Table 5.4. Comparison of the measured wavenumbers of the Balmer series and the calculated values obtained from the Rydberg formula

	n	λ_{air}/Å	$\bar{\nu}_{vac}$/cm^{-1}	ν_{Ry}/cm^{-1}
H_α	3	6562.79	15,233.21	15,233.00
H_β	4	4861.33	20,564.77	20,564.55
H_γ	5	4340.46	23,032.54	23,032.29
H_δ	6	4101.73	24,373.07	24,372.80
H_ε	7	3970.07	25,181.33	25,181.08
H_ζ	8	3889.06	25,705.84	25,705.68
H_η	9	3835.40	26,065.53	26,065.35
H_ϑ	10	3797.91	26,322.80	26,322.62
H_ι	11	3770.63	26,513.21	26,512.97
H_κ	12	3750.15	26,658.01	26,657.75
H_λ	13	3734.37	26,770.65	26,770.42
H_μ	14	3721.95	26,860.01	26,859.82
H_ν	15	3711.98	26,932.14	26,931.94

c) The experimentally observed splittings of the Zeeman components agrees only for a few atomic species with the prediction of the normal Zeeman pattern. For most atoms it is more complicated. For the H atom, for instance, it looks completely different from the regular triplet pattern in Fig. 5.12.

d) The ground state of the H atom ($n = 1, l = 0$) shows a very narrow splitting into two components (hyperfine structure), which differs for the two isotopes ^{1}H and ^{2}H = ^{2}D.

In order to explain these deviations, the Schrödinger theory has to be extended and new atomic parameters have to be included. This will be discussed in the next sections.

5.4 Relativistic Correction of Energy terms

Part of the deviation between experimental results and theoretical predictions of the energy term values (5.18) can be explained when the relativistic mass increase of the electron during its motion around the nucleus is taken into account.

Instead of the nonrelativistic energy relation

$$E = p^2/2m + E_{pot} \tag{5.38}$$

anticipated by the Schrödinger theory, we have to use the relativistic energy relation

$$E = c\sqrt{m_0^2c^2 + p^2} - m_0c^2 + E_{pot} . \tag{5.39}$$

For the electron in the hydrogen atom, the velocity v of the electron is still small compared to the velocity of light c, which means that $E_{kin} \ll m_0c^2$ or $p^2/m_0^2c^2 \ll 1$. We can therefore expand the square root in (5.39) into the power series

$$\sqrt{1 + \frac{p^2}{m_0^2c^2}} = 1 + \frac{1}{2}\frac{p^2}{m_0^2c^2} - \frac{1}{8}\frac{p^4}{m_0^4c^4} + \dots ,$$

which gives for the energy expression (5.38)

$$E = \left(\frac{p^2}{2m_0} + E_{pot}\right) - \frac{p^4}{8m_0^3c^2} + \dots = E_{nr} - \Delta E_r . \tag{5.40}$$

For $E_{kin} \ll m_0c^2$ we can neglect the higher order terms. In this approximation the last term in (5.40) represents the relativistic correction ΔE_r to the nonrelativistic energy (5.38).

We can obtain the quantum mechanical expectation value of this correction by substituting $p \to ih$, which leads to the expression

$$\Delta E_r = \frac{\hbar^4}{8m_0^3c^2}\int \psi^*_{n,l,m}\nabla^4\psi_{n,l,m}\,d\tau . \tag{5.41}$$

Inserting for ψ the wave functions of the hydrogen atom $\psi_{n,l,m}$ gives the "Darwin term" (see Problem 5.6)

$$\Delta E_r = E_{nr}\frac{Z^2\alpha^2}{n}\left(\frac{3}{4n} - \frac{1}{l+1/2}\right) . \tag{5.42}$$

The constant

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} = 7.297353 \times 10^{-3} = \frac{1}{137} \tag{5.43}$$

is called ***Sommerfeld's fine structure constant.***

The total energy of an eigen-state for the H atom is then

$$E_{n,l} = -Ry\frac{Z^2}{n^2}\left[1 - \frac{\alpha^2Z^2}{n}\left(\frac{3}{4n} - \frac{1}{l+1/2}\right)\right] , \tag{5.44}$$

which now depends not only on n but also on l! The relativistic correction is maximum for $n = 1$ and $l = 0$.

not be explained by the Schrödinger theory. Since this splitting is very small and can be only resolved with high resolution spectrographs, where the hydrogen lines appear as a fine substructure, it was named fine structure.

