First of all, we shall briefly review the predictions of the vector model of the atom (in which the various angular momenta are treated like classical vectors) as far as the hyperfine coupling between **I** and **S** is concerned. In a zero field, $\mathbf{F} = \mathbf{I} + \mathbf{S}$ is a constant of the motion. **I** and **S** precess about their resultant **F** with an angular velocity proportional to the coupling constant $\mathcal{A}$ between **I** and **S**. If the system is, in addition, placed in a weak static field $\mathbf{B}_0$ parallel to Oz, onto the rapid precessional motion of **I** and **S** about **F** is superposed a slow precessional motion of **F** about Oz (Larmor precession; fig. 6).

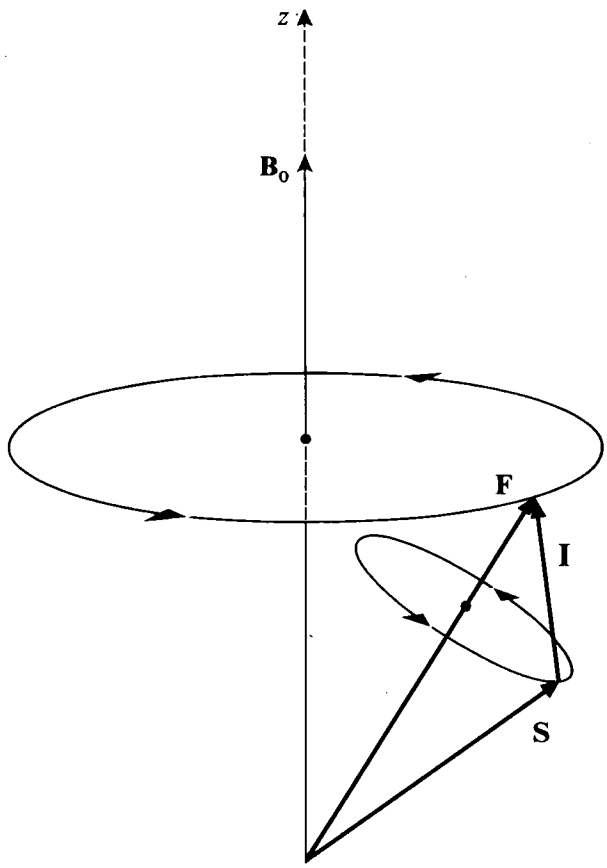

FIGURE 6

The motion of S, I and F in the vector model of the atom. S and I precess rapidly about F under the effect of the hyperfine coupling. In a weak field, F slowly precesses about B (Larmor precession).

F_z is therefore a constant of the motion, while S_z has a static part (the projection onto Oz of the component of **S** parallel to **F**), and a part which is modulated by the hyperfine precession frequency (the projection onto Oz of the component of **S** perpendicular to **F**, which precesses about **F**).

Let us compare these semi-classical results with those of the quantum theory presented earlier in this section. To do so, we must consider the time evolution of the mean values $\langle F_z \rangle$ and $\langle S_z \rangle$. According to the discussion of § D-2-d of chapter III, the mean value $\langle G \rangle(t)$ of a physical quantity G contains a series of components which oscillate at the various Bohr frequencies $(E - E')/h$ of the system. Also, a given Bohr frequency appears in $\langle G \rangle(t)$ only if the matrix element of G between the states corresponding to the two energies is different from zero. In the problem which concerns us here, the eigenstates of the weak-field Hamiltonian are the $|F, m_F\rangle$ states. Now consider the two matrices (E-10) and (E-11) which represent S_z and F_z in this basis. Since F_z has only diagonal matrix elements, no Bohr frequency different from zero can appear in $\langle F_z \rangle(t)$: $\langle F_z \rangle$ is therefore static. On the other hand, S_z has, not only diagonal matrix elements (with which is associated a static component of $\langle S_z \rangle$), but also a non-diagonal element between the $|F = 1, m_F = 0\rangle$ and $|F = 0, m_F = 0\rangle$ states, whose energy

difference is $\mathscr{A}\hbar^2$, according to table (E-15) (or figure 5). It follows that $\langle S_z \rangle$ has, in addition to a static component, a component modulated at the angular frequency $\mathscr{A}\hbar$. This result recalls the one obtained using the vector model of the atom★.

COMMENT:

A relation can be established between perturbation theory and the vector model of the atom. The influence of a weak field B_0 on the $F = 1$ and $F = 0$ levels can be obtained by retaining in the Zeeman Hamiltonian $2\omega_0 S_z$ only the matrix elements in the $F = 1$ and $F = 0$ levels, "forgetting" the matrix element of S_z between $|F = 1; m_F = 0\rangle$ and $|F = 0; m_F = 0\rangle$. Proceeding in this way, we also "forget" the modulated component of $\langle S_z \rangle$, which is proportional to this matrix element. We therefore keep only the component of $\langle \mathbf{S} \rangle$ parallel to $\langle \mathbf{F} \rangle$.

