Chapter 19
Perturbation Theory

Due to the lack of analytic solutions of physical problems, several perturbative methods have been developed. The time-independent perturbation theory discussed in this chapter is an important and much-used technique by which we can calculate the fine structure of the spectrum of the hydrogen atom.

Studying physics, one may get in the beginning the impression that there are closed analytical solutions for all problems. That impression is deceptive, as is well known.[1] All in all, in physics, the set of explicitly and exactly solvable problems is of measure zero; and this is particularly relevant to quantum mechanics. There are a handful of potentials for which one can specify an explicit analytic solution of the SEq, but that's about the end of it. If we pick at random any more or less physically reasonable model potential of an appropriate function space, the chance that we know an explicit analytic solution is practically zero. For this reason, one either depends on numerical calculations or, if one wants to have more or less analytic results, on some form of approximation. There are various methods[2]; here, we address the so-called *perturbation theory*.[3]

This method can be applied when the interaction being considered can be decomposed into a part V which covers the essential physical effects, and another relatively small part W (the 'perturbation') which describes more detailed structures. Of course it is an especially favorable case when there exist closed analytic solutions for V.

One distinguishes between time-independent (=stationary) and time-dependent perturbation theory. Since we consider only time-independent potentials in this text, we restrict ourselves in the following to stationary perturbation theory.

[1] Physics is regarded as an exact science. That does not mean that physical models are always exact or can be solved exactly. Physical models are inherently approximations, and only a few can indeed be solved exactly. A main characteristic of physics is that it deliberately keeps track of the inaccuracies of its approaches. To repeat a quote from Bertrand Russell: "Although this may be seen as a paradox, all exact science is dominated by the idea of approximation".

[2] In Chap. 23, we will discuss the Ritz variational principle, a different approximation procedure.

[3] Also called Rayleigh–Schrödinger perturbation theory.

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19.1 Stationary Perturbation Theory, Nondegenerate

We start with a Hamiltonian H:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V + W = H^{(0)} + W. \tag{19.1}$$

The prerequisite for the following considerations is that W be sufficiently 'small', i.e. that for all states occurring in the calculation, it holds that: $|\langle\varphi| W |\psi\rangle| \ll \left|\langle\varphi| H^{(0)} |\psi\rangle\right|$. In this case, we can write

$$H = H^{(0)} + W = H^{(0)} + \varepsilon\hat{W} \tag{19.2}$$

with the smallness parameter $\varepsilon \ll 1$, where the matrix elements $\left|\langle\varphi| \hat{W} |\psi\rangle\right|$ and $\left|\langle\varphi| H^{(0)} |\psi\rangle\right|$ are of the same order of magnitude.

The superscripted zero denotes quantities in the unperturbed problem (which, at best, is itself analytically solvable). Eigenvalues and eigenvectors of $H^{(0)}$ are solutions of

$$H^{(0)} \left|\varphi_k^{(0)}\right\rangle = E_k^{(0)} \left|\varphi_k^{(0)}\right\rangle;\ k = 1, 2, \ldots \tag{19.3}$$

We assume that the spectrum of $H^{(0)}$ is discrete and nondegenerate, and that its eigenvectors form a CONS. The initial state is $\left|\varphi_n^{(0)}\right\rangle$ and the initial energy is $E_n^{(0)}$.

If we now 'turn on' the perturbation W, we no longer have the unperturbed eigenvalue problem (19.3). Instead, states and eigenvalues are determined by

$$H |\varphi\rangle = E |\varphi\rangle . \tag{19.4}$$

We assume that for sufficiently weak W, we have approximately

$$|\varphi\rangle \approx \left|\varphi_n^{(0)}\right\rangle;\ E \approx E_n^{(0)} \text{ for } \varepsilon \text{ sufficiently small.} \tag{19.5}$$

We formalize this by assuming that we can expand states and energies in power series of the smallness parameter ε. Thus, we use the *ansatz*:

$$|\varphi\rangle = \left|\varphi_n^{(0)}\right\rangle + \varepsilon \left|\varphi_n^{(1)}\right\rangle + \varepsilon^2 \left|\varphi_n^{(2)}\right\rangle + \ldots;\ E = E_n^{(0)} + \varepsilon E_n^{(1)} + \varepsilon^2 E_n^{(2)} + \cdots \tag{19.6}$$

The basic idea of perturbation theory is now to insert these formulations into the SEq (19.4) and to sort by powers of ε. Terms with ε^0 give the unperturbed system, which is labelled by the superscript $^{(0)}$; the terms with ε^1 give the first-order corrections which are labelled by $^{(1)}$, and so on. The procedure is simple in principle, although, at first glance, it looks perhaps somewhat opaque due to the accumulation of indices. In addition, it should be noted that the convergence of the series (19.6) in ε is difficult to establish. We assume again that quantum mechanics and the method considered here are 'well behaved', and estimate the quality of our

approximation a posteriori by comparison with experimental data. Apart from that, such an approximation method in general makes sense in practice only if the essential corrections can be described with a few terms (proportional to ε^1, or at most to ε^2).

