
Atoms and Ions

This chapter summarizes the traditional theory of one- and many-electron systems, which has been developed and successfully applied to many atomic problems for almost a century. The presentation is deliberately brief. A more detailed introduction to atomic physics can be found in the textbook by Bransden and Joachain [BJ83]. At a much more formal level there is “Atomic Many-Body Theory” by Lindgren and Morrison [LM85]. Finally we mention “Atomic Structure” by Condon and Odabasi [CO80], where a comprehensive account of conventional atomic structure calculations can be found.

2.1 One-Electron Systems

2.1.1 The Hydrogen Atom

In non-relativistic quantum mechanics a system consisting of a proton of mass m_p and an electron of mass m_e is described by the following Hamiltonian:

$$\hat{H}_H = \frac{\hat{\mathbf{p}}_p^2}{2m_p} + \frac{\hat{\mathbf{p}}_e^2}{2m_e} - \frac{e^2}{|\mathbf{r}_e - \mathbf{r}_p|}, \quad (2.1)$$

where $\hat{\mathbf{p}}_p$ and $\hat{\mathbf{p}}_e$ are the momentum operators for the proton and the electron respectively, and \mathbf{r}_p and \mathbf{r}_e are the respective spatial coordinates. Introducing the centre-of-mass coordinate \mathbf{R} and the relative distance coordinate \mathbf{r} ,

$$\mathbf{R} = \frac{m_p \mathbf{r}_p + m_e \mathbf{r}_e}{m_p + m_e}, \quad \mathbf{r} = \mathbf{r}_e - \mathbf{r}_p, \quad (2.2)$$

we can rewrite (2.1) as

$$\hat{H}_H = \frac{\hat{\mathbf{P}}^2}{2(m_p + m_e)} + \frac{\hat{\mathbf{p}}^2}{2\mu} - \frac{e^2}{r}, \quad (2.3)$$

where $\hat{\mathbf{P}}$ is the total momentum and $\hat{\mathbf{p}}$ the relative momentum in the two-body system:

$$\hat{\mathbf{P}} = \hat{\mathbf{p}}_p + \hat{\mathbf{p}}_e, \quad \hat{\mathbf{p}} = \frac{\hat{\mathbf{p}}_e}{\mu} - \frac{\hat{\mathbf{p}}_p}{m_p}. \quad (2.4)$$

In coordinate representation the momentum operators have the explicit form:

$$\hat{\mathbf{P}} = \frac{\hbar}{i} \nabla_{\mathbf{R}}, \quad \hat{\mathbf{p}} = \frac{\hbar}{i} \nabla_{\mathbf{r}}. \quad (2.5)$$

The mass μ appearing in (2.3) and (2.4) is the *reduced mass*

$$\mu = \frac{m_e m_p}{m_e + m_p} = \frac{m_e}{1 + m_e/m_p}. \quad (2.6)$$

Since the ratio $m_e/m_p = 0.0005446170234$ (12) is very small (the numerical value is taken from [MT00]), the reduced mass μ is only little smaller than the rest mass m_e of the electron, namely by about $0.5^0/00$.

Thus the Hamiltonian \hat{H}_H consists of a part $\hat{\mathbf{P}}^2/[2(m_p + m_e)]$ describing the free motion of the centre of mass and an *internal Hamiltonian*,

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2\mu} - \frac{e^2}{r}, \quad (2.7)$$

describing the motion of the electron relative to the position of the proton. Eigenfunctions $\psi_{\text{cm}}(\mathbf{R})$ and eigenvalues E_{cm} for the centre-of-mass motion are known, $\psi_{\text{cm}}(\mathbf{R}) \propto \exp(i\mathbf{K} \cdot \mathbf{R})$, $E_{\text{cm}} = \hbar^2 K^2/[2(m_p + m_e)]$, so solving the two-body problem (2.1) or (2.3) is reduced to the problem of solving the one-body Schrödinger equation with the internal Hamiltonian (2.7).

