14. Atoms in a Magnetic Field: Quantum Mechanical Treatment

14.1 Quantum Theory of the Ordinary Zeeman Effect

The ordinary Zeeman effect is a beautiful example of the fact that even with classical physics, one can obtain results similar to those of strict quantum theory. In order to set our earlier results on a firm basis, however, we shall now go through the strict quantum theoretical treatment.

This chapter is somewhat more demanding, because we shall have to make use of some of the basic theory of electromagnetism. As is shown in this theory, a magnetic field $\boldsymbol{B}$ can be expressed as the curl of the vector potential $\boldsymbol{A}$:

$$\boldsymbol{B} = \operatorname{curl} \boldsymbol{A} . \tag{14.1}$$

The electric field strength $\boldsymbol{F}$[1] can be obtained in a similar way from the electric potential $\tilde{V}$ and the vector potential $\boldsymbol{A}$ according to the rule

$$\boldsymbol{F} = -\operatorname{grad} \tilde{V} - \frac{d\boldsymbol{A}}{dt} . \tag{14.2}$$

Furthermore, we remember that the equation of motion of a particle with charge $-e$ (we are thinking specifically of electrons here) and mass m_0 is

$$m_0 \ddot{\boldsymbol{r}} = (-e)(\boldsymbol{F}) + (-e)(\boldsymbol{v} \times \boldsymbol{B}) . \tag{14.3}$$

The second term on the right is the so-called Lorentz force, $\boldsymbol{v}$ is the particle velocity. It can be shown that this equation of motion can be obtained, using the Hamilton equations

$$\dot{\boldsymbol{p}} = -\operatorname{grad}_r H(\boldsymbol{p}, \boldsymbol{r}) \quad \text{and} \tag{14.4}$$

$$\dot{\boldsymbol{r}} = \operatorname{grad}_p H(\boldsymbol{p}, \boldsymbol{r}) , \tag{14.5}$$

from the Hamiltonian function

$$H = \frac{1}{2m_0} (\boldsymbol{p} + e\boldsymbol{A})^2 + V . \tag{14.6}$$

The potential energy V of the electron is related to the electric potential $\tilde{V}$: $V = -e\tilde{V}$.

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[1] In order to avoid confusion between the energy E and the electric field strength, we denote the latter by $\boldsymbol{F}$

At this point, it is only important to remember that in quantum theory, we always start from a Hamiltonian function. As we saw in Sect. 9.3.4, the Hamiltonian function is converted to an *operator* in quantum mechanics by using the Jordan rule to replace the momentum, according to

$$p \rightarrow \frac{\hbar}{\mathrm{i}} \operatorname{grad} . \tag{14.7}$$

By applying this technique here, we arrive at the Hamiltonian operator

$$\mathscr{H} = [(1/2 m_0)[\hbar/\mathrm{i}) \operatorname{grad} + e\boldsymbol{A}]^2 + V . \tag{14.8}$$

When we multiply out the squared term, taking care to maintain the order of the factors, we obtain

$$\mathscr{H} = -\frac{\hbar^2}{2m_0}\nabla^2 + \frac{\hbar e}{2m_0\mathrm{i}}\boldsymbol{A} \operatorname{grad} + \frac{\hbar e}{2m_0\mathrm{i}} \operatorname{grad}\boldsymbol{A} + \frac{e^2\boldsymbol{A}^2}{2m_0} + V . \tag{14.9}$$

In applying the various differential operators, however, we must be careful, since we know that $\mathscr{H}$ is to operate on the wavefunction ψ. Thus we must interpret

$$\operatorname{grad}\boldsymbol{A} \tag{14.10}$$

exactly as

$$\operatorname{grad}(\boldsymbol{A}\,\psi) . \tag{14.11}$$

On differentiating the product in (14.11) and then again applying (14.7), we obtain for the Hamiltonian

$$\mathscr{H} = -\frac{\hbar^2}{2m_0}\nabla^2 + \frac{e}{m_0}\boldsymbol{A}\boldsymbol{p} + \frac{e\hbar}{2m_0\mathrm{i}} \operatorname{div}\boldsymbol{A} + \frac{e^2\boldsymbol{A}^2}{2m_0} + V . \tag{14.12}$$

(The operators *grad*ient, *div*ergence, and curl used here are vector differential operators which are often abbreviated using the Nabla symbol ∇, with $\nabla f \equiv \operatorname{grad} f$, $\nabla \cdot \boldsymbol{F} \equiv \operatorname{div}\boldsymbol{F}$, $\nabla \times \boldsymbol{F} \equiv \operatorname{curl}\boldsymbol{F}$, and $\nabla \cdot \nabla f = \nabla^2 f =$ Laplacian f, where f is a scalar function and $\boldsymbol{F}$ a vector function.)

We now choose, as always in this book, the constant magnetic field $\boldsymbol{B}$ in the z direction:

$$\boldsymbol{B} = (0, 0, B_z) . \tag{14.13}$$

It can be demonstrated that the vector potential $\boldsymbol{A}$ in (14.1) cannot be uniquely determined. One possible representation, which is convenient for the present calculation, is

$$A_x = -\frac{B_z}{2} y , \quad A_y = \frac{B_z}{2} x , \quad A_z = 0 . \tag{14.14}$$

With this, the Schrödinger equation with the Hamiltonian (14.12) becomes

$$\left[-\frac{\hbar^2}{2m_0}\nabla^2 + B_z\frac{e}{2m_0}\,\frac{\hbar}{\mathrm{i}}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) + \frac{e^2B_z^2}{8m_0}(x^2+y^2) + V(r)\right]\psi = E\psi\,. \tag{14.15}$$

In the following, we shall assume a spherically symmetrical potential for V.

We recall the following relation from Sect. 10.2:

$$\frac{\hbar}{\mathrm{i}}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = \hat{l}_z = \frac{\hbar}{\mathrm{i}}\,\frac{\partial}{\partial\phi}\,, \tag{14.16}$$

where $\hat{l}_z$ is the angular momentum operator in the z direction. In general, the term in (14.15) containing (x^2+y^2) can be neglected in comparison to the preceding term with $\hat{l}_z$, if the magnetic field is not too large, and as long as the magnetic quantum number $m \neq 0$. Leaving out the term with x^2+y^2, and using the usual formula for the wavefunction,

$$\psi(\boldsymbol{r}) = R_{n,l}(r)\,\mathrm{e}^{\mathrm{i}m\phi}\mathrm{P}_l^m(\cos\theta)\,, \tag{14.17}$$

we recognise that (14.15) is identically satisfied. The energy is now

$$E = E_n^0 + B_z\frac{e\hbar}{2m_0}\cdot m\,, \qquad -l \leqq m \leqq l\,. \tag{14.18}$$

The energy E is thus shifted with respect to the unperturbed energy E_n^0 by an amount which depends on the magnetic quantum number m, and the energy level is split. The factor $\mu_\mathrm{B} = e\hbar/(2m_0)$ is the Bohr magneton which was introduced earlier. With the addition of the selection rules for optical transitions,

$$\Delta m = 0 \quad \text{or} \quad \pm 1\,,$$

the above derivation leads to the splitting of spectral lines known as the ordinary Zeeman effect (Sect. 13.3).

14.2 Quantum Theoretical Treatment of the Electron and Proton Spins

14.2.1 Spin as Angular Momentum

As we saw in Sect. 12.4, the electron has three degrees of freedom in its translational motion, and a fourth in its spin. As we know, a number of other elementary particles, including the proton, have spins too. Our quantum mechanical calculations to this point, especially our derivation of the Schrödinger equation and its application to the hydrogen atom, have not included spin. In the following, we shall show how spin is included in the quantum theoretical treatment of atomic states. This is necessary, for example in spin-orbit coupling, in the anomalous Zeeman effect, in spin resonance, and in an adequate formulation of the Pauli principle, which will be discussed later. Like every angular momentum, the spin of the electron is a vector with three spatial components s_x, s_y and s_z:

$$s = (s_x, s_y, s_z) \,. \tag{14.19}$$

In the following development of the spin formalism, we must account for the experimental observation that the spin has only two possible orientations such that the spin component in a chosen direction, e.g. the z direction, can only have the value $+\hbar/2$ or $-\hbar/2$. In this sense, it is a genuine two-level system.

14.2.2 Spin Operators, Spin Matrices and Spin Wavefunctions

Since it is intuitive to think of one of the states of spin as "spin up" and the other as "spin down", we shall first introduce in a purely formal way two "wave" functions which correspond to these spin directions, i.e. $\phi_\uparrow$ and $\phi_\downarrow$. If we proceed strictly according to quantum formalism, measurement of the z component of the spin corresponds to applying the operator $\hat{s}_z$ to a wavefunction. (As with the angular momentum $\boldsymbol{l}$, we distinguish the spin operator from the corresponding classical parameter by using the "hat" sign.) We can choose the wavefunctions in such a way that the application of the operator gives the observed values of the wavefunction. Because we have only two observed values, namely $\hbar/2$ and $-\hbar/2$, we expect that

$$\hat{s}_z \phi_\uparrow = \frac{\hbar}{2} \phi_\uparrow \,, \quad \text{and} \tag{14.20a}$$

$$\hat{s}_z \phi_\downarrow = -\frac{\hbar}{2} \phi_\downarrow \,. \tag{14.20b}$$

These can be summarised as

$$\hat{s}_z \phi_{m_s} = \hbar m_s \phi_{m_s} \,, \tag{14.21}$$

where $m_s = +1/2$ (corresponding to $\uparrow$) or
$m_s = -1/2$ (corresponding to $\downarrow$).

m_s is thus the quantum number of the z component of the spin.

We are now looking for a formalism which will more or less automatically give us the relations (14.20a, b). It has been found that this is most easily done by using matrices. A matrix, in mathematics, is a square array, for example

$$M = \begin{pmatrix} a & b \\ c & d \end{pmatrix} . \tag{14.22}$$

There is a multiplication rule for this array. As an example, let us imagine a vector $\boldsymbol{v}$ with the components x and y in a plane, or $\boldsymbol{v} = \begin{pmatrix} x \\ y \end{pmatrix}$. We can produce a new vector x', y' by multiplying $\begin{pmatrix} x \\ y \end{pmatrix}$ by M. This is done according to the rule

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = M \begin{pmatrix} x \\ y \end{pmatrix} \equiv \begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} ax+by \\ cx+dy \end{pmatrix} . \tag{14.23}$$

We thus are looking for a "vector" ϕ and a matrix M such that $M\phi$ yields exactly either $\frac{\hbar}{2}\phi$ or $-\frac{\hbar}{2}\phi$.

We shall simply give the result, and then verify it. We choose $\hat{s}_z$ in the form

$$\hat{s}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{14.24}$$

and the spin functions in the form

$$\phi_\uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \phi_\downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix} . \tag{14.25}$$

With the help of (14.23), it can be immediately calculated that substitution of (14.24 and 25) in (14.20a and b) actually yields the relations $M\phi_\uparrow = (\hbar/2)\phi_\uparrow$, $M\phi_\downarrow = -(\hbar/2)\phi_\downarrow$. We obtain the most general spin function by superposition of $\phi_\uparrow$ and $\phi_\downarrow$ with the coefficients a and b, as we have done before with wave packets:

$$\phi = a\phi_\uparrow + b\phi_\downarrow = \begin{pmatrix} a \\ b \end{pmatrix} . \tag{14.26}$$

In order to arrive at a normalisation condition, we must now introduce the "scalar product" for the ϕ's. If we have a general ϕ_1 in the form

$$\phi_1 = \begin{pmatrix} a_1 \\ b_1 \end{pmatrix} \tag{14.27}$$

and another ϕ_2 in the form

$$\phi_2 = \begin{pmatrix} a_2 \\ b_2 \end{pmatrix}, \tag{14.28}$$

we define the scalar product as

$$\bar{\phi}_1 \phi_2 = (a_1^*, b_1^*) \begin{pmatrix} a_2 \\ b_2 \end{pmatrix} = (a_1^* a_2 + b_1^* b_2) . \tag{14.29}$$

These are calculation rules, which should be familiar to the reader from vector calculations. If we substitute in (14.29) $\bar{\phi}_1 = \bar{\phi}_\uparrow$, $\phi_2 = \phi_\uparrow$, we obtain

$$\bar{\phi}_\uparrow \phi_\uparrow = 1 \tag{14.30}$$

and correspondingly,

$$\bar{\phi}_{\downarrow}\phi_{\downarrow} = 1 \ . \tag{14.31}$$

Thus the wavefunctions are normalised. With $\bar{\phi}_1 = \bar{\phi}_{\downarrow}$ and $\phi_2 = \phi_{\uparrow}$, we have

$$\bar{\phi}_{\downarrow}\phi_{\uparrow} = 0 \ , \tag{14.32}$$

i.e. the wavefunctions are mutually orthogonal.

With (14.24), we have the first part of the solution of the entire problem. The representation of the operators for the x and y directions of the angular momentum is naturally still open. Because we are talking about *angular momenta*, it seems reasonable to require the usual commutation relations for angular momenta (10.14). We do not wish to go into the mathematics of the problem here. For the purposes of this book, it is sufficient simply to choose $\hat{s}_x$ and $\hat{s}_y$ appropriately. It turns out that

$$\hat{s}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{14.33 a}$$

and

$$\hat{s}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \tag{14.33 b}$$

are suitable. If we calculate $\hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2$ with the matrices (14.24, 33 a and 33 b), we obtain after a short calculation

$$\hat{s}^2 = \frac{\hbar^2}{4}\begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix} = \hbar^2 \frac{3}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \hbar^2 \frac{3}{4} \cdot (\text{unit matrix}) \ .$$

Therefore, it we apply $\hat{s}^2$ to any spin function ϕ, in particular to ϕ_{m_s}, it will always yield

$$\hat{s}^2 \phi_{m_s} = \hbar^2 \tfrac{3}{4} \phi_{m_s} \ .$$

The analogy between this equation and the eigenvalue equation for the orbital angular momentum $\boldsymbol{l}^2$ with the eigenvalue $\hbar^2 l(l+1)$ (10.6) is especially clear if we write $\hbar^2\,3/4$ in the form $\hbar^2 s(s+1)$, with $s = 1/2$:

$$\hat{s}^2 \phi_{m_s} = \hbar^2 s(s+1)\, \phi_{m_s} \ . \tag{14.34}$$

14.2.3 The Schrödinger Equation of a Spin in a Magnetic Field

We shall now proceed to the formulation of a Schrödinger equation for the spin in a magnetic field. A magnetic moment

$$\mu_{\mathrm{B}} = \frac{e\hbar}{2m_0} \tag{14.35}$$

is associated with the electron spin of $\hbar/2$. Here m_0 is the rest mass of the electron and e is the positive unit charge. This magnetic moment, the "Bohr magneton", was presented in Sect. 12.2. Since the magnetic moment is a vector oriented antiparallel to the electron spin, we can write more generally

$$\boldsymbol{\mu} = -\frac{e}{m_0}\boldsymbol{s}\,, \tag{14.36}$$

where the factor $\hbar/2$ is now naturally included in the angular momentum $\boldsymbol{s}$. The following calculations can be directly applied to the spin of a proton, if the Bohr magneton μ_{B} is consistently replaced by the so-called nuclear magneton $-\mu_{\mathrm{N}}$ and $-e/m_0$ by e/m_{p}. μ_{N} is defined as $-(m_0/m_{\mathrm{p}})\mu_{\mathrm{B}}$, and m_{p} is the mass of the proton. The negative sign comes from the fact that the charge of the proton is the negative of the electron charge.

The energy of a spin in a spatially homogeneous magnetic field $\boldsymbol{B}$ is, as is shown in electrodynamics,

$$V_S = -\boldsymbol{\mu}\cdot\boldsymbol{B}\,. \tag{14.37}$$

We are trying to find an equation analogous to the Schrödinger equation, and we realise from the previous discussion of quantum mechanics that the Schrödinger equation was obtained from energy expressions (Sect. 9.2). There the energy expressions were the Hamilton functions, which were then converted to the Hamiltonian operator. In a similar way, we now make the energy expression (14.37) into an operator and write the equation

$$\frac{e}{m_0}\boldsymbol{B}\cdot\hat{\boldsymbol{s}}\,\phi = E\phi\,. \tag{14.38}$$

If the magnetic field has the components B_x, B_y and B_z, the left side of (14.38) is

$$\frac{e}{m_0}(B_x\hat{s}_x + B_y\hat{s}_y + B_z\hat{s}_z)\,\phi\,. \tag{14.39}$$

Now $\hat{s}_x$, $\hat{s}_y$ and $\hat{s}_z$ are the matrices (14.33 a, b and 24), respectively. Therefore (14.39) is also a matrix. According to the rules for the addition of matrices, it is

$$\frac{e\hbar}{2m_0}\begin{pmatrix} B_z & B_x - \mathrm{i}B_y \\ B_x + \mathrm{i}B_y & -B_z \end{pmatrix}. \tag{14.40}$$

The characteristic of being an operator thus accrues to the left side of (14.38) from $\hat{\boldsymbol{s}}$, which was defined above as the spin operator. If we choose the field $\boldsymbol{B}$ in the z direction, as above,

$$\boldsymbol{B} = (0, 0, B_z)\,, \tag{14.41}$$

the left side of (14.38) is the same, except for the numerical factor eB_z/m_0, as the left side of (14.20 a or b) which shows us that the functions introduced above (14.25) are also eigenfunctions of the operator in (14.38) with the corresponding eigenvalues

$$E = \pm \mu_{\mathrm{B}} B_z \, . \tag{14.42}$$

The spin energy in a constant magnetic field in the z direction is thus just given by the expression which we would expect in classical theory for the interaction of an antiparallel spin moment with a magnetic field. Of course, instead of (14.38), we could have formulated the corresponding time-dependent Schrödinger equation

$$\frac{e}{m_0} \boldsymbol{B} \cdot \hat{s} \, \phi = \mathrm{i} \hbar \frac{d\phi}{dt} \, . \tag{14.43}$$

This equation must be used, in particular, if we are dealing with a time-dependent magnetic field.