One more note before we go through perturbation theory: We can assume from the outset that the correction terms are orthogonal to the initial state

$$\left\langle \varphi_n^{(0)} \middle| \varphi_n^{(j)} \right\rangle = 0; \;\; j \neq 0. \tag{19.7}$$

For if it would turn out during the calculation that this were not the case (implying that $\left|\varphi_n^{(1)}\right\rangle = c\left|\varphi_n^{(0)}\right\rangle + |\psi_{\text{rest}}\rangle$ with $|\psi_{\text{rest}}\rangle$ orthogonal to $\left|\varphi_n^{(0)}\right\rangle$), we could add this part to the undisturbed state and renormalize:

$$\left|\varphi_n^{(0)}\right\rangle + \varepsilon c \left|\varphi_n^{(0)}\right\rangle + \varepsilon |\psi_{\text{rest}}\rangle \to \frac{1}{\sqrt{1+\varepsilon^2 |c|^2}} \left|\varphi_n^{(0)}\right\rangle + \varepsilon |\psi_{\text{rest}}\rangle = \left|\varphi_n^{(0)}\right\rangle_{\text{new}} + \varepsilon |\psi_{\text{rest}}\rangle , \tag{19.8}$$

so that with this new initial state $\left|\varphi_n^{(0)}\right\rangle_{\text{new}}$, the orthogonality relation (19.7) is satisfied. We point out that this issue plays a role in the following argument.

We insert the power series (19.6) into (19.4) and obtain, sorted by powers of ε,

$$\begin{aligned} &H^{(0)} \left|\varphi_n^{(0)}\right\rangle + \varepsilon \left[H^{(0)} \left|\varphi_n^{(1)}\right\rangle + \hat{W} \left|\varphi_n^{(0)}\right\rangle \right] + \cdots \\ &\quad = E_n^{(0)} \left|\varphi_n^{(0)}\right\rangle + \varepsilon \left[E_n^{(0)} \left|\varphi_n^{(1)}\right\rangle + E_n^{(1)} \left|\varphi_n^{(0)}\right\rangle \right] + \cdots \end{aligned} \tag{19.9}$$

To make the principle clear, it will suffice to consider the terms $\sim\varepsilon^0$ and $\sim\varepsilon^1$. For terms $\sim\varepsilon^2$, see the exercises. Comparing powers of ε leads to

$$H^{(0)} \left|\varphi_n^{(0)}\right\rangle = E_n^{(0)} \left|\varphi_n^{(1)}\right\rangle \tag{19.10}$$

$$H^{(0)} \left|\varphi_n^{(1)}\right\rangle + \hat{W} \left|\varphi_n^{(0)}\right\rangle = E_n^{(0)} \left|\varphi_n^{(1)}\right\rangle + E_n^{(1)} \left|\varphi_n^{(0)}\right\rangle . \tag{19.11}$$

Equation (19.10) is automatically satisfied. From (19.11), the correction terms $\left|\varphi_n^{(1)}\right\rangle$ and $E_n^{(1)}$ have to be calculated.

19.1.1 Calculation of the First-Order Energy Correction

In the first step, we multiply (19.11) from the left by $\left\langle \varphi_n^{(0)} \right|$ and find, with $\left\langle \varphi_n^{(0)} \middle| \varphi_n^{(1)} \right\rangle = 0$ and $\left\langle \varphi_n^{(0)} \right| H^{(0)} \left|\varphi_n^{(1)}\right\rangle = E_n^{(0)} \left\langle \varphi_n^{(0)} \middle| \varphi_n^{(1)} \right\rangle = 0$, immediately as the first correction term for the energy the matrix element:

$$E_n^{(1)} = \left\langle \varphi_n^{(0)} \right| \hat{W} \left|\varphi_n^{(0)}\right\rangle . \tag{19.12}$$

Therefore, the energy in first-order correction is given by

$$E = E_n^{(0)} + \varepsilon \left\langle \varphi_n^{(0)} \right| \hat{W} \left|\varphi_n^{(0)}\right\rangle = E_n^{(0)} + \left\langle \varphi_n^{(0)} \right| W \left|\varphi_n^{(0)}\right\rangle . \tag{19.13}$$

