Complement D_{VII}

THE HYDROGEN ATOM PLACED IN A UNIFORM MAGNETIC FIELD. PARAMAGNETISM AND DIAMAGNETISM. THE ZEEMAN EFFECT

In chapter VII, we studied the quantum mechanical properties of a free hydrogen atom, that is, of the system formed by an electron and a proton exerting an electrostatic attraction on each other but not interacting with any external field. This complement is devoted to the study of the new effects which appear when this atom is placed in a static magnetic field. We shall confine ourselves to the case in which this field is uniform, as it always is, moreover, in practice, since the magnetic fields that can be produced in the laboratory vary very little in relative value over distances comparable to atomic dimensions.

We have already studied the behavior of an electron subjected either to an electric field alone (*cf.* for example, chapter VII) or to a magnetic field alone (*cf.* complement E_{VI}). Here, we shall generalize these discussions by calculating the energy levels of an electron subjected both to the influence of the internal electric field of the atom and to an external magnetic field. Under these conditions, the exact solution of the Schrödinger equation may seem to be a very complicated problem. However, we shall see that this problem can be simplified considerably by means of certain approximations. In the first place, we shall totally neglect the nuclear finite mass effect*. Then we shall use the fact that, in practice, the effect of the external magnetic field is much smaller than that of the internal electric field of the atom : the atomic level shifts due to the magnetic field are much smaller than the energy separations in a zero field.

The discussion presented in this complement will enable us to introduce and explain certain effects which are important in atomic physics. We shall see, in

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* For the hydrogen atom, such an approximation is justified by the fact that the proton is considerably heavier than the electron. For muonium (*cf.* complement A_{VII}), the approximation is not as good and it becomes totally inapplicable for the case of positronium. We note, moreover, that, in the presence of a magnetic field, it is not rigorously possible to separate the motion of the center of mass. If one wished to take the nuclear finite mass effect into account in this complement, it would not suffice to replace the mass m_e of the electron by the reduced mass μ of the electron-proton system.

particular, how atomic paramagnetism and diamagnetism appear in the quantum mechanical formalism. In addition, we shall be able to predict the modifications occurring in the optical spectrum emitted by hydrogen atoms when they are placed in a static magnetic field (the Zeeman effect).

1. The Hamiltonian of the problem. The paramagnetic term and the diamagnetic term

a. EXPRESSION FOR THE HAMILTONIAN

Consider a spinless particle, of mass m_e and charge q, subjected simultaneously to a scalar central potential $V(r)$ and a vector potential $\mathbf{A}(\mathbf{r})$. Its Hamiltonian is :

$$H = \frac{1}{2m_e}[\mathbf{P} - q\mathbf{A}(\mathbf{R})]^2 + V(\mathbf{R}) \tag{1}$$

When the magnetic field $\mathbf{B} = \nabla \times \mathbf{A}(\mathbf{r})$ is uniform, the vector potential $\mathbf{A}$ can be put into the form:

$$\mathbf{A}(\mathbf{r}) = -\frac{1}{2}\mathbf{r} \times \mathbf{B} \tag{2}$$

To substitute this expression into (1), we shall calculate the quantity:

$$[\mathbf{P} - q\mathbf{A}(\mathbf{R})]^2 = \mathbf{P}^2 + \frac{q}{2}[\mathbf{P}\,.\,(\mathbf{R} \times \mathbf{B}) + (\mathbf{R} \times \mathbf{B})\,.\,\mathbf{P}] + \frac{q^2}{4}(\mathbf{R} \times \mathbf{B})^2 \tag{3}$$

Now, $\mathbf{B}$ is actually a constant and not an operator. All observables therefore commute with $\mathbf{B}$, so we can write, using the rules of vector calculus:

$$[\mathbf{P} - q\mathbf{A}(\mathbf{R})]^2 = \mathbf{P}^2 + \frac{q}{2}[\mathbf{B}\,.\,(\mathbf{P} \times \mathbf{R}) - (\mathbf{R} \times \mathbf{P})\,.\,\mathbf{B}] + \frac{q^2}{4}[\mathbf{R}^2\mathbf{B}^2 - (\mathbf{R}\,.\,\mathbf{B})^2] \tag{4}$$

On the right-hand side of this expression, the angular momentum $\mathbf{L}$ of the particle appears :

$$\mathbf{L} = \mathbf{R} \times \mathbf{P} = -\,\mathbf{P} \times \mathbf{R} \tag{5}$$