14.2.4 Description of Spin Precession by Expectation Values

It is, however, also interesting to determine the time-dependent solution of (14.43) for a constant magnetic field. If we choose a magnetic field in the z direction, the Schrödinger equation is given by

$$\mu_{\mathrm{B}} B_z \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \phi = \mathrm{i} \hbar \frac{d\phi}{dt} \, . \tag{14.44}$$

The general solution is found as a superposition of $\phi_\uparrow$ and $\phi_\downarrow$ (14.26). Since the Schrödinger equation contains a derivative with respect to time on the right-hand side, we have to include in $\phi_\uparrow$ and $\phi_\downarrow$ the corresponding time functions

$$\exp(-\mathrm{i} E_\uparrow t/\hbar) \quad \text{and} \quad \exp(-\mathrm{i} E_\downarrow t/\hbar) \, ,$$

where $E_\uparrow$ and $E_\downarrow$ may be written in the form

$$E_\uparrow = (\hbar/2)\, \omega_0 \, , \quad E_\downarrow = -(\hbar/2)\, \omega_0 \, , \quad \text{and} \quad \omega_0 = \frac{e}{m_0} B_z \, . \tag{14.45}$$

Since a linear combination may also contain constant coefficients, we use the more general trial solution for (14.44):

$$\phi(t) = a \exp(-\mathrm{i} \omega_0 t/2)\, \phi_\uparrow + b \exp(\mathrm{i} \omega_0 t/2)\, \phi_\downarrow \, . \tag{14.46}$$

We require ϕ to be normalised, as always in quantum mechanics, i.e. that the scalar product $\bar{\phi}\phi$ (14.29) be equal to one. This means

$$|a|^2 + |b|^2 = 1 \, . \tag{14.47}$$

The physical meaning of (14.46) will become clear when we form the expectation value of the spin operator $\hat{s}$ with this wavefunction. To do this, we must first recall how expectation values are to be calculated, and refer to Sect. 9.3. The "recipe" given there states:

1) Take the wavefunction ψ,
2) allow the "operator for the measurable quantity" Ω of which the expectation value is to be found, to operate on it,
3) then multiply with ψ^* and integrate:

$$\int \psi^*(x)\,\Omega\,\psi(x)\,dx\,.$$

The steps 1 – 3) can easily be transformed into three analogous rules for calculating with the spin formalism:

1) Take the spinfunction ϕ, e.g. (14.46),
2) let the spin operator $\hat{s}_x$, $\hat{s}_y$, or $\hat{s}_z$ operate on (14.46), i.e. form, for example $\hat{s}_z\phi$;
3) multiplication by $\bar{\phi}$ and integration are replaced by the rules for calculating the scalar product:
   we multiply $\hat{s}_z\phi$ from the left by $\bar{\phi}$.
   As an abbreviation we set

$$\begin{aligned} a\exp(-\mathrm{i}\,\omega_0 t/2) &= \alpha\,, \\ b\exp(\mathrm{i}\,\omega_0 t/2) &= \beta\,. \end{aligned} \tag{14.48}$$

The individual steps 1 – 3) are now as follows:

$$1)\quad \phi = \alpha\phi_\uparrow + \beta\phi_\downarrow = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \tag{14.49}$$

$$2)\quad \hat{s}_z\phi = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix}. \tag{14.50}$$

Using the rule (14.23), this is equal to

$$\frac{\hbar}{2}\begin{pmatrix} \alpha \\ -\beta \end{pmatrix}. \tag{14.51}$$

$$3)\quad \bar{\phi}\hat{s}_z\phi = \bar{\phi}\,\frac{\hbar}{2}\begin{pmatrix} \alpha \\ -\beta \end{pmatrix}. \tag{14.52}$$

According to rule (14.29), the right-hand side is equal to

$$\frac{\hbar}{2}(|\alpha|^2 - |\beta|^2)\,.$$

Writing the expectation value of $\hat{s}_z$ as $\langle\hat{s}_z\rangle$, we have found:

$$\langle\hat{s}_z\rangle = \frac{\hbar}{2}(|\alpha|^2 - |\beta|^2)\,. \tag{14.53}$$

We leave it to the reader as an exercise to show that

$$\langle\hat{s}_x\rangle = \frac{\hbar}{2}(\alpha^*\beta + \alpha\beta^*)\,, \tag{14.54}$$

and

$$\langle \hat{s}_y \rangle = \frac{\hbar}{2}\mathrm{i}(\alpha\beta^* - \alpha^*\beta) . \tag{14.55}$$

Since we can see all the essentials by assuming a and b in (14.48) to be real numbers, we shall do so and insert (14.48) into (14.53 – 55). This yields

$$\langle \hat{s}_z \rangle = \frac{\hbar}{2}(a^2 - b^2) = \text{const w.r.t. time} . \tag{14.56}$$

The expectation value of the z component of the spin thus remains constant in time.

$$\langle \hat{s}_x \rangle = ab\hbar \cos \omega_0 t , \tag{14.57}$$

$$\langle \hat{s}_y \rangle = ab\hbar \sin \omega_0 t . \tag{14.58}$$

The component of the spin in the $x-y$ plane rotates with the angular velocity ω_0. The expectation values (14.56 – 58) can be interpreted as a *precessional motion* of the spin (Fig. 14.1). Thus the model used in Chap. 13 is justified by quantum theory.

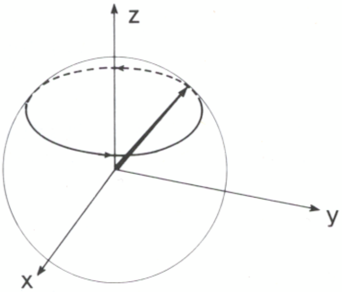

Fig. 14.1. Precessional motion of the spin

14.3 Quantum Mechanical Treatment of the Anomalous Zeeman Effect with Spin-Orbit Coupling*

In this section we shall continue the complete quantum mechanical treatment of spin-orbit coupling. The goal is to give an exact justification for the vector model of spin-orbit coupling introduced in Chap. 12. Specifically, we are concerned with LS coupling and wish to show the justification for the rule that l^2, s^2 and j^2 can be replaced by $l(l+1)$, $s(s+1)$ and $j(j+1)$, respectively. If we ignore spin-orbit coupling for a moment, then the energies of the orbital motion and of the spin (magnetic moment) in a magnetic field are additive. This means that the total Hamiltonian is simply the sum of the Hamiltonians for orbital motion (14.8) and for the spin (14.38). Thus we have the Schrödinger equation

$$\left[\frac{1}{2m_0}\left(\frac{\hbar}{\mathrm{i}}\,\mathrm{grad} + e\boldsymbol{A}\right)^2 + V + \frac{e}{m_0}\hat{\boldsymbol{s}}\cdot\boldsymbol{B}\right]\psi = \mathrm{i}\hbar\frac{\partial\psi}{\partial t} . \tag{14.59}$$

This is also known in the literature as the Pauli equation.

Because the Hamiltonians (14.8) and (14.38) are additive and apply to entirely different degrees of freedom, the wavefunction ψ can be written as a product of the wavefunction of the orbital motion and that of the spin motion. Finally, we can also treat the spin-orbit coupling introduced in Sect. 12.8 quantum mechanically. For this we need only to introduce the previously derived expression (12.27), which represents an interaction energy, into quantum mechanics. This is done, as usual, by assigning the angular momentum $\boldsymbol{l}$ to the angular momentum *operator* $\hat{\boldsymbol{l}}$ (Sect. 9.3.4.) and the spin $\boldsymbol{s}$ to the spin operator $\hat{\boldsymbol{s}}$ [compare with (9.61)]. The resulting term

$$W(\hat{\boldsymbol{l}},\hat{\boldsymbol{s}}) = \frac{\mu_0 Z e^2}{8\pi m_0^2}\,\frac{1}{r^3}(\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}}) = \frac{\mu_0 Z}{4\pi r^3}(\hat{\boldsymbol{\mu}}_{\text{orbit}}\cdot\hat{\boldsymbol{\mu}}_{\text{spin}}) \tag{14.60}$$

is introduced into the Schrödinger equation to give the Schrödinger equation of an electron with spin in a magnetic field, where spin-orbit coupling is taken into account. The time-independent form of this equation is

$$\left[-\frac{\hbar^2}{2m_0}\nabla^2 + \frac{e\hbar}{m_0\mathrm{i}}\boldsymbol{A}\,\mathrm{grad} + \frac{e\hbar}{2m_0\mathrm{i}}\mathrm{div}\boldsymbol{A} + \frac{e^2\boldsymbol{A}^2}{2m_0} + V\right.$$
$$\left. + \frac{e}{m_0}\hat{\boldsymbol{s}}\cdot\boldsymbol{B} + \frac{\mu_0 Z e^2}{8\pi m_0^2}\,\frac{1}{r^3}(\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}})\right]\psi = E\psi\,. \tag{14.61}$$

As we saw in Sect. 13.3, spin-orbit coupling dominates in low magnetic fields. Therefore we shall first examine the Schrödinger equation in the absence of a magnetic field:

$$\left[-\frac{\hbar^2}{2m_0}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{\mu_0 Z e^2}{8\pi m_0^2}\,\frac{1}{r^3}(\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}})\right]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})\,. \tag{14.62}$$

Equation (14.62) includes the spin operator $\hat{\boldsymbol{s}}$ which, as we know, is a matrix. Therefore the wavefunction $\psi(\boldsymbol{r})$ has two components:

$$\psi(\boldsymbol{r}) = \begin{pmatrix}\psi_1(\boldsymbol{r})\\ \psi_2(\boldsymbol{r})\end{pmatrix},$$

where ψ_1 corresponds to spin ↑ and ψ_2 to spin ↓.

Spin-orbit coupling mixes orbital and spin states, and makes it necessary to introduce new quantum numbers. Without spin-orbit coupling, the wavefunction would have the form

$$\psi_{n,l,m,m_s} = \underbrace{R_{n,l}(r)F_{l,m}(\theta,\phi)}_{\text{orbit}}\ \underbrace{\phi_{m_s}}_{\text{spin}}\,. \tag{14.63}$$ [2]

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[2] The letter ϕ in (14.63) has two entirely different meanings: in $F_{l,m}(\theta,\phi)$, it indicates an angular coordinate, while in ϕ_{m_s} it indicates one of the spin wavefunctions (14.25)

It is characterised by the principal quantum number n, the orbital angular momentum quantum number l, the magnetic quantum number $m(\equiv m_l)$ and the spin quantum number m_s. In order to determine the quantum numbers applicable to spin-orbit coupling, we must expand on the considerations on orbital angular momentum presented in Sect. 10.2, and examine the parameters to decide which can be observed simultaneously. As we know, this can be done with the help of commutation relations (Sect. 9.3). If, as in Sect. 12.7, we introduce the total spin operator $\hat{\boldsymbol{j}} = \hat{\boldsymbol{l}} + \hat{\boldsymbol{s}}$, and its component in the z direction, $\hat{j}_z$, the following parameters can be observed to any desired precision simultaneously:

The square of the orbital angular momentum $\boldsymbol{l}^2$

The square of the spin $\boldsymbol{s}^2$

The square of the total angular momentum $\boldsymbol{j}^2$

Component j_z

$\boldsymbol{l}\cdot\boldsymbol{s}$ and $\boldsymbol{j}\cdot\boldsymbol{s}$.

Because $\boldsymbol{l}\cdot\boldsymbol{s}$ occurs in (14.62), we can characterise the wavefunction by choosing those quantum numbers which are eigenvalues for the operators $\hat{\boldsymbol{j}}^2$, $\hat{\boldsymbol{l}}^2$, $\hat{\boldsymbol{s}}^2$ and $\hat{j}_z$. We therefore obtain the following relations between operators and quantum numbers

$$\begin{array}{ll} \hat{\boldsymbol{j}}^2\text{: quantum number } j & \hat{j}_z\text{: quantum number } m_j \\ \hat{\boldsymbol{s}}^2\text{: quantum number } s & \hat{\boldsymbol{l}}^2\text{: quantum number } l\,. \end{array} \tag{14.64}$$

Since the spin-orbit coupling is much smaller than the term spacing, the principal quantum number n is still a good quantum number, i.e. it still characterises the eigenfunction to a good approximation. The wavefunction is now characterised by

$$\psi_{n,j,m_j,l,s} = R(r)\cdot(\text{Function of angle and spin})\,. \tag{14.65}$$

The spin-orbit coupling leads to the relative orientations of the spin and orbital moments, as was discussed in detail in Sect. 12.8.

We now examine the effect of a magnetic field on an electron, taking spin-orbit coupling into account. It can be shown that in the Schrödinger equation (14.59), the $\boldsymbol{A}^2$ term is much smaller than the other terms, if the magnetic field is not too large, and can be ignored. Let us again choose the magnetic field $\boldsymbol{B}$ in the z direction and

$$A_x = -\tfrac{1}{2}B_y\,,\quad A_y = \tfrac{1}{2}B_x\quad\text{and}\quad A_z = 0\,.$$

$\operatorname{div}\boldsymbol{A}$ is then zero. The Schrödinger equation is then

$$\Bigg[\underbrace{-\frac{\hbar^2}{2m_0}\nabla^2-\frac{Ze^2}{4\pi\varepsilon_0 r}}_{\mathscr{H}^0}+\underbrace{\frac{e}{2m_0}B\hat{l}_z+\frac{e}{m_0}\hat{s}_z B}_{W_{\text{magn}}}+\underbrace{\frac{Ze^2\mu_0}{8\pi m_0^2 r^3}(\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}})}_{W_{\text{spin-orbit}}}\Bigg]\psi=E\psi\,. \tag{14.66}$$

We are treating the case of a weak magnetic field in which the spin-orbit coupling is larger than the interaction with the external magnetic field. We are now in a position to justify quantum mechanically the vector model introduced in Chap. 13. Let us consider the operator occurring in (14.66):

$$W_{\text{magn}}\equiv\frac{eB}{2m_0}(\hat{l}_z+2\hat{s}_z)=\frac{eB}{2m_0}(\hat{j}_z+\hat{s}_z) \tag{14.67}$$

(it leads to an additional magnetic energy, which we called V_{m_j} in Sects. 13.3.4, 5). If we here had $\hat{l}_z+\hat{s}_z$ instead of $\hat{l}_z+2\hat{s}_z$, the solution would be very simple, and analogous to the treatment of an electron without a spin in the magnetic field (Sect. 14.1). In that case, the wavefunction ψ, which is already characterised by the quantum number m_j, would also be an eigenfunction of the operator $\hat{j}_z=\hat{l}_z+\hat{s}_z$. We must therefore see how we can deal with the additional $\hat{s}_z$ in (14.67). Let us consider

$$\hat{s}_z\hat{\boldsymbol{j}}^2=\hat{s}_z(\hat{j}_x^2+\hat{j}_y^2+\hat{j}_z^2)\,, \tag{14.68}$$

which can be rewritten as

$$\hat{j}_z(\hat{\boldsymbol{s}}\cdot\hat{\boldsymbol{j}})+\underbrace{(\hat{s}_z\hat{j}_x-\hat{j}_z\hat{s}_x)\hat{j}_x+(\hat{s}_z\hat{j}_y-\hat{j}_z\hat{s}_y)\hat{j}_y}_{q}\,. \tag{14.69}$$

It can be shown that the matrix elements of the operator q disappear when it is applied to wavefunctions with the same quantum number j, or, in other words, the operator q can only couple wavefunctions with different values of j. If the externally applied field is small, we can also expect that such transitions will make only a small contribution and can therefore be ignored. In the following, we shall therefore leave out the operator q. With this approximation, (14.68) can then be written as

$$\hat{s}_z\hat{\boldsymbol{j}}^2=\hat{j}_z\tfrac{1}{2}(\hat{\boldsymbol{j}}^2-\hat{\boldsymbol{l}}^2+\hat{\boldsymbol{s}}^2)\,, \tag{14.70}$$

where we have replaced $\hat{\boldsymbol{s}}\cdot\hat{\boldsymbol{j}}$ by the corresponding expression on the right side of (14.70). It is important to note that all the parameters in (14.70) are *operators*. We now apply both sides of (14.70) to a wavefunction ψ, which is characterised by the *quantum numbers* j, m_j, l, and s. We obtain

$$\begin{aligned}\underset{\substack{\uparrow\,\uparrow\\ \text{Operators}}}{\hat{s}_z\hat{\boldsymbol{j}}^2}\cdot\psi &= \underset{\substack{\uparrow\\ \text{Operator}}}{\hat{s}_z}\cdot\underset{\substack{\uparrow\,\uparrow\\ \text{Numbers}}}{\hbar^2 j(j+1)}\,\psi\\ &=\hbar^2\cdot\underset{\substack{\uparrow\\ \text{Operator}}}{\hat{j}_z}\cdot\underbrace{\tfrac{1}{2}[j(j+1)-l(l+1)+s(s+1)]}_{\text{Numbers}}\,\psi\,.\end{aligned} \tag{14.71}$$

If we divide the right half of the double equation (14.71) by $\hbar^2 j(j+1)$, we obtain

$$\hat{s}_z \psi = \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} \hat{j}_z \psi \,, \qquad s = 1/2 \,. \tag{14.72}$$

If we write W_{magn} (14.67) in the form

$$W_{\text{magn}} = \frac{eB}{2m_0} (\underset{\uparrow}{\hat{j}_z} + \underset{\uparrow}{\hat{s}_z}) \,, \quad \text{Operators} \tag{14.73}$$

we finally obtain

$$W_{\text{magn}} \psi = \frac{eB}{2m_0} \cdot \underset{\substack{\uparrow \\ \text{Operator}}}{\hat{j}_z} \cdot \left[1 + \underbrace{\frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}}_{\text{Numbers}} \right] \psi \,. \tag{14.74}$$

The additional energy due to the orientation of the total moment $\boldsymbol{j}$ in the magnetic field is represented by (14.74).

If we write the energy change of a quantum state n, j, l, m_j in the form

$$\Delta E_{j,l,m_j} = \frac{e\hbar}{2m_0} B g \cdot m_j \,, \tag{14.75}$$

we can infer the *Landé factor* by comparison with (14.74) to be

$$g = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} \,. \tag{14.76}$$

We derived this Landé factor earlier, in an intuitive way with the help of the vector model, but we had to make use of the law of cosines in an ad hoc fashion when we replaced $\boldsymbol{j}^2$ by $j(j+1)\hbar^2$, $\boldsymbol{l}^2$ by $l(l+1)\hbar^2$ and $\boldsymbol{s}^2$ by $s(s+1)\hbar^2$. The quantum mechanical calculation presented here gives the exact basis for this substitution.

14.4 Quantum Theory of a Spin in Mutually Perpendicular Magnetic Fields, One Constant and One Time Dependent

A number of important experiments on spin have been carried out with the following arrangement: both a constant, spatially homogeneous magnetic field in the z direction and an oscillating field in the x-y plane are applied. We shall see that this leads to the interesting phenomenon of spin flipping. These experiments make possible, among other things, the exact measurement of magnetic moments, and permit detailed analysis of the structure of and relaxation processes in liquids and solids.