This is just the one-body problem in an attractive Coulomb potential which was discussed in detail in Sect. 1.3.3. The energy eigenvalues are

$$E_n = -\frac{\mathcal{R}}{n^2}, \quad n = 1, 2, 3, \dots, \\ l = 0, 1, \dots, n-1, \\ m = -l, -l+1, \dots, l-1, l, \quad (2.8)$$

where the Rydberg energy $\mathcal{R} = \mu e^4/(2\hbar^2)$ is smaller by a factor μ/m_e than the Rydberg energy $\mathcal{R}_\infty = m_e e^4/(2\hbar^2)$ corresponding to a proton of infinite mass [BN97, UH97, MT00]:

$$\mathcal{R}_\infty = 2.1798719(2) \times 10^{-18} \text{ J} = 13.605692(2) \text{ eV}, \\ \mathcal{R}_\infty/(2\pi\hbar c) = 109737.315686(1) \text{ cm}^{-1}, \\ \mathcal{R}_\infty/(2\pi\hbar) = 3.28984196037(3) \times 10^{15} \text{ Hz}. \quad (2.9)$$

In coordinate space, the bound eigenfunctions of the Hamiltonian (2.7) have the form (1.74) and the radial wave functions are given by (1.138). The Bohr radius $a = \hbar^2/(\mu e^2)$ is larger by a factor m_e/μ than the Bohr radius $a_0 = \hbar^2/(m_e e^2)$ corresponding to an infinite proton mass. According to [MT00] the numerical value for a_0 is:

$$a_0 = 0.529177208(2) \times 10^{-8} \text{ cm}. \quad (2.10)$$

In *atomic units* we measure energies in units of twice the Rydberg energy and lengths in units of the Bohr radius, $\mathbf{r} \rightarrow a\mathbf{r}$, $\hat{\mathbf{p}} \rightarrow \hat{\mathbf{p}}\hbar/a$, $\hat{H} \rightarrow 2\mathcal{R}\hat{H}$. The time scale in atomic units is $t_0 = \hbar/(2\mathcal{R})$. Inserting the Rydberg energy \mathcal{R}_∞ corresponding to infinite proton mass we have [MT00], $t_0^\infty = \hbar/(2\mathcal{R}_\infty) = 0.241888432650(2) \times 10^{-16}$ s.

In atomic units and coordinate representation, the (internal) Hamiltonian for the hydrogen atom is:

$$\hat{H} = -\frac{1}{2}\Delta - \frac{1}{r}, \quad (2.11)$$

which corresponds to $\mu = 1$, $\hbar = 1$ and $e = 1$. In atomic units, the bound spectrum of the hydrogen atom is simply $E_n = -1/(2n^2)$ and the Bohr radius is unity.

2.1.2 Hydrogenic Ions

The considerations of the preceding section apply almost without change to a system consisting of an electron and an arbitrary atomic nucleus with charge number Z . Such a system is a *hydrogenic* ion which is $(Z - 1)$ -fold positively charged. In the formula for the reduced mass, the mass m_p must now be replaced by the mass m_{nuc} of the nucleus which depends not only on the charge number Z , but also on the mass number A (or equivalently, on the number of neutrons $A - Z$):

$$\mu = \frac{m_e m_{\text{nuc}}}{m_e + m_{\text{nuc}}} = \frac{m_e}{1 + m_e/m_{\text{nuc}}}. \quad (2.12)$$

Since $m_{\text{nuc}} > m_p$ for all nuclei barring the proton itself, μ is now even closer to the electron mass m_e .