We can therefore write H in the form:

$$H = H_0 + H_1 + H_2 \tag{6}$$

where H_0, H_1 and H_2 are defined by:

$$H_0 = \frac{\mathbf{P}^2}{2m_e} + V(\mathbf{R}) \tag{7-a}$$

$$H_1 = -\frac{\mu_B}{\hbar}\mathbf{L}\,.\,\mathbf{B} \tag{7-b}$$

$$H_2 = \frac{q^2\mathbf{B}^2}{8m_e}\mathbf{R}_\perp^2 \tag{7-c}$$

In these relations, μ_B denotes the Bohr magneton (whose dimensions are those of a magnetic moment):

$$\mu_B = \frac{q\hbar}{2m_e} \tag{8}$$

and the operator $\mathbf{R}_\perp$ is the projection of $\mathbf{R}$ onto a plane perpendicular to $\mathbf{B}$:

$$\mathbf{R}_\perp^2 = \mathbf{R}^2 - \frac{(\mathbf{R}\cdot\mathbf{B})^2}{\mathbf{B}^2} \tag{9}$$

If we choose a system of orthonormal axes $Oxyz$ such that $\mathbf{B}$ is parallel to Oz, we have:

$$\mathbf{R}_\perp^2 = X^2 + Y^2 \tag{10}$$

COMMENT:

When the field $\mathbf{B}$ is zero, H becomes equal to H_0, which is the sum of the kinetic energy $\mathbf{P}^2/2m_e$ and the potential energy $V(\mathbf{R})$. Nevertheless, we must not conclude from this that when $\mathbf{B}$ is not zero, $\mathbf{P}^2/2m_e$ still represents the kinetic energy of the electron. We have seen (*cf.* complement H_{III}) that the physical meaning of operators acting in the state space changes when the vector potential is not zero. For example, the momentum $\mathbf{P}$ no longer represents the mechanical momentum $\mathbf{\Pi} = m_e\mathbf{V}$, and the kinetic energy is then equal to :

$$\frac{\mathbf{\Pi}^2}{2m_e} = \frac{1}{2m_e}[\mathbf{P} - q\mathbf{A}(\mathbf{R})]^2 \tag{11}$$

The meaning of the term $\mathbf{P}^2/2m_e$, taken alone, depends on the gauge chosen. With the one defined by (2), it can easily be shown to correspond to the "relative" kinetic energy $\mathbf{\Pi}_R^2/2m_e$, where $\mathbf{\Pi}_R$ is the mechanical momentum of the particle with respect to the "Larmor frame" rotating about $\mathbf{B}$ with angular velocity $\omega_L = -qB/2m_e$. The term H_2 then describes the kinetic energy $\mathbf{\Pi}_E^2/2m_e$ related to the drag velocity of the frame. As for H_1, it corresponds to the cross term $\mathbf{\Pi}_E\cdot\mathbf{\Pi}_R/m_e$.

b. ORDER OF MAGNITUDE OF THE VARIOUS TERMS

In the presence of the magnetic field $\mathbf{B}$, two new terms, H_1 and H_2, therefore appear in H. Before examining their physical meaning in greater detail, we shall calculate the order of magnitude of the energy differences ΔE (or the frequency differences $\Delta E/h$) associated with them.

As far as H_0 is concerned, we already know the corresponding energy differences ΔE_0 (*cf.* chap. VII). The associated frequencies are of the order of:

$$\frac{\Delta E_0}{h} \simeq 10^{14} \text{ to } 10^{15} \text{ Hz} \tag{12}$$

Also, by using (7-b), we see that ΔE_1 is approximately given by:

$$\frac{\Delta E_1}{h} \simeq \frac{1}{h}\left(\frac{\mu_B}{\hbar}\hbar B\right) = \frac{\omega_L}{2\pi} \tag{13}$$

where ω_L is the Larmor angular velocity*:

$$\omega_L = -\frac{qB}{2\mu} \tag{14}$$

A simple numerical calculation shows that, for an electron, the Larmor frequency is such that:

$$\frac{\nu_L}{B} = \frac{\omega_L}{2\pi B} \simeq 1.40 \times 10^{10}\ \text{Hz/tesla} = 1.40\ \text{MHz/gauss} \tag{15}$$