We shall see that we can easily solve these problems using the spin formalism introduced in Sect. 14.2. We write the magnetic field expressed as a time-dependent and a time-independent part:

$$\boldsymbol{B} = \boldsymbol{B}_0 + \boldsymbol{B}^{\mathrm{s}}(t)\,, \tag{14.77}$$

where the vectors of the magnetic fields are defined as

$$\boldsymbol{B}_0 = (0, 0, B_z^0) \qquad \text{and} \tag{14.78}$$

$$\boldsymbol{B}^{\mathrm{s}}(t) = (B_x^{\mathrm{s}}(t), B_y^{\mathrm{s}}(t), 0)\,. \tag{14.79}$$

Naturally we cannot expect that the spin will always point up or down in a time-dependent magnetic field. Rather, we must expect time-dependent transitions. We take these into account by writing the wave function which is to be a solution of the Schrödinger equation (14.43) in the general form

$$\phi(t) = c_1(t)\,\phi_\uparrow + c_2(t)\,\phi_\downarrow \equiv \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}. \tag{14.80}$$

To arrive at equations for the still unknown coefficients c_1 and c_2, we substitute (14.80) in (14.43), observing the decomposition (14.77 – 79). If we multiply (14.39) out like a normal scalar product and observe the matrix form of $\hat{s}_x$, $\hat{s}_y$, and $\hat{s}_z$ – see (14.40) – we obtain the Schrödinger equation (14.43) in the form

$$\mu_{\mathrm{B}} \begin{pmatrix} B_z^0 & B_x^{\mathrm{s}} - \mathrm{i} B_y^{\mathrm{s}} \\ B_x^{\mathrm{s}} + \mathrm{i} B_y^{\mathrm{s}} & -B_z^0 \end{pmatrix} \cdot \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \mathrm{i}\hbar \begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \end{pmatrix}. \tag{14.81}$$

If we multiply the matrices according to the rule (14.23), we obtain these equations instead of (14.81):

$$(\tfrac{1}{2}\hbar\omega_0)\,c_1 + \mu_{\mathrm{B}}(B_x^{\mathrm{s}} - \mathrm{i} B_y^{\mathrm{s}})\,c_2 = \mathrm{i}\hbar\dot{c}_1\,, \tag{14.82}$$

$$\mu_{\mathrm{B}}(B_x^{\mathrm{s}} + \mathrm{i} B_y^{\mathrm{s}})\,c_1 - \tfrac{1}{2}\hbar\omega_0 c_2 = \mathrm{i}\hbar\dot{c}_2\,. \tag{14.83}$$

Here we have introduced the frequency

$$\hbar\omega_0 = 2\mu_{\mathrm{B}} B_z^0 \tag{14.84}$$

as an abbreviation. In order to simplify the following calculation, let us think of the transverse magnetic field as rotating with the frequency ω. In other words, the magnetic field has the form

$$\begin{aligned} B_x^{\mathrm{s}} &= F\cos\omega t\,, \\ B_y^{\mathrm{s}} &= F\sin\omega t\,. \end{aligned} \tag{14.85}$$

Since B_x^{s} and B_y^{s} appear in (14.82, 83) in a combined form, let us first consider these expressions. We can express them as an exponential function, due to elementary relationships between sines and cosines:

$$B_x^{\mathrm{s}} \pm \mathrm{i} B_y^{\mathrm{s}} = F(\cos\omega t \pm \mathrm{i}\sin\omega t) = F\exp(\pm\mathrm{i}\omega t)\,. \tag{14.86}$$

Then (14.82, 83) simplify to

$$(\hbar\omega_0/2)c_1+\mu_B F\exp(-\mathrm{i}\omega t)c_2=\mathrm{i}\hbar\dot{c}_1\,, \tag{14.87}$$

$$\mu_B F\exp(\mathrm{i}\omega t)c_1-(\hbar\omega_0/2)c_2=\mathrm{i}\hbar\dot{c}_2\,. \tag{14.88}$$

We shall solve these two equations in two steps. In the first, we put the coefficients $c_j(t)$ into the form

$$c_1(t)=d_1(t)\exp(-\mathrm{i}\omega_0 t/2)\,;\qquad c_2(t)=d_2(t)\exp(\mathrm{i}\omega_0 t/2)\,. \tag{14.89}$$

If we differentiate (14.89) with respect to time and rearrange slightly, we obtain

$$\mathrm{i}\hbar\dot{c}_1=(\hbar\omega_0/2)c_1+\mathrm{i}\hbar\dot{d}_1\exp(-\mathrm{i}\omega_0 t/2)\,. \tag{14.90}$$

If we substitute this in (14.87), we see that the term $(\hbar\omega_0/2)c_1$ on both sides cancels out. The same thing happens with c_2 in (14.88), so that (14.87) and (14.88) simplify to

$$\mu_B F\exp[-\mathrm{i}(\omega-\omega_0)t]\,d_2=\mathrm{i}\hbar\dot{d}_1\,, \tag{14.91}$$

$$\mu_B F\exp[\mathrm{i}(\omega-\omega_0)t]\,d_1=\mathrm{i}\hbar\dot{d}_2\,. \tag{14.92}$$

These equations become very simple when we set the rotational frequency of the magnetic field ω equal to the spin frequency ω_0:

$$\omega=\omega_0\,. \tag{14.93}$$

We then obtain

$$\mu_B F d_2=\mathrm{i}\hbar\dot{d}_1\,, \tag{14.94}$$

$$\mu_B F d_1=\mathrm{i}\hbar\dot{d}_2\,. \tag{14.95}$$

To solve these equations, we first take the time derivative of (14.94):

$$\mu_B F\dot{d}_2=\mathrm{i}\hbar\,\ddot{d}_1\,, \tag{14.96}$$

and then, according to (14.95), we replace $\dot{d}_2$ by $(\mu_B F d_1)/(\mathrm{i}\hbar)$, and thus obtain

$$\ddot{d}_1+\frac{\mu_B^2F^2}{\hbar^2}d_1=0\,. \tag{14.97}$$

If we simplify the expression by setting $\mu_B F/\hbar=\Omega$, we recognise (14.97) as a typical oscillator equation with the general solution

$$d_1=a\sin(\Omega t+\Phi)\,, \tag{14.98}$$

where the amplitude a and phase Φ are free to vary. Using (14.98) and (14.94) we obtain

$$d_2=\mathrm{i}a\cos(\Omega t+\Phi)\,. \tag{14.99}$$

With the proper choice of the zero time, we can set $\Phi=0$. The normalisation conditions for the spin wavefunction require that $a=1$. If we substitute (14.99) in (14.89) and this in (14.80), and do the same with (14.98), we obtain the desired spin wavefunction

$$\phi(t) = \sin(\Omega t)\exp(-\mathrm{i}\,\omega_0 t/2)\,\phi_\uparrow + \mathrm{i}\cos(\Omega t)\exp(\mathrm{i}\,\omega_0 t/2)\,\phi_\downarrow\,. \tag{14.100}$$

The spin functions and the spin formalism naturally seem very unintuitive. In order to see the meaning of the above equations, let us remember that the immediate predictions of quantum mechanics can be read from the corresponding expectation values (Sect. 9.3). We will first develop the expectation value of the spin operator in the z direction. A comparison of (14.49) with (14.100) shows that we can now express the α and β of (14.49) in the form

$$\begin{aligned} \alpha &= \sin(\Omega t)\exp(-\mathrm{i}\,\omega_0 t/2)\,,\\ \beta &= \mathrm{i}\cos(\Omega t)\exp(\mathrm{i}\,\omega_0 t/2)\,. \end{aligned} \tag{14.101}$$

These can be immediately substituted into the end results (14.53 – 55), however, to give

$$\begin{aligned} \langle \hat{s}_z\rangle &= (\hbar/2)\sin^2(\Omega t) - \cos^2(\Omega t)\\ &= -(\hbar/2)\cos(2\,\Omega t)\,. \end{aligned} \tag{14.102}$$

According to (14.102), the z component of the spin oscillates with the frequency $2\,\Omega$. If the spin is originally down at $t = 0$, it flips up, then down again, and so on.

For the other components,

$$\langle \hat{s}_x\rangle = -\frac{\hbar}{2}\sin(2\,\Omega t)\sin(\omega_0 t)\,, \tag{14.103}$$

$$\langle \hat{s}_y\rangle = \frac{\hbar}{2}\sin(2\,\Omega t)\cos(\omega_0 t)\,. \tag{14.104}$$

These equations indicate that the spin motion in the x-y plane is a superposition of two motions, a rapid rotational motion with the frequency ω_0 and a modulation with the frequency $2\,\Omega$. The entire result (14.102 – 104) can be very easily interpreted if we think of the expectation value of the spin as a vector $\boldsymbol{s}$ with the components $\langle \hat{s}_x\rangle$, $\langle \hat{s}_y\rangle$, and $\langle \hat{s}_z\rangle$. Obviously the projection of the vector on the z axis is $(-\hbar/2)\cos(2\,\Omega t)$, while the projection in the x-y plane is $(\hbar/2)\sin(2\,\Omega t)$. As can be seen from the formulae, the spin gradually tips out of the $-z$ direction toward the horizontal, and then further into the $+z$ direction, while simultaneously precessing. The spin thus behaves exactly like a top under the influence of external forces, as we indicated in previous chapters.

We shall consider this process again, in more detail. At a time $t = 0$,

$$\langle \hat{s}_z\rangle = -\hbar/2\,. \tag{14.105}$$

We now ask when the spin, considered intuitively, is in the horizontal position, i.e. when

$$\langle \hat{s}_z\rangle = 0\,. \tag{14.106}$$

This is clearly the case when the cosine function vanishes, that is when

$$2\Omega t = \pi/2 \tag{14.107}$$

holds, or when the time

$$t = \pi/(4\Omega) = \pi\hbar/(4\mu_B F) \tag{14.108}$$

has passed. If one allows the transverse magnetic field to act upon the spins for this time, they will be pointing in the horizontal position (Fig. 14.2). In other words, they have been rotated by an angle $\pi/2$. We therefore speak of a $\pi/2$ or of a 90° pulse. Naturally, we may allow the magnetic field to act for a longer time, for example until the spins are pointing up, i.e.

$$\langle \hat{s}_z \rangle = \hbar/2 \,. \tag{14.109}$$

This occurs when

$$\cos(2\Omega t) = -1 \tag{14.110}$$

is fulfilled, i.e. after the time

$$t = \pi\hbar/(2\mu_B F) \,. \tag{14.111}$$

In this case, we speak of a π or of a 180° pulse (Fig. 14.2).

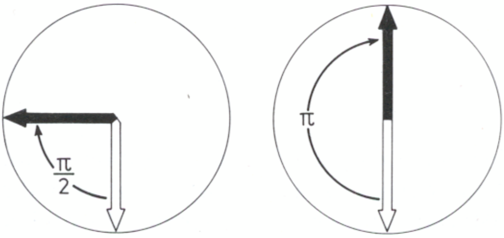

Fig. 14.2. *Left:* Spin flip through $\pi/2$. *Right:* Spin flip through π

With these considerations, we have sketched the most important traits of spin resonance. By applying a rotating magnetic field, we can cause the spin to flip from one direction to another. In practice, of course, one does not apply a magnetic field rotating with the spin frequency, but a linearly oscillating magnetic field. This can be pictured as a superposition of two fields rotating in opposite directions. Then one of the fields rotates with the spin, as before, while the other rotates with twice the frequency, as seen from the point of view of the rotating spin system.

The corresponding equations have practically the same form as those above, except for an additional, rapidly oscillating term, which comes from the "oppositely rotating" magnetic field. To a good approximation, this can be ignored; the result is the "rotating wave approximation".

14.5 The Bloch Equations

As we have just seen, the behaviour of the expectation values of the spin operators can be very simply interpreted. It is thus reasonable to ask whether it would not be possible to derive equations for these expectation values themselves. This is in fact the case. To derive these equations, we use the explicit form which we have just derived for the expectation values of the spin operator. We differentiate $\langle \hat{s}_x \rangle$ with respect to time and make use of (14.103) to obtain

$$\frac{d}{dt}\langle \hat{s}_x \rangle = -(\hbar/2)2\,\Omega\cos(2\,\Omega t)\sin(\omega_0 t) - (\hbar/2)\,\omega_0\sin(2\,\Omega t)\cos(\omega_0 t)\,. \tag{14.112}$$

The first term on the right side contains $-(\hbar/2)\cos(2\,\Omega t)$, which, however, is none other than the expectation value of the z component of the spin. We also recognise that the second term on the right side contains the expectation value of the y component of the spin. Equation (14.112) therefore has the form

$$\frac{d}{dt}\langle \hat{s}_x \rangle = \hbar^{-1} 2\mu_{\mathrm{B}} F\sin(\omega_0 t)\,\langle \hat{s}_z \rangle - \omega_0 \langle s_y \rangle\,. \tag{14.113}$$

However, we have seen the factors in front of the expectation values on the right side before. $F\sin(\omega_0 t)$ is just B_y, while ω_0 is proportional to B_z. If we also take into account the relationships (14.84) and (14.85), (14.112) becomes

$$\frac{d}{dt}\langle \hat{s}_x \rangle = \frac{e}{m_0}\langle \hat{s}_z \rangle B_y - \frac{e}{m_0} B_z \langle \hat{s}_y \rangle\,. \tag{14.114}$$

In a similar way, we find that the time derivative of the y component of the spin is

$$\frac{d}{dt}\langle \hat{s}_y \rangle = -\frac{e}{m_0}\langle \hat{s}_z \rangle B_x + \frac{e}{m_0} B_z \langle \hat{s}_x \rangle\,. \tag{14.115}$$

If we differentiate the expression (14.102) for $\langle \hat{s}_z \rangle$, we immediately obtain

$$\frac{d}{dt}\langle \hat{s}_z \rangle = \frac{\hbar}{2} 2\,\Omega\sin(2\,\Omega t)\,. \tag{14.116}$$

Since we expect that the right side of (14.116) can be expressed in terms of the expectation values of the spin components, like (14.114) and (14.115), we take advantage of the relation

$$\sin^2\omega_0 t + \cos^2\omega_0 t = 1 \tag{14.117}$$

to write the right side of (14.116) in the form

$$\hbar\,\Omega\sin(2\,\Omega t)[\sin(\omega_0 t)\sin(\omega_0 t) + \cos(\omega_0 t)\cos(\omega_0 t)]\,. \tag{14.118}$$

It is now easy to convince oneself that (14.116) can also be written in the form

$$\frac{d}{dt}\langle\hat{s}_z\rangle = -\frac{e}{m_0}\langle\hat{s}_x\rangle B_y + \frac{e}{m_0}\langle\hat{s}_y\rangle B_x . \tag{14.119}$$

Equations (14.114, 115 and 119) can be written in the form

$$\frac{d}{dt}\langle\hat{s}\rangle = \boldsymbol{\mu}\times\boldsymbol{B} , \tag{14.120}$$

as can be easily seen from the rules of vector multiplication. Here we have assembled the expectation values of the three components of the spin operator into the vector

$$\langle\hat{s}\rangle = \begin{pmatrix} \langle\hat{s}_x\rangle \\ \langle\hat{s}_y\rangle \\ \langle\hat{s}_z\rangle \end{pmatrix} . \tag{14.121}$$

This is strongly reminiscent of the torque equation for a top, if we identify $\boldsymbol{s}$ as the angular momentum and take into account that

$$\boldsymbol{\mu} = -\frac{e}{m_0}\langle\hat{s}\rangle . \tag{14.122}$$

Equation (14.120) is not quite adequate for the interpretation of many experiments, because in many cases, the spin of the particle interacts with its environment. For example, the orbital motion of the spins is continually perturbed by lattice oscillations. This results in continual phase shifts in the precession of the spin. In this case, it is no longer sufficient to regard the equations of a single spin as representative for those of all the spins, as we have implicitly done up to this point. Instead we must consider an "ensemble" of spins, and accordingly, we must in a certain sense subject the pure quantum mechanical expectation values we have used so far to another averaging process. We have to take into account the fact, for instance, that the x component of the spin no longer has a definite value at a definite time, but rather a distribution of values. As time passes, the distribution of values widens out, so that the probability that the value of $\langle\hat{s}_x\rangle$ is positive approaches the same value as the probability that it is negative. This means, however, that in the course of time, the average value of s_x goes to zero. In order to take this decay into account, we add more terms to (14.120) which reflect this incoherent spin motion.

These qualitative considerations are reflected by the phenomenological rule

$$\frac{d}{dt}\langle\hat{s}_x\rangle_{\text{incoh}} = -\frac{1}{T_2}\langle\hat{s}_x\rangle . \tag{14.123}$$

Since $\hat{s}_x$ and $\hat{s}_y$ play the same rôle, we must naturally assume the corresponding rule for $\langle\hat{s}_y\rangle$:

$$\frac{d}{dt}\langle\hat{s}_y\rangle_{\text{incoh}} = -\frac{1}{T_2}\langle\hat{s}_y\rangle . \tag{14.124}$$

Since the spins precess around the z axis, (14.123) and (14.124) indicate how quickly the components transverse to s_z decay. T_2 is therefore often called the transverse relaxation time. It is a measure of the speed with which the individual precessional movements of the spins get out of phase.

Since the z component of the spin is directed along a predetermined, constant field, it must be treated differently from the other two. In this case, too, we would expect a relaxation due to the interaction of the spin with its environment. It will naturally depend upon the orientation of the spin with respect to the external magnetic field – whether the field lies in the positive or negative z direction. The spin can give up energy through its coupling to the environment, and will attempt to reach the lowest state if the environment is at the absolute zero of temperature, $T = 0$. On the other hand, if the environment is at a finite temperature, the system of the spins and their environment will attempt to come to thermal equilibrium. At thermal equilibrium, some of the spins will be in the higher state, and others in the lower. If the spin system is displaced from thermal equilibrium, it will naturally attempt to return to it, and in a certain time interval which we call T_1. T_1 is often referred to as the longitudinal relaxation time. What we have just said can be put in mathematical form, if we take

$$\frac{d}{dt}\langle\hat{s}_z\rangle_{\text{incoh}} = \frac{s_0 - \langle\hat{s}_z\rangle}{T_1} \tag{14.125}$$

for the incoherent relaxation of $\langle\hat{s}_z\rangle$. Here s_0 is the value of $\langle\hat{s}_z\rangle$ which the spin component would assume at thermal equilibrium. We arrive at the Bloch equations by adding the "incoherent" terms (14.123 – 125) to the equation (14.120) describing the "coherent" motion of the spin.

The Bloch equations thus have the form

$$\frac{d}{dt}\langle\hat{s}\rangle = -\frac{e}{m_0}\langle\hat{s}\rangle \times \boldsymbol{B} + \begin{pmatrix} -\dfrac{1}{T_2}\langle\hat{s}_x\rangle \\ -\dfrac{1}{T_2}\langle\hat{s}_y\rangle \\ \dfrac{s_0 - \langle\hat{s}_z\rangle}{T_1} \end{pmatrix} . \tag{14.126}$$

The relaxation times T_1 and T_2 are a measure of the strength of the coupling of the electron (or proton) spin to its environment. Measurement of T_1 and T_2 often provides important information about processes in the environment of the spin being investigated, e.g. motion in liquids and solids. We shall discuss a typical and especially elegant experiment in Sect. 15.4.

14.6 The Relativistic Theory of the Electron. The Dirac Equation

In order to correctly describe the interaction of an electron with a magnetic field, we introduced spin operators, which represent the intrinsic degree of freedom of the electron. It was shown by *Dirac* that this intrinsic degree of freedom follows quite automatically from relativistic quantum theory. We therefore wish to treat the Dirac equation in this section. In order to arrive at a relativistic wave equation, it would seem appropriate to attempt to derive it in the same manner as the non-relativistic Schrödinger equation (see Sect. 9.2).

The derivation given there can be summarised in the following "recipe" (cf. also Sect. 9.3): one starts with the classical relation between energy and momentum for a force-free particle

$$E = \boldsymbol{p}^2/2m_0 \tag{14.127}$$

and replaces the energy E and the components of the momentum $\boldsymbol{p}$ by operators according to

$$E \rightarrow \mathrm{i}\hbar \frac{\partial}{\partial t} \tag{14.128}$$

and

$$p_x \rightarrow \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial x}, \quad p_y \rightarrow \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial y}, \quad p_z \rightarrow \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial z}. \tag{14.129}$$

The last equivalence can be abbreviated as

$$\boldsymbol{p} \rightarrow \frac{\hbar}{\mathrm{i}} \nabla. \tag{14.130}$$

Following the computational rules of quantum mechanics (cf. Sect. 9.2, 3), these operators act on wavefunctions Ψ, whereby (14.127) thus becomes the well-known Schrödinger equation

$$\mathrm{i}\hbar \frac{\partial}{\partial t} \Psi = -\frac{\hbar^2}{2m_0} \nabla^2 \Psi. \tag{14.131}$$

We shall now attempt to apply this recipe to the relativistic relation between energy and momentum. The latter is

$$E = \sqrt{\boldsymbol{p}^2 c^2 + m_0^2 c^4}\,. \tag{14.132}$$

If we replace E and $\boldsymbol{p}$ by operators according to (14.128) and (14.130) and allow the resulting expressions on both sides of (14.132) to act upon a wavefunction Ψ, we obtain the equation

$$\mathrm{i}\hbar \frac{\partial}{\partial t} \Psi = \sqrt{-c^2 \hbar^2 \nabla^2 + m_0^2 c^4}\, \Psi. \tag{14.133}$$

This equation contains the Laplace operator ∇^2 under a square-root sign, which may at first appear to be only a cosmetic defect. However, this approach failed utterly when the attempt was made to include the effects of electric and magnetic fields on the electron in such a wave equation. The theory had entered a cul-de-sac. Physicists chose two routes to lead it out again:

Route 1: The Klein-Gordon Equation

Since all of the difficulties stem from the square root in (14.133), one has to consider ways to avoid it. To this end, we square both sides of (14.132) and obtain

$$E^2 = p^2 c^2 + m_0^2 c^4 , \tag{14.134}$$

which, of course, may be immediately translated into the wave equation

$$-\hbar^2 \frac{\partial^2}{\partial t^2} \Psi = (-c^2 \hbar^2 \nabla^2 + m_0^2 c^4)\, \Psi , \tag{14.135}$$

called the *Klein-Gordon equation.*

The latter may be arranged in a more elegant (and relativistically more obvious) form by dividing both sides by $c^2 \hbar^2$ and introducing the operator

$$\Box^2 = \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} . \tag{14.136}$$

The Klein-Gordon equation is then given as

$$\Box^2 \Psi = \frac{m_0^2 c^2}{\hbar^2} \Psi . \tag{14.137}$$

Let us examine its solutions. Since, for a force-free particle, we expect the solutions to be de Broglie waves, we use the trial function

$$\Psi = \exp[\mathrm{i}(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)] \tag{14.138}$$

in which, as usual,

$$\omega = \frac{E}{\hbar} \quad \text{and} \quad \boldsymbol{p} = \hbar \boldsymbol{k} . \tag{14.139}$$

If we insert (14.138) in (14.135), we obtain (14.134) as the immediate result.