Now, this is precisely what we do in the vector model of the atom when we want to evaluate the interaction energy with the field $\mathbf{B}_0$. In a weak field, $\mathbf{F}$ does precess about $\mathbf{B}_0$ much more slowly than $\mathbf{S}$ does about $\mathbf{F}$. The interaction of $\mathbf{B}_0$ with the component of $\mathbf{S}$ perpendicular to $\mathbf{F}$ therefore has no effect, on the average; only the projection of $\mathbf{S}$ onto $\mathbf{F}$ counts. This is how, for example, the Landé factor is calculated.

3. The strong-field Zeeman effect

We must now start by diagonalizing the Zeeman term.

a. EIGENSTATES AND EIGENVALUES OF THE ZEEMAN TERM

This term is diagonal in the $\{ |m_S, m_I\rangle \}$ basis:

$$2\omega_0 S_z |m_S, m_I\rangle = 2m_S\hbar\omega_0 |m_S, m_I\rangle \tag{E-17}$$

Since $m_S = \pm 1/2$, the eigenvalues are equal to $\pm \hbar\omega_0$. Each of them is therefore two-fold degenerate, because of the two possible values of m_I. We therefore have★★:

$$\begin{cases} 2\omega_0 S_z |+, \pm\rangle = +\hbar\omega_0 |+, \pm\rangle \\ 2\omega_0 S_z |-, \pm\rangle = -\hbar\omega_0 |-, \pm\rangle \end{cases} \tag{E-18}$$

★ A parallel could also be established between the evolution of $\langle F_x \rangle$, $\langle S_x \rangle$, $\langle F_y \rangle$, $\langle S_y \rangle$, and that of the projections of the vectors $\mathbf{F}$ and $\mathbf{S}$ of figure 6 onto Ox and Oy. However, the motion of $\langle \mathbf{F} \rangle$ and $\langle \mathbf{S} \rangle$ does not coincide perfectly with that of the classical angular momenta. In particular, the modulus of $\langle \mathbf{S} \rangle$ is not necessarily constant (in quantum mechanics, $\langle \mathbf{S}^2 \rangle \neq \langle \mathbf{S} \rangle^2$); see discussion of complement F_X.

★★ To simplify the notation, we shall often write $|\varepsilon_S, \varepsilon_I\rangle$ instead of $|m_S, m_I\rangle$, where ε_S and ε_I are equal to + or −, depending on the signs of m_S and m_I.

b. EFFECTS OF THE HYPERFINE TERM CONSIDERED AS A PERTURBATION

The corrections to first order in $\mathscr{A}$ can be obtained by diagonalizing the restrictions of the operator $\mathscr{A}\,\mathbf{I}\,.\,\mathbf{S}$ to the two subspaces $\{\,|\,+,\pm\,\rangle\,\}$ and $\{\,|\,-,\pm\,\rangle\,\}$ corresponding to the two different eigenvalues of $2\omega_0 S_z$.

First of all, notice that, in each of these two subspaces, the two basis vectors $|\,+,+\,\rangle$ and $|\,+,-\,\rangle$ (or $|\,-,+\,\rangle$ and $|\,-,-\,\rangle$) are also eigenvectors of F_z, but do not correspond to the same value of $m_F = m_S + m_I$. Since the operator $\mathscr{A}\,\mathbf{I}\,.\,\mathbf{S} = \dfrac{\mathscr{A}}{2}\,(\mathbf{F}^2 - \mathbf{I}^2 - \mathbf{S}^2)$ commutes with F_z, it has no matrix elements between the two states $|\,+,+\,\rangle$ and $|\,+,-\,\rangle$, or $|\,-,+\,\rangle$ and $|\,-,-\,\rangle$. The two matrices representing $\mathscr{A}\,\mathbf{I}\,.\,\mathbf{S}$ in the two subspaces $\{\,|\,+,\pm\,\rangle\,\}$ and $\{\,|\,-,\pm\,\rangle\,\}$ are then diagonal, and their eigenvalues are simply the diagonal elements:

$$\langle\, m_S;\, m_I \,|\, \mathscr{A}\,\mathbf{I}\,.\,\mathbf{S} \,|\, m_S;\, m_I\,\rangle,$$

which can also be written, using the relation:

$$\mathbf{I}\,.\,\mathbf{S} = I_z S_z + \frac{1}{2}(I_+ S_- + I_- S_+) \tag{E-19}$$

in the form:

$$\langle\, m_S, m_I \,|\, \mathscr{A}\,\mathbf{I}\,.\,\mathbf{S} \,|\, m_S, m_I\,\rangle = \langle\, m_S, m_I \,|\, \mathscr{A} I_z S_z \,|\, m_S, m_I\,\rangle = \mathscr{A}\hbar^2 m_S m_I \tag{E-20}$$