Now, with the fields usually produced in the laboratory (which rarely exceed 100,000 gauss), we have:

$$\frac{\omega_L}{2\pi} \lesssim 10^{11}\ \text{Hz} \tag{16}$$

Comparing (12) and (16), we see that:

$$\Delta E_1 \ll \Delta E_0 \tag{17}$$

Let us show, similarly, that:

$$\Delta E_2 \ll \Delta E_1 \tag{18}$$

To do so, we shall evaluate the order of magnitude ΔE_2 of the energies associated with H_2. The matrix elements of the operator $\mathbf{R}_\perp^2 = X^2 + Y^2$ are of the same order of magnitude as a_0^2, where $a_0 = \hbar^2/m_e e^2$ characterizes atomic dimensions. Thus we obtain:

$$\Delta E_2 \simeq \frac{q^2B^2}{m_e} a_0^2 \tag{19}$$

We then find the ratio:

$$\frac{\Delta E_2}{\Delta E_1} \simeq \frac{q^2B^2}{m_e} a_0^2 \frac{1}{\hbar\omega_L} = 2\hbar \frac{qB}{m_e} \frac{m_e a_0^2}{\hbar^2} \tag{20}$$

Now, according to formulas (C-12-a) and (C-12-b) of chapter VII:

$$\Delta E_0 \simeq \frac{\hbar^2}{m_e a_0^2} \tag{21}$$

Relation (20) therefore yields, with (13) taken into account:

$$\frac{\Delta E_2}{\Delta E_1} \simeq \frac{\Delta E_1}{\Delta E_0} \tag{22}$$

which, according to (17), proves (18).

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* Note that the Larmor frequency $\frac{\omega_L}{2\pi}$ is half the cyclotron frequency.

Therefore, the effects of the magnetic field always remain, in practice, much smaller than those due to the internal field of the atom. Moreover, it is generally sufficient, when we study them, to retain only the term H_1, compared to which H_2 is negligible (H_2 will be taken into account only in the special cases in which the contribution of H_1 is zero)*.

c. INTERPRETATION OF THE PARAMAGNETIC TERM

Consider, first of all, the term H_1 given by (7-b). We shall see that it can be interpreted to be the coupling energy $-\mathbf{M}_1 \cdot \mathbf{B}$ of the field **B** and the magnetic moment $\mathbf{M}_1$ related to the revolution of the electron in its orbit.

For this purpose, we shall begin by calculating the magnetic moment $\mathcal{M}$ classically associated with a charge q in a circular orbit of radius r (fig. 1). If the speed of the particle is v, its motion is equivalent to a current:

$$i = q\frac{v}{2\pi r} \tag{23}$$

Since the surface S defined by this current is:

$$S = \pi r^2 \tag{24}$$

the magnetic moment $\mathcal{M}$ is given by:

$$|\mathcal{M}| = i \times S = \frac{q}{2} rv \tag{25}$$

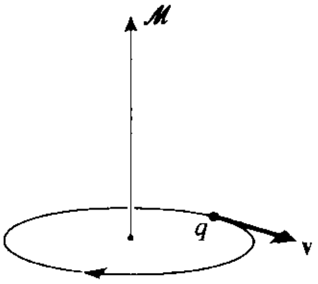

FIGURE 1

Classically, the motion of an electron in its orbit can be regarded as a current loop of magnetic moment $\mathcal{M}$.

Introducing the angular momentum $\mathcal{L}$, which, since the velocity is tangential, has a modulus of:

$$|\mathcal{L}| = m_e rv \tag{26}$$

we can write (25) in the form:

$$\mathcal{M} = \frac{q}{2m_e}\mathcal{L} \tag{27}$$

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* The Zeeman effect of a three-dimensional harmonic oscillator can be calculated without approximations (*cf.* problem 2 of complement G_{VII}). This is true because $V(\mathbf{R})$ and H_2 then have analogous forms. This example is interesting since it enables us to analyze the contributions of H_1 and H_2 in a soluble case.

(this is a vector relation since $\mathscr{L}$ and $\mathscr{M}$ are parallel, as both are perpendicular to the plane of the classical orbit).

The quantum mechanical analogue of (27) is the operator relation:

$$\mathbf{M}_1 = \frac{q}{2m_e}\mathbf{L} \tag{28}$$

We can therefore write H_1 in the form:

$$H_1 = -\mathbf{M}_1 \,.\, \mathbf{B} \tag{29}$$

This confirms the interpretation given above: H_1 corresponds to the coupling between the magnetic field $\mathbf{B}$ and the permanent atomic magnetic moment ($\mathbf{M}_1$ is independent of $\mathbf{B}$). H_1 is called the paramagnetic coupling term.