For charge numbers $Z > 1$, the essential difference between a hydrogenic ion and the hydrogen atom lies in the potential energy which is stronger by a factor Z :

$$\hat{H}_Z = \frac{\hat{\mathbf{p}}^2}{2\mu} - \frac{Ze^2}{r}. \quad (2.13)$$

Looking at the formula (1.135) for the Rydberg energy and (1.102) for the Bohr radius we see that the formulae (2.8) for the energy eigenvalues and (1.138) for the radial wave functions still hold, provided we insert the Rydberg energy \mathcal{R}_Z instead of \mathcal{R} ,

$$\mathcal{R}_Z = \frac{Z^2 \mu e^4}{2\hbar^2}, \quad (2.14)$$

and the Bohr radius a_Z ,

$$a_Z = \frac{\hbar^2}{Z\mu e^2}, \quad (2.15)$$

instead of a . In atomic units the Hamiltonian \hat{H}_Z and the energy eigenvalues E_n are given by

$$\hat{H}_Z = -\frac{1}{2}\Delta - \frac{Z}{r}, \quad E_n = -\frac{Z^2}{2n^2}, \quad (2.16)$$

while the Bohr radius is $a_Z = 1/Z$.

The hydrogen atom and the hydrogenic ions He^+ , Li^{++} , Be^{+++} , ..., U^{91+} , ... constitute the simplest example of an *iso-electronic sequence*: atoms and ions with the same number of electrons have very similar spectra. In sequences with more than one electron however, the energies don't follow such a simple scaling rule as (2.16), because only the electron-nucleus part of the potential energy is proportional to Z , while the electron-electron interaction is independent of Z (see Sect. 2.2 and Sect. 2.3).

2.1.3 The Dirac Equation

The time-dependent Schrödinger equation (1.39) violates the symmetry requirements of special relativity, as is already obvious from the different roles played by the spatial coordinates and the time; the Schrödinger equation contains second derivatives with respect to the spatial coordinates, but only first derivatives with respect to time. As a way out of this situation Dirac proposed a Hamiltonian containing the momentum components $\hat{p}_x = (\hbar/i)\partial/\partial x$ etc. linearly. For a free particle of mass m_0 Dirac's Hamiltonian is

$$\hat{H} = c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}} + \beta m_0 c^2. \quad (2.17)$$

Here $c = 2.99792458 \times 10^8 \text{ ms}^{-1}$ is the speed of light, which is included so that the coefficient β and the vector of coefficients $(\alpha_x, \alpha_y, \alpha_z) \equiv (\alpha_1, \alpha_2, \alpha_3)$ are physically dimensionless.

The square of Dirac's Hamiltonian,

$$\begin{aligned} \hat{H}^2 = c^2 \sum_{i,k=1}^3 \frac{1}{2} (\alpha_i \alpha_k + \alpha_k \alpha_i) \hat{p}_i \hat{p}_k + m_0 c^3 \sum_{i=1}^3 (\alpha_i \beta + \beta \alpha_i) \hat{p}_i \\ + \beta^2 m_0^2 c^4, \end{aligned} \quad (2.18)$$

can only fulfill the relativistic energy momentum relation $E^2 = p^2 c^2 + m_0^2 c^4$, if the coefficients α_i , β fulfill the following *anticommutation relations*:

$$\alpha_i \alpha_k + \alpha_k \alpha_i = 2\delta_{i,k}, \quad \alpha_i \beta + \beta \alpha_i = 0, \quad \beta^2 = 1. \quad (2.19)$$

This means they can't simply be numbers. As square matrices they must at least be 4×4 matrices in order to fulfill (2.19). We thus replace the Schrödinger equation by an equation

$$(c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}} + \beta m_0 c^2)\psi = i\hbar \frac{\partial \psi}{\partial t} \quad (2.20)$$

for four-component quantities called *four-component spinors*:

$$\psi(\mathbf{r}, t) = \begin{pmatrix} \psi_1(\mathbf{r}, t) \\ \psi_2(\mathbf{r}, t) \\ \psi_3(\mathbf{r}, t) \\ \psi_4(\mathbf{r}, t) \end{pmatrix}. \quad (2.21)$$