Finally, in a strong field, the eigenstates (to zeroeth order in $\mathscr{A}$) and the eigenvalues (to first order in $\mathscr{A}$) are:

Eigenstates	*Eigenvalues*
$\|\,+,+\,\rangle$	$\hbar\omega_0 + \dfrac{\mathscr{A}\hbar^2}{4}$
$\|\,+,-\,\rangle$	$\hbar\omega_0 - \dfrac{\mathscr{A}\hbar^2}{4}$
$\|\,-,+\,\rangle$	$-\hbar\omega_0 - \dfrac{\mathscr{A}\hbar^2}{4}$
$\|\,-,-\,\rangle$	$-\hbar\omega_0 + \dfrac{\mathscr{A}\hbar^2}{4}$

(E-21)

In figure 7, the solid-line curves on the right-hand side (for $\hbar\omega_0 \gg \mathscr{A}\hbar^2$) represent the strong-field energy levels: we obtain two parallel straight lines of slope + 1, separated by an energy $\mathscr{A}\hbar^2/2$, and two parallel straight lines of slope − 1, also separated by $\mathscr{A}\hbar^2/2$. The perturbation treatments presented in this section and the preceding one therefore give the strong-field asymptotes and the tangents at the origin of the energy levels.

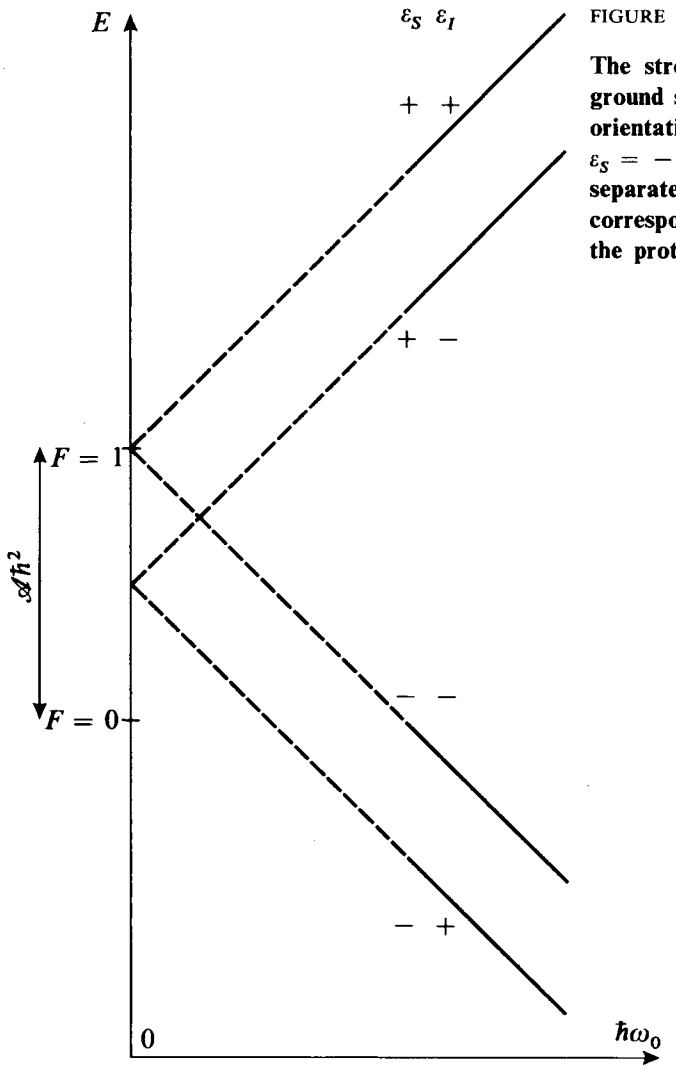

FIGURE 7

The strong-field Zeeman diagram of the 1*s* ground state of the hydrogen atom. For each orientation of the electronic spin ($\varepsilon_S = +$ or $\varepsilon_S = -$), we obtain two parallel straight lines separated by an energy $\mathscr{A}\hbar^2/2$, each one corresponding to a different orientation of the proton spin ($\varepsilon_I = +$ or $\varepsilon_I = -$).

