives the following expression for the matrix representing Sz in the { | F; m_F > } basis (the basis vectors are arranged in the order I l, I I l, 0〉, | 1, − 1 〉, | 0, 0 〉):

$$= \frac{\hbar}{2} \times \begin{array}{|c|c|c|c|} \hline 1 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 1 \\ \hline 0 & 0 & -1 & 0 \\ \hline 0 & 1 & 0 & 0 \\ \hline \end{array}$$

COMMENT :

It is instructive to compare the preceding matrix with the one which represents FZ in the same basis :

$$(F_z) = \hbar \times \begin{pmatrix} & & & \\ 0 & 0 & & \\ & & & \\ & & & \end{pmatrix}$$

We see, first of all, that the two matrices are not proportional: the (Fz) matrix is diagonal, while the (Sz) one is not.

However, if we confine ourselves to the restrictions of the two matrices in the F = I subspace [limited by the darker line in expressions (E-10) and (E-l I we see that they are proportional. Denoting by PI the projector onto the F I subspace (cf. complement BIO, we have :

$$P_1 S_z P_1 = \frac{1}{2} P_1 F_z P_1$$

It would be simple to •show that the same relation exists between sx and Fx on the one hand, and Sy and Fy, on the other.

We have thus found a special case of the Wigner-Eckart theorem (complement Dx), according to which, in a given eigensubspace of the total angular momentum, all the matrices which represent vector operators are proportional. It is clear from this example that this proportionality exists only for the restrictions of operators to a given eigensubspace of the total angular momentum, and not for the operators themselves.

Moreover, the proportionality coefficient 1/2 which appears in (E-12) can be obtained immediately from the projection theorem. According to formula (30) of complement Ex, this coefficient is equal to :

$$\frac{\langle \mathbf{S} \cdot \mathbf{F} \rangle_{F=1}}{\langle \mathbf{F}^2 \rangle_{F=1}} = \frac{F(F+1) + s(s+1) - I(I+1)}{2F(F+1)}$$

Since s — I = 1/2, (E-13) is indeed equal to 1/2.

b. WEAK-FIELD EIGENSTATES AND EIGENVALUES

According to the results of Sa, the matrix which represents 200Sz in the F I level can be written :

hoo	0	0
o	0	
0	0	hoo

In the F = 0 level, this matrix reduces to a number, equal to 0.

Since these two matrices are diagonal, we can immediately find the weak-field eigenstates (to zeroth order in 00) and the eigenvalues (to first order in 00):

Eigenstates	Eigenvalues
	dh2
I F — 1 ;m_F =+ hoo	
$\| F = 1 ; m_F = 0 \rangle$	$\leftrightarrow \frac{\mathscr{A}\hbar^2}{4} + 0$
I F= 1 ; $m_F = -1 \rangle$	$\leftrightarrow \frac{\mathscr{A}\hbar^2}{4}$ –hoo

$$F = 0;\ m_F = 0\rangle \qquad \longleftrightarrow \qquad -3\frac{\hbar\omega_0}{4}$$

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In figure 5, we have plotted hoo on the x-axis and the energies of the four Zeeman sublevels on the y-axis (Zeeman diagram). In a zero field, we have the two hyperfine levels, F = I and F = 0. When the field Bo is turned on, the I F = 0, = 0 > sublevel, which is not degenerate, starts horizontally; as for the F = I level, its three-fold degeneracy is completely removed : three equidistant sublevels are obtained, varying linearly with hoo, with slopes of + l, O, I respectively.

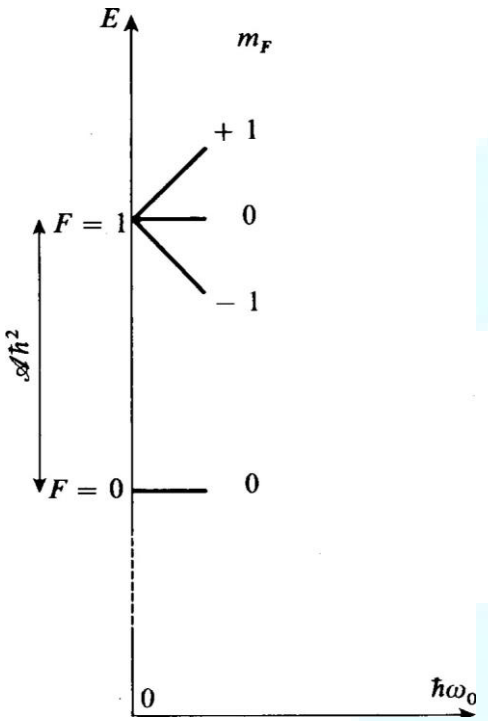

FIGURE 5

The weak-field Zeeman diagram of the Is ground state of the hydrogen atom. The hyperfine F = I level splits into three equidistant levels, each of which corresponds to a well-defined value of the quantum number niF. The F = O level does not undergo any shift to first order in oo.

The preceding treatment is valid as long as the difference hoo between two adjacent Zeeman sublevels of the F I level remains much smaller than the zerofield difference between the F = I and F = 0 levels (the hyperfine structure).

COMMENT :

The Wigner-Eckart theorem, mentioned above, makes it possible to show that, in a given level F of the total angular momentum, the Zeeman Hamiltonian oo(Lz + 2Sz) is represented by a matrix proportional to Fz. Thus, we can write, denoting the projector onto the F level by PA.

$$\omega_0(L_z + \qquad = \text{gF00PFFzPF}$$

gF is called the Landéfactor of the F state. In the case which concerns us here, —1.

c. THE BOHR FREQUENCIES INVOLVED IN THE EVOLUTION OF < F > AND < S). COMPARISON WITH THE VECTOR MODEL OF THE ATOM

In this section, we shall determine the different Bohr frequencies which appear in the evolution of < F > and < S and show that certain aspects of the results obtained recall those found by using the vector model of the atom (cf. complement Fx).