In order to determine the energy E itself, we must naturally take the square root. We thus obtain not only a positive energy

$$E = +\sqrt{p^2 c^2 + m_0^2 c^4} \tag{14.140}$$

but also a negative energy

$$E = -\sqrt{p^2 c^2 + m_0^2 c^4} . \tag{14.141}$$

Since free particles can have only positive energies, we are faced here with a difficulty! Furthermore, the analysis of the solutions reveals that the particle *density* can also become negative, which is also an unphysical result. The Klein-Gordon equation was reinterpreted by Pauli and Weisskopf, who used the charge density instead of the mass density, and thus found it to be applicable in quantum field theory to particles with spin zero. However, further development of that topic lies outside the framework of this book.

Route 2: The Dirac Equation

Dirac considered the question as to whether the root in (14.132) could not be extracted in some simple manner. In the limit $p=0$, we find

$$\sqrt{p^2c^2+m_0^2c^4}\rightarrow m_0c^2\,;$$

and, for $m_0=0$, (14.142)

$$\sqrt{p^2c^2+m_0^2c^4}\rightarrow pc\,.$$

In order to understand Dirac's approach, let us first consider the one dimensional case and generalise (14.142) to

$$\sqrt{p_x^2c^2+m_0^2c^4}=\alpha c p_x+\beta m_0c^2\,. \tag{14.143}$$

This relation can clearly not be fulfilled in the general case $p_x\neq 0$, $m_0\neq 0$ by ordinary numbers α and β; however, it can be, when α and β are *matrices*, as we shall proceed to demonstrate. We square both sides of (14.143), remembering that matrices do not commute, in general, so that we must maintain the order of α and β in multiplying out the right-hand side of (14.143). We then obtain

$$p_x^2c^2+m_0^2c^4=\alpha^2c^2p_x^2+(\alpha\beta+\beta\alpha)m_0c^3p_x+\beta^2m_0^2c^4\,. \tag{14.144}$$

For the left and right sides of this equation to be equal, we clearly require that

$$\alpha^2=1\,;\qquad \alpha\beta+\beta\alpha=0\,;\qquad \beta^2=1\,. \tag{14.145}$$

These relations are familiar from the (Pauli) spin matrices! (compare Problem 14.2). Unfortunately, we cannot use the latter directly, since we wish to describe a three-dimensional, not a one-dimensional motion. Thus, we require

$$\sqrt{(p_x^2+p_y^2+p_z^2)c^2+m_0^2c^4}=\alpha_1cp_x+\alpha_2cp_y+\alpha_3cp_z+\beta m_0c^2\,. \tag{14.146}$$

Squaring (14.146) leads, analogously to the one-dimensional case, to

$$\begin{aligned}&\alpha_j^2=1\,;\qquad \beta^2=1\,;\qquad \alpha_j\beta+\beta\alpha_j=0\,;\qquad\text{and}\\&\alpha_j\alpha_k+\alpha_k\alpha_j=0\quad\text{for}\quad j\neq k\,;\quad j=1,2,3\quad\text{and}\quad k=1,2,3\,.\end{aligned} \tag{14.147}$$

In addition, as always in quantum mechanics, the operators (matrices) are Hermitian. These relations may be fulfilled in various (but physically equivalent) ways, for example

$$\alpha_j=\begin{bmatrix}0&\sigma_j\\\sigma_j&0\end{bmatrix},\qquad \beta=\begin{bmatrix}1&0\\0&-1\end{bmatrix}, \tag{14.148}$$

where the σ_j are the Pauli spin matrices (cf. 14.24, 33 without $\hbar$). The "1"s in β represent 2×2 identity matrices, so that β may be written in the conventional notation as

$$\beta = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \quad . \tag{14.149}$$

After these intermediate steps, we can again attack the Dirac equation, employing the translation rules (14.128) and (14.130) and applying them to the equation

$$E = \alpha_1 c p_x + \alpha_2 c p_y + \alpha_3 c p_z + \beta m_0 c^2 \quad . \tag{14.150}$$

This leads to

$$\mathrm{i}\hbar \frac{\partial}{\partial t} \Psi = (\alpha_1 c p_x + \alpha_2 c p_y + \alpha_3 c p_z + \beta m_0 c^2)\,\Psi \,, \tag{14.151}$$

the *Dirac equation*.

Since α_j and β are 4×4 matrices, they must operate on *vectors* with four components, i.e. Ψ must be of the form

$$\Psi = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} \quad . \tag{14.152}$$

In the preceding sections dealing with the electronic spin, we became acquainted with wavefunctions having 2 components; in the Dirac theory, they have four! This is a result of the fact that the Dirac equation allows both positive and negative-energy solutions for free particles.

As the reader may verify in one of the problems to this chapter, the Dirac equation yields the same energy spectrum as the Klein-Gordon equation; it is given in (14.140, 141), and in Fig. 14.3. One can easily convince oneself that the solutions of the Dirac equation for force-free particles are plane waves having the form

$$\Psi(\boldsymbol{r},t) = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r} - \mathrm{i}\omega t)\,, \tag{14.153}$$

where the constants $\Psi_1, \ldots \Psi_4$ are computed in Problem 14.6.

In the Dirac equation in the form (14.151), the time derivative plays a special rôle relative to the spatial-coordinate derivatives. However, in relativity theory, time and space coordinates have a symmetric position as components of space-time four-vectors; thus, in the literature, a symmetrised form of the Dirac equation is often used. It is obtained by multiplying (14.151) on both sides from the left by $\gamma^0 = \beta$, and introducing new matrices

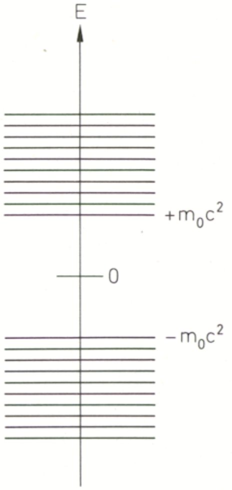

Fig. 14.3. Energy spectrum of the Klein-Gordon equation and the Dirac equation

$$\gamma^j = \beta \alpha_j\,, \quad \text{with} \quad j = 1, 2, 3\,. \tag{14.154}$$

It may be shown that the resulting equation is "Lorenz covariant":

$$\mathrm{i}\hbar\left(\gamma^0 \frac{\partial}{\partial x^0} + \gamma^1 \frac{\partial}{\partial x_1} + \gamma^2 \frac{\partial}{\partial x_2} + \gamma^3 \frac{\partial}{\partial x_3}\right)\Psi = m_0 c \Psi\,, \tag{14.155}$$

with $x^0 = ct$, $x_1 = x$, $x_2 = y$, $x_3 = z$.

The explicit forms for the matrices γ^0 and γ^j are

$$\gamma^0 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \gamma^j = \begin{bmatrix} 0 & \sigma^j \\ -\sigma^j & 0 \end{bmatrix} \tag{14.156}$$

where the σ^j are again the Pauli matrices.

Finally, we discuss the inclusion of the action of electric and magnetic fields on the electron in the Dirac equation. For this purpose, we use the procedure of the Schrödinger theory once again:

1) The potential energy $V(\boldsymbol{r}) = -e\tilde{V}$, which results from the electrostatic potential $\tilde{V}$, is added in analogy to (9.32). This can also be expressed by adopting the following expression:

$$\mathrm{i}\hbar\frac{\partial}{\partial t} \rightarrow \mathrm{i}\hbar\frac{\partial}{\partial t} + e\tilde{V}\,. \tag{14.157}$$

2) The magnetic field is taken into account by replacing the momentum operator (as in Sect. 14.1) by

$$\frac{\hbar}{\mathrm{i}}\nabla \rightarrow \frac{\hbar}{\mathrm{i}}\nabla + e\boldsymbol{A} \tag{14.158}$$

where $\boldsymbol{A}$ is the vector potential.

The resulting Dirac equation has been solved for several cases, in particular for the hydrogen atom. The results are in very good agreement with experiment, apart from the corrections due to quantum electrodynamics (Lamb shift).

In spite of the success of the Dirac theory, the question of the meaning of the negative energy values for free particles remained open. They would permit an electron with a positive energy to emit light and drop down to deeper-lying, i.e. negative energy levels, and thus all particles with positive energies would finally fall into this energy chasm.

Dirac had the ingenious idea of assuming that all the states of negative energies were already occupied with electrons, following the Pauli principle, according to which each state can contain at most two electrons with antiparallel spins. The infinitely large negative charge of this so-called "Dirac sea" can be thought to be compensated by the positive charges of the protons, which likewise obey the Dirac equation and must fill a corresponding positively charged Dirac sea. The vacuum would, in this interpretation, consist of the two filled Dirac seas.

If we now add sufficient energy that an electron from the Dirac sea can cross over the energy gap of $2m_0c^2$, an electron with positive energy would appear, leaving behind a hole in the Dirac sea. Since this hole is a missing negative charge, but the Dirac sea(s) were previously electrically neutral, the hole acts like a positive charge $(+e)$. Furthermore, it has the same properties as a particle, so that it appears as such. The creation of electron-hole pairs can indeed be observed; the positively charged particles are experimentally known as *positrons*.

In modern quantum field theory, the creation of positrons can be described directly by means of a formal trick, without having to invoke the infinite filled Dirac sea. On the other hand, precisely this idea of a Dirac sea provides an intuitive picture for the appearance of positively charged electrons, i.e. the positrons.

Problems

14.1 *The Landau levels*

If an otherwise free electron is moving in a magnetic field, it is forced into a circular path in the plane perpendicular to the magnetic field. It thus has a periodic motion and would be subject to quantisation, even in the Sommerfeld formulation. This quantisation leads to discrete levels, the Landau levels. These also result from an exact quantum mechanical calculation.

Problem: Solve the time-independent Schrödinger equation of a particle with charge $(-e)$ which is moving in the x-y plane perpendicular to a constant magnetic field $\boldsymbol{B}$. Do not take the electron spin into account.

Hint: Use the vector potential $\boldsymbol{A}$ in the form $\boldsymbol{A} = (0, B_x, 0)$ and the trial solution

$$\psi(x,y,z) = \mathrm{e}^{iky}\phi(x) .$$

In addition, make use of the fact that $\phi(x)$ satisfies the Schrödinger equation for a displaced harmonic oscillator.

14.2 Show that for the spin operators $\hat{s}_x$ and $\hat{s}_y$ (14.33 a, b), the following relations hold:

$$\hat{s}_x\hat{s}_y + \hat{s}_y\hat{s}_x = 0 , \quad \left(\frac{2}{\hbar}\hat{s}_x\right)^2 = 1 , \quad \left(\frac{2}{\hbar}\hat{s}_y\right)^2 = 1 .$$

Hint: Use the explicit matrix form.

14.3 Demonstrate that the relativistic expression for the energy, (14.132), may be written in the form

$$E \approx m_0c^2 + \frac{1}{2}\frac{p^2}{m_0}$$

provided that

$$\frac{p^2}{2m_0} \ll \frac{1}{2}m_0c^2 .$$

Hint: Expand the square root in a series.

14.4 Show that the (charge) conservation law in the form

$$\frac{d\varrho}{dt} + \operatorname{div} \boldsymbol{j} = 0$$

may be derived from the Klein-Gordon equation.

Hint: Multiply the Klein-Gordon equation (written with $\square^2$) by Ψ^* and subtract from the result its complex conjugate. Use:

$$\varrho = \frac{\mathrm{i}\hbar}{2m_0c^2}\left(\Psi^*\frac{\partial\Psi}{\partial t} - \Psi\frac{\partial\Psi^*}{\partial t}\right),$$

$$\boldsymbol{j} = \frac{\hbar}{2\mathrm{i}m_0}\left(\Psi^* \operatorname{grad}\Psi - \Psi \operatorname{grad}\Psi^*\right).$$

14.5 Show that each component of (14.153) satisfies the Klein-Gordon equation.

Hint: Write the Dirac equation (14.151) in the form

$$\mathrm{i}\hbar\frac{\partial\Psi}{\partial t} = \mathscr{H}\Psi \tag{1}$$

then take $\mathrm{i}\hbar(\partial/\partial t)$ on both sides; use (1) again and rearrange $\mathscr{H}^2$ using the Dirac matrices.

14.6 Solve the Dirac equation for a force-free particle moving in the z direction.

Hint: Substitute the trial solution

$$\Psi(\boldsymbol{r}, t) = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} \exp(\mathrm{i}kz - \mathrm{i}\omega t)$$

into (14.151) and solve the resulting algebraic equation.

Which energies correspond to the various solutions?

15. Atoms in an Electric Field

15.1 Observations of the Stark Effect

In 1913, *Stark* observed a splitting of the lines of the Balmer series of hydrogen (8.2) in an electric field. He was studying the light emission of H atoms in the field of a condenser (Figs. 15.1, 2). Since then, frequency shifts in optical spectra in the presence of eletric fields have been generally called the Stark effect.

The effect is experimentally more difficult to observe than the Zeeman effect, because it is necessary to generate strong electric fields without sparking over. It has been far less important to experimental atomic physics than the Zeeman effect.

One observes:

- With hydrogen and similar atoms, such as He^+, Li^{++}, etc., a splitting of the terms with $l \neq 0$ and the spectral lines associated with them. The splitting is proportional to the field strength F. This so-called *linear* Stark effect is present when the l degeneracy – the degeneracy of states with the same principal quantum number n and different orbital angular momentum quantum numbers l – is lifted by the external electric field, when it is not already lifted by internal atomic fields;
- Displacement and splitting of terms in all atoms proportional to F^2. This is the *quadratic* Stark effect.

The quadratic Stark effect can be understood qualitatively in an intuitive model. The lifting of the l degeneracy by the other electrons in an atom always leads to states which have no electric dipole moment averaged over time. This can be demonstrated

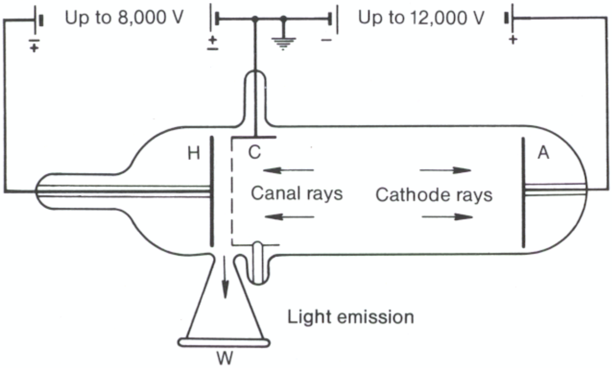

Fig. 15.1. Canal ray tube for investigation of the emission of atoms in an electric field: the Stark effect. The potential between the cathode C and the electrode H can be as high as 8000 V. The resulting splitting of spectral lines is observed through the window W. In order to observe neutral H atoms, the positive ions of the canal rays must be neutralised. This is not shown in the figure

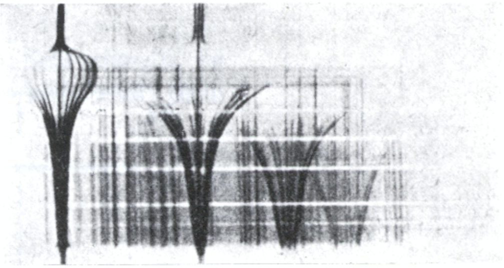

Fig. 15.2. Splitting of the hydrogen atom lines in an electric field. The strength of the field varies along the light source, the image of which is shown after passage through a spectrograph slit. The field is 10^5 V/cm in the region of smaller splitting near the bottom of the figure and rises to a value of $1.14 \cdot 10^6$ V/cm in the region of the greatest splitting. From K. H. Hellwege, *Einführung in die Physik der Atome*, Heidelberger Taschenbücher, Vol. 2, 4th ed. (Springer, Berlin, Heidelberg, New York 1974) Fig. 45

exactly by quantum mechanics. The applied electric field induces an electric dipole moment $\boldsymbol{p} = \alpha \boldsymbol{F}$ in the atom, where α is the atomic polarisability. The latter is naturally a function of the quantum numbers of the atomic state and is different for each electron configuration.

The electric field acts on this induced dipole moment. The interaction energy is given by

$$V_{\mathrm{el}} = \tfrac{1}{2}\boldsymbol{p} \cdot \boldsymbol{F} = \tfrac{1}{2}\alpha F^2 . \tag{15.1}$$

We have thus explained qualitatively the proportionality between the term shifts and the square of the electric field strength.

The linear Stark effect, which is observed in the hydrogen atom, cannot be so easily understood on an intuitive basis. This is an effect which can be understood only in terms of quantum mechanics. The degeneracy of the l-states in the absence of a field $\boldsymbol{F}$ is lifted by the electric field, because the Coulomb potential of the nucleus is perturbed by the field $\boldsymbol{F}$. This effect will be treated in greater detail in Sect. 15.2.

The linear Stark effect, which is observed in the hydrogen atom, cannot be so easily understood on an intuitive basis. This is an effect which can be understood only in terms of quantum mechanics. The originally present degeneracy of the l-states is lifted by the electric field. This effect will be treated in greater detail in Sect. 15.2.

The fundamental difference between the Stark effect and the splitting of spectral lines in a magnetic field is the fact that in an electric field, states with the same absolute value of the magnetic quantum number m_j, i.e. m_j and $-m_j$, behave in an identical manner. This can be easily understood: the effect of an electric field on a "clockwise" and on a "counterclockwise" rotating electron, when the spatial distribution of the electrons is otherwise the same, is, averaged over time, the same. The number of split components is therefore smaller in the Stark effect than in the Zeeman effect: the number of different terms is not $2j+1$, but rather $j+1$ for integral j and $j+1/2$ for half-integral j.