19.1.2 Calculation of the First-Order State Correction

In the second step, we determine the correction to the state vector in the lowest order. To calculate the correction term $\left|\varphi_n^{(1)}\right\rangle$, we multiply (19.11) from the left by $\left\langle\varphi_m^{(0)}\right|$, with $m \neq n$:

$$\left\langle\varphi_m^{(0)}\right| H^{(0)} \left|\varphi_n^{(1)}\right\rangle + \left\langle\varphi_m^{(0)}\right| \hat{W} \left|\varphi_n^{(0)}\right\rangle = \left\langle\varphi_m^{(0)}\right| E_n^{(0)} \left|\varphi_n^{(1)}\right\rangle + \left\langle\varphi_m^{(0)}\right| E_n^{(1)} \left|\varphi_n^{(0)}\right\rangle . \tag{19.14}$$

We can transform this to (note: $m \neq n$)

$$E_m^{(0)} \left\langle\varphi_m^{(0)} \left|\varphi_n^{(1)}\right\rangle + \left\langle\varphi_m^{(0)}\right| \hat{W} \left|\varphi_n^{(0)}\right\rangle = E_n^{(0)} \left\langle\varphi_m^{(0)} \left|\varphi_n^{(1)}\right\rangle , \tag{19.15}$$

and this gives

$$\left\langle\varphi_m^{(0)} \left|\varphi_n^{(1)}\right\rangle = \frac{\left\langle\varphi_m^{(0)}\right| \hat{W} \left|\varphi_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}};\ m \neq n \tag{19.16}$$

or

$$\sum_{m\neq n} \left|\varphi_m^{(0)}\right\rangle \left\langle\varphi_m^{(0)} \left|\varphi_n^{(1)}\right\rangle = \sum_{m\neq n} \frac{\left\langle\varphi_m^{(0)}\right| \hat{W} \left|\varphi_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \left|\varphi_m^{(0)}\right\rangle . \tag{19.17}$$

To make use of the completeness relation of the eigenvectors $\left|\varphi_m^{(0)}\right\rangle$, we add on the left $\left|\varphi_n^{(0)}\right\rangle \left\langle\varphi_n^{(0)} \left|\varphi_n^{(1)}\right\rangle = 0$ (this follows from (19.7)) and obtain the correction term

$$\left|\varphi_n^{(1)}\right\rangle = \sum_{m\neq n} \frac{\left\langle\varphi_m^{(0)}\right| \hat{W} \left|\varphi_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \left|\varphi_m^{(0)}\right\rangle . \tag{19.18}$$

Correspondingly, the state with first-order correction is given by

$$|\varphi\rangle = \left|\varphi_n^0\right\rangle + \varepsilon \sum_{m\neq n} \frac{\left\langle\varphi_m^{(0)}\right| \hat{W} \left|\varphi_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \left|\varphi_m^{(0)}\right\rangle = \left|\varphi_n^0\right\rangle + \sum_{m\neq n} \frac{\left\langle\varphi_m^{(0)}\right| W \left|\varphi_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \left|\varphi_m^{(0)}\right\rangle . \tag{19.19}$$

With (19.12) and (19.18), the corrections which are of first order in the smallness parameter ε are known. In principle and if necessary, one can perform the calculation for higher powers of ε, but we will not do that here.

19.2 Stationary Perturbation Theory, Degenerate

We now assume that the initial spectrum is degenerate:

$$H^{(0)} \left|\varphi_{n,i}^{(0)}\right\rangle = E_n^{(0)} \left|\varphi_{n,i}^{(0)}\right\rangle;\ i = 1, \ldots, g_n \tag{19.20}$$

where g_n is the degree of degeneracy of $E_n^{(0)}$. The states are pairwise orthogonal[4]:

$$\left\langle\varphi_{n,j}^{(0)} \middle| \varphi_{n,k}^{(0)}\right\rangle = \delta_{jk}. \tag{19.21}$$

The initial state of energy $E_n^{(0)}$ is then a superposition of all the degenerate states:

$$\left|\varphi_n^{(0)}\right\rangle = \sum_i c_i \left|\varphi_{n,i}^{(0)}\right\rangle;\ c_i \in \mathbb{C}. \tag{19.22}$$

For simplicity, we restrict ourselves to the calculation of the energy correction. We start from (19.11) and multiply from the left by $\left\langle\varphi_{n,k}^{(0)}\right|$. This gives

$$\left\langle\varphi_{n,k}^{(0)}\right| H^{(0)} \left|\varphi_n^{(1)}\right\rangle + \left\langle\varphi_{n,k}^{(0)}\right| \hat{W} \left|\varphi_n^{(0)}\right\rangle = \left\langle\varphi_{n,k}^{(0)}\right| E_n^{(0)} \left|\varphi_n^{(1)}\right\rangle + \left\langle\varphi_{n,k}^{(0)}\right| E_n^{(1)} \left|\varphi_n^{(0)}\right\rangle. \tag{19.23}$$