COMMENTS:

(*i*) According to (28), the eigenvalues of any component of the magnetic moment $\mathbf{M}_1$ are of the form:

$$\left(\frac{q}{2m_e}\right) \times (m\hbar) = m\mu_B \tag{30}$$

where m is an integer. μ_B therefore gives the order of magnitude of the magnetic moment associated with the orbital moment of the electron. This is why definition (8) is useful. In the MKSA system:

$$\mu_B \simeq -9.27 \times 10^{-24} \text{ Joule/tesla} \tag{31}$$

(*ii*) As we shall see in chapter IX, the electron possesses, in addition to the orbital angular momentum $\mathbf{L}$, a spin angular momentum $\mathbf{S}$. With this observable is associated a magnetic moment, $\mathbf{M}_S$, proportional to $\mathbf{S}$:

$$\mathbf{M}_S = 2\frac{\mu_B}{\hbar}\mathbf{S} \tag{32}$$

Although the magnetic effects due to the spin are important, we shall ignore them for now (we shall return to them in complement D_{XII}).

(*iii*) The classical argument presented above is not completely correct. We have confused the angular momentum:

$$\mathscr{L} = \mathbf{r} \times \mathbf{p} \tag{33}$$

with the moment of the mechanical momentum:

$$\lambda = \mathbf{r} \times m_e\mathbf{v} = \mathscr{L} - q\,\mathbf{r} \times \mathbf{A}(\mathbf{r}) \tag{34}$$

In fact, the error is small. As we shall see in the next section it simply amounts to neglecting H_2 relative to H_1.

d. INTERPRETATION OF THE DIAMAGNETIC TERM

Consider a zero angular momentum state of the hydrogen atom (for example, the ground state). The correction supplied by H_1 to the energy of this state is also zero. Thus, to determine the effect of the field **B**, we must now take into account the presence of H_2. How should the corresponding energy be interpreted?

We have seen (*cf.* complement C_{VII}, §2-b) that, in the presence of a uniform magnetic field, the probability current associated with the electron is modified. This current is cylindrically symmetrical with respect to **B**. It corresponds to a uniform rotation of the probability fluid, clockwise if q is positive and counterclockwise if q is negative. With the corresponding electric current is then associated a magnetic moment $\langle \mathbf{M}_2 \rangle$ antiparallel to **B**, and, therefore, a positive coupling energy, which explains the physical origin of the term H_2.

To see this more precisely, we shall return to the classical argument of the preceding section, taking into account the fact [*cf.* comment (*iii*) of §c] that the magnetic moment $\mathcal{M}$ is in fact proportional to $\boldsymbol{\lambda} = \mathbf{r} \times m_e \mathbf{v}$ (and not to $\mathcal{L} = \mathbf{r} \times \mathbf{p}$):

$$\mathcal{M} = \frac{q}{2m_e}\boldsymbol{\lambda} = \frac{q}{2m_e}[\mathcal{L} - q\,\mathbf{r} \times \mathbf{A}(\mathbf{r})] \tag{35}$$

When $\mathcal{L}$ is zero, $\mathcal{M}$ reduces, in gauge (2), to:

$$\mathcal{M}_2 = \frac{q^2}{4m_e}\mathbf{r} \times (\mathbf{r} \times \mathbf{B}) = \frac{q^2}{4m_e}[(\mathbf{r} \cdot \mathbf{B})\mathbf{r} - \mathbf{r}^2\mathbf{B}] \tag{36}$$

$\mathcal{M}_2$ is proportional to the value of the magnetic field*. It therefore represents the *moment induced* by **B** in the atom. Its coupling energy with **B** is:

$$\begin{aligned} W_2 &= -\int_0^{\mathbf{B}} \mathcal{M}_2(\mathbf{B}') \cdot \mathrm{d}\mathbf{B}' = -\frac{1}{2}\mathcal{M}_2(\mathbf{B}) \cdot \mathbf{B} \\ &= \frac{q^2}{8m_e}[\mathbf{r}^2\mathbf{B}^2 - (\mathbf{r} \cdot \mathbf{B})^2] \\ &= \frac{q^2}{8m_e}\mathbf{r}_\perp^2\,\mathbf{B}^2 \end{aligned} \tag{37}$$

as we found in (7-c). Therefore, the interpretation given above has been confirmed : H_2 describes the coupling between the field **B** and the magnetic moment $\mathbf{M}_2$ induced in the atom. Since the induced moment, according to Lenz' law, opposes the applied field, the coupling energy is positive. H_2 is called the diamagnetic term of the Hamiltonian.

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* $\mathcal{M}_2$ is not collinear with **B**. However, it can be shown that, in the ground state of the hydrogen atom, the mean value $\langle \mathbf{M}_2 \rangle$ of the operator associated with $\mathcal{M}_2$ is antiparallel to **B**. This is in agreement with the result obtained above from the structure of the probability current.