Equation (2.20) is the *Dirac equation* representing four partial differential equations for the four components of ψ . In the so-called *standard representation* the coefficients α_i , β are expressed through the Pauli spin matrices (1.345):

$$\begin{aligned} \alpha_x &= \begin{pmatrix} 0 & \hat{\sigma}_x \\ \hat{\sigma}_x & 0 \end{pmatrix}, & \alpha_y &= \begin{pmatrix} 0 & \hat{\sigma}_y \\ \hat{\sigma}_y & 0 \end{pmatrix}, \\ \alpha_z &= \begin{pmatrix} 0 & \hat{\sigma}_z \\ \hat{\sigma}_z & 0 \end{pmatrix}, & \beta &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \end{aligned} \quad (2.22)$$

Each entry in a matrix in (2.22) stands for a 2×2 matrix, e.g.

$$\alpha_x = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \quad (2.23)$$

Inserting an ansatz for a stationary solution,

$$\psi(\mathbf{r}, t) = \psi(\mathbf{r}, t=0) e^{-i/\hbar Et}, \quad (2.24)$$

turns the Dirac equation (2.20) into a time-independent Dirac equation,

$$(c \boldsymbol{\alpha} \cdot \hat{\mathbf{p}} + \beta m_0 c^2) \psi = E \psi. \quad (2.25)$$

In order to simplify notation and interpretation we write the four-component spinors ψ as pairs of two-component quantities:

$$\psi = \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix}, \quad \psi_A = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}, \quad \psi_B = \begin{pmatrix} \psi_3 \\ \psi_4 \end{pmatrix}. \quad (2.26)$$

Inserting (2.26) into (2.25) and using the representation (2.22) of the coefficients α_i , β leads to two coupled equations for the two-component spinors ψ_A and ψ_B :

$$\begin{aligned} \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \psi_B &= \frac{1}{c} (E - m_0 c^2) \psi_A, \\ \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \psi_A &= \frac{1}{c} (E + m_0 c^2) \psi_B. \end{aligned} \quad (2.27)$$

For a particle at rest, $\hat{\mathbf{p}}\psi_A = 0$, $\hat{\mathbf{p}}\psi_B = 0$, we obtain two (linearly independent) solutions of (2.27) with positive energy $E = m_0 c^2$, namely $\psi_A = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ or $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ and $\psi_B = 0$, and two solutions with negative energy $E = -m_0 c^2$, namely $\psi_B = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ or $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ and $\psi_A = 0$. The positive energy solutions are interpreted as the two spin states of the ordinary particle (of spin $s = 1/2$), and the negative energy solutions are related to the corresponding states of the associated *anti-particle*. (For a discussion of the concept of anti-particles

see textbooks on relativistic quantum mechanics, e.g. [BD64].) In situations more general than a particle at rest, the positive energy solutions of (2.27) usually have non-vanishing lower components ψ_B , but these are small, except in the extremely relativistic case ($E \gg m_0c^2$), and are consequently called *small components* in contrast to the *large components* ψ_A .

In order to describe e.g. a hydrogen atom, we must extend the above treatment of a free particle to the case of a particle in a potential. The concept of a particle in a static potential $V(\mathbf{r})$ obviously contradicts the basic requirements of relativity, because it distinguishes one reference frame from all others. On the other hand, a relativistic theory does *not* allow the simple separation of a two-body problem into a centre-of-mass part and an internal relative motion part, as was possible in the non-relativistic case (Sect. 2.1.1). We can nevertheless justify the relativistic treatment of an electron in the potential of an atomic nucleus, because the nucleus is comparatively heavy and can be assumed to be at rest (in an appropriate reference frame). This picture makes sense as long as the energy of the electron is small compared with the rest energy $m_{\text{nuc}}c^2$ of the atomic nucleus.