Again, we have

$$\left\langle\varphi_{n,i}^{(0)} \middle| \varphi_n^{(1)}\right\rangle = 0;\ i = 1, \ldots, g_n \tag{19.24}$$

The first terms on both sides vanish. What remains is

$$\sum_i \left\langle\varphi_{n,k}^{(0)}\right| \hat{W} \left|\varphi_{n,i}^{(0)}\right\rangle c_i = \sum_i \left\langle\varphi_{n,k}^{(0)}\right| E_n^{(1)} \left|\varphi_{n,i}^{(0)}\right\rangle c_i = E_n^{(1)} c_k. \tag{19.25}$$

On the left, we use the abbreviation $\left\langle\varphi_{n,k}^{(0)}\right| \hat{W} \left|\varphi_{n,i}^{(0)}\right\rangle = \hat{W}_{ki}$. The equation (dimension g_n) is then written as follows:

$$\sum_i \hat{W}_{ki} c_i = E_n^{(1)} c_k;\ i, k = 1, \ldots, g_n \tag{19.26}$$

and this is an eigenvalue problem with the matrix $\mathbb{W} = \left(\hat{W}_{ki}\right)$ and the column vector $\mathbf{c}$:

$$\mathbb{W}\mathbf{c} = E_n^{(1)}\mathbf{c}. \tag{19.27}$$

[4] We can always make this assumption. It is guaranteed by standard methods of linear algebra that one can construct such states, if necessary.

At this point, the usual machinery of linear algebra takes over. We obtain the characteristic polynomial; according to the fundamental theorem of algebra, there are g_n solutions for $E_n^{(1)}$ which can partially coincide. If all eigenvalues are unequal, the degeneracy is removed completely, otherwise only partly. The simplest case is that $\mathbb{W}$ is diagonal from the outset and the $\hat{W}_{kk}$ are all unequal; then the solution values $E_n^{(1)}$ are just the g_n different diagonal elements $\hat{W}_{kk}$, $k = 1, \ldots, g_n$.

19.3 Hydrogen: Fine Structure

In this section, we want to look at the hydrogen spectrum in more detail using perturbation theory. We first describe some correction terms W and then explore their consequences.

Concerning the Hamiltonian and the spectrum of the hydrogen atom, we have thus far not considered the electron's *spin*. In fact, the spin is a purely relativistic phenomenon and can be 'patched' into the SEq only heuristically. As we have already noted in Chap. 17, the hydrogen atom is described in a relativistically correct manner by the Dirac equation (see also Appendix U, Vol. 1, and Appendix F, Vol. 2). Performing an expansion in terms of powers of $(v/c)^2$ of this equation, one finds relativistic corrections of various kinds to the nonrelativistic Hamiltonian $H^{(0)}$. This operator, which was the starting point of our consideration of the hydrogen atom in Sect. 17.2, is the unperturbed Hamiltonian for the following perturbation calculation[5]:

$$H^{(0)} = \frac{\mathbf{p}^2}{2m} - \frac{\gamma}{r}; \quad \gamma = \frac{e^2}{4\pi\varepsilon_0}; \quad E_n^{(0)} = -\frac{mc^2\alpha^2}{2n^2}. \tag{19.28}$$

There are three different correction terms:

$$H = H^{(0)} + W_{mp} + W_{ls} + W_D. \tag{19.29}$$

19.3.1 Relativistic Corrections to the Hamiltonian

The term W_{mp} takes into account the relativistic dependence of the mass on its velocity in a first approximation. We expand $E = \sqrt{m^2c^4 + p^2c^2}$ for small momentum and find $E = mc^2 + \frac{\mathbf{p}^2}{2m} - \frac{\mathbf{p}^4}{8m^3c^2} + \cdots$, i.e.

$$W_{mp} = -\frac{\mathbf{p}^4}{8m^3c^2}. \tag{19.30}$$

[5] We use here the rest mass m and not the reduced mass μ, since an equivalent one-body problem does not exist for the Dirac equation. For nuclear charge (proton number) $Z \neq 1$, we have $\gamma = \frac{Ze^2}{4\pi\varepsilon_0}$.