An example is the Stark effect of the Na D lines, shown in Fig. 15.3. The magnitude of the Stark shift is about 0.05 Å for the Na D lines in fields of about 10^7 V/m (10^5 V/cm). It increases with the principal quantum number n, since orbits with a larger

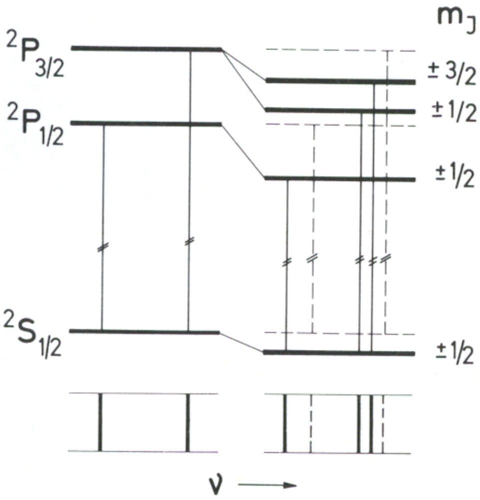

Fig. 15.3. Energy level diagram showing the Stark effect on the sodium doublet $3^2P_{3/2,1/2} - 3^2S_{1/2}$ and the splitting pattern of the D lines

principal quantum number also have a larger polarisability. Therefore the Stark effect is extremely important for the investigation of Rydberg atoms (cf. Sect. 8.12).

The Stark effect which is caused by the strong electric fields resulting from the chemical bonding between atoms, is extremely important to the understanding of molecular spectra. It is also important for the clarification of the influence of the crystal electric field in solids on the atomic term diagrams of component atoms, as well as in gases at high densities. In the latter, the Stark effect is the most important source of spectral line broadening.

15.2 Quantum Theory of the Linear and Quadratic Stark Effects

15.2.1 The Hamiltonian

We shall treat the quantum theoretical explanation of the Stark effect in some detail here, since we shall, in the process, be able to introduce the general and important methods of perturbation theory.

We wish to investigate how the wavefunctions and the energy levels of an electron are changed, when, in addition to the attractive nuclear potential $V(r)$, a constant electric field is acting on it. We write the Hamiltonian of the complete problem in the form

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}^{\mathrm{P}}, \tag{15.2}$$

where

$$\mathscr{H}_0 = -\frac{\hbar^2}{2m_0}\nabla^2 + V(r) \tag{15.3}$$

is the original Hamiltonian without the applied field. In (15.2), as in the following, the upper index "P" indicates "perturbation".

If the electric field has the field strength $\boldsymbol{F}$, the electron is acted on by the force

$$-e\boldsymbol{F}\,. \tag{15.4}$$

(In order to avoid confusion between the energy E and the electric field strength, we denote the latter here by $\boldsymbol{F}$.) The corresponding potential energy, which results from "force times distance", is then

$$V^{\mathrm{P}} = e\boldsymbol{F}\cdot\boldsymbol{r}\,, \tag{15.5}$$

provided $\boldsymbol{F}$ is homogeneous.

Since the formalism which we are about to develop may be applied to perturbations which are more general than (15.5), we have written $\mathscr{H}^{\mathrm{P}}$ instead of V^{P} in (15.2). It is found in many cases that the applied electric field produces only a small change in the electron wavefunctions and energies, i.e. it acts as a so-called small perturbation. In order to express the smallness of this perturbation explicitly, we write $\mathscr{H}^{\mathrm{P}}$ in the form

$$\mathscr{H}^{\mathrm{P}} = \lambda\,\mathscr{H}^{1}, \tag{15.6}$$

where λ is a small parameter. In the following, we also assume that the time-independent Schrödinger equation without the external perturbation potential has already been solved:

$$\mathscr{H}_0 \phi_\nu = E_\nu^0 \phi_\nu . \tag{15.7}$$

The indices 0 on $\mathscr{H}_0$ and E_ν^0 indicate that these quantities refer to the unperturbed problem. We shall at first assume that the energies E_ν^0 are all different from one another.

15.2.2 The Quadratic Stark Effect. Perturbation Theory Without Degeneracy*[1]

To be able to solve the Schrödinger equation which also contains the perturbation potential, namely

$$\mathscr{H} \psi = E \psi , \tag{15.8}$$

we represent the solution for which we are searching, ψ, as the superposition of the unperturbed solutions ϕ_ν. We expect, indeed, that the electric field will shift and perhaps also change the shapes of the wavefunctions. These modified wavefunctions may be constructed from the unperturbed ones by adding them to wavefunctions belonging to other energy levels (Fig. 15.4). On the basis of such considerations, which also may be justified mathematically in a strict sense, we arrive at the following trial solution for the wavefunctions we are seeking:

$$\psi(\boldsymbol{r}) = \sum_{\nu=1}^{\infty} c_\nu \phi_\nu(\boldsymbol{r}) . \tag{15.9}$$

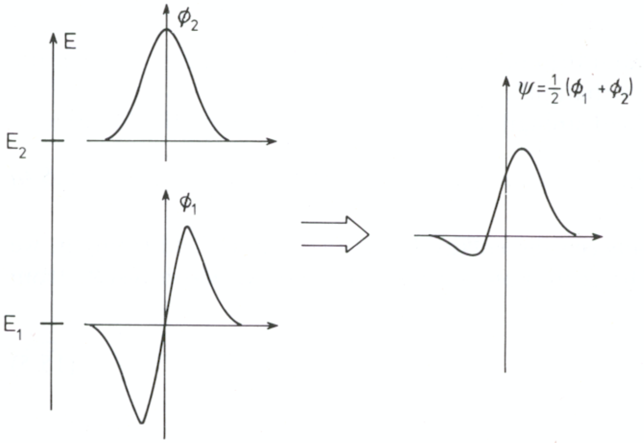

Fig. 15.4. Example of how the superposition of two wavefunctions ϕ_1 and ϕ_2 (*left*) can lead to a new wavefunction with a shifted centre of gravity (centre of charge) (*right*)

Here it is important to note that the wavefunctions ϕ_ν depend upon the position coordinate $\boldsymbol{r}$, but that the coefficients c_ν do *not*. To fix the latter, we insert (15.9) into (15.8) and obtain immediately

$$\mathscr{H}_0 \sum_\nu c_\nu \phi_\nu(\boldsymbol{r}) + \mathscr{H}^{\mathrm{P}} \sum_\nu c_\nu \phi_\nu(\boldsymbol{r}) = E \sum_\nu c_\nu \phi_\nu(\boldsymbol{r}) . \tag{15.10}$$

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[1] In this book, we treat *time independent* perturbation theory. *Time dependent* perturbation theory, which is also very important, is described in detail in Vol. 2, H. Haken and H.C. Wolf: *Molecular Physics and Elements of Quantum Chemistry*.

In the first term on the left side, we shall use the fact that the wavefunctions ϕ_ν obey (15.7) and we may thus replace $\mathscr{H}_0\phi_\nu$ by $E_\nu^0\phi_\nu$. In order to free ourselves from the $\boldsymbol{r}$ dependence in (15.10), we multiply from the left by ϕ_μ^* and integrate over all space. As we shall show in the appendix, the wavefunctions are orthonormal, i.e. the following relations hold:

$$\int \phi_\mu^* \phi_\nu dV = \delta_{\mu\nu} . \tag{15.11}$$

Furthermore, we introduce the abbreviations

$$H_{\mu\nu}^{\mathrm{P}} = \int \phi_\mu^* \mathscr{H}^{\mathrm{P}} \phi_\nu dV . \tag{15.12}$$

Since the parameters $H_{\mu\nu}^{\mathrm{P}}$ carry the two subscripts μ and ν, one often thinks of the $H_{\mu\nu}^{\mathrm{P}}$ arranged in a square array. Such an array is called a "matrix" in mathematics, and the $H_{\mu\nu}^{\mathrm{P}}$ are thus also called "matrix elements", or more exactly, "matrix elements of the perturbation operator $\mathscr{H}^{\mathrm{P}}$". With the help of (15.11) and (15.12), we obtain the following equation from (15.10)

$$(E_\mu^0 - E)c_\mu + \sum_\nu H_{\mu\nu}^{\mathrm{P}} c_\nu = 0 , \tag{15.13}$$

which one must imagine as written out for all indices μ. Thus far, our procedure is completely generally valid and makes no use of the small magnitude of the perturbation. We now assume, however, that the perturbation is small, in that we imagine, according to (15.6), that the parameter λ increases from zero. If the perturbation is exactly equal to zero, the solution sought, (15.9), must naturally be the same as one of the starting solutions ϕ_ν. The coefficients which result for $\lambda = 0$ are indicated by the superscript 0. The initial state is denoted by a subscript κ. We thus obtain the relation

$$c_\nu^0 = \begin{cases} 1 & \text{for} \quad \nu = \kappa \\ 0 & \text{for} \quad \nu \neq \kappa \end{cases} \tag{15.14}$$

or in shorter form,

$$c_\nu^0 = \delta_{\nu\kappa} . \tag{15.15}$$

If we now let λ increase, the coefficients c_ν will also change, of course. We shall expect that as a first approximation, the coefficients c_ν increase proportionally to λ. As the next approximation, we must then take into account changes proportional to λ^2, and so on. The same will naturally also hold for the new energy values E. We thus arrive at

$$c_\nu = \delta_{\nu\kappa} + \lambda c_\nu^{(1)} + \lambda^2 c_\nu^{(2)} + \ldots \tag{15.16}$$

and

$$E = E_\kappa^0 + \lambda \varepsilon^{(1)} + \lambda^2 \varepsilon^{(2)} + \ldots . \tag{15.17}$$

We subsitute these expressions in (15.13) and thereby obtain

$$(E_\mu^0 - E_\kappa^0 - \lambda \varepsilon^{(1)} - \lambda^2 \varepsilon^{(2)} - \ldots)(\delta_{\mu\kappa} + \lambda c_\mu^{(1)} + \ldots) + \sum_\nu \lambda H_{\mu\nu}^1 (\delta_{\nu\kappa} + \lambda c_\nu^{(1)} + \ldots) = 0 . \tag{15.18}$$

Expressions (15.16) and (15.17) define orders of magnitude, as one can easily convince oneself by setting, e.g. $\lambda = 0.1$. In this case, $\lambda^2 = 0.01$, which is only 10% of λ. Speaking a bit loosely, what we are doing is to solve (15.18) for the different decimal places. In strict mathematical terms, this means that we must multiply out all the terms of (15.18) and arrange them according to powers of λ. We then have to require that the coefficients of the individual powers of λ cancel out independently. For the zeroth power, we obtain

$$(E^0_\mu - E^0_\kappa)\,\delta_{\mu\kappa} = 0\,, \tag{15.19}$$

which is identically fulfilled. For the 1st power of λ,

$$-\,\varepsilon^{(1)}\,\delta_{\mu\kappa} + (E^0_\mu - E^0_\kappa)\,c^{(1)}_\mu + H^1_{\mu\kappa} = 0\,. \tag{15.20}$$

For further discussion of this equation, we differentiate between the cases where $\mu = \kappa$ and $\mu \neq \kappa$. For $\mu = \kappa$, (15.20) reduces to

$$\varepsilon^{(1)} = H^1_{\kappa,\kappa} \equiv \int \phi^*_\kappa \mathscr{H}^1 \phi_\kappa\, dV\,. \tag{15.21}$$

For the perturbed energy, this means according to (15.17) that the 1st order perturbation approximation,

$$E = E^0_\kappa + H^{\mathrm{P}}_{\kappa,\kappa}\,, \tag{15.22}$$

applies. If we choose $\mu \neq \kappa$, the coefficients of the 1st order perturbation approximation can be calculated from (15.20):

$$c^{(1)}_\mu = \frac{H^1_{\mu,\kappa}}{E^0_\kappa - E^0_\mu}\,, \qquad \mu \neq \kappa\,. \tag{15.23}$$

So far, the coefficient $c^{(1)}_\kappa$ has not been determined. As can be shown from the normalisation coefficient, it must be set equal to zero:

$$c^{(1)}_\kappa = 0\,. \tag{15.24}$$

If we substitute the coefficients we have calculated into (15.9), the perturbed wavefunction is, in the 1st order perturbation approximation,

$$\psi(\boldsymbol{r}) = \phi_\kappa(\boldsymbol{r}) + \sum_{\mu \neq \kappa} \frac{H^{\mathrm{P}}_{\mu,\kappa}}{E^0_\kappa - E^0_\mu}\,\phi_\mu(\boldsymbol{r})\,. \tag{15.25}$$

Now we can take into account the terms in second order, i.e. with λ^2. A short calculation yields

$$\varepsilon^{(2)} = \sum_{\nu \neq \kappa} \frac{|H^1_{\kappa,\nu}|^2}{E^0_\kappa - E^0_\nu}\,. \tag{15.26}$$

With this, the energy in the second order perturbation approximation can be expressed as

$$E = E^0_\kappa + H^{\mathrm{P}}_{\kappa,\kappa} + \sum_{\nu \neq \kappa} \frac{|H^{\mathrm{P}}_{\kappa,\nu}|^2}{E^0_\kappa - E^0_\nu}\,. \tag{15.27}$$

We shall now examine the meaning of the formulae (15.25) and (15.27) in the case when an external electric field $\boldsymbol{F}$ is applied. It can be shown (see Sect. 16.1.3 on selection rules), for example that for the hydrogen atom $H^{\mathrm{P}}_{\kappa,\kappa}=0$. The matrix elements which are not equal to zero are, according to (15.5) and (15.12), proportional to the field strength F. Thus the energy E is shifted from the unperturbed energy E^0_κ by an amount, according to (15.27), which is proportional to F^2. One therefore speaks of the *quadratic Stark effect.*

15.2.3 The Linear Stark Effect. Perturbation Theory in the Presence of Degeneracy*

In addition to this quadratic Stark effect, observations have shown a *linear Stark effect*. We approach it as follows. In a purely formal way, we can see from (15.23 – 27) that the method we used above will not work if the denominator, i.e. $E^0_\kappa - E^0_\nu$ cancels and at same time the matrix element in the numerator is not equal to zero. This can actually happen, however, if we are considering degenerate states, such as we have seen in the hydrogen atom. There we have an entire set of different wavefunctions with the same principal quantum number n, but different l and m, which belong to a given energy. To treat this case in the presence of a perturbation, one must fall back on the so-called *perturbation theory in the presence of degeneracy.*

Let us briefly review what was done in the first step of perturbation theory in the absence of degeneracy. We set up the requirement (15.14). In the case of degeneracy, as we know, it is not only the mutually degenerate wavefunctions which can be solutions to the Schrödinger equation for the energy E^0_κ, but also any linear combination of these wavefunctions. Thus if we think of the perturbation being turned off, the perturbed solution can be transformed into a linear combination of unperturbed solutions whose coefficients are not known. The basic idea of perturbation theory in the presence of degeneracy is to find these coefficients, in the zero order approximation, by a systematic procedure. To this end we write

$$\psi(\boldsymbol{r}) = \sum_{\substack{\nu \text{ only over} \\ \text{degenerate} \\ \text{states}}} c^{(0)}_\nu \phi_\nu(\boldsymbol{r}) + \text{corrections}\,, \tag{15.28}$$

where the summation includes *only* the mutually degenerate states. We ignore the correction terms. Equation (15.28) is formally the same as our earlier (15.9), but now we are not summing over all states. However, the coefficients $c^{(0)}_\nu$ can be formally determined if we return to the equation system of the form of (15.13), and allow the set of coefficients $c^{(0)}_\nu$ to replace the coefficients c_ν there. If we have N mutually degenerate states, we now have N equations with N unknown coefficients before us. In order that the homogeneous system of equations be soluble, the determinant of the coefficients must vanish. This provides the condition

$$\begin{vmatrix} (E^0_\kappa - E + H^{\mathrm{P}}_{1,1}) & H^{\mathrm{P}}_{1,2} & \dots & H^{\mathrm{P}}_{1,N} \\ H^{\mathrm{P}}_{2,1} & (E^0_\kappa - E + H^{\mathrm{P}}_{2,2}) & \dots & H^{\mathrm{P}}_{2,N} \\ \vdots & & & \\ H^{\mathrm{P}}_{N,1} & \dots & & (E^0_\kappa - E + H^{\mathrm{P}}_{N,N}) \end{vmatrix} = 0\,. \tag{15.29}$$

The determinant here is also called a secular determinant. If calculated, it yields an Nth degree polynomial in the energy E. When this is set equal to zero, it becomes an algebraic equation for E which has N roots, some of which may be equal to each other.

As a concrete example, let us treat the first excited state of the hydrogen atom with the principal quantum number $n=2$. The wavefunctions of hydrogen are, as we know, indicated by the quantum numbers n, l and m. To relate these to the present system of indices, we write

$$\phi_{\underbrace{n,l,m}_{\nu}}, \quad n=2\,, \tag{15.30}$$

where we use the table

$$\nu=\begin{cases} 1 & \text{for} \quad l=0\,, \quad m=0 \\ 2 & \text{for} \quad l=1\,, \quad m=0 \\ 3 & \text{for} \quad l=1\,, \quad m=1 \\ 4 & \text{for} \quad l=1\,, \quad m=-1\,. \end{cases} \tag{15.31}$$

The trial solution (15.28) thus becomes

$$\psi(\boldsymbol{r})=c_1^{(0)}\phi_1(\boldsymbol{r})+c_2^{(0)}\phi_2(\boldsymbol{r})+c_3^{(0)}\phi_3(\boldsymbol{r})+c_4^{(0)}\phi_4(\boldsymbol{r})\,, \tag{15.32}$$

where, to repeat once more, the ϕ's are wavefunctions of the hydrogen atom in the $n=2$ state, which are all degenerate. The matrix elements (15.12) are then, in concrete terms,

$$H_{\mu\nu}^{\mathrm{P}}=\int\phi^*_{\underbrace{n,l,m}_{\mu}}(\boldsymbol{r})\,eFz\,\phi_{\underbrace{n,l',m'}_{\nu}}(\boldsymbol{r})\,dV\,, \tag{15.33}$$

where it is assumed that the field is applied in the z direction. Using selection rules, it can be shown, as in Sect. 16.1, that all the matrix elements disappear except for

$$H_{1,2}^{\mathrm{P}}=H_{2,1}^{\mathrm{P}}\,. \tag{15.34}$$

This can be written in the form

$$H_{1,2}^{\mathrm{P}}=H_{2,1}^{\mathrm{P}}=eFd \tag{15.35}$$

because the wavefunctions referred to are real. In the present case, where $N=4$ and all matrix elements except for (15.35) disappear, (15.13) reduces to

$$(E_2^0-E)\,c_1+eF\,dc_2=0\,, \tag{15.36}$$

$$eF\,dc_1+(E_2^0-E)\,c_2=0\,, \tag{15.37}$$

$$(E_2^0-E)\,c_3=0\,, \tag{15.38}$$

$$(E_2^0-E)\,c_4=0\,. \tag{15.39}$$

It is obvious that this system of equations breaks down into two groups of two: (15.36) and (15.37) in one group, and (15.38) and (15.39) in the other. The determinant for (15.36, 37) is

$$\begin{vmatrix} E_2^0-E & eFd \\ eFd & E_2^0-E \end{vmatrix} = 0 . \tag{15.40}$$

This goes to zero when E assumes the values

$$E_\pm = E_2^0 \pm eFd . \tag{15.41}$$

It can be shown that the positive sign is associated with $c_1 = c_2$, and the negative sign with $c_1 = -c_2$. The energy E is increased or decreased with respect to the unperturbed energy, by an amount proportional to the field strength F. Equation (15.38) or (15.39) requires that the perturbed energy be the same as the unperturbed energy. In particular, it turns out that the wavefunctions $\phi_3(r)$ and $\phi_4(r)$ are in each case the "right linear combination". This can also be seen from the fact that for $\phi_3(r)$ and $\phi_4(r)$, the perturbation theory without degeneracy actually does not fail, because for the critical terms (zero energy difference in the denominator), the matrix elements of the numerator also go to zero.