We extend the Dirac equation (2.20) or (2.27) to a particle in a static potential $V(\mathbf{r})$ by simply adding $V(\mathbf{r})$ to the Hamiltonian. Equation (2.27) then becomes

$$\begin{aligned}\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \psi_B &= \frac{1}{c} (E - V(\mathbf{r}) - m_0c^2) \psi_A, \\ \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \psi_A &= \frac{1}{c} (E - V(\mathbf{r}) + m_0c^2) \psi_B.\end{aligned}\quad (2.28)$$

If the potential is radially symmetric, $V = V(r)$, then the radial motion can be separated from the angular motion as in the non-relativistic case. To this end we use the generalized spherical harmonics $\mathcal{Y}_{j,m,l}$ introduced in Sect. 1.7.3 and make the following ansatz for the two-component spinors ψ_A and ψ_B :

$$\psi_A = \frac{F(r)}{r} \mathcal{Y}_{j,m,l_A}, \quad \psi_B = i \frac{G(r)}{r} \mathcal{Y}_{j,m,l_B} . \quad (2.29)$$

We make use of the identity (Problem 2.1)

$$\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} = \frac{1}{r^2} (\hat{\boldsymbol{\sigma}} \cdot \mathbf{r}) \left(\frac{\hbar}{i} r \frac{\partial}{\partial r} + i \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{L}} \right), \quad (2.30)$$

of the properties

$$\begin{aligned}\frac{1}{r} (\hat{\boldsymbol{\sigma}} \cdot \mathbf{r}) \mathcal{Y}_{j,m,l=j+1/2} &= -\mathcal{Y}_{j,m,l=j-1/2}, \\ \frac{1}{r} (\hat{\boldsymbol{\sigma}} \cdot \mathbf{r}) \mathcal{Y}_{j,m,l=j-1/2} &= -\mathcal{Y}_{j,m,l=j+1/2},\end{aligned}\quad (2.31)$$

and of the fact that the operator $\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{L}} = (2/\hbar) \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}$ can be expressed through $\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2$, in other words, through $[j(j+1) - l(l+1) - 3/4] \hbar^2$ (1.360). From (2.30), (2.31) we see that each total angular momentum quantum number j

allows exactly two possibilities for the orbital angular momentum quantum numbers l_A and l_B in the ansatz (2.29):

$$(i) \ l_A = j - \frac{1}{2}, \ l_B = j + \frac{1}{2}; \quad (ii) \ l_A = j + \frac{1}{2}, \ l_B = j - \frac{1}{2}. \quad (2.32)$$

Inserting (2.29) into (2.28) and using (2.30), (2.31) leads to the *radial Dirac equation* for the radial wave functions $F(r)$ and $G(r)$:

$$\begin{aligned} \hbar c \left(\frac{dF}{dr} + \frac{\kappa}{r} F \right) &= (E - V(r) + m_0 c^2) G, \\ \hbar c \left(\frac{dG}{dr} - \frac{\kappa}{r} G \right) &= -(E - V(r) - m_0 c^2) F. \end{aligned} \quad (2.33)$$

The absolute value of the constant κ is $j + 1/2$; its sign depends on the orbital angular momentum numbers given by (2.32):¹

$$\kappa = -j - \frac{1}{2} \quad \text{for (i)}, \quad \kappa = j + \frac{1}{2} \quad \text{for (ii)}. \quad (2.34)$$

The radial Dirac equation (2.33) is a system of two coupled ordinary differential equations of first order. Solving the radial Dirac equation is in general no more difficult than solving the radial Schrödinger equation (1.75) or (1.362). For an attractive Coulomb potential, $V(r) = -Ze^2/r$, the energy eigenvalues can be given analytically in the regime of bound particle states $0 < E < m_0 c^2$:

$$\begin{aligned} E_{n,j} &= m_0 c^2 \left[1 + \frac{(Z\alpha_{\text{fs}})^2}{(n - \delta_j)^2} \right]^{-\frac{1}{2}}, \\ \delta_j &= j + \frac{1}{2} - \sqrt{(j + 1/2)^2 - (Z\alpha_{\text{fs}})^2}. \end{aligned} \quad (2.35)$$

Here $\alpha_{\text{fs}} = e^2/(\hbar c) = 0.007297352533$ (27) $\approx 1/137$ [MT00] is the dimensionless *fine-structure constant* which characterizes the strength of the electromagnetic interaction. Note that, in atomic units corresponding to $\hbar = 1$, $e = 1$, the speed of light is $1/\alpha_{\text{fs}}$.