The term W_{ls} (called the spin-orbit coupling) describes the interaction between the electron's orbital angular momentum $\mathbf{l}$ and its spin $\mathbf{s}$. Heuristically, one can explain this effect by the fact that a magnetic moment is associated with each of the two angular momenta; these moments interact. The result is[6]

$$W_{ls} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{\mathrm{d}V\,(r)}{\mathrm{dr}}\mathbf{l}\cdot\mathbf{s} = \frac{1}{2m^2c^2}\frac{\gamma}{r^3}\mathbf{l}\cdot\mathbf{s}. \tag{19.31}$$

The term W_D (called the Darwin term[7]) also follows from the Dirac equation. It is given by

$$W_D = \frac{\hbar^2}{8m^2c^2}\boldsymbol{\nabla}^2 V\,(r) = \frac{\pi\hbar^2\gamma}{2m^2c^2}\delta\,(\mathbf{r}) \tag{19.32}$$

where we have used[8] $\boldsymbol{\nabla}^2\frac{1}{r} = -4\pi\delta\,(\mathbf{r})$. Due to the delta function, this term affects only s orbitals, since only for these is $\psi\,(0) \neq 0$ (because of $R_{nl} \sim r^l$ for $r \to 0$).

Taking into account the correction terms in (19.29) has immediately two consequences: First, the spin *must* occur in the wavefunction. In the simplest case, the space-dependent part, which we have hitherto considered exclusively, is multiplied by a two-component vector which describes the two possibilities of spin orientation (similar to the polarization states for light). The degeneracy of the n levels then increases by a factor of 2, to $2n^2$.

Secondly, we must look for a new CSCO. For the unperturbed problem (19.28), the three commuting Hermitian operators $H^{(0)}$, $\mathbf{l}^2$ and l_z form a CSCO, as we have seen in Sect. 17.3. Accordingly, we can denote the states by the three quantum numbers n, l and m_l, for example in the form $|n, l, m_l\rangle$. If we consider also the spin $\mathbf{s}$ in the eigenfunctions of (19.28), we can write $|n, l, m_l, m_s\rangle$ (since the total spin value s does not change, one omits the $\frac{1}{2}$ in $\left|n, l, m_l, \frac{1}{2}, m_s\right\rangle$).[9] The CSCO thus consists of $H^{(0)}$, $\mathbf{l}^2$, l_z and s_z.

But for the problem (19.29), H, $\mathbf{l}^2$, l_z and s_z do *not form* a CSCO. This is due to the spin-orbit coupling W_{ls}, which prevents l_z and s_z from commuting with H, $\left[H, l_z\right] \neq 0$ and $\left[H, s_z\right] \neq 0$. The total angular momentum $\mathbf{j}$, i.e. the sum of orbital angular momentum and spin

$$\mathbf{j} = \mathbf{l} + \mathbf{s} \tag{19.33}$$

provides a remedy, since $\mathbf{j}^2$ and j_z commute with H and $\mathbf{l}^2$ (see the exercises). Hence, H, $\mathbf{j}^2$, j_z and $\mathbf{l}^2$ form a (new) suitable CSCO and the states can be classified according

[6] See also Chap. 16 (angular momentum). There, we abbreviated the prefactor of $\mathbf{l}\cdot\mathbf{s}$ by $F(r)$.

[7] No, not an evolutionary term. Charles Galton Darwin (1887–1962), physicist, was a grandson of *the* Charles Darwin. Also known as the *Zitterbewegung* ('dithering motion', from the German).

[8] See Appendix F, Vol. 1.

[9] In the position representation, the states take the form

$$\psi_{n,l,m_l,m_s}\,(\mathbf{r}) = \langle\mathbf{r}|\,n, l, m_l\rangle\begin{pmatrix} m_{s\uparrow} \\ m_{s\downarrow}\end{pmatrix}$$

.

to the four quantum numbers n, j, m_j and l. So we can write $\left|n;\ j, m_{j;} l\right\rangle$. These states form a CONS,

$$\left\langle n;\ j', m'_{j;} l' \right| n;\ j, m_{j;} l\rangle = \delta_{j\acute{j}'} \delta_{m_j m'_j} \delta_{ll'} . \tag{19.34}$$

According to the rules of angular-momentum addition, we start out from the following states:

$$\left|\varphi_n^{(0)}\right\rangle = \left|n;\ j, m_{j;} l\right\rangle ;\ \ j = l \pm \frac{1}{2} \text{ for } l \geq 1 \ ; \ j = \frac{1}{2} \text{ for } l = 0. \tag{19.35}$$

Note that in the position representation, the radial component is given by the function $R_{nl}(r)$, introduced in Chap. 17. Although we do not need the explicit form of the states which we derived in Chap. 16 for the following, we give it here for the sake of completeness:

$$\left|n;\ j = l \pm 1/2, m_{j;} l\right\rangle = \begin{pmatrix} \pm\sqrt{\frac{l \pm m_j + 1/2}{2l+1}} \left|n; l, m_j - 1/2\right\rangle \\ \sqrt{\frac{l \mp m_j + 1/2}{2l+1}} \left|n; l, m_j + 1/2\right\rangle \end{pmatrix}$$
$$\text{with } \ m_j = l \pm 1/2, \ldots, -(l \pm 1/2) . \tag{19.36}$$