We thus obtain overall the scheme shown in Fig. 15.5 for the energy splitting. The same figure shows the wavefunctions in the presence of the field.

The linear Stark effect discussed here is a special case, in that it is only observed in the hydrogen atom. The reason for this is easy to understand: the matrix element (15.33) differs from zero only when $l \neq l'$. In contrast to hydrogen, the l degeneracy is lifted in other atoms, i.e.

$$E^0_{n,l,m} \neq E^0_{n,l',m'}$$

as was shown in Chap. 11.

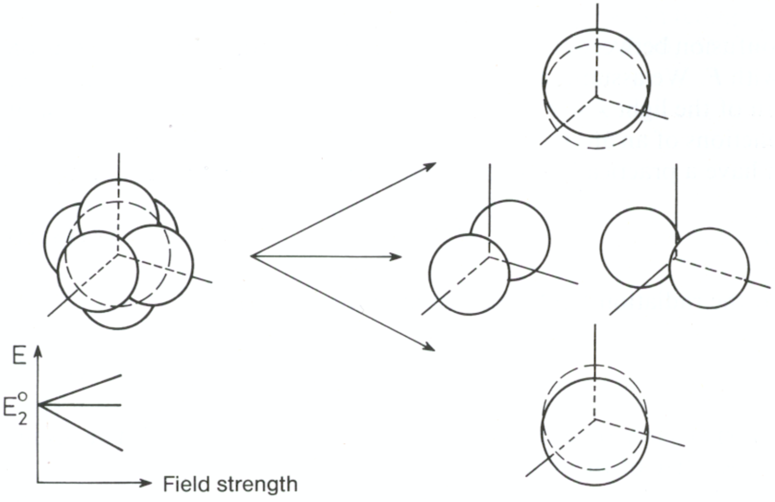

Fig. 15.5. The linear Stark effect. *Lower left:* As the field strength F increases, the energy level E_2^0 is split into three levels. *Upper left:* Representation of four mutually degenerate wavefunctions in a single figure. Dotted line, s functions; solid lines, the p function "dumbbells" in the x, y and z directions. *Upper right:* Superposition of s function and p dumbbell in the z direction causes a shift in the centre of charge of the electron. *Middle right:* The dumbbells in the x and y directions are not affected. *Lower right:* Superposition of s function and p dumbbell (with amplitude in the opposite direction compared to the previous case) leads to a shift of the centre of charge in the negative z direction

15.3 The Interaction of a Two-Level Atom with a Coherent Radiation Field

In the previous chapters on the interaction of a spin with a changing magnetic field, we came upon the interesting phenomenon of spin flipping, which has found numerous applications in physics and chemistry. In this section, we shall show that a two-level atom interacts with a coherent radiation field in a manner which is exactly analogous to spin flipping. Although the spin is a system with exactly two levels, this assumption is only an approximation for an atom. We simply assume that a radiation field induces transitions between two neighbouring levels, and that all the other levels of the atom are energetically so far from the two under consideration that we can neglect the effects of the other states on the two at hand. This is understandable in light of the perturbation theory in the absence of degeneracy which was treated above, because combinations of the wavefunctions associated with distant levels with the wavefunctions belonging to the two close levels will have large energy differences in the denominator, and will thus make only small contributions (15.25).

In the quantum mechanical treatment, we begin with a Schrödinger equation for an electron which is moving in the potential field V of the nucleus and in the additional potential of the radiation field V_a. This equation has the form

$$\left(-\frac{\hbar^2}{2m_0}\nabla^2+V+V_a\right)\psi(\boldsymbol{r},t)=\mathrm{i}\hbar\frac{d\psi(\boldsymbol{r},t)}{dt}\,. \tag{15.42}$$

To find the explicit form of V_a, let us think of the radiation field in the form of a plane wave:

$$\boldsymbol{F}=\boldsymbol{F}_0\cos(kx-\omega t)\,. \tag{15.43}$$

In order to avoid confusion between the energy and the electric field strength, we again indicate the latter with $\boldsymbol{F}$. We assume, furthermore, that the atom is localised at $\boldsymbol{r}=0$. Since the wavelength of the light $\lambda=2\pi/k$ is in general much larger than the extent of the electron wavefunctions of an atom, we can, to a very good approximation, set $x=0$ in (15.43). We then have a practically homogeneous radiation field over the atom,

$$\boldsymbol{F}=\boldsymbol{F}_0\cos(\omega t)\,. \tag{15.44}$$

We also assume that the radiation field is polarised in the z direction:

$$\boldsymbol{F}_0=(0,0,F_0)\,. \tag{15.45}$$

The force exerted on an electron by an electric field $\boldsymbol{F}$ is given by $-e\cdot\boldsymbol{F}$. The resulting potential energy (negative of the force times the z vector) is

$$V_a=eF_0z\cos\omega t\,. \tag{15.46}$$

In the following, we shall use this V_a in (15.42). We assume that we have already solved the Schrödinger equation in the absence of an external field:

$$\left(-\frac{\hbar^2}{2m_0}\nabla^2+V\right)\phi_j=E_j\phi_j\,,\qquad j=1,2\,,\tag{15.47}$$

i.e. we assume that the wavefunctions and energies are known, at least for the indices $j=1,2$.

Since we expect transitions only between the two levels 1 and 2, we cast the wavefunction of (15.42) in the form of a superposition of the unperturbed wavefunctions of (15.47),

$$\psi(\boldsymbol{r},t)=c_1(t)\,\phi_1(\boldsymbol{r})+c_2(t)\,\phi_2(\boldsymbol{r})\,.\tag{15.48}$$

In order to determine the still unknown coefficients c_1 and c_2, we substitute (15.48) into (15.42), multiply from the left by ϕ_1^* or ϕ_2^*, exactly as in Sect. 15.2, and integrate over the total space. By introducing the abbreviation

$$H_{ij}^{\mathrm{P}}=\int\phi_i^*(\boldsymbol{r})\,eF_0z\,\phi_j(\boldsymbol{r})\,dV\cos\omega t\,,\tag{15.49}$$

we obtain the equations

$$\dot{c}_1=\frac{1}{\mathrm{i}\hbar}\left[(E_1+H_{11}^{\mathrm{P}})\,c_1+H_{12}^{\mathrm{P}}c_2\right]\tag{15.50}$$

and

$$\dot{c}_2=\frac{1}{\mathrm{i}\hbar}\left[H_{21}^{\mathrm{P}}c_1+(E_2+H_{22}^{\mathrm{P}})\,c_2\right]\,,\tag{15.51}$$

in analogy with Sect. 15.2.

In many cases, we can assume that H_{11}^{P} and H_{22}^{P} vanish (compare Chap. 16 on symmetries and selection rules). For the solution of (15.50, 51), we attempt the trial function

$$c_j=d_j(t)\,\mathrm{e}^{(-\mathrm{i}/\hbar)E_jt}\,.\tag{15.52}$$

With this equation, (15.50) and (15.51) reduce to

$$\dot{d}_1=\frac{1}{\mathrm{i}\hbar}\left(H_{12}^{\mathrm{P}}d_2\,\mathrm{e}^{\mathrm{i}(E_1-E_2)t/\hbar}\right)\tag{15.53}$$

and

$$\dot{d}_2=\frac{1}{\mathrm{i}\hbar}\left(H_{21}^{\mathrm{P}}d_1\,\mathrm{e}^{-\mathrm{i}(E_1-E_2)t/\hbar}\right)\,.\tag{15.54}$$

Meanwhile we have assumed, according to (15.43), that the radiation field is monochromatic. We now introduce the further assumption that the field is in resonance with the electronic transition. This means that the following relation is valid:

$$E_2-E_1=\hbar\omega\,.\tag{15.55}$$

If we now extract the factor

$$\cos\omega t = \tfrac{1}{2}(e^{i\omega t}+e^{-i\omega t}) \tag{15.56}$$

from (15.49), and multiply by the exponential function in (15.53), we obtain the overall factor

$$\tfrac{1}{2}(1+e^{-2i\omega t})\,. \tag{15.57}$$

As we shall see in the following, d_1 and d_2 vary quite slowly in time compared to the frequency ω, so long as the field strength is not too great. This makes it possible for us to average (15.53) and (15.54) over a time which is long compared to $1/\omega$, but still short compared to the time constant which determines the change in d_j, see (15.61).

The result of this averaging is that the rapidly changing term $\exp(-2i\omega t)$ makes a contribution which is much less than 1 and can therefore be neglected compared to 1. This is called the "rotating wave approximation" in the literature. The expression comes from spin resonance. (In Sect. 14.4 the term $\exp(-i\omega t)$ did not appear, because we had applied a *rotating* magnetic field in the first place.) In (15.54) there is a term with $\exp(+2i\omega t)$ which corresponds to (15.57), and in this case too, it is negligibly small. If we abbreviate the integral in (15.49) by substituting the dipole moment matrix element $(\theta_z)_{ij} \equiv \int \phi_i^*(\boldsymbol{r})\, ez\, \phi_j(\boldsymbol{r})\, dV$, (15.53) and (15.54) reduce to

$$\dot{d}_1 = \frac{1}{i\hbar}\,\tfrac{1}{2}F_0(\theta_z)_{12}d_2 \tag{15.58}$$

and

$$\dot{d}_2 = \frac{1}{i\hbar}\,\tfrac{1}{2}F_0(\theta_z)_{21}d_1\,. \tag{15.59}$$

These equations are strikingly similar to the spin equations (14.94) and (14.95) which we met in Sect. 14.4. It can be shown that $(\theta_z)_{12}=(\theta_z)_{21}^*$ can be chosen to be real. By introducing another abbreviation,

$$\Omega = \frac{1}{2\hbar}F_0(\theta_z)_{12}\,, \tag{15.60}$$

where Ω is to be understood as a frequency, we obtain as a solution to (15.58, 59)

$$d_1 = \cos\Omega t\,, \tag{15.61}$$

$$d_2 = -i\sin\Omega t\,. \tag{15.62}$$

We have based this on the assumption that at time $t=0$, the electron is known for certain to be in the lower level. Thus the Schrödinger equation (15.42) for a two-level system interacting with an external monochromatic radiation field is solved. The coefficients c_1 and c_2 in (15.48) now obviously have the form

$$c_1 = e^{-(i/\hbar)E_1 t}\cos\Omega t\,, \tag{15.63}$$

$$c_2 = -i\,e^{-(i/\hbar)E_2 t}\sin\Omega t\,. \tag{15.64}$$

As we know, the square of the absolute value of c_j gives the probability of finding the system in state j. $|c_j|^2$ can thus be unterstood as the *occupation number* N_j of the state j. As indicated by the corresponding formulae

$$N_1 \equiv |c_1|^2 = \cos^2 \Omega t \, , \tag{15.65}$$

$$N_2 \equiv |c_2|^2 = \sin^2 \Omega t \, , \tag{15.66}$$

the electron oscillates with the frequency Ω between states 1 and 2. It is instructive to calculate the dipole matrix element according to

$$\theta_z = \int \psi^* e z \psi \, dV = (\theta_z)_{12} c_1^* c_2 + (\theta_z)_{21} c_2^* c_1 \, . \tag{15.67}$$

The final result of the whole process is

$$\theta_z = -(\theta_z)_{12} \sin(2\Omega t) \sin \omega t \, . \tag{15.68}$$

This says that the dipole moment swings back and forth with the rapidly oscillating component $\sin \omega t$, and that its magnitude is also modulated by $\sin 2\Omega t$. The dipole moment is thus largest when the electron has exactly the occupation number $N_1 = N_2 = \frac{1}{2}$, that is, its probability of occupying either level is the same. The result (15.68) and the formulae (15.65) and (15.66) are very closely analogous to the results obtained for spin resonance in Sect. 14.4. We shall examine this analogy more closely in the next chapter. It makes it possible to extend a series of spin experiments to optical transitions between electronic states in atoms. Such experiments require coherent light with a high field strength. The latter, F_0, is necessary so that the transitions can occur in a time $t_0 \sim 1/\Omega \sim 1/F_0$ – [compare (15.60)!] – which is so short that the electron motion is not appreciably perturbed by other effects, e.g. collisions between atoms in gases or the spontaneous emission of light from excited states. Typical values for t_0 lie between 10^{-9} and 10^{-11} s.

15.4 Spin and Photon Echoes

In this section we shall treat two especially interesting phenomena, spin echo and photon echo. If we compare the results of Sect. 14.4 with those of the preceding section, we see a very close analogy between the behaviour of a spin subjected to both a constant magnetic field and a transverse oscillating magnetic field, and an electron in a two-level atom which is subjected to an oscillating electric field. In both cases we assume that the frequency of the applied field is in resonance with the transition frequency of the spin or of the electron transition from the lower to the upper state. With reference to the analogy which we shall wish to use, we shall first discuss the behaviour of a spin.

As we saw in Sect. 14.4, the application of a coherent, resonant field causes the spin eventually to flip. How far it flips depends on the length of time the external field is applied. If one lets the field work just long enough to flip the spin by $\pi/2$, one speaks of a $\pi/2$ or a 90° pulse. If the field is left on twice as long, the spin will flip completely over. In this case one speaks of a π or 180° pulse. The so-called spin echo is an important application of these ideas. Here one first applies a $\pi/2$ pulse (Fig. 15.6). In a

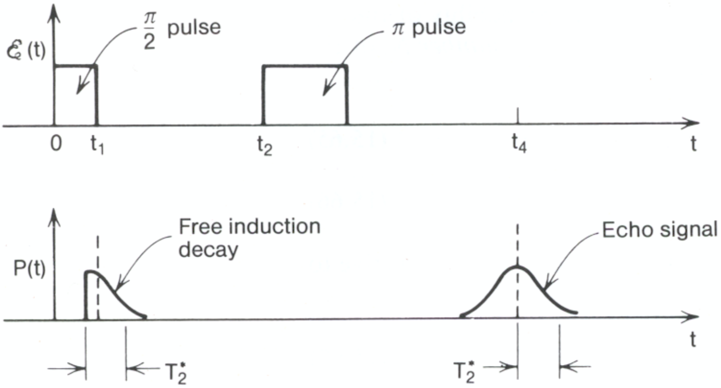

Fig. 15.6. The spin echo (photon echo) experiment. *Above:* the applied pulses of electric field strength (photon echo) or magnetic field (spin echo) as a function of time. *Below:* magnitude of the dipole moment (spin) of the atom as a function of time (schematically)

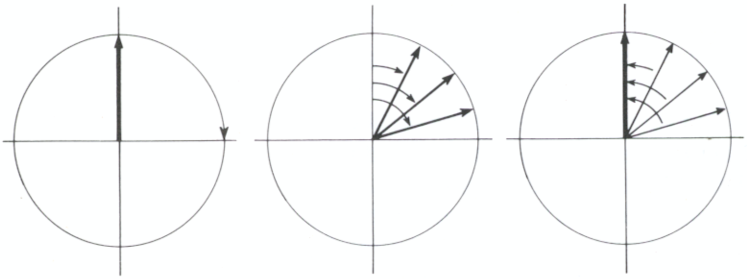

Fig. 15.7. Spreading out and moving together of spins. *Left:* Starting condition, all spins parallel. *Middle:* Spreading out of spins. *Right:* Moving back together after 180° pulse (schematically)

number of practical cases, the spins do not precess with the same velocity, due to spatially varying static magnetic fields. They therefore spread out in the course of time (see Fig. 15.7). Denoting the frequency width of the precession by $\Delta\omega^*$, we may define a mean time, T_2^*, within which the spins spread, by $\Delta\omega^* = 2\pi/T_2^*$. $\Delta\omega^*$ is called "inhomogeneous width". A single precessing spin can emit electromagnetic radiation. Because the spins get out of phase with each other, so do their electromagnetic emissions, which leads to a reduction in the total intensity. If one now applies another pulse, this time a 180° pulse (Fig. 15.6), the spins are flipped. What happens here can best be compared with runners on a track. At the beginning of the race, all the runners are at the same place, the starting line. After the starting gun (the 90° pulse), they have, however, moved different distances away from the starting line because of their different velocities. The effect of the 180° pulse is the same as that of a second gun, which signals the runners to turn around and return to the start at the same speed as before. Obviously, they all reach the start at the same time. For the spins, this means that at a certain time after the 180° pulse, they will again all be in phase, and thus their radiation will be in phase. As a result, the original radiation intensity is reached again. This picture must be somewhat modified, because there are also irreversible phase changes of the spins, which are characterised by the so-called homogeneous linewidth, which we shall discuss in Sect. 16.2. Due to this homogeneous linewidth, the original starting intensity can no longer quite be attained (see Fig. 15.8). If one repeats the 180° pulse, the result is that shown in Fig. 15.9. The decay time T_2, which we met earlier in Sect. 14.5 in the Bloch equations, can be calculated from the decay of the peaks. The homogeneous linewidth can then be determined from T_2: $\Delta\omega = 2\pi/T_2$. The analogy between the spin and the two-level atom has now made it possible to apply the entire

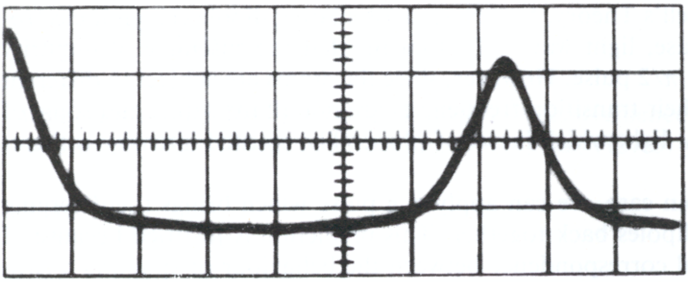

Fig. 15.8. Decay of the spin emission and echo emission of protons in water. From A. Abragam: *The Principles of Nuclear Magnetism* (Oxford 1962)

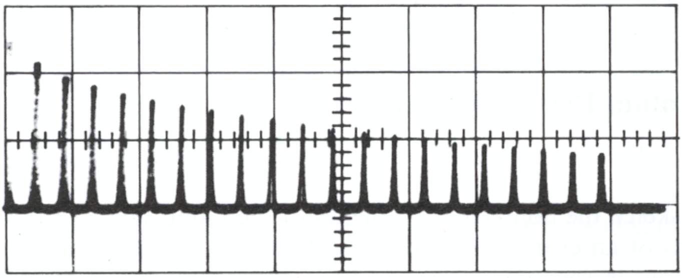

Fig. 15.9. A series of spin echos obtained from protons in ordinary water. In this method, a 90° pulse is applied at time $t = 0$, and is followed at times τ, 3τ, $5\tau, \ldots, (2n-1)\tau$ by a 180° pulse. The echoes are observed at the times 2τ, $4\tau, \ldots, 2n\tau$ (n an integer). It can be shown that the height of the peaks decays according to the formula $f(n) = \exp(-2n\tau/T_2)$. From A. Abragam: *The Principles of Nuclear Magnetism* (Oxford, 1962)

process of spin echo to the radiation field in the case of the photon echo. We leave it to the reader to develop this analogy on the basis of the above.

To this end, let us consider a system of two-level atoms. An example is the ruby, in which chromium ions are included as impurities in a basic lattice of aluminium oxide. To a certain approximation, these ions can be treated as two-level atoms. As we saw in Sect. 15.4, the occupation number of the upper state increases due to the applied resonant oscillating electric field (15.66). The electron of the impurity atom is thus to be found more and more frequently in the upper state, while the occupation of the lower state decreases correspondingly. Eventually a state is reached in which the occupation numbers are equal. Because this is an exact analogy to the state in which the spin has flipped through 90°, or in other words, the occupation numbers of the "spin up" and "spin down" states are equal, one speaks in this case, too, of a $\pi/2$ or 90° pulse. If one applies the external electric field to the electron for twice as long, it goes completely into the upper state, again in analogy to the spin, which is at this point rotated through 180°. Therefore one speaks again, in the two-level atom case, of a 180° or π pulse. As (15.66) and (15.60) show, the "flipping" occurs more rapidly when the applied field strength F_0 is larger.