COMMENT:

The strong-field splitting $\mathscr{A}\hbar^2/2$ of the two states, $|+, + \rangle$ and $|+, - \rangle$ or $|-, + \rangle$ and $|-, - \rangle$, can be interpreted in the following way. We have seen that only the term $I_z S_z$ of expression (E-19) for $\mathbf{I} \cdot \mathbf{S}$ is involved in a strong field, when the hyperfine coupling is treated like a perturbation of the Zeeman term. The total strong-field Hamiltonian (E-8) can therefore be written:

$$2\omega_0 S_z + \mathscr{A} I_z S_z = 2\left(\omega_0{}^{\bullet} + \frac{\mathscr{A}}{2} I_z\right) S_z \qquad \text{(E-22)}$$

It is as if the electronic spin "saw", in addition to the external field $\mathbf{B}_0$, a smaller "internal field", arising from the hyperfine coupling between $\mathbf{I}$ and $\mathbf{S}$ and having two possible values, depending on whether the nuclear spin points up or down. This field adds to or substracts from $\mathbf{B}_0$ and is responsible for the energy difference between $|+, + \rangle$ and $|+, - \rangle$ or between $|-, + \rangle$ and $|-, - \rangle$.

c. THE BOHR FREQUENCIES INVOLVED IN THE EVOLUTION OF $\langle S_z \rangle$

In a strong field, the Zeeman coupling of **S** with $\mathbf{B}_0$ is more important than the hyperfine coupling of **S** with **I**. If we start by neglecting this hyperfine coupling, the vector model of the atom predicts that **S** will precess (very rapidly since $|\mathbf{B}_0|$ is large) about the Oz direction of $\mathbf{B}_0$ (**I** remains motionless, since we have assumed ω_n to be negligible).

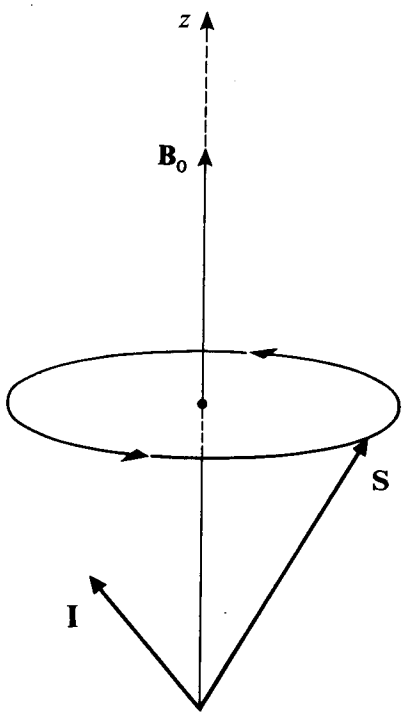

FIGURE 8

The motion of S in the vector model of the atom. In a strong field, S precesses rapidly about $\mathbf{B}_0$ (here we are neglecting both the Zeeman coupling between I and $\mathbf{B}_0$ and the hyperfine coupling between I and S, so that I remains motionless).

Expression (E-19) for the hyperfine coupling remains valid for classical vectors. Because of the very rapid precession of **S**, the terms S_+ and S_- oscillate very fast and have, on the average, no effect, so that only the term $I_z S_z$ counts. The effect of the hyperfine coupling is therefore to add a small field parallel to Oz and proportional to I_z (*cf.* comment of the preceding section), which accelerates or slows down the precession of **S** about Oz, depending on the sign of I_z. The vector model of the atom thus predicts that S_z will be static in a strong field.

We shall show that quantum theory gives an analogous result for the mean value $\langle S_z \rangle$ of the observable S_z. In a strong field, the well-defined energy states are, as we have seen, the states $| m_S, m_I \rangle$. Now, in this basis, the operator S_z has only diagonal matrix elements. No non-zero Bohr frequency can therefore appear in $\langle S_z \rangle$, which, consequently, is a static quantity*, unlike its weak-field counterpart (*cf.* § E-2-c).

* The study of $\langle S_x \rangle$ and $\langle S_y \rangle$ presents no difficulty. We find two Bohr angular frequencies : one, $\omega_0 + \mathscr{A}\hbar/2$, slightly larger than ω_0, and the other one, $\omega_0 - \mathscr{A}\hbar/2$, slightly smaller. They correspond to the two possible orientations of the "internal field", produced by I_z, which adds to the external field B_0.

Similarly, we find that **I** precesses about the "internal field" produced by S_z.