19.3.2 Results of Perturbation Theory

With the functions (19.35), we now carry out the perturbation treatment for degenerate states,[10] cf. (19.26). We have seen there that the corrections $E_n^{(1)}$ can be quite easily calculated, if the matrix $\left(\hat{W}_{ki}\right)$ is diagonal. As it turns out, this is the case for all three relativistic corrections. For brevity, we use the notation $\langle A\rangle = \left\langle n;\ j', m'_j; l\right| A \left|n;\ j, m_j; l\right\rangle$. In particular, we obtain (a somewhat more detailed analysis is given in Appendix H, Vol. 2):

$$\left\langle W_{mp}\right\rangle = -\frac{1}{2mc^2} \left\{ \left(E_n^{(0)}\right)^2 + 2E_n^{(0)} \gamma \left\langle \frac{1}{r} \right\rangle + \gamma^2 \left\langle \frac{1}{r^2} \right\rangle \right\} \delta_{j'j} \delta_{m'_j m_j} . \tag{19.37}$$

The next term exists for $l \neq 0$ only:

$$\left\langle W_{ls}\right\rangle = \frac{\gamma\hbar^2}{2m^2c^2} \frac{1}{2} \left[j\,(j+1) - l\,(l+1) - \frac{3}{4} \right] \left\langle \frac{1}{r^3} \right\rangle \delta_{j'j} \delta_{m'_j m_j} . \tag{19.38}$$

The last term occurs only for $l = 0$; it is given by

[10] In the following, we treat the degeneracy of n and l; the removal of the m-degeneracy is possible only by applying external fields.

$$\langle W_D \rangle = \frac{\pi \hbar^2 \gamma}{2m^2 c^2} \left| R_{n0}(0) \right|^2 \delta_{j'j} \delta_{m'_j m_j}. \tag{19.39}$$

We add these fine-structure corrections and obtain initially

$$E_n^{(1)} = -\frac{1}{2mc^2} \left\{ \begin{array}{c} \left(E_n^{(0)}\right)^2 + 2E_n^{(0)} \gamma \left\langle \frac{1}{r} \right\rangle + \gamma^2 \left\langle \frac{1}{r^2} \right\rangle \\ -\frac{\gamma \hbar^2}{m} \frac{1}{2} \left[j(j+1) - l(l+1) - \frac{3}{4} \right] \left\langle \frac{1}{r^3} \right\rangle \\ -\frac{\pi \hbar^2 \gamma}{m} \left| R_{n0}(0) \right|^2 \end{array} \right\} \delta_{j'j} \delta_{m'_j m_j}. \tag{19.40}$$

The mean values within the brackets can be calculated (see Appendix B, Vol. 2). We do not need to do this explicitly here and simply adopt the results. For the proton number $Z = 1$ (i.e. $\gamma = \frac{e^2}{4\pi\varepsilon_0}$), we obtain

$$E^{(1)}_{n,j\,=\,l\pm\frac{1}{2},l} = \frac{mc^2\alpha^4}{2n^4} \left\{ \frac{3}{4} - \frac{n}{j+\frac{1}{2}} \right\} \tag{19.41}$$

where α is the fine-structure constant, $\alpha \approx 1/137$.

19.3.3 Comparison with the Results of the Dirac Equation

With these corrections, we obtain the following energy levels for the hydrogen atom:

$$E_{nj} = -mc^2 \frac{\alpha^2}{2n^2} \left\{ 1 - \frac{\alpha^2}{n^2} \left(\frac{3}{4} - \frac{n}{j+\frac{1}{2}} \right) \right\}. \tag{19.42}$$

For comparison: the Dirac equation gives (see Appendix F, Vol. 2)

$$E_{nj} = mc^2 \left\{ 1 + \alpha^2 \left[n - j - \frac{1}{2} + \sqrt{\left(j+\frac{1}{2}\right)^2 - \alpha^2} \right]^{-2} \right\}^{-\frac{1}{2}} - mc^2. \tag{19.43}$$

Expanding this expression in powers of α^2 and retaining only the terms $\sim\alpha^2$ and $\sim\alpha^4$, one obtains the approximate expression (19.42).[11] We see that the energy corrections are smaller than the initial values by a (relative) factor of $\alpha^2 \approx 5 \cdot 10^{-5}$—hence the name 'fine structure'. In addition, the energy levels evidently depend not only on the principal quantum number n but also on j. So we have a partial lifting of the degeneracy of the hydrogen levels. These levels are denoted by the quantum

[11] Numerical values: $mc^2\alpha^2 = 2 \cdot 13.6\,\text{eV}$, $mc^2\alpha^4 = 1.45 \cdot 10^{-3}\,\text{eV}$ (see also Appendix B, Vol. 1).