We start with a semiclassical model, treating the angular momenta as vectors with quantized absolute values and quantized z components. In Sect. 5.2 it was shown that an electron with charge $-e$, moving with the orbital angular momentum l on a circle around the nucleus, produces a magnetic moment

$$\mu_l = -\frac{e}{2m_e} l = -(\mu_B/\hbar)\cdot l\,.$$

That is proportional to l.

In a coordinate system where the electron rests at the origin, the nucleus with positive charge $Z\cdot e$ moves with the frequency ν on a circle around the electron. This causes a circular current $Ze\nu$ that produces a magnetic field B at the location of the electron (Fig. 5.18). According to Biot–Savart's law (see textbooks on magnetic fields) this magnetic field is

$$B_l = \frac{\mu_0 Ze}{4\pi r^3}(v\times(-r)) = -\frac{\mu_0 Ze}{4\pi r^3}(v\times r)$$
$$= +\frac{\mu_0 Ze}{4\pi r^3 m_e} l \qquad (5.54)$$

because the angular momentum l_p of the proton equals the negative angular momentum $l = m_e(r\times v)$ of the electron in a coordinate system where the electron moves around the proton at rest.

The magnetic spin moment of the electron has two spatial orientations in this field according to the two spin directions $s_z = \pm h/2$. This causes an additional energy (in addition to the Coulomb energy)

$$\Delta E = -\mu_s\cdot B_l = g_s\mu_B\frac{\mu_0 Ze}{4\pi r^3 m_e\hbar}(s\cdot l)$$
$$\approx \frac{\mu_0 Ze^2}{4\pi m_e^2 r^3}(s\cdot l)\,.$$

Transforming the coordinate system back to the rest frame of the nucleus by a Lorentz transformation gives a factor 1/2 (Thomas factor [5.2]), which is due to the fact that the electron spin in the rest-frame of the nucleus precesses when moving around the nucleus (Thomas precession).

The energy levels E_n of (5.18), which had been obtained without taking into account the electron spin, now split, due to the spin-orbit coupling, into the fine structure components with energies

$$E_{n,l,s} = E_n - \mu_s\cdot B_l = E_n + \frac{\mu_0 Ze^2}{\pi m_e^2 r^3}(s\cdot l)\,. \qquad (5.5$$

The scalar product $(s\cdot l)$ may be positive or negative depending on the orientation of the spin relative to the orbital angular momentum.

When we introduce the total angular momentum

$$j = l + s \quad \text{with} \quad |j| = \sqrt{j(j+1)}\hbar \qquad (5.57$$

as a vector sum of orbital angular momentum l and electron spin s (Fig. 5.19), we can square this sum and obtain

$$j^2 = l^2 + s^2 + 2l\cdot s\,. \qquad (5.57b)$$

This gives for the scalar product

$$l\cdot s = \frac{1}{2}\hbar^2[j(j+1) - l(l+1) - s(s+1)]\,. \qquad (5.58$$

With this relation we can write (5.56) as

$$E_{n,l,j} = E_n + \frac{a}{2}[j(j+1) - l(l+1) - s(s+1)]\,. \qquad (5.59$$

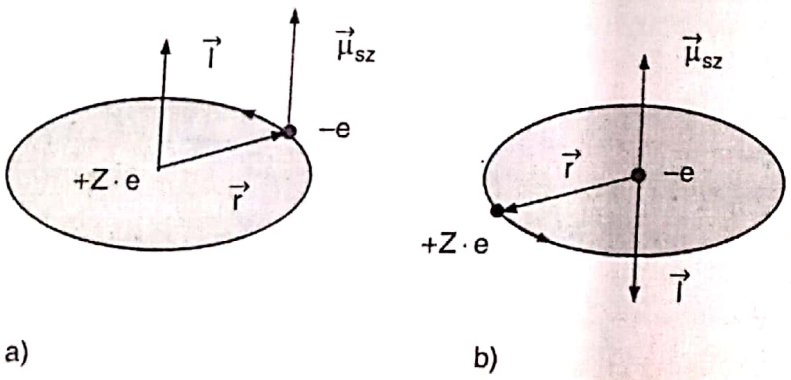

Fig. 5.18a,b. Vector model of spin-orbit interaction. **(a)** vector model. **(b)** transformation to a coordinate system, where the electron rests at $r = 0$

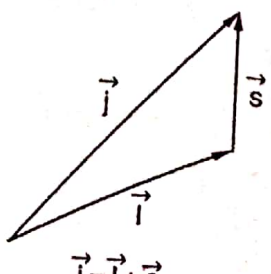

Fig. 5.19. Vector coupling of orbital angular momentum l and electron spin s to form the total angular momentum j of the electron