COMMENT:

As we have already pointed out [*cf.* (18)], atomic diamagnetism is a weak phenomenon which is concealed by paramagnetism when both are present. As is shown by (37) (and the calculations of § 1-b), this result is related to the small size of the atomic radius: for magnetic fields of the type usually produced, the magnetic flux intercepted by an atom is very small. It must not be concluded that we can always neglect H_2 relative to H_1, whatever the physical problem. For example, in the case of a free electron (for which the radius of the classical orbit would be infinite in a zero magnetic field), we saw in complement $\mathrm{E_{VI}}$ that the contribution of the diamagnetic term is as important as that of the paramagnetic term.

2. The Zeeman effect

Now that we have explained the physical significance of the various terms appearing in the Hamiltonian, we shall look more closely at their effects on the spectrum of the hydrogen atom. More precisely, we shall examine the way in which the emission of the optical line called the "resonance line" ($\lambda \simeq 1\,200$ Å) is modified when the hydrogen atom is placed in a static magnetic field. We shall see that this changes not only the frequency, but also the polarization, of the atomic lines: this is what is usually called the "Zeeman effect".

Important comment: In reality, because of the existence of electron and proton spins, the resonance line of hydrogen includes several neighboring components (fine and hyperfine structure; *cf.* chap. XII). Moreover, the spin degrees of freedom profoundly modify the effect of a magnetic field on the various components of the resonance line (the Zeeman effect of the hydrogen atom is sometimes called "anomalous"). Since we are ignoring the effects of spin here, the following calculations do not truly correspond to the real physical situation. However, they can easily be generalized to take spins into account (*cf.* complement $\mathrm{D_{XII}}$). Moreover, the results we shall obtain (the appearance of several Zeeman components of different frequencies and polarizations) remain qualitatively valid.

a. ENERGY LEVELS OF THE ATOM IN THE PRESENCE OF THE MAGNETIC FIELD

The resonance line of hydrogen corresponds to an atomic transition between the ground state 1*s* ($n = 1$; $l = m = 0$) and the excited state 2*p* ($n = 2$; $l = 1$; $m = +1, 0, -1$). While the angular momentum is zero in the ground state, it is not so in the excited state; in calculating optical line modifications in the presence of the magnetic field **B**, we therefore make a small error by neglecting the effects of the diamagnetic term H_2, which amounts to taking $H_0 + H_1$ for the Hamiltonian.

We denote by $|\varphi_{n,l,m}\rangle$ the common eigenstates of H_0 (eigenvalue $E_n = -E_I/n^2$), $\mathbf{L}^2$ [eigenvalue $l(l+1)\hbar^2$] and L_z (eigenvalue $m\hbar$). The wave functions of these states are those which were calculated in chapter VII:

$$\varphi_{n,l,m}(r,\theta,\varphi) = R_{n,l}(r)\, Y_l^m(\theta,\varphi) \tag{38}$$

We choose the Oz axis parallel to $\mathbf{B}$; it is not difficult to see that the states $|\varphi_{n,l,m}\rangle$ are then also eigenvectors of $H_0 + H_1$:

$$\begin{aligned}(H_0 + H_1)\,|\varphi_{n,l,m}\rangle &= \left(H_0 - \frac{\mu_B}{\hbar} B\, L_z\right)|\varphi_{n,l,m}\rangle \\ &= (E_n - m\mu_B B)\,|\varphi_{n,l,m}\rangle\end{aligned} \tag{39}$$

If we neglect the diamagnetic term, the stationary states of the atom placed in the field $\mathbf{B}$ are therefore still the $|\varphi_{n,l,m}\rangle$; only the corresponding energies are modified.

In particular, for the states involved in the resonance line, we see that:

$$(H_0 + H_1)\,|\varphi_{1,0,0}\rangle = -E_I\,|\varphi_{1,0,0}\rangle \tag{40-a}$$

$$(H_0 + H_1)\,|\varphi_{2,1,m}\rangle = [-E_I + \hbar(\Omega + m\omega_L)]\,|\varphi_{2,1,m}\rangle \tag{40-b}$$

where:

$$\Omega = \frac{E_2 - E_1}{\hbar} = \frac{3E_I}{4\hbar} \tag{41}$$

is the angular frequency of the resonance line in a zero field.

b. ELECTRIC DIPOLE OSCILLATIONS

α. *Matrix elements of the operator associated with the dipole*

Let:

$$\mathbf{D} = q\mathbf{R} \tag{42}$$

be the electric dipole operator of the atom. To calculate the mean value $\langle \mathbf{D} \rangle$ of this dipole, we begin by evaluating the matrix elements of $\mathbf{D}$.