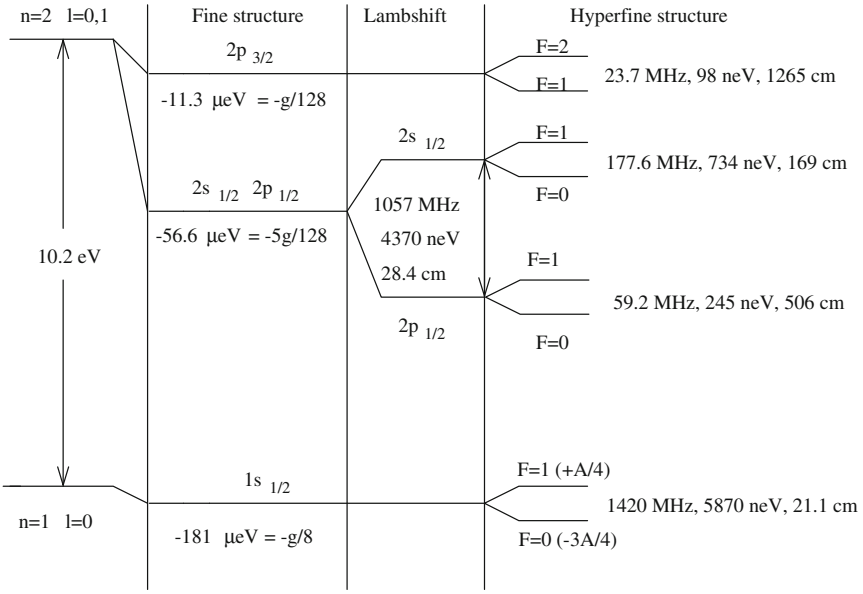

Fig. 19.1 Fine and hyperfine structure of the hydrogen atom. Abbreviations: $g = mc^2\alpha^4 = 1.45 \cdot 10^{-3}$ eV, $A = 1,420$ MHz. The finite size of the nucleus is not taken into account. Scales are not preserved

numbers n, l, j in the form nl_j, where for l the nomenclature $s, p, d, \ldots$ is used.[12] As a result of perturbation theory, we have for $n = 1$ a slight lowering of the $1s_{1/2}$ levels and for $n = 2$ a splitting into a $2p_{3/2}$ level and a degenerate $2s_{1/2} - 2p_{1/2}$ level. Similar statements hold for higher principal quantum numbers. In the context of the assumptions made here, the $2s_{1/2} - 2p_{1/2}$ degeneracy is valid for any power of α^2 (compare the relativistically correct expression (19.43)). The changes in the spectrum are shown schematically in Fig. 19.1.

19.4 Hydrogen: Lamb Shift and Hyperfine Structure

A particularly accurate (denoted by 'hyperfine') consideration of the hydrogen spectrum shows that further corrections have to be applied to the previously obtained results. They are also shown schematically in Fig. 19.1. The reasons for these additional corrections are:

[12] Another common notation uses s, l, j and reads $^{2s+1}l_j$.

1. Quantum electrodynamic effects remove the $2s_{1/2} - 2p_{1/2}$ -degeneracy. This so-called Lamb shift is about $4 \cdot 10^{-6}$ eV.
2. Hyperfine structure: the spins of the nucleus and of the electron interact with each other. They can add up to the total spin $F = 0$ (singlet) or $F = 1$ (triplet). The interaction term is proportional to $\mathbf{s}_N \cdot \mathbf{s}_e = \frac{\mathbf{F}^2 - \mathbf{s}_N^2 - \mathbf{s}_e^2}{2} = \frac{\hbar^2}{2}\left[F\,(F+1) - \frac{3}{2}\right]$ and leads to a splitting of the $1s_{1/2}$ levels of the form

$$E_{F=1} = E^{(0)} + \frac{1}{4}A;\;\; E_{F\,=\,0} = E^{(0)} - \frac{3}{4}A;\;\; E_{F=1} - E_{F=0} = A$$
$$\text{with} \quad A = (1420405751.768 \pm 0.001)\ \text{Hz}. \tag{19.44}$$

   The term $A \approx 1,420\,\text{MHz}$ is one of the most precisely measured quantities in physics; the theory describes correctly the first six digits. The transition $E_{F\,=\,1} - E_{F\,=\,0}$ is used in the hydrogen maser, but also plays an important role in astrophysics. By detecting it, one gains information about the interstellar hydrogen clouds, which at 10–50% account for a significant proportion of the mass of galaxies. In this context, one also speaks of the 21 cm line; see the conversion table for energy units in Appendix B, Vol. 1. Because of their greater probability density at the nucleus, the hyperfine correction is most noticeable for s levels; in addition, the splitting of energy levels is proportional to n^{-3}.
3. Equation (19.28) contains the Coulomb or point interaction $-\frac{\gamma}{r}$, but the nucleus has finite dimensions. This effect also leads to a correction, namely to a shift of the levels, which again is most marked for the s levels and is proportional to n^{-3}. For the lowest s level, the correction is about $4 \cdot 10^{-9}$ eV. Finally, there are isotope effects in the hyperfine structure; on the one hand, isotopes lead to different reduced masses; on the other hand, different nuclear isotopes have different charge distributions (volume effect).