Fig. 5.20. Energy level scheme of fine structure splitting of $3^2P(l=1)$ state

ith the spin-orbit coupling constant

$$a = \frac{\mu_0 Z e^2 \hbar^2}{8\pi m_e^2 r^3} \,. \tag{5.59b}$$

he energy levels split, depending on the orientation of e spin, into the two components with $j = l + 1/2$ and $= l - 1/2$ (see Fig. 5.20). Finestructure splittings are bserved only for levels with $l \geq 1$, i.e. for $p, d, f, \ldots$ vels, *not* for s-levels with $l = 0$.

> The fine structure may be regarded as Zeeman splitting due to the interaction of the magnetic spin moment with the internal magnetic field generated by the orbital motion of the electron.

In the quantum mechanical model the distance r f the electron from the nucleus cannot be given exactly. Only the time-averaged value of r related to the probability of finding the electron at the location r is a measurable quantity

$$\langle r \rangle = \int \psi^*_{n,l,m} r \psi_{n,l,m} \, d\tau \Rightarrow$$

$$\left\langle \frac{1}{r^3} \right\rangle = \int \psi_{n,l,m} \frac{1}{r^3} \psi_{n,l,m} \, d\tau \,. \tag{5.60a}$$

The quantum mechanical average $\langle a \rangle$ of the spin-orbit coupling constant is then

$$\langle a \rangle = \frac{\mu_0 Z e^2 \hbar^2}{8\pi m_e^2} \int \psi^*_{n,l,m} \frac{1}{r^3} \psi_{n,l,m} \, d\tau \,. \tag{5.60b}$$

Inserting the hydrogen wave functions $\psi_{n,l,m}(r, \vartheta, \varphi)$, the integral can be solved and one obtains

$$\langle a \rangle = -E_n \frac{Z^2 \alpha^2}{nl(l+1/2)(l+1)} \,, \tag{5.61}$$

where the constant

$$\alpha = \frac{\mu_0 c e^2}{4\pi h} = \frac{e^2}{4\pi \varepsilon_0 \hbar c} \approx \frac{1}{137} \tag{5.62}$$

is Sommerfeld's fine structure constant, which was already introduced in Sect. 5.4 for the relativistic correction of the level energies.

The energy separation of the two fine structure components $(n, l, j = l + 1/2)$ and $(n, l, j = l - 1/2)$ is then, according to (5.59) and (5.61),

$$\Delta E_{l,s} = \langle a \rangle \left(l + \frac{1}{2} \right) = -E_n \frac{Z^2 \alpha^2}{nl(l+1)}$$

$$\approx -5.3 \times 10^{-5} E_n \frac{Z^2}{nl(l+1)} \,. \tag{5.63}$$

This shows that the splitting is very small compared to the energy $E_{n,l}$ of the levels (n, l) and justifies the name "fine structure."

As can be seen from (5.63), the fine structure splitting decreases with increasing quantum numbers n and l, but it increases proportionally to the product $Z^2 E_n$. Since the energies E_n of the levels with principal quantum number n follow the relation $E_n \propto Z^2/n^2$, we can write the fine structure splitting as

$$\Delta E_{l,s} \propto \frac{Z^4}{n^3 l(l+1)} \,. \tag{5.64}$$

EXAMPLE

For the $2p$ level of the H atom, we have $Z = 1$, $n = 2$, $l = 1$ and $E_n = -3.4\,\text{eV}$. From (5.63) we therefore obtain for the fine structure splitting $\Delta E_{l,s} = 4.6 \times 10^{-5}\,\text{eV} \Rightarrow \Delta E_{l,s}/hc = \Delta\tilde{\nu} = 0.37\,\text{cm}^{-1}$.

If both effects, the relativistic increase of the electron mass and the spin-orbit coupling, are taken into account we have to add (5.42) and (5.63) and obtain for the energy of a fine structure component (n, l, j) (see Problem 5.7)

$$E_{n,j} = E_n \left[1 + \frac{Z^2 \alpha^2}{n} \left(\frac{1}{j + 1/2} - \frac{3}{4n} \right) \right] \,, \tag{5.65}$$

which turns out to be independent of l.

> In the Coulomb field with $E_{\text{pot}} \propto 1/r$ the energy of a fine structure component (n, l, j) does not depend on the quantum number l. All levels with equal quantum numbers n and j have the same energy (Fig. 5.21).