Under reflection through the origin, $\mathbf{D}$ is changed into $-\mathbf{D}$: the electric dipole is therefore an odd operator (*cf.* complement F_{II}). Now, the states $|\varphi_{n,l,m}\rangle$ also have a well-defined parity: since their angular dependence is given by $Y_l^m(\theta,\varphi)$, their parity is $+1$ if l is even and -1 if l is odd (*cf.* complement A_{VI}). It follows, in particular, that:

$$\begin{cases}\langle \varphi_{1,0,0}|\,\mathbf{D}\,|\varphi_{1,0,0}\rangle = \mathbf{0} \\ \langle \varphi_{2,1,m'}|\,\mathbf{D}\,|\varphi_{2,1,m}\rangle = \mathbf{0}\end{cases} \tag{43}$$

for all m and m'.

The non-zero matrix elements of $\mathbf{D}$ are therefore necessarily non-diagonal elements. To calculate the matrix elements $\langle \varphi_{2\,1\,m}|\,\mathbf{D}\,|\varphi_{1\,0\,0}\rangle$, it is convenient to note that x, y and z can easily be expressed in terms of the spherical harmonics:

$$\begin{cases} x = \sqrt{\dfrac{2\pi}{3}}\, r[Y_1^{-1}(\theta, \varphi) - Y_1^1(\theta, \varphi)] \\ y = i\sqrt{\dfrac{2\pi}{3}}\, r[Y_1^{-1}(\theta, \varphi) + Y_1^1(\theta, \varphi)] \\ z = \sqrt{\dfrac{4\pi}{3}}\, r Y_1^0(\theta, \varphi) \end{cases} \tag{44}$$

In the expressions for the desired matrix elements, we therefore have:

– on the one hand, a radial integral, which we shall set equal to χ:

$$\chi = \int_0^\infty R_{2,1}(r)\, R_{1,0}(r)\, r^3\, \mathrm{d}r \tag{45}$$

– and on the other hand, an angular integral which, thanks to relations (44), reduces to a scalar product of spherical harmonics, which can be calculated directly from their orthogonality relations. We obtain, finally:

$$\begin{cases} \langle \varphi_{2,1,1} \mid D_x \mid \varphi_{1,0,0} \rangle = -\langle \varphi_{2,1,-1} \mid D_x \mid \varphi_{1,0,0} \rangle = -\dfrac{q\chi}{\sqrt{6}} \\ \langle \varphi_{2,1,0} \mid D_x \mid \varphi_{1,0,0} \rangle = 0 \end{cases} \tag{46-a}$$

$$\begin{cases} \langle \varphi_{2,1,1} \mid D_y \mid \varphi_{1,0,0} \rangle = \langle \varphi_{2,1,-1} \mid D_y \mid \varphi_{1,0,0} \rangle = \dfrac{iq\chi}{\sqrt{6}} \\ \langle \varphi_{2,1,0} \mid D_y \mid \varphi_{1,0,0} \rangle = 0 \end{cases} \tag{46-b}$$

$$\begin{cases} \langle \varphi_{2,1,1} \mid D_z \mid \varphi_{1,0,0} \rangle = \langle \varphi_{2,1,-1} \mid D_z \mid \varphi_{1,0,0} \rangle = 0 \\ \langle \varphi_{2,1,0} \mid D_z \mid \varphi_{1,0,0} \rangle = \dfrac{q\chi}{\sqrt{3}} \end{cases} \tag{46-c}$$

β. *Calculation of the mean value of the dipole*

The results of §α indicate that, if the system is in a stationary state, the mean value of the operator **D** is zero. Let us assume, rather, that the state vector of the system is initially a linear superposition of the ground state $1s$ and one of the $2p$ states:

$$| \psi_m(0) \rangle = \cos\alpha \,| \varphi_{1,0,0} \rangle + \sin\alpha \,| \varphi_{2,1,m} \rangle \tag{47}$$

with $m = +1, 0$ or -1 (α is a real parameter). We then immediately obtain the state vector at time t:

$$| \psi_m(t) \rangle = \cos\alpha \,| \varphi_{1,0,0} \rangle + \sin\alpha \, \mathrm{e}^{-i(\Omega + m\omega_L)t} \,| \varphi_{2,1,m} \rangle \tag{48}$$

(we have omitted the global phase factor $\mathrm{e}^{iE_I t/\hbar}$, which is of no physical consequence).