4. The intermediate-field Zeeman effect

a. THE MATRIX WHICH REPRESENTS THE TOTAL PERTURBATION IN THE $\{|F, m_F\rangle\}$ BASIS

The $|F, m_F\rangle$ states are eigenstates of the operator $\mathscr{A}\mathbf{I}\cdot\mathbf{S}$. The matrix which represents this operator in the $\{|F, m_F\rangle\}$ basis is therefore diagonal. The diagonal elements corresponding to $F = 1$ are equal to $\mathscr{A}\hbar^2/4$, and those corresponding to $F = 0$, to $-3\mathscr{A}\hbar^2/4$. Furthermore, we have already written, in (E-10), the matrix representation of S_z in the same basis. It is now very simple to write the matrix which represents the total perturbation (E-8). Arranging the basis vectors in the order $|1, 1\rangle, |1, -1\rangle, |1, 0\rangle, |0, 0\rangle$, we thus obtain:

$\frac{\mathscr{A}\hbar^2}{4} + \hbar\omega_0$	0	0	0
0	$\frac{\mathscr{A}\hbar^2}{4} - \hbar\omega_0$	0	0
0	0	$\frac{\mathscr{A}\hbar^2}{4}$	$\hbar\omega_0$
0	0	$\hbar\omega_0$	$-\frac{3\mathscr{A}\hbar^2}{4}$

(E-23)

COMMENT:

S_z and F_z commute; $2\omega_0 S_z$ can therefore have non-zero matrix elements only between two states with the same m_F. Thus, we could have predicted all the zeros of matrix (E-23).

b. ENERGY VALUES IN AN ARBITRARY FIELD

Matrix (E-23) can be broken into two 1×1 matrices and one 2×2 matrix. The two 1×1 matrices immediately yield two eigenvalues:

$$\begin{cases} E_1 = \frac{\mathscr{A}\hbar^2}{4} + \hbar\omega_0 \\ E_2 = \frac{\mathscr{A}\hbar^2}{4} - \hbar\omega_0 \end{cases} \tag{E-24}$$

corresponding respectively to the state $|1, 1\rangle$ (that is, the state $|+, +\rangle$) and to the state $|1, -1\rangle$ (that is, the state $|-, -\rangle$). In figure 9, the two straight lines of slopes $+1$ and -1 passing through the point whose ordinate is $+\mathscr{A}\hbar^2/4$ for a zero field (for which the perturbation theory treatment gave only the initial and asymptotic behavior) therefore represent, for any B_0, two of the Zeeman sublevels.

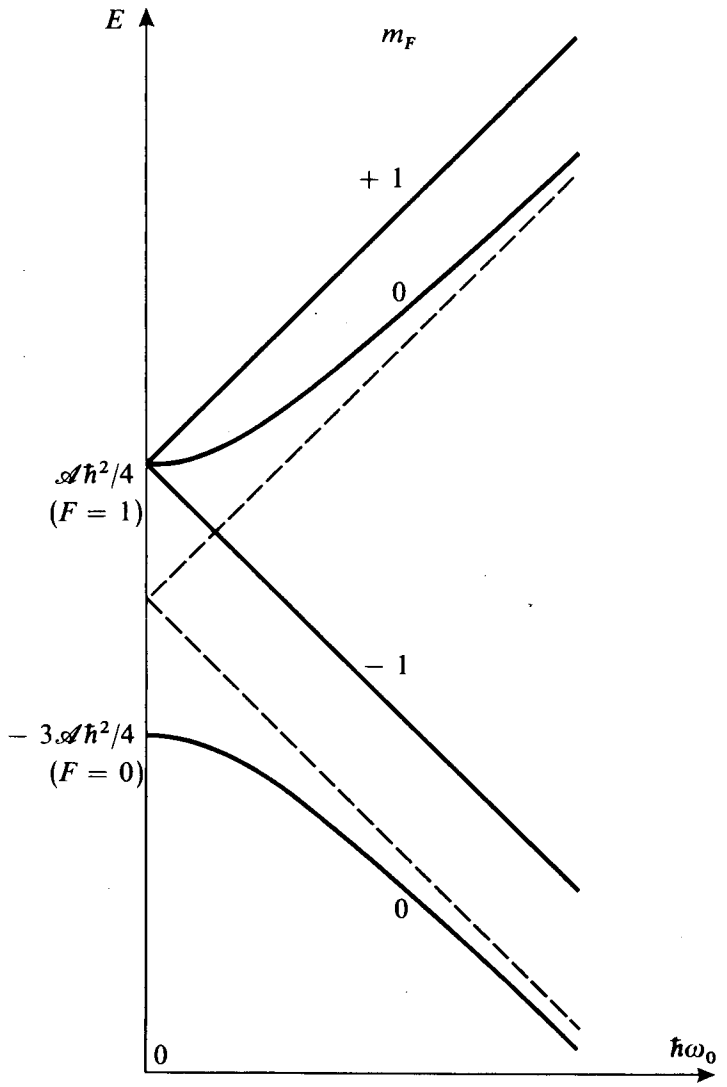

FIGURE 9

The Zeeman diagram (for an arbitrary field) of the $1s$ 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 + 1 and − 1 of m_F, as well as a hyperbola whose two branches are associated with the two $m_F = 0$ levels. Figures 5 and 7 give, respectively, the tangents at the origin and the asymptotes of the levels shown in this diagram.