The energies (2.35) depend not only on the principal quantum number $n = 1, 2, 3, \dots$, but also on the total angular momentum quantum number j , which, for given n , can assume the values $j = 1/2, 3/2, \dots, n - 1/2$. For each j with $1/2 \leq j < n - 1/2$ (i.e. $j \neq n - 1/2$) there are two linearly independent solutions of the radial Dirac equation characterized by the orbital angular momentum quantum numbers $l_A = j + 1/2$ and $l_A = j - 1/2$ in the large components. Obviously the formula (2.35) is only valid for $Z\alpha_{\text{fs}} < 1$. This implies $Z < 137$, which is fulfilled for all known atomic nuclei.

Expanding (2.35) in powers of $Z\alpha_{\text{fs}}$ yields

$$E_{n,j} = m_0 c^2 \left[1 - \frac{(Z\alpha_{\text{fs}})^2}{2n^2} - \frac{(Z\alpha_{\text{fs}})^4}{2n^3} \left(\frac{1}{j + 1/2} - \frac{3}{4n} \right) + \dots \right]. \quad (2.36)$$

¹ The constant κ is related to the factor $F(j, l)$ in front of the spin-orbit contribution in the radial Schrödinger equation (1.362) by $\kappa = -1 - F(j, l_A)$.

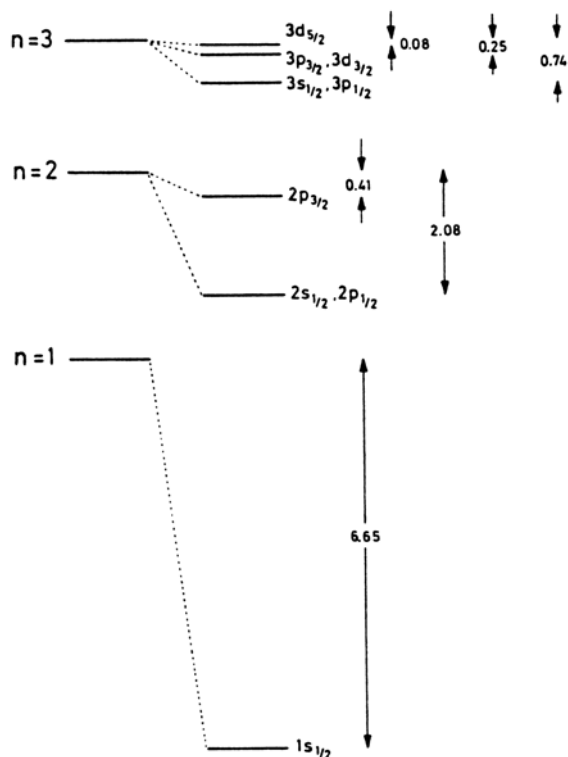


Fig. 2.1. Fine-structure splitting of the energy levels up to $n = 3$ in the hydrogen atom, as predicted by the Dirac equation (2.35). The numbers are energies in 10^{-6} atomic units; on this scale the non-relativistic binding energies are $0.5 \times 10^6/n^2$

The first term is simply the rest energy m_0c^2 of the particle and the second term corresponds to the non-relativistic spectrum with binding energies \mathcal{R}/n^2 . The next term contains corrections which are smaller than the non-relativistic binding energies by at least a factor of $(Z\alpha_{\text{fs}})^2/n$. This *fine structure* causes an n - and j -dependent lowering of all energy levels. For a given n the shift is largest for $j = 1/2$ and smallest for $j = n - 1/2$.