We now imagine that the electron has been excited by a $\pi/2$ pulse. It can be shown that the dipole moment of the electron then oscillates freely with the frequency of the optical transition, ω. This can be shown by a calculation of the expectation value of the dipole which is analogous to (15.67) and (15.68), although there is no external applied field. According to Maxwell's Theory, however, an oscillating dipole can emit electromagnetic waves, in this case, light waves. This means that the ensemble of impurity atoms emits light after the $\pi/2$ pulse. However, since the atoms are subject to different fields within the crystal, their transition frequencies are not all the same, and some of the oscillating dipoles emit light which is out of phase. The emitted intensity is therefore reduced.

Now, just as in the spin case, we can apply a π pulse which brings the diverging phases of the oscillating dipoles back together. This prediction is justified because of the complete mathematical correspondence between the behaviour of spin and a two-level atom. As the oscillating dipole moments come back into phase, they emit a light pulse which can be seen as the "echo" of the previously applied π pulse. In the optical range, the phases of the dipoles diverge very rapidly, so it is necessary in these experiments to use short pulses of about 10^{-10} s and less.

15.5 A Glance at Quantum Electrodynamics*

15.5.1 Field Quantization

In this section we want to sketch the nonrelativistic theory of the Lamb shift. To this end we first show by means of an example how the light field can be quantized. We start with Maxwell's equations in vacuum which reads:

$$\operatorname{curl} \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}, \tag{15.69}$$

$$\operatorname{curl} \boldsymbol{B} = \varepsilon_0 \mu_0 \frac{\partial \boldsymbol{E}}{\partial t}, \tag{15.70}$$

$$\operatorname{div} \boldsymbol{E} = 0, \tag{15.71}$$

$$\operatorname{div} \boldsymbol{B} = 0 \tag{15.72}$$

where

$$\mu_0 \varepsilon_0 = \frac{1}{c^2} \tag{15.73}$$

and where c is the light velocity in vacuum. Let us consider a standing electric wave with wave vector k and with its electric vector in the z-direction

$$\boldsymbol{E} = (0, 0 E_z), \quad E_z = p(t) N \sin(kx) \tag{15.74}$$

and where $p(t)$ is a still unknown function of time. To derive the corresponding magnetic induction we insert (15.74) into (15.69). One can convince oneself readily that only the y-component of this equation is non-vanishing.

$$-\frac{\partial E_z}{\partial x} = -\frac{\partial B_y}{\partial t}. \tag{15.75}$$

Since the left-hand side of this equation is proportional to $\cos(kx)$ it suggests that we put B_y proportional to $\cos(kx)$. This leads us to the ansatz

$$B_y = q(t)\frac{N}{c}\cos(kx) \tag{15.76}$$

where we have included the factor $1/c$ for later convenience. This factor gives p and q the same physical dimension. Inserting (15.76) into (15.75) yields

$$\frac{dq}{dt} = \omega p \tag{15.77}$$

where we have used the abbreviation

$$\omega = ck\,. \tag{15.78}$$

Since k is a wave number and c a velocity, ω in (15.78) is a circular frequency. Inserting $\boldsymbol{E}$ (15.74) and $\boldsymbol{B}$ (15.76) into (15.70) yields

$$\frac{dp}{dt} = -\omega q\,. \tag{15.79}$$

When we differentiate (15.77) with respect to time and eliminate p from it by means of (15.79), we obtain

$$\frac{d^2q}{dt^2} + \omega^2 q = 0\,. \tag{15.80}$$

This equation is the well-known equation of a harmonic oscillator with circular frequency ω. Equations (15.77) and (15.79) can be written in a very elegant form by introducing the Hamiltonian

$$\mathscr{H} = \tfrac{1}{2}\omega(p^2+q^2)\,. \tag{15.81}$$

With its aid we can write (15.77) and (15.79) in the form

$$\frac{dq}{dt} = \frac{\partial\mathscr{H}}{\partial p} \tag{15.82}$$

$$\frac{dp}{dt} = -\frac{\partial\mathscr{H}}{\partial q}\,. \tag{15.83}$$

Quite evidently we are dealing here with the Hamiltonian equations of a harmonic oscillator. This then allows us to identify p with the momentum and q with the coordinate of an harmonic oscillator. With this identification we have the key in our hands to quantize the electromagnetic field. This is done by a purely formal analogy. In Sect. 9.4 we saw how to quantize the motion of the harmonic oscillator. Here we want to do exactly the same. To put this analogy between the harmonic oscillator and the electromagnetic field on firm ground we show that $\mathscr{H}$ (15.81) is identical with the energy of the electromagnetic field mode. According to electrodynamics, the field energy in the volume $\mathscr{V} \equiv L^3$ is given by

$$\bar{U} = \int \frac{1}{2}\left(\varepsilon_0 \boldsymbol{E}^2 + \frac{1}{\mu_0}\boldsymbol{B}^2\right) d^3\boldsymbol{x} \,. \tag{15.84}$$

By inserting (15.74) and (15.76) into the energy expression (15.84) we obtain

$$\bar{U} = \frac{1}{2} N^2 \varepsilon_0 \left\{ L^2 \int_0^L [p^2 \sin^2(kx) + q^2 \cos^2(kx)]\, dx \right\} . \tag{15.85}$$

Under the assumption of periodic boundary conditions, the integration over x can easily be performed so that we are left with

$$\bar{U} = \tfrac{1}{4}\, \mathscr{V} N^2 \varepsilon_0 (p^2 + q^2) \,. \tag{15.86}$$

We find exactly the same function of p and q as occurring in (15.81). However, this identification now allows us to determine the still unknown normalization factor N. Comparing (15.86) with (15.81) we obtain

$$N = \sqrt{\frac{\omega}{\varepsilon_0}} \sqrt{\frac{2}{\mathscr{V}}} \,. \tag{15.87}$$

Now let us return to the quantization problem. We wish to utilize the analogy between the Hamiltonian (15.81) and that of the harmonic oscillator. It is convenient to use its Hamiltonian in the form

$$\tfrac{1}{2} \hbar \omega (\Pi^2 + \xi^2) \,. \tag{15.88}$$

The equivalence of (15.81) with (15.88) is achieved by putting

$$p = \sqrt{\hbar}\, \Pi \,, \qquad q = \sqrt{\hbar}\, \xi \tag{15.89}$$

so that the Hamiltonian (15.81) acquires exactly the same form (15.88). Here, however, we known what the quantum version looks like. We have to replace Π by the operator $\partial / \mathrm{i} \partial \xi$ exactly in analogy to Sect. 9.4. By exploiting that analogy further we introduce creation and annihilation operators by

$$\frac{1}{\sqrt{2}}\left(-\frac{\partial}{\partial \xi} + \xi\right) = b^+ \,, \tag{15.90}$$

$$\frac{1}{\sqrt{2}}\left(\frac{\partial}{\partial \xi} + \xi\right) = b \tag{15.91}$$

or, solving for p and q

$$p = \mathrm{i} \sqrt{\frac{\hbar}{2}} (b^+ - b) \,, \tag{15.92}$$

$$q = \sqrt{\frac{\hbar}{2}} (b^+ + b) \,. \tag{15.93}$$

The creation and annihilation operators b^+ and b obey the commutation relation

$$bb^+ - b^+b = 1 \,. \tag{15.94}$$

By using (15.92) and (15.93), we can express the free fields $\boldsymbol{E}$ and $\boldsymbol{B}$ by means of these operators in the form

$$E_z = \mathrm{i}(b^+ - b)\sqrt{\frac{\hbar}{2}}\,N\sin(kx) \tag{15.95}$$

$$B_y = (b^+ + b)\sqrt{\frac{\hbar}{2}}\,\frac{N}{c}\cos(kx) \,. \tag{15.96}$$

The normalization factor is given by

$$N = \sqrt{\frac{\omega}{\varepsilon_0}}\sqrt{\frac{2}{\mathscr{V}}}\,, \qquad \varepsilon_0\mu_0 = \frac{1}{c^2} \,. \tag{15.97}$$

With the transformations (15.90) and (15.91), the Hamiltonian (15.88) can be expressed by the creation and annihilation operators exactly as in Sect. 9.4.

$$\mathscr{H} = \hbar\omega(b^+b + \tfrac{1}{2}) \,. \tag{15.98}$$

We leave it as an exercise to the reader to convince himself that this Hamiltonian could be also derived by inserting (15.95) and (15.96) into (15.84). For a number of problems dealing with the interaction between electrons and the electromagnetic field we need the vector potential $\boldsymbol{A}$. $\boldsymbol{A}$ is connected with the magnetic induction by

$$\boldsymbol{B} = \mathrm{curl}\,\boldsymbol{A} \,. \tag{15.99}$$

In our book we choose the "Coulomb gauge"

$$\mathrm{div}\,\boldsymbol{A} = 0 \,. \tag{15.100}$$

For $\boldsymbol{B}$ in the form (15.96) the relations (15.99) and (15.100) are fulfilled by

$$A_x = 0\,, \quad A_y = 0\,, \quad A_z = -(b^+ + b)\sqrt{\frac{\hbar\omega\mu_0}{2}}\sqrt{\frac{2}{\mathscr{V}}}\,\frac{1}{k}\sin(kx) \,. \tag{15.101}$$

Let us summarize the above results. When we quantize the electromagnetic field, the electric field strength, the magnetic induction, and the vector potential become operators that can be expressed by the familiar creation and annihilation operators b^+, b of a harmonic oscillator. The total energy of the field also becomes a Hamiltonian operator of the form (15.98).

Since the normalization of waves in infinite space provides some formal difficulties (which one may overcome, however), we shall use a well-known trick. We subject the wavefunctions

$$\exp(\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r}) \tag{15.102}$$

to periodic boundary conditions. In order to apply the above formalism in particular to the Lamb shift, two changes must be made:

1) Instead of using a single (standing) wave, the electromagnetic field must be written as a superposition of all possible waves.
2) Instead of standing waves, the use of running waves has some advantages.

Since the derivation of the corresponding relations does not give us any physical insight beyond what we gained above, we immediately write down these relations.

$$\boldsymbol{E}(\boldsymbol{r}) = \sum_\lambda \boldsymbol{e}_\lambda \sqrt{\frac{\hbar\omega_\lambda}{2\varepsilon_0 \mathscr{V}}}\,[\mathrm{i}b_\lambda \exp(\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r}) - \mathrm{i}b_\lambda^+ \exp(-\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r})] \tag{15.103}$$

$$\boldsymbol{B}(\boldsymbol{r}) = \sum_\lambda \hat{\boldsymbol{k}} \times \boldsymbol{e}_\lambda \sqrt{\frac{\hbar\omega_\lambda \mu_0}{2 \mathscr{V}}}\,[\mathrm{i}b_\lambda \exp(\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r}) - \mathrm{i}b_\lambda^+ \exp(-\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r})] \,. \tag{15.104}$$

The individual expressions have the following meaning:

λ	index labeling the individual waves
$\boldsymbol{e}_\lambda$	vector of polarization of wave
ω_λ	circular frequency
$\boldsymbol{k}_\lambda$	wave vector of wave

$$\hat{\boldsymbol{k}} = \boldsymbol{k}/|\boldsymbol{k}| \,. \tag{15.105}$$

The vector potential $\boldsymbol{A}$ reads

$$\boldsymbol{A} = \sum_\lambda \boldsymbol{e}_\lambda \sqrt{\frac{\hbar}{2\omega_\lambda \varepsilon_0 \mathscr{V}}}\,[b_\lambda \exp(\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r}) + b_\lambda^+ \exp(-\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r})] \,. \tag{15.106}$$

The operators b_λ^+, b_λ again obey the commutation relations

$$b_\lambda b_{\lambda'}^+ - b_{\lambda'}^+ b_\lambda = \delta_{\lambda\lambda'} \tag{15.107}$$

$$b_\lambda b_{\lambda'} - b_{\lambda'} b_\lambda = 0 \tag{15.108}$$

$$b_\lambda^+ b_{\lambda'}^+ - b_{\lambda'}^+ b_\lambda^+ = 0 \,. \tag{15.109}$$

The Hamiltonian operator reads

$$\mathscr{H}_{\text{field}} = \sum_\lambda \hbar\omega_\lambda (b_\lambda^+ b_\lambda + \tfrac{1}{2}) \,. \tag{15.110}$$

As usual, the Schrödinger equation is obtained by applying the Hamiltonian operator to a wavefunction, which we call Φ:

$$\mathscr{H}_{\text{field}}\, \Phi = E\Phi \,. \tag{15.111}$$

We shall determine the wavefunction and energies in the exercises. For what follows, we need only the ground state defined by $b_\lambda \Phi_0 = 0$ for all λ, and the states which are occupied by a single light quantum (photon).

$$\Phi_\lambda = b_\lambda^+ \Phi_0 \tag{15.112}$$

with quantum energy

$$E_\lambda = \hbar\omega_\lambda (+E_0) \, . \tag{15.113}$$

It has the zero point energy

$$E_0 = \sum_\lambda \tfrac{1}{2} \hbar\omega_\lambda \, . \tag{15.114}$$

This expression is infinite, but it is also unobservable and therefore dropped.

15.5.2 Mass Renormalization and Lamb Shift

We shall now treat the interaction of a hydrogen atom with the quantized light-field. The interaction is brought about by the vector potential $\boldsymbol{A}$ occurring in (14.12). Since $\boldsymbol{A}$ is small in the present case, we shall retain only terms linear in $\boldsymbol{A}$, and assume $\operatorname{div} \boldsymbol{A} = 0$. But in contrast to that former case, the fields are not externally given, but become now by themselves variables of the system. Therefore we must not only write $\boldsymbol{A}$ in the form (15.106), but we must also add to the Hamiltonian $\mathscr{H}_{\text{el}} + \mathscr{H}_{\text{int}}$ that of the quantized field, i.e. $\mathscr{H}_{\text{field}}$. Thus the Schrödinger equation to be solved reads:

$$(\mathscr{H}_{\text{el}} + \mathscr{H}_{\text{field}} + \mathscr{H}_{\text{int}}) \Psi = E \Psi \tag{15.115}$$

where

$$\mathscr{H}_{\text{el}} = -\frac{\hbar^2}{2m_0} \Delta + V(\boldsymbol{r}) \tag{15.116}$$

$$\mathscr{H}_{\text{field}} = \sum_\lambda \hbar\omega_\lambda b_\lambda^+ b_\lambda \tag{15.117}$$

$$\mathscr{H}_{\text{int}} = \frac{e}{m_0} \boldsymbol{A} \cdot \hat{\boldsymbol{p}} \equiv \frac{e}{m_0} \sum_\lambda \boldsymbol{e}_\lambda \sqrt{\frac{\hbar}{2\omega_\lambda \varepsilon_0 \mathscr{V}}} \, [b_\lambda \exp(\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r}) + b_\lambda^+ \exp(\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r})] \, \hat{\boldsymbol{p}}$$

where

$$\hat{\boldsymbol{p}} \equiv \frac{\hbar}{\mathrm{i}} \operatorname{grad} \, . \tag{15.118}$$

In order to solve the Schrödinger equation (15.115), we shall apply perturbation theory, where

$$\mathscr{H}_0 = \mathscr{H}_{\text{el}} + \mathscr{H}_{\text{field}} \tag{15.119}$$

serves as unperturbed Hamiltonian and $\mathscr{H}_{\text{int}}$ as perturbation. The eigenfunctions Φ_ν of $\mathscr{H}_0$ are products of an eigenfunction of $\mathscr{H}_{\text{el}}$, i.e. ψ and of an eigenfunction of $\mathscr{H}_{\text{field}}$, i.e. Φ. We shall abbreviate the set of quantum numbers n, l, m of ψ by n. In the following we shall be concerned with the vacuum state Φ_0 and one-photon states $\Phi_\lambda \equiv b_\lambda^+ \Phi_0$. Identifying the index ν of ϕ_ν with $(n, 0)$, or (n, λ) we may write the unperturbed wavefunction as

$$\phi_\nu = \psi_n(\boldsymbol{r})\, \Phi_\kappa \quad \text{where} \tag{15.120}$$

$$\kappa = 0 \;, \quad \text{or} \quad \lambda \;. \tag{15.121}$$

The corresponding energy levels are

$$E^0_{\nu,\text{tot}} = E^0_n \quad (\kappa = 0) \qquad \text{and} \qquad E^0_{\nu,\text{tot}} = E^0_n + \hbar\omega_\lambda \quad (\kappa = \lambda) \;. \tag{15.122}$$

For the perturbation theory we need the matrix elements of $\mathscr{H}_\text{int}$ which read in bra and ket notation:

$$H^1_{\mu\nu} = \left\langle \psi_n \Phi_\kappa \left| \frac{e}{m_0} \sum_\lambda \boldsymbol{e}_\lambda \sqrt{\frac{\hbar}{2\,\omega_\lambda\, \varepsilon_0\, \mathscr{V}}}\, [b_\lambda \exp(\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r}) + b_\lambda^+ \exp(-\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r})]\hat{\boldsymbol{p}} \right| \psi_{n'} \Phi_{\kappa'} \right\rangle \tag{15.123}$$

which may be rearranged as

$$\begin{aligned} H^1_{\mu\nu} = \frac{e}{m_0} \sum_\lambda \sqrt{\frac{\hbar}{2\,\omega_\lambda\, \varepsilon_0\, \mathscr{V}}}\, [&\langle n | \exp(\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r}) \boldsymbol{e}_\lambda \cdot \hat{\boldsymbol{p}} | n' \rangle \langle \Phi_\kappa | b_\lambda | \Phi_{\kappa'} \rangle \\ &+ \langle n | \exp(-\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r}) \boldsymbol{e}_\lambda \cdot \hat{\boldsymbol{p}} | n' \rangle \langle \Phi_\kappa | \, b_\lambda^+ \, | \Phi_{\kappa'} \rangle] \;. \end{aligned} \tag{15.124}$$

As we know from the quantized harmonic oscillator,

$$\langle \Phi_\kappa | b_\lambda^+ \, | \Phi_\kappa \rangle = \langle \Phi_\kappa | b_\lambda | \Phi_\kappa \rangle = 0 \;. \tag{15.125}$$

Therefore the perturbation energy in first order vanishes. Starting from the vacuum as unperturbed state, i.e. $\kappa' = 0$, we further have

$$\langle \Phi_\kappa | b_\lambda | \Phi_0 \rangle = 0 \;, \qquad \langle \Phi_\kappa | b_\lambda^+ \, | \Phi_0 \rangle = \delta_{\lambda\kappa} \tag{15.126}$$

In other words, a single photon λ may be generated. We assume that the atom sits at the origin and that the extension of the electronic wave function is small compared to the wavelength of the light waves $\exp[\mathrm{i}\boldsymbol{k}_\lambda \cdot \boldsymbol{r}]$. This allows us to ignore this factor in the matrix elements. In this way $H^1_{\mu\nu}$ is reduced to (with $\kappa = \lambda$!)

$$H^1_{\mu\nu} \equiv H^1_{n,\lambda;n',0} = \frac{e}{m_0} \sqrt{\frac{\hbar}{2\,\omega_\lambda\, \varepsilon_0\, \mathscr{V}}} \langle n | \boldsymbol{e}_\lambda \cdot \hat{\boldsymbol{p}} | n' \rangle \;. \tag{15.127}$$

The expression for the perturbed energy in second order therefore reads

$$\varepsilon^{(2)} = \sum_{n',\lambda} \frac{|H^1_{n',\lambda;n,0}|^2}{E^0_n - E^0_{n'} - \hbar\omega_\lambda} \;. \tag{15.128}$$

In quantum electrodynamics, the processes which lead to $\varepsilon^{(2)}$ are usually visualized as follows:

An electron is in its initial state n, and there is no photon. Then a photon of kind λ is emitted, [creation operation b_λ^+ in (15.124) and (15.128)!] and the electron goes into the state n'. Finally the photon is reabsorbed [annihilation operator b_λ in (15.124) and (15.128)!] and the electron returns to its state n. This process is described by the following "Feynman diagram" (Fig. 15.10).