The eigenvalue equation of the remaining 2 × 2 matrix can be written:

$$\left(\frac{\mathscr{A}\hbar^2}{4} - E\right)\left(-\frac{3\mathscr{A}\hbar^2}{4} - E\right) - \hbar^2\omega_0^2 = 0 \tag{E-25}$$

The two roots of this equation can easily be found:

$$E_3 = -\frac{\mathscr{A}\hbar^2}{4} + \sqrt{\left(\frac{\mathscr{A}\hbar^2}{2}\right)^2 + \hbar^2\omega_0^2} \tag{E-26}$$

$$E_4 = -\frac{\mathscr{A}\hbar^2}{4} - \sqrt{\left(\frac{\mathscr{A}\hbar^2}{2}\right)^2 + \hbar^2\omega_0^2} \tag{E-27}$$

When $\hbar\omega_0$ varies, the two points of abscissas $\hbar\omega_0$ and ordinates E_3 and E_4 follow the two branches of a hyperbola (fig. 9). The asymptotes of this hyperbola are the two straight lines whose equation is $E = -(\mathcal{A}\hbar^2/4) \pm \hbar\omega_0$, obtained in §3 above. The two turning points of the hyperbola have abscissas of $\omega_0 = 0$ and ordinates of $-(\mathcal{A}\hbar^2/4) \pm \mathcal{A}\hbar^2/2$, that is, $\mathcal{A}\hbar^2/4$ and $-3\mathcal{A}\hbar^2/4$. The tangents at both these points are horizontal. This is in agreement with the results of §2 for the states $|F = 1; m_F = 0\rangle$ and $|F = 0; m_F = 0\rangle$.

The preceding results are summarized in figure 9, which is the Zeeman diagram of the $1s$ ground state.

c. PARTIAL HYPERFINE DECOUPLING

In a weak field, the well-defined energy states are the states $|F, m_F\rangle$; in a strong field, the states $|m_S, m_I\rangle$; in an intermediate field, the eigenstates of matrix (E-23), which are intermediate between the states $|F, m_F\rangle$ and the states $|m_S, m_I\rangle$.

One thus moves continuously from a strong coupling between **I** and **S** (coupled bases) to a total decoupling (uncoupled bases) via a partial coupling.

COMMENT:

An analogous phenomenon exists for the Zeeman fine structure effect. If, for simplicity, we neglect W_{hf}, we know (§ C) that, in a zero field, the eigenstates of the Hamiltonian H are the $|J, m_J\rangle$ states corresponding to a strong coupling between **L** and **S** (the spin-orbit coupling). This property remains valid as long as $W_Z \ll W_f$. If, on the other hand, B_0 is strong enough to make $W_Z \gg W_f$, we find that the eigenstates of H are the $|m_L, m_S\rangle$ states corresponding to a total decoupling of **L** and **S**. The intermediate zone ($W_Z \simeq W_f$) corresponds to a partial coupling of **L** and **S**. See, for example, complement D_{XII}, in which we study the Zeeman effect of the $2p$ level (without taking W_{hf} into account).

References and suggestions for further reading:

The hydrogen atom spectrum: Series (11.7), Bethe and Salpeter (11.10).

The Dirac equation : the subsection "Relativistic quantum mechanics" of section 2 of the bibliography and Messiah (1.17), chap. XX, especially §§ V and IV-27.

The fine structure of the $n = 2$ level and the Lamb shift: Lamb and Retherford (3.11); Frisch (3.13); Series (11.7), chaps. VI, VII and VIII.

The hyperfine structure of the ground state: Crampton et al (3.12).

The Zeeman effect and the vector model of the atom: Cagnac and Pebay-Peyroula (11.2), chap. XVII, §§3E and 4C; Born (11.4), chap. 6, §2.

Interstellar hydrogen: Roberts (11.17); Encrenaz (12.11), chap. IV.

A. INTRODUCTION

The most important forces inside atoms are Coulomb electrostatic forces. We took them into account in chapter VII by choosing as the hydrogen atom Hamiltonian:

$$H_0 = \frac{\mathbf{P}^2}{2\mu} + V(R) \tag{A-1}$$

The first term represents the kinetic energy of the atom in the center of mass frame (μ is the reduced mass). The second term:

$$V(R) = -\frac{q^2}{4\pi\varepsilon_0}\frac{1}{R} = -\frac{e^2}{R} \tag{A-2}$$

represents the electrostatic interaction energy between the electron and the proton (q is the electron charge). In §C of chapter VII, we calculated in detail the eigenstates and eigenvalues of H_0.

Actually, expression (A-1) is only approximate: it does not take any relativistic effects into account. In particular, all the magnetic effects related to the electron spin are ignored. Moreover, we have not introduced the proton spin and the corresponding magnetic interactions. The error is, in reality, very small, since the hydrogen atom is a weakly relativistic system (recall that, in the Bohr model, the velocity v in the first orbit $n = 1$ satisfies $v/c = e^2/\hbar c = 1/137 \ll 1$). In addition, the magnetic moment of the proton is very small.