To calculate the mean value of the electric dipole:

$$\langle \mathbf{D} \rangle_m(t) = \langle \psi_m(t) \,|\, \mathbf{D} \,|\, \psi_m(t) \rangle \tag{49}$$

we shall use results (46) and (48), and cite three cases:

(*i*) if $m = 1$, we obtain:

$$\begin{cases} \langle D_x \rangle_1 = -\dfrac{q\chi}{\sqrt{6}} \sin 2\alpha \cos [(\Omega + \omega_L)t] \\ \langle D_y \rangle_1 = -\dfrac{q\chi}{\sqrt{6}} \sin 2\alpha \sin [(\Omega + \omega_L)t] \\ \langle D_z \rangle_1 = 0 \end{cases} \tag{50}$$

The vector $\langle \mathbf{D} \rangle_1(t)$ therefore rotates in the xOy plane about the Oz axis, in the counterclockwise direction and with the angular velocity $\Omega + \omega_L$.

(*ii*) if $m = 0$:

$$\begin{cases} \langle D_x \rangle_0 = \langle D_y \rangle_0 = 0 \\ \langle D_z \rangle_0 = \dfrac{q\chi}{\sqrt{3}} \sin 2\alpha \cos \Omega t \end{cases} \tag{51}$$

The motion of $\langle \mathbf{D} \rangle_0(t)$ is now a linear oscillation along the Oz axis, of angular frequency Ω.

(*iii*) if $m = -1$:

$$\begin{cases} \langle D_x \rangle_{-1} = \dfrac{q\chi}{\sqrt{6}} \sin 2\alpha \cos [(\Omega - \omega_L)t] \\ \langle D_y \rangle_{-1} = -\dfrac{q\chi}{\sqrt{6}} \sin 2\alpha \sin [(\Omega - \omega_L)t] \\ \langle D_z \rangle_{-1} = 0 \end{cases} \tag{52}$$

The vector $\langle \mathbf{D} \rangle_{-1}(t)$ again rotates in the xOy plane about Oz, but this time in the clockwise direction and with the angular velocity $\Omega - \omega_L$.

c. FREQUENCY AND POLARIZATION OF EMITTED RADIATION

In the three cases ($m = +1, 0$ and -1), the mean value of the electric dipole is an oscillating function of time. It is clear that such a dipole radiates electromagnetic energy.

Since the atomic dimensions are negligible compared to the optical wavelength, the atom's radiation at great distances can be treated like that of a dipole. We shall assume that the characteristics of the light emitted (or absorbed) by the atom during transition between a state $|\varphi_{2,1,m}\rangle$ and the ground state are correctly given by the classical calculation of radiation of a dipole* which is equal to the mean quantum mechanical value $\langle \mathbf{D} \rangle_m(t)$.

To state the problem precisely, we shall assume that we want to study the radiation emitted by a sample containing a great number of hydrogen atoms, which have somehow been excited into a $2p$ state. In most experiments actually performed, the excitation of the atoms is isotropic, and the three states $|\varphi_{2,1,1}\rangle$, $|\varphi_{2,1,0}\rangle$ and $|\varphi_{2,1,-1}\rangle$ occur with equal probability. Therefore, we shall begin by calculating the radiation diagram for each of the cases of the preceding sections. Then we shall obtain the radiation actually emitted by the atomic system by taking, for each spatial direction, the sum of the light intensities emitted in each case.

(*i*) If $m = 1$, the angular frequency of the emitted radiation is $(\Omega + \omega_L)$. The optical line frequency is therefore slightly shifted by the magnetic field. In accordance with the laws of classical electromagnetism applied to a rotating dipole such as $\langle \mathbf{D} \rangle_1(t)$, the radiation emitted in the Oz direction is circularly polarized (the corresponding polarization is called σ_+). However, the radiation emitted in a direction of the xOy plane is linearly polarized (parallel to this plane). In other directions, the polarization is elliptical.

(*ii*) If $m = 0$, we must consider a dipole oscillating linearly along Oz, with angular frequency Ω, that is, the same as in a zero field. The wavelength of the radiation is therefore not changed by the field $\mathbf{B}$. Its polarization is always linear, whatever the propagation direction being considered. For example, for a propagation direction situated in the xOy plane, this polarization is parallel to Oz (π polarization). No radiation is emitted in the Oz direction (an oscillating linear dipole does not radiate along its axis).

(*iii*) If $m = -1$, the results are analogous to those for $m = 1$. The only difference is that the angular frequency of the radiation is $(\Omega - \omega_L)$ instead of $(\Omega + \omega_L)$, and the dipole rotates in the opposite direction; this changes, for example, the direction of the circular polarization (σ_- polarization).