Figure 2.1 shows the fine-structure splitting of the low-lying levels of the hydrogen atom, as predicted by the Dirac equation. The standard nomenclature for hydrogenic single-particle states is as follows: Energy levels are labelled nl_j , where n is the Coulomb principal quantum number and j is the total angular momentum quantum number. The orbital angular momentum quantum numbers $l_A \equiv l = 0, 1, 2, 3, \dots$ are denoted by the letters s, p, d, f, \dots (continue alphabetically). Examples: $2s_{1/2}$ stands for $n = 2, l = 0, j = 1/2$ and $7g_{9/2}$ stands for $n = 7, l = 4, j = 9/2$.

Going beyond the Dirac equation, the electron-proton interaction can be treated with the methods of quantum electrodynamics which leads to still finer corrections to the energy levels, the *Lamb shift*. Further corrections follow from the fact that the proton is not a structureless point particle. Such higher-order corrections to the energy eigenvalues are more important for states of

low angular momentum and thus lift the degeneracy of the $l_A = j \pm 1/2$ states for given n and j . The Lamb shift has been measured to a high degree of precision [BH95] and amounts to about 1.24×10^{-6} atomic units for the $1s$ state in hydrogen, whereas the $2s_{1/2}$ level comes to lie 0.16×10^{-6} atomic units above the $2p_{1/2}$ level, a separation corresponding to about 10% of the fine-structure splitting to the $2p_{3/2}$ level.

2.1.4 Relativistic Corrections to the Schrödinger Equation

The Dirac equation (2.28) can be rewritten as one second-order partial differential equation for the large components ψ_A . To see this, resolve the lower equation for ψ_B ,

$$\psi_B = \frac{c}{E - V(\mathbf{r}) + m_0 c^2} \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \psi_A, \quad (2.37)$$

and insert the result into the upper equation:

$$\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \frac{c^2}{m_0 c^2 + E - V} \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \psi_A = (E - V - m_0 c^2) \psi_A, \quad (2.38)$$

or, replacing $E - m_0 c^2$ by ε :

$$\frac{1}{2m_0} \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \left[1 + \frac{\varepsilon - V}{2m_0 c^2} \right]^{-1} \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \psi_A = (\varepsilon - V) \psi_A. \quad (2.39)$$

In the weakly relativistic case the energy E of the particle is not very different from its rest energy $m_0 c^2$, so the difference $\varepsilon = E - m_0 c^2$ is small compared with $m_0 c^2$, as is the potential V . It then makes sense to expand the square bracket in (2.39), and the left-hand side becomes

$$\begin{aligned} & \frac{1}{2m_0} \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \left(1 - \frac{\varepsilon - V}{2m_0 c^2} \right) \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \psi_A \\ &= \left[\left(1 - \frac{\varepsilon - V}{2m_0 c^2} \right) \frac{(\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}})(\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}})}{2m_0} + \frac{\hbar}{i} \frac{(\hat{\boldsymbol{\sigma}} \cdot \nabla V)(\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}})}{4m_0^2 c^2} \right] \psi_A. \end{aligned} \quad (2.40)$$

Using the identity (Problem 2.1)

$$(\hat{\boldsymbol{\sigma}} \cdot \mathbf{A})(\hat{\boldsymbol{\sigma}} \cdot \mathbf{B}) = \mathbf{A} \cdot \mathbf{B} + i \hat{\boldsymbol{\sigma}} \cdot (\mathbf{A} \times \mathbf{B}) \quad (2.41)$$