However, the considerable accuracy of spectroscopic experiments makes it possible to observe effects that cannot be explained in terms of the Hamiltonian (A-1). Therefore, we shall take into account the corrections we have just mentioned by writing the complete hydrogen atom Hamiltonian in the form:

$$H = H_0 + W \tag{A-3}$$

where H_0 is given by (A-1) and where W represents all the terms neglected thus far. Since W is much smaller than H_0, it is possible to calculate its effects by using the perturbation theory presented in chapter XI. This is what we propose to do in this chapter. We shall show that W is responsible for a "fine structure", as well as for a "hyperfine structure" of the various energy levels calculated in chapter VII. Furthermore, these structures can be measured experimentally with very great accuracy (the hyperfine structure of the $1s$ ground state of the hydrogen atom is the physical quantity currently known to the largest number of significant figures). We shall also consider, in this chapter and its complements, the influence of an external static magnetic or electric field on the various levels of the hydrogen atom (the Zeeman effect and the Stark effect).

This chapter actually has two goals. On the one hand, we want to use a concrete and realistic case to illustrate the general stationary perturbation theory discussed in the preceding chapter. On the other hand, this study, which bears on one of the most fundamental systems of physics (the hydrogen atom), brings out certain

concepts which are basic to atomic physics. For example, §B is devoted to a thorough discussion of various relativistic and magnetic corrections. This chapter, while not indispensable for the study of the last two chapters, presents concepts fundamental to atomic physics.

B. ADDITIONAL TERMS IN THE HAMILTONIAN

The first problem to be solved obviously consists of finding the expression for W.

1. The fine-structure Hamiltonian

a. THE DIRAC EQUATION IN THE WEAKLY RELATIVISTIC DOMAIN

In chapter IX, we mentioned that the spin appears naturally when we try to establish an equation for the electron which satisfies both the postulates of special relativity and those of quantum mechanics. Such an equation exists: it is the *Dirac equation*, which makes it possible to account for numerous phenomena (electron spin, the fine structure of hydrogen, etc.) and to predict the existence of positrons.

The most rigorous way of obtaining the expression for the relativistic corrections [appearing in the term W of (A-3)] therefore consists of first writing the Dirac equation for an electron placed in the potential $V(r)$ created by the proton (considered to be infinitely heavy and motionless at the coordinate origin). One then looks for its limiting form when the system is weakly relativistic, as is the case for the hydrogen atom. We then recognize that the description of the electron state must include a two-component spinor (*cf.* chap. IX, § C-1). The spin operators S_x, S_y, S_z, introduced in chapter IX then appear naturally. Finally, we obtain an expression such as (A-3) for the Hamiltonian H, in which W appears in the form of a power series expansion in v/c which we can evaluate.

It is out of the question here to study the Dirac equation, or to establish its form in the weakly relativistic domain. We shall confine ourselves to giving the first terms of the power series expansion in v/c of W and their interpretation.

$$H = m_e c^2 + \underbrace{\frac{\mathbf{P}^2}{2m_e} + V(R)}_{H_0} - \underbrace{\frac{\mathbf{P}^4}{8m_e^3 c^2}}_{W_{mv}} + \underbrace{\frac{1}{2m_e^2 c^2}\frac{1}{R}\frac{dV(R)}{dR}\mathbf{L}\cdot\mathbf{S}}_{W_{SO}} + \underbrace{\frac{\hbar^2}{8m_e^2 c^2}\Delta V(R)}_{W_D} + \ldots \tag{B-1}$$

We recognize in (B-1) the rest-mass energy $m_e c^2$ of the electron (the first term)

and the non-relativistic Hamiltonian H_0 (the second and third terms)*. The following terms are called fine structure terms.

COMMENT:

Note that it is possible to solve the Dirac equation exactly for an electron placed in a Coulomb potential. We thus obtain the energy levels of the hydrogen atom without having to make a limited power series expansion in v/c of the eigenstates and eigenvalues of H. The "perturbation" point of view which we are adopting here is, however, very useful in bringing out the form and physical meaning of the various interactions which exist inside an atom. This will later permit a generalization to the case of many-electron atoms (for which we do not know how to write the equivalent of the Dirac equation).

