4.5   The Hydrogen Atom

The simplest of all atoms is the Hydrogen atom, which is made up of a positively charged proton with rest mass $m_p = 1.6726231 \times 10^{-27}\,\mathrm{kg}$, and a negatively charged electron with rest mass $m_e = 9.1093897 \times 10^{-31}\,\mathrm{kg}$. Therefore, the hydrogen atom is the only atom which consists of only two particles. This makes an analytical solution of both the classical as well as the quantum mechanical dynamics of the hydrogen atom possible. All other atomes are composed of a nucleus and more than one electron. According
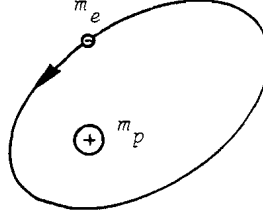
Figure 4.8: Bohr Sommerfeld model of the Hydrogen atom.

to the Bohr-Somerfeld model of hydrogen, the electron circles the proton on a planetary like orbit, see Figure 4.8.The stationary Schroedinger Equation for the Hydrogen atom is

$$\Delta\psi\left(\vec{r}\right) + \frac{2m_0}{\hbar^2}\left(E - V\left(\vec{r}\right)\right)\,\psi\left(\vec{r}\right) = 0 \tag{4.88}$$

The potential is a Coulomb potential between the proton and the electron such that

$$V\left(\vec{r}\right) = -\frac{e_0^2}{4\,\pi\,\varepsilon_0\,\left|\vec{r}\right|} \tag{4.89}$$

and the mass is actually the reduced mass

$$m_0 = \frac{m_p\,\cdot\,me}{m_p + m_e} \tag{4.90}$$

that arises when we transform the two body problem between electron and proton into a problem for the center of mass and relative coordinate motion. Due to the large, but finite, mass of the proton, i.e. the proton mass is 1836 times the electron mass, both bodies circle around a common center of mass. The center of mass is very close to the position of the proton and the reduced mass is almost identical to the proton mass. Due to the spherical symmetry of the potential the use of spherical coordinates is advantageous

$$\Delta\psi = \frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\,\frac{\partial\psi}{\partial r} + \frac{1}{r^2}\left[\frac{1}{\sin\vartheta}\,\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial\psi}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\,\frac{\partial^2\psi}{\partial\,\varphi^2}\right] \tag{4.91}$$

We will derive separate equations for the radial and angular coordinates by assuming trial solutions which are products of functions only depending on

one of the coordinates r, ϑ, or φ

$$\psi(r, \vartheta, \varphi) = R(r) \ \theta(\vartheta) \ \phi(\varphi) \ . \tag{4.92}$$

Substituting this trial solution into the stationary Schroedinger Eq.(4.91) and separating variables leads to radial equation

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left(\frac{2m_0 E}{\hbar^2} + \frac{m_0 e_0^2}{2\pi\varepsilon_0 \hbar^2 r} - \frac{\alpha}{r^2} \right) R = 0 \quad , \tag{4.93}$$

the azimuthal equation

$$\frac{1}{\sin \vartheta} \frac{d}{d\vartheta} \left(\sin \vartheta \frac{d\theta}{d\vartheta} \right) + \left(\alpha - \frac{m^2}{\sin^2 \vartheta} \right) \theta = 0 \quad , \tag{4.94}$$

and the polar equation

$$\frac{d^2 \phi}{d\varphi^2} + m^2 \phi = 0 \quad , \tag{4.95}$$

where α and m are constants yet to be determined. The polar equation has the complex solutions

$$\phi(\varphi) = \text{const. } e^{jm\varphi}, \text{ with } m = \ldots - 2, -1, 0, 1, 2 \ldots \tag{4.96}$$

because of the symmetry of the problem in the polar angle φ, i.e. the wavefunction must be periodic in φ with period 2π.

4.5.1 Spherical Harmonics

The azimuthal equation is transformed by the substitution

$$\xi = \cos \vartheta \tag{4.97}$$

into

$$\left(1 - \xi^2 \right) \frac{d^2 \theta}{d\xi^2} - 2\xi \frac{d\theta}{d\xi} + \left(\alpha - \frac{m^2}{1 - \xi^2} \right) \theta = 0 \quad . \tag{4.98}$$