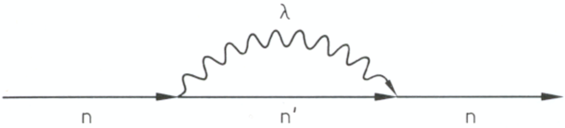

Fig. 15.10. Example of a Feynman diagram: virtual emission and reabsorption of a photon

In the following we have to distinguish the different field modes more carefully. To this end we replace the general mode index λ by the wave vector $\boldsymbol{k}$ and an index j indicating one of the two directions of polarization. Furthermore we use the relation between frequency and wave number

$$\omega_\lambda \equiv \omega_k = ck \quad . \tag{15.129}$$

While we initially start with waves normalized in a volume $\mathscr{V}$ we will eventually go over to an integration which is done by the rule

$$\frac{1}{\mathscr{V}} \sum_\lambda \to \sum_{j=1,2} \int \frac{d^3\boldsymbol{k}}{(2\pi)^3} \quad . \tag{15.130}$$

Using (15.127, 129) and (15.130) we may cast (15.128) into the form

$$\varepsilon^{(2)} = \frac{1}{(2\pi)^3} \frac{e^2\hbar}{2m_0^2\varepsilon_0} \int d^3\boldsymbol{k} \frac{1}{\omega_k} \sum_{n',j} \frac{|\langle n|\boldsymbol{e}_j \cdot \hat{\boldsymbol{p}}|n'\rangle|^2}{E_n^0 - E_{n'}^0 - \hbar\omega_k} \quad . \tag{15.131}$$

For further evaluation we split the integral over $\boldsymbol{k}$-space into one over the space angle Ω and one over the magnitude of $\boldsymbol{k}$, i.e. k,

$$\int d^3\boldsymbol{k} = \int k^2 dk \int d\Omega \quad . \tag{15.132}$$

We then first perform the integration over the space angle and sum up over the two directions of polarizations. Since the evaluation is purely formal we immediately write down the result

$$\int d\Omega \sum_j |\langle n|\boldsymbol{e}_j \cdot \hat{\boldsymbol{p}}|n'\rangle|^2 = 4\pi \tfrac{2}{3} |\langle n|\hat{\boldsymbol{p}}|n'\rangle|^2 \quad . \tag{15.133}$$

This leads us to the following result for the self-energy

$$\varepsilon^{(2)} = \frac{1}{(2\pi)^2} \frac{2e^2\hbar}{3m_0^2\varepsilon_0 c^3} \int_0^\infty \omega\, d\omega \sum_{n'} \frac{|\langle n|\hat{\boldsymbol{p}}|n'\rangle|^2}{E_n^0 - E_{n'}^0 - \hbar\omega} \quad . \tag{15.134}$$

A detailed discussion of the sum over n' reveals that this sum certainly does not vanish more strongly than $1/\omega$. We thus immediately recognize that the integral over ω in (15.134) diverges which means that the energy shift is infinitely great. This seemingly absurd result presented a great difficulty to theoretical physics. It was overcome by ideas of Bethe, Schwinger and Weisskopf which we will now explain.

When we do similar calculations for free electrons we again find an infinite result, which can be seen as follows. We repeat the whole calculation above but instead of eigenfunctions ψ_n of the hydrogen atom we use the wave functions of free electrons

$$\psi_n(\boldsymbol{r}) \rightarrow \psi_{\boldsymbol{p}} = N \exp(\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}/\hbar) \tag{15.135}$$

Note that in this formula $\boldsymbol{p}$ is a usual vector whereas $\hat{\boldsymbol{p}}$ occurring for instance in (15.127) and (15.131) is the momentum operator $(\hbar/\mathrm{i})$ grad. Instead of matrix elements, which were between the eigenstates of the hydrogen atom, we now have to evaluate matrix elements between plane waves. We immediately obtain

$$\langle\boldsymbol{p}'|\hat{\boldsymbol{p}}|\boldsymbol{p}\rangle = N^2 \int \exp(-\mathrm{i}\boldsymbol{p}'\cdot\boldsymbol{r}/\hbar)\hat{\boldsymbol{p}} \exp(\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}/\hbar)\,d^3\boldsymbol{r} \tag{15.136}$$

and

$$\langle\boldsymbol{p}'|\hat{\boldsymbol{p}}|\boldsymbol{p}\rangle = \boldsymbol{p}\,\delta_{\boldsymbol{p},\boldsymbol{p}'} \ . \tag{15.137}$$

Furthermore, we have to make the substitution

$$E_n^0 - E_{n'}^0 \rightarrow E_p - E_{p'} \tag{15.138}$$

but we immediately find

$$(E_p - E_{p'})\,\delta_{p,p'} = 0 \tag{15.139}$$

on account of (15.137). By putting all the results together we obtain the self-energy of a free electron in the form

$$\varepsilon_p^{(2)} = -\frac{1}{(2\pi)^2}\,\frac{2e^2}{3m_0^2\varepsilon_0 c^3}\,\boldsymbol{p}^2 \sum_0^\infty d\omega \ . \tag{15.140}$$

We notice that the self-energy of a free electron of momentum $\boldsymbol{p}$ is proportional to $\boldsymbol{p}^2$. Equation (15.140) can be interpreted as giving rise to a shift in the mass of the electron, which can be seen as follows: The energy of the free electron without interaction with the electromagnetic field ("bare electron") reads

$$E_p = \boldsymbol{p}^2/(2\bar{m}_0) \ . \tag{15.141}$$

In it, $\bar{m}_0$ is the "bare" mass. The energy shift just calculated is

$$\Delta E_p = -\frac{1}{(2\pi)^2}\,\frac{2e^2}{3m_0^2\varepsilon_0 c^3}\,\boldsymbol{p}^2 \int_0^\infty d\omega \ . \tag{15.142}$$

Thus the total energy reads

$$E_p + \Delta E_p = \frac{p^2}{2\,m_0} \tag{15.143}$$

While the mass of the "bare" electron neglecting electromagnetic interaction is $\bar{m}_0$, taking this interaction into account the electron mass is m_0. Note that in this type of consideration one uses m_0 and not $\bar{m}_0$ in (15.142). This follows from the "renormalization" procedure we will describe now.

Since we always make observations on free electrons with the electromagnetic interaction present, (15.143) must be just the expression we normally write down for the energy of a free electron where m_0 is the observed mass. Thus we can make the identification

$$\frac{1}{m_0} = \frac{1}{\bar{m}_0} - \frac{1}{(2\pi)^2}\,\frac{4\,e^2}{3\,m_0^2\,\varepsilon_0\,c^3}\int_0^\infty d\omega \equiv \frac{1}{\bar{m}_0} - 2\tilde{a} \tag{15.144}$$

where $2\tilde{a}$ is merely an abbreviation of the last term of the middle part of (15.144). The electromagnetic self-energy can be interpreted as a shift of the mass of an electron from its "bare" value to its observed value m_0. This shift is called renormalization of the mass.

The argument used in renormalization theory is now as follows. The reason that the result (15.134) is infinite lies in the fact that it included an infinite energy change that is already counted when we use the observed mass in the Hamiltonian rather than the bare mass. In other words, we should in fact start with the Hamiltonian for the hydrogen atom in the presence of the radiation field given by

$$\mathscr{H} = \frac{\hat{p}^2}{2\,\bar{m}_0} - \frac{e^2}{4\,\pi\,\varepsilon_0\,r} + \mathscr{H}_{\text{int}}\ . \tag{15.145}$$

Then using (15.144) we can rewrite $\mathscr{H}$ as

$$\mathscr{H} = \frac{\hat{p}^2}{2\,m_0} - \frac{e^2}{4\,\pi\,\varepsilon_0\,r} + \{\mathscr{H}_{\text{int}} + \tilde{a}\hat{p}^2\}\ . \tag{15.146}$$

Thus if we use the observed free particle mass in the expression for the kinetic energy (which we always do) we should not count that part of $\mathscr{H}_{\text{int}}$ that produces the mass shift, i.e. we should regard

$$\mathscr{H}_{\text{int}} + \tilde{a}\hat{p}^2 \tag{15.147}$$

as the effective interaction of an electron of a renormalized mass m_0 with the radiation field.

Returning then to the calculation of the Lamb shift, we see that to first order in $e^2/\hbar c$ we must add the expectation value of the second term in (15.147) to (15.134) in order to avoid counting the electromagnetic interaction twice, once in m_0 and once in $\mathscr{H}_{\text{int}}$. Thus more correctly the shift of the level n is given by

$$\varepsilon^{(2)}=\frac{1}{(2\pi)^2}\,\frac{2e^2\hbar}{3m_0^2\varepsilon_0c^3}\int\limits_0^\infty\omega\,d\omega\left[\sum_{n'}\frac{|\langle n'|\hat{p}|n\rangle|^2}{E_n^0-E_{n'}^0-\hbar\omega}+\frac{\langle n|\hat{p}^2|n\rangle}{\hbar\omega}\right]. \qquad (15.148)$$

The second term under the integral in (15.148) can be brought into a form similar to the first term under the integral by means of the relation

$$\langle n|\hat{p}^2|n\rangle=\sum_{n'}\langle n|\hat{p}|n'\rangle\langle n'|\hat{p}|n\rangle \qquad (15.149)$$

In order not to interrupt the main discussion we will postpone the proof of this relation to the exercises. Using (15.149) and (15.148) we find after a slight rearrangement of terms

$$\varepsilon^{(2)}=\frac{1}{(2\pi)^2}\,\frac{2e^2}{3m_0^2\varepsilon_0c^3}\sum_{n'}|\langle n'|\hat{p}|n\rangle|^2\int\limits_0^\infty d\omega\,\frac{E_n^0-E_{n'}^0}{E_n^0-E_{n'}^0-\hbar\omega}. \qquad (15.150)$$

We note that the integral over ω is still divergent, however, only logarithmically. This divergence is not present in a more sophisticated relativistic calculation. Such a calculation yields a result quite similar to (15.150), but with an integrand falling off more rapidly at high frequencies $\hbar\omega\geq m_0c^2$. We can mimic the result of such a calculation by cutting off the integral at $\omega=m_0c^2/\hbar$. The integral can be immediately performed and yields

$$\varepsilon^{(2)}=\frac{1}{(2\pi)^2}\,\frac{2e^2}{3m_0\varepsilon_0\hbar c^3}\sum_{n'}|\langle n'|\hat{p}|n\rangle|^2(E_{n'}^0-E_n^0)\ln\left|\frac{m_0c^2}{E_{n'}^0-E_n^0}\right| \qquad (15.151)$$

where we have neglected $|E_n^0-E_{n'}^0|$ compared to m_0c^2. The further evaluation of (15.151) requires some formal tricks which are purely mathematical. Namely,

$$\ln\left|\frac{m_0c^2}{(E_{n'}^0-E_n^0)}\right|$$

is replaced by an average

$$\ln\frac{|m_0c^2|}{\langle|E_{n'}^0-E_n^0|\rangle}.$$

Clearly, we may now rewrite (15.151) in the form

$$\varepsilon^{(2)}=\frac{1}{(2\pi)^2}\,\frac{2e^2}{3m_0^2\varepsilon_0\hbar c^3}\ln\frac{|m_0c^2|}{\langle|E_{n'}^0-E_n^0|\rangle}\sum_{n'}|\langle n'|\hat{p}|n\rangle|^2(E_{n'}^0-E_n^0). \qquad (15.152)$$

To simplify (15.152) further we use the relation

$$\sum_{n'}|\langle n'|\hat{p}|n\rangle|^2(E_{n'}^0-E_n^0)=-\tfrac{1}{2}\langle n|[\hat{p},[\hat{p},\mathscr{H}_{\mathrm{el}}]]|n\rangle \qquad (15.153)$$

which will be proved in the exercises. The double commutator on the right-hand side can be easily evaluated. We assume $\mathscr{H}_{\text{el}}$ in the form

$$\mathscr{H}_{\text{el}} = -\frac{\hbar^2}{2m_0}\Delta + V(r) \ . \tag{15.154}$$

We readily obtain (cf. Sect. 9.3)

$$[\hat{p}_x, \mathscr{H}_{\text{el}}] = \frac{\hbar}{\mathrm{i}}\frac{\partial V(r)}{\partial x} \tag{15.155}$$

and in a similar fashion

$$[\hat{\boldsymbol{p}}, [\hat{\boldsymbol{p}}, \mathscr{H}_{\text{el}}]] = -\hbar^2 \Delta V(r) \ . \tag{15.156}$$

Using for V the Coulomb potential of the electron in the hydrogen atom, $V = -e^2/(4\pi\varepsilon_0|\boldsymbol{r}|)$, we can readily evaluate the right-hand side of (15.156). Using a formula well known from electrostatics (potential of a point charge!) we find

$$\Delta\frac{1}{|\boldsymbol{r}|} = -4\pi\delta(\boldsymbol{r}) \tag{15.157}$$

where $\delta(\boldsymbol{r})$ is Dirac's delta function in three dimensions. Using this result and the definition of bra and kets (see Problem 9.19), we readily obtain

$$(15.153) = \frac{\hbar^2}{2}\left\langle n \middle| \Delta\frac{-e^2}{4\pi\varepsilon_0|\boldsymbol{r}|}\middle| n\right\rangle = \frac{e^2\hbar^2}{2\varepsilon_0}\int|\psi_n(\boldsymbol{r})|^2\delta(\boldsymbol{r})\,d^3r \tag{15.158}$$

and making use of the properties of the δ-function

$$(15.158) = \frac{e^2\hbar^2}{2\varepsilon_0}|\psi_n(0)|^2 \ . \tag{15.159}$$

We are now in a position to write down the final formula for the renormalized self-energy shift by inserting the result (15.156) with (15.153) and (15.159) into (15.152). We then obtain

$$\varepsilon^{(2)} = \frac{1}{(2\pi)^2}\,\frac{2e^2}{3m_0^2\varepsilon_0\hbar c^3}\ln\frac{|m_0c^2|}{\langle|E_{n'}^0 - E_n^0|\rangle}\,\frac{e\hbar^2}{2\varepsilon_0}|\psi_n(0)|^2 \ . \tag{15.160}$$

To obtain final numerical results we have to calculate numerically the average as well as $|\psi_n(0)|^2$. For the hydrogen atom $|\psi_n(0)|^2$ is well known and is nonzero only for *s*-states. The average value was calculated by Bethe for the $2S$ level. Inserting all the numerical values we eventually find $\varepsilon^{(2)}/\hbar = 1040$ megacycles. According to these considerations a shift between an S and a P level must be expected. Such a shift was first discovered between the $2S_{1/2}$ and $2P_{1/2}$ level of hydrogen by Lamb and Retherford.

At first sight, it may seem strange that it is possible to obtain reasonable results by a subtraction procedure in which two infinitely large quantities are involved. However, it has turned out that such a subtraction procedure can be formulated in the frame of a beautiful theory, called renormalization, and such procedures are now a legitimate part of theoretical physics giving excellent agreement between theory and experiment. Unfortunately it is beyond the scope of our introductory book to cover the details of these renormalization techniques.

Problems

15.1 A harmonic oscillator with mass m, charge e and eigenfrequency ω is subjected to a constant electric field. Calculate the wavefunctions to the first and second approximations by perturbation theory, and compare the result with the exact solution and energy values (see Problem 9.13).
As an example, one might choose the perturbation of the $n = 1$ and $n = 2$ levels.

Hint: Use the b^+, b formalism in perturbation theory and the results of the corresponding problems from Chap. 9.

15.2 The rotational motion of a two-atom molecule or of a rotating atomic nucleus can be approximately described by the Schrödinger equation

$$-\frac{\hbar^2}{Mr_0^2}\frac{d^2}{d\theta^2}\phi(\theta) = E\phi(\theta)\,,$$

where M is a mass and r_0 is an "effective" distance. Let the wavefunction $\phi(\theta)$ be periodic in the angular coordinate θ: $\phi(\theta+2\pi) = \phi(\theta)$. What are the wavefunctions and energy values of this system? Then assume the system is perturbed by the additional potential $a\cos(2\theta)$. Calculate E and ϕ in this case using perturbation theory with degeneracy.

15.3 Prove that (15.112) fulfills (15.111) and verify (15.113).

Hint: Insert (15.112) into (15.111), use the commutation relations (15.107), (15.109) and $b_\lambda \Phi_0 = 0$ for all λ's.

15.4 Prove that the general wavefunction

$$\Phi = \frac{1}{\sqrt{n_1!\,n_2!\dots n_N!}}(b_1^+)^{n_1}(b_2^+)^{n_2}\dots(b_N^+)^{n_N}\Phi_0 \qquad (*)$$

fulfills (15.111) and determine E.

Hint: Insert (*) into (15.111), use the relations

$$b_\lambda(b_\kappa^+)^n - (b_\kappa^+)b_\lambda = n\,b_\kappa^{n-1}\delta_{\lambda,\kappa}\ ,$$

(15.109) and $b_\lambda\Phi_0 = 0$ for all λ's.

15.5 Prove $\langle n|\hat{p}^2|n\rangle = \sum_{n'} \langle n|\hat{p}|n'\rangle\langle n'|\hat{p}|n\rangle$.

Hint: Write the bra-ket as integrals $\int \psi_n^* \hat{p}\, \psi_{n'}\, dx\, dy\, dz$ and use the completeness relation

$$\sum_{n'} \psi_{n'}(\boldsymbol{r})\, \psi_{n'}^*(\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}') \tag{**}$$

where δ is Dirac's function.

15.6 Prove $\sum_{n'} |\langle n'|\hat{p}|n\rangle|^2 (E_{n'}^0 - E_n^0) = -\frac{1}{2}\langle n|[\hat{p}, [\hat{p}, \mathscr{H}_{\mathrm{el}}]]|n\rangle$.

Hint: Start from the expression

$$\sum_{n'} \langle n|\hat{p}|n'\rangle\, \langle n'|\hat{p}|n\rangle E_{n'}^0$$

and use the fact that the ψ_n's are eigenfunctions of $\mathscr{H}_{\mathrm{el}}$. Use the completeness relation (**).

15.7 Show that the Lamb shift can be understood qualitatively by the assumption that the zero-point fluctuations of the field (≡ set of harmonic oscillators!) cause a shift of the potential energy of the electron.

Hint: Write the electron coordinate as

$$\boldsymbol{r}' = \boldsymbol{r} + \boldsymbol{s}$$

where $\boldsymbol{r}$ corresponds to the unperturbed motion, and $\boldsymbol{s}$ to the field fluctuations.

Expand

$$\langle \psi_n(\boldsymbol{r})\, V(\boldsymbol{r}')\, \psi_n(\boldsymbol{r})\rangle$$

in the first two powers of $\boldsymbol{s}$, where $\langle \boldsymbol{s}\rangle = 0$ and convince yourself, that an expression analogous to (15.158) results.