If we now assume that there are equal numbers of excited atoms in the three states $m = +1, 0$ and -1, we see that:

- in an arbitrary spatial direction, three optical frequencies are emitted: $\Omega/2\pi$, $(\Omega \pm \omega_L)/2\pi$. The polarization associated with the first one is linear, and that associated with the others is, in general, elliptical;

- in a direction perpendicular to the field $\mathbf{B}$, the three polarizations are linear (*cf.* fig. 2). The first one is parallel to $\mathbf{B}$, and the other two are perpendicular. The intensity of the central line is twice that of each of the shifted lines [*cf.* formulas (50), (51) and (52)]. In a direction parallel to $\mathbf{B}$, only the two shifted frequencies $(\Omega \pm \omega_L)/2\pi$ are emitted, and the associated light polarizations are both circular but opposite in direction (*cf.* fig. 3).

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* If we wanted to treat the problem entirely quantum mechanically, we should have to use the quantum mechanical theory of radiation. In particular, the return of the atom to the ground state by spontaneous emission of a photon could only be understood in the framework of this theory. However, the results we shall obtain here semi-classically would remain essentially valid as far as radiation is concerned.

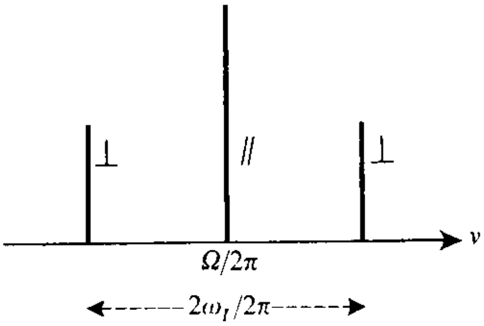

FIGURE 2

The Zeeman components of the resonance line of hydrogen observed in a direction perpendicular to the magnetic field B (ignoring electron spin). We obtain a component of unshifted frequency ν, polarized parallel to B, and two shifted components $\pm\ \omega_L/2\pi$, polarized perpendicularly to B.

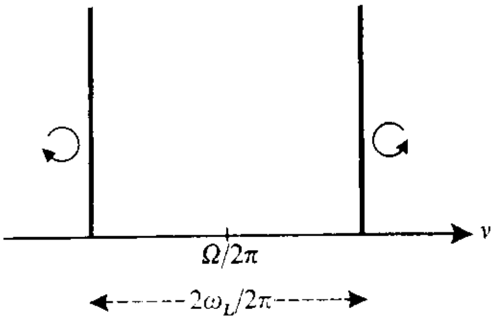

FIGURE 3

When the observation is carried out along the direction of the field B, only two Zeeman components are obtained, circularly polarized in opposite directions and shifted by $\pm\ \omega\ /2\pi$.

COMMENT:

The atom therefore emits σ_+-polarized radiation in going from the state $|\varphi_{2,1,1}\rangle$ to the state $|\varphi_{1,0,0}\rangle$, σ_- in going from $|\varphi_{2,1,-1}\rangle$ to $|\varphi_{1,0,0}\rangle$, and π in going from $|\varphi_{2,1,0}\rangle$ to $|\varphi_{1,0,0}\rangle$. Formulas (46) furnish a simple rule for finding these polarizations. Consider the operators $D_x + iD_y$, $D_x - iD_y$ and D_z; their only non-zero matrix elements between the $2p$ and $1s$ states taken in this order are:

$$\langle\varphi_{2,1,1}|D_x + iD_y|\varphi_{1,0,0}\rangle, \quad \langle\varphi_{2,1,-1}|D_x - iD_y|\varphi_{1,0,0}\rangle$$
$$\text{and} \quad \langle\varphi_{2,1,0}|D_z|\varphi_{1,0,0}\rangle.$$

To the σ_+, σ_- and π polarizations, therefore, correspond the operators $D_x + iD_y$, $D_x - iD_y$ and D_z, respectively. This is a general rule: there is emission of electric dipole radiation when the operator **D** has a non-zero matrix element between the atom's initial state and its final state. The polarization of this radiation is σ_+, σ_- or π depending on whether the non-zero matrix element* is that of $D_x + iD_y$, $D_x - iD_y$ or D_z.

References and suggestions for further reading:

Paramagnetism and diamagnetism: Feynman II (7.2), chaps. 34 and 35; Cagnac and Pebay-Peyroula (11.2), chaps. VIII and IX; Kittel (13.2), chap. 14; Slater (1.6), chap. 14; Flügge (1.24), §§128 and 160.

Dipole radiation: Cagnac and Pebay-Peyroula (11.2), Annex III; Panofsky and Phillips (7.6), §14-7; Jackson (7.5), §9-2.

Angular momentum of radiation and selection rules : Cagnac and Pebay-Peyroula (11.2), chap. XI.

* The order of the states in the matrix element must be respected in order not to confuse σ_+ with σ_-.