(in particular $(\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}})(\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}}) = \hat{\mathbf{p}}^2$) and assuming a radially symmetric potential, $V = V(r)$, $\nabla V = (\mathbf{r}/r)dV/dr$, we obtain the equation

$$\begin{aligned} & \left[\left(1 - \frac{\varepsilon - V}{2m_0 c^2} \right) \frac{\hat{\mathbf{p}}^2}{2m_0} + \frac{\hbar}{i} \frac{1}{4m_0^2 c^2} \frac{1}{r} \frac{dV}{dr} (\mathbf{r} \cdot \hat{\mathbf{p}}) \right. \\ & \left. + \frac{\hbar}{4m_0^2 c^2} \frac{1}{r} \frac{dV}{dr} \hat{\boldsymbol{\sigma}} \cdot (\mathbf{r} \times \hat{\mathbf{p}}) \right] \psi_A = (\varepsilon - V) \psi_A. \end{aligned} \quad (2.42)$$

In the first term on the left-hand side we approximate $\varepsilon - V$ by $\hat{\mathbf{p}}^2/(2m_0)$. In the last term we have $\hbar \hat{\boldsymbol{\sigma}} \cdot (\mathbf{r} \times \hat{\mathbf{p}}) = 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$. The middle term is not Hermitian.

This is due to the fact that we are trying to account for the coupling between the large components ψ_A and the small components ψ_B in a Schrödinger-type equation for the large components alone. Darwin introduced the Hermitian average,

$$\begin{aligned}\hat{H}_D &= \frac{1}{8m_0^2c^2} \left[\frac{\hbar}{i} \frac{1}{r} \frac{dV}{dr} (\mathbf{r} \cdot \hat{\mathbf{p}}) - \frac{\hbar}{i} (\hat{\mathbf{p}} \cdot \mathbf{r}) \frac{1}{r} \frac{dV}{dr} \right] \\ &= \frac{\hbar^2}{8m_0^2c^2} \left(\frac{2}{r} \frac{dV}{dr} + \frac{d^2V}{dr^2} \right) = \frac{\hbar^2}{8m_0^2c^2} \Delta V(r).\end{aligned}\quad (2.43)$$

With these manipulations we obtain a Schrödinger equation including relativistic corrections to first order in $\hat{\mathbf{p}}^2/(m_0c)^2$:

$$\left(\frac{\hat{\mathbf{p}}^2}{2m_0} - \frac{\hat{\mathbf{p}}^2 \hat{\mathbf{p}}^2}{8m_0^3c^2} + V(r) + \hat{H}_{LS} + \hat{H}_D \right) \psi_A = \varepsilon \psi_A. \quad (2.44)$$

Besides the *Darwin term* (2.43) the Hamiltonian in (2.44) contains the spin-orbit coupling

$$\hat{H}_{LS} = \frac{1}{2m_0^2c^2} \frac{1}{r} \frac{dV}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \quad (2.45)$$

and a correction to the kinetic energy including the fourth power of the momentum operator. This makes (2.44) a differential equation of fourth order, which is actually no progress compared with the original Dirac equation (2.28) or (2.33). However, the effects of the relativistic corrections to the non-relativistic Schrödinger equation are small and can usually be calculated with perturbative methods.

In an attractive Coulomb potential $V(r) = -Ze^2/r$, the spin-orbit coupling and the Darwin term are explicitly:

$$\hat{H}_{LS} = \frac{Ze^2}{2m_0^2c^2} \frac{1}{r^3} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \quad \hat{H}_D = \frac{\pi\hbar^2 Ze^2}{2m_0^2c^2} \delta(\mathbf{r}). \quad (2.46)$$

In this case the Darwin term contributes only for $l = 0$; the spin-orbit coupling always contributes only for $l > 0$. We can recover the result (2.36) using first-order perturbation theory with the perturbing operator consisting of the two terms (2.46) and the $\hat{\mathbf{p}}^2 \hat{\mathbf{p}}^2$ term (Problem 2.2).

As indicated at the end of Sect. 2.1.3, further corrections can be obtained by considering that the atomic nucleus isn't a structureless point particle, but has a finite spatial size of the order of 10^{-12} cm and an internal angular momentum called the *nuclear spin*. These corrections are even smaller than the fine structure effects discussed above and appear in the spectrum as *hyperfine structure*.