It turns out, that this equation has only bounded solutions on the interval $\xi \epsilon [-1, 1]$, if the constant α is a whole number

$$\alpha = l(l+1) \quad \text{with,} \quad l = 0, 1, 2 \ldots \tag{4.99}$$

and

$$m = -l, -l+1, \ldots \quad -1, 0, 1 \ldots l-1, l \tag{4.100}$$

For $m = 0$, Eq.(4.98) is Legendre's Differential Equation and the solutions are the Legendre-Polynomialsm [5]

$$
\begin{aligned}
P_0\left(\xi\right) &= 1\,, & P_3\left(\xi\right) &= \tfrac{5}{2}\xi^3 - \tfrac{3}{2}\xi\,, \\
P_1\left(\xi\right) &= \xi\,, & P_4\left(\xi\right) &= \tfrac{35}{8}\xi^4 - \tfrac{15}{4}\xi^2 + \tfrac{3}{8}\,, \\
P_2\left(\xi\right) &= \tfrac{3}{2}\xi^2 - \tfrac{1}{2}\,, & P_5\left(\xi\right) &= \tfrac{63}{8}\xi^5 - \tfrac{35}{4}\xi^3 + \tfrac{15}{8}\xi\,.
\end{aligned} \tag{4.101}
$$

For $m \neq 0$, Eq.(4.98) is the associated Legendre's Differential Equation and the solutions are the associated Legendre-Polynomials, which can be generated from the Legendre-Polynomials by

$$P_1^m\left(\xi\right) = \left(1 - \xi^2\right)^{m/2} \frac{d^m P_1\left(\xi\right)}{d\xi^m}. \tag{4.102}$$

Overall the angular functions can be combined to form the spherical harmonics

$$Y_1^m\left(\vartheta, \varphi\right) = (-1)^m \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}}\ P_1^m\left(\cos\vartheta\right) e^{jm\,\varphi}\,, \tag{4.103}$$

which play an important role whenever a partial differential equation that contains the Laplace operator is solved in spherical coordinates. The spherical harmonics form a system of orthogonal functions on the full volume angle 4π, i.e. $\vartheta\epsilon[0, \pi]$ and $\varphi\epsilon[-\pi, \pi]$

$$\int\limits_0^\pi \int\limits_0^{2\pi} Y_l^{m*}(\vartheta, \varphi)\, Y_{l'}^{m'}\left(\vartheta, \varphi\right) \sin\vartheta\ d\vartheta\ d\varphi = \delta_{ll'}, \delta_{mm'}. \tag{4.104}$$

Therefore, a function of the angular variable (ϑ, φ) can be expanded in spherical harmonics. The spherical harmonics with negative azimuthal number -m can be expressed in terms of those with positive azimuthal number m.

$$Y_1^{-m}\left(\vartheta, \varphi\right) = (-1)^m \left(Y_l^m(\vartheta, \varphi)\right)^* \quad . \tag{4.105}$$

The lowest order spherical harmonics are listed in Table 4.1. Figure 4.9 shows a cut through the spherical harmonics $Y_1^m\left(\vartheta, \varphi\right)$ along the meridional plane.

$$Y_0^0(\vartheta,\varphi) = \tfrac{1}{\sqrt{4\pi}}, \qquad Y_1^0(\vartheta,\varphi) = \sqrt{\tfrac{3}{4\pi}}\cos\vartheta\,, \qquad Y_1^1(\vartheta,\varphi) = -\sqrt{\tfrac{3}{8\pi}}\sin\vartheta\;e^{\mathrm{j}\varphi}\,,$$

$$Y_2^0(\vartheta,\varphi) = \sqrt{\tfrac{5}{16\pi}}\left(3\cos^2\vartheta - 1\right), \; Y_2^1(\vartheta,\varphi) = -\sqrt{\tfrac{15}{8\pi}}\sin\vartheta\cos\varphi\;e^{\mathrm{j}\varphi}, \; Y_2^2(\vartheta,\varphi) = \sqrt{\tfrac{15}{32\pi}}\sin^2\vartheta\;e^{2\mathrm{j}\varphi},$$

$$Y_3^0(\vartheta,\varphi) = \sqrt{\tfrac{7}{16\pi}}\left(5\;\cos^3\vartheta - 3\;\cos\vartheta\right), \qquad Y_3^1(\vartheta,\varphi) = -\sqrt{\tfrac{21}{64\pi}}\sin\vartheta\left(5\;\cos^2\vartheta - 1\right)e^{\mathrm{j}\varphi}\,,$$

$$Y_3^2(\vartheta,\varphi) = \sqrt{\tfrac{105}{32\pi}}\sin^2\vartheta\;\cos\vartheta\;e^{\mathrm{j}2\varphi}\,, \qquad Y_3^3(\vartheta,\varphi) = -\sqrt{\tfrac{35}{64\pi}}\sin^3\vartheta\;e^{\mathrm{j}3\varphi} \qquad.$$