b. INTERPRETATION OF THE VARIOUS TERMS OF THE FINE-STRUCTURE HAMILTONIAN

α. *Variation of the mass with the velocity (W_{mv} term)*

(*i*) The physical origin

The physical origin of the W_{mv} term is very simple. If we start with the relativistic expression for the energy of a classical particle of rest-mass m_e and momentum $\mathbf{p}$:

$$E = c\sqrt{\mathbf{p}^2 + m_e^2 c^2} \tag{B-2}$$

and perform a limited expansion of E in powers of $|\mathbf{p}|/m_e c$, we obtain:

$$E = m_e c^2 + \frac{\mathbf{p}^2}{2m_e} - \frac{\mathbf{p}^4}{8m_e^3 c^2} + \ldots \tag{B-3}$$

In addition to the rest-mass energy ($m_e c^2$) and the non-relativistic kinetic energy ($\mathbf{p}^2/2m_e$), we find the term $-\mathbf{p}^4/8m_e^3 c^2$, which appears in (B-1). This term represents the first energy correction, due to the relativistic variation of the mass with the velocity.

(*ii*) Order of magnitude

To evaluate the size of this correction, we shall calculate the order of magnitude of the ratio W_{mv}/H_0:

$$\frac{W_{mv}}{H_0} \simeq \frac{\dfrac{\mathbf{p}^4}{8m_e^3 c^2}}{\dfrac{\mathbf{p}^2}{2m_e}} = \frac{\mathbf{p}^2}{4m_e^2 c^2} = \frac{1}{4}\left(\frac{v}{c}\right)^2 \simeq \alpha^2 \simeq \left(\frac{1}{137}\right)^2 \tag{B-4}$$

* Expression (B-1) was obtained by assuming the proton to be infinitely heavy. This is why it is the mass m_e of the electron that appears, and not, as in (A-1), the reduced mass μ of the atom. As far as H_0 is concerned, the proton finite mass effect is taken into account by replacing m_e by μ. However, we shall neglect this effect in the subsequent terms of H, which are already corrections. It would, moreover, be difficult to evaluate, since the relativistic description of a system of two interacting particles poses serious problems [it is not sufficient to replace m_e by μ in the last terms of (B-1)].

since we have already mentioned that, for the hydrogen atom, $v/c \simeq \alpha$. Since $H_0 \simeq 10$ eV, we see that $W_{mv} \simeq 10^{-3}$ eV.

β. *Spin-orbit coupling (W_{SO} term)*

(*i*) The physical origin

The electron moves at a velocity $\mathbf{v} = \mathbf{p}/m_e$ in the electrostatic field $\mathbf{E}$ created by the proton. Special relativity indicates that there then appears, in the electron frame, a magnetic field $\mathbf{B}'$ given by:

$$\mathbf{B}' = -\frac{1}{c^2}\mathbf{v} \times \mathbf{E} \tag{B-5}$$

to first order in v/c. Since the electron possesses an intrinsic magnetic moment $\mathbf{M}_S = q\mathbf{S}/m_e$, it interacts with this field $\mathbf{B}'$. The corresponding interaction energy can be written:

$$W' = -\mathbf{M}_S \cdot \mathbf{B}' \tag{B-6}$$

Let us express W' more explicitly. The electrostatic field $\mathbf{E}$ appearing in (B-5) is equal to $-\frac{1}{q}\frac{dV(r)}{dr}\frac{\mathbf{r}}{r}$, where $V(r) = -\frac{e^2}{r}$ is the electrostatic energy of the electron. From this, we get:

$$\mathbf{B}' = \frac{1}{qc^2}\frac{1}{r}\frac{dV(r)}{dr}\frac{\mathbf{p}}{m_e} \times \mathbf{r} \tag{B-7}$$

In the corresponding quantum mechanical operator, there appears:

$$\mathbf{P} \times \mathbf{R} = -\mathbf{L} \tag{B-8}$$

Finally, we obtain:

$$W' = \frac{1}{m_e^2 c^2}\frac{1}{R}\frac{dV(R)}{dR}\mathbf{L} \cdot \mathbf{S} = \frac{e^2}{m_e^2 c^2}\frac{1}{R^3}\mathbf{L} \cdot \mathbf{S} \tag{B-9}$$

Thus we find, to within the factor 1/2★, the spin-orbit term W_{SO} which appears in (B-1). This term then represents the interaction of the magnetic moment of the electron spin with the magnetic field "seen" by the electron because of its motion in the electrostatic field of the proton.

(*ii*) Order of magnitude

Since $\mathbf{L}$ and $\mathbf{S}$ are of the order of $\hbar$, we have:

$$W_{SO} \simeq \frac{e^2}{m_e^2 c^2}\frac{\hbar^2}{R^3} \tag{B-10}$$

★ It can be shown that the factor 1/2 is due to the fact that the motion of the electron about the proton is not rectilinear. The electron spin therefore rotates with respect to the laboratory reference frame (Thomas precession; see Jackson (7.5) section 11-8, Omnès (16.13) chap. 4 §2, or Bacry (10.31) chap. 7 §5-d).