A practical application of the interaction of nuclear spins with their environment is *nuclear magnetic resonance spectroscopy* (NMR spectroscopy). The simplified operating principle is as follows: A sample contains hydrogen atoms whose nuclear spins (nucleus = proton) are aligned by an external homogeneous magnetic field. The sample is additionally irradiated with a single radio frequency pulse (RF pulse) or with a sequence of RF pulses. After the decay of the RF pulse, the protons in the sample exchange energy with each other and with the surrounding environment. This leads to a return to the equilibrium state (relaxation), i.e. to a measurable change in the (nuclear) magnetization. The decay time of this signal depends on the environment of the proton—in solid matter, the damping is much stronger than in liquids, for instance.

19.5 Exercises

1. Given
$$H = H^{(0)} + F(r)\,\mathbf{l}\cdot\mathbf{s} = \frac{\mathbf{p}^2}{2m} + V(r) + F(r)\,\mathbf{l}\cdot\mathbf{s}. \tag{19.45}$$
(a) Show that:
$$\left[H^{(0)}, l_z\right] = \left[H^{(0)}, s_z\right] = 0; \tag{19.46}$$
(b) Show that:
$$\left[H, l_z\right] \neq 0;\ \ \left[H, s_z\right] \neq 0;\ \ \left[H, j_z\right] = 0. \tag{19.47}$$
Hint: See the exercises for Chap. 16.
2. Expand the expression for the relativistic energy levels of the hydrogen atom:
$$E_{nj} = mc^2\left\{1 + \alpha^2\left[n - j - \frac{1}{2} + \sqrt{\left(j+\frac{1}{2}\right)^2 - \alpha^2}\right]^{-2}\right\}^{-\frac{1}{2}} - mc^2 \tag{19.48}$$
and compare with the approximation deduced in the text.
3. Given the Hamiltonian
$$H\,|\varphi\rangle = \left(H^{(0)} + W\right)|\varphi\rangle = \left(H^{(0)} + \varepsilon\hat{W}\right)|\varphi\rangle = E\,|\varphi\rangle\,, \tag{19.49}$$
where the states and the eigenvalues of $H^{(0)}\left|\varphi_n^{(0)}\right\rangle = E_n^{(0)}\left|\varphi_n^{(0)}\right\rangle$ are known (discrete, nondegenerate). The initial state is $\left|\varphi_n^{(0)}\right\rangle$ and the corresponding energy is $E_n^{(0)}$. States and energies are expanded in terms of ε
$$|\varphi\rangle = \left|\varphi_n^{(0)}\right\rangle + \varepsilon\left|\varphi_n^{(1)}\right\rangle + \varepsilon^2\left|\varphi_n^{(2)}\right\rangle + \cdots;\ E = E_n^{(0)} + \varepsilon E_n^{(1)} + \varepsilon^2 E_n^{(2)} + \cdots \tag{19.50}$$
We can assume from the outset that the correction terms are orthogonal to the initial state, $\left\langle\varphi_n^{(0)}\ \middle|\ \varphi_n^{(j)}\right\rangle = 0$ for $j \neq 0$. Calculate the corrections to the energy and the state to first order ($\sim\varepsilon^1$, repetition) and to second order ($\sim\varepsilon^2$).
4. We add a perturbation $\sim q^3$ to the Hamiltonian of the harmonic oscillator:
$$H = H^0 + W = -\frac{\hbar^2}{2m}\frac{d^2}{dq^2} + \frac{1}{2}m\omega^2 q^2 + \varepsilon q^3. \tag{19.51}$$
Calculate the correction term of the energy $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$ to first order.
5. Finite nuclear size: For a hydrogen atom, we model the finite core size by the potential

$$V(r) = \begin{cases} -\frac{\gamma}{r} & \text{for } r \geq r_0 \\ \frac{\gamma}{2r_0}\left[\left(\frac{r}{r_0}\right)^2 - 3\right] & \text{for } r \leq r_0 \end{cases} \tag{19.52}$$

(Thus, we replace the point nucleus by a homogenously-charged sphere of radius r_0 with the charge density ρ_0). Calculate the corrections to the energy in first order. Assume that the radial functions $R_{nl}(r)$ can be approximated for $r \leq r_0$ by $R_{nl}(0)$.