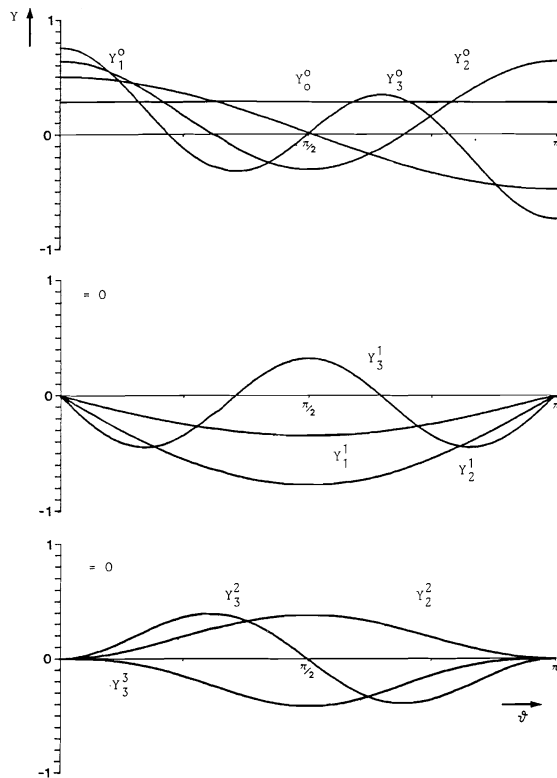Table 4.1: Lowest order spherical harmonics

Figure 4.9: Lowest order spherical harmonics $Y_1^m(\vartheta,\varphi)$, along the meridional plane, i.e. $\varphi = 0$.

4.5.2   Radial Wave Functions

Obviously, the spherical harmonics are related to the angular momentum L of the particle, because after choosing the spherical harmonic with indices l, m the radial Equation (4.93) is

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left(\frac{2m_0 E}{\hbar^2} + \frac{m_0 e_0^2}{2\pi\varepsilon_0 \hbar^2 r} - \frac{l\,(l+1)}{r^2} \right) R = 0. \qquad (4.106)$$

The radial equation has in addition to the $1/r$ Coulomb potential the centrifugal potential

$$E_{rot} = \frac{\hbar^2}{2m_0} \frac{l\,(l+1)}{r^2} = \frac{\vec{L}^2}{2m_0 r^2}, \qquad (4.107)$$

which is the rotation energy of a particle with angular momentum $\left| \vec{L} \right| = \sqrt{l\,(l+1)}\hbar$ and moment of inertia $m_0 r^2$. Thus quantum mechanically, the particle can no longer access arbitrary values for the angular momentum. The angular momentum can only have values $\left| \vec{L} \right| = \sqrt{l\,(l+1)}\hbar$ with $l = 0, 1, 2, \dots$. For large radii, the radial equation simplifies to

$$\frac{d^2 R}{dr^2} + \frac{2m_0 E}{\hbar^2} R = 0, \qquad (4.108)$$

which indicates that the radial wave function must decay exponentially for large radii. Therefore, we rescale the radius accoring to

$$\rho = Ar \qquad (4.109)$$

with

$$A^2 = -\frac{8m_0 E}{\hbar^2}, \text{ because } E < 0, \qquad (4.110)$$

and form the trial solution

$$R\,(\rho) = \rho^s \, w\,(\rho) \, e^{-\rho/2}. \qquad (4.111)$$

Substitution into Eq.(4.109) leads to the following differential equation for $w\,(\rho)$

$$\rho^2 \frac{d^2 w}{d\rho^2} + \rho\,[2\,(s+1) - \rho] \frac{dw}{d\rho} + [\rho\,(\lambda - s - 1) + s\,(s+1) - l\,(l+1)] \; w = 0, \qquad (4.112)$$

with

$$\lambda = \frac{m_0 e^2}{2\pi\varepsilon_0 \hbar^2 A} = \frac{\sqrt{m_0} e^2}{4\sqrt{2}\pi\varepsilon_0 \hbar\sqrt{-E}}. \tag{4.113}$$

Evaluation of this differential equation at $\rho = 0$ leads to

$$l = s,$$

and we are left with the much simpler equation

$$\rho\frac{d^2 w}{d\rho^2} + [2(l+1) - \rho]\frac{dw}{d\rho} + (\lambda - l - 1)\ w = 0. \tag{4.114}$$

One way to solve this equation is by using a polynomial trial solution.

$$w(\rho) = b_0 + b_1\rho + b_2\rho^2 + \dots b_p\rho^p \tag{4.115}$$

Substitution into Eq.(4.114) leads to the following recursion relation for the coefficients

$$b_{k+1} = \frac{k + l + 1 - \lambda}{(k+1)\ (k+2l+2)}\ b_k \tag{4.116}$$

For

$$\lambda = p + l + 1 \tag{4.117}$$

the recursion breaks off and we obtain a polynomial of finite order. If λ is not an integer the polynomial does not stop and the corresponding series converges against a $w(\rho)$ that has an asymptotic behavior $w(\rho) \sim e^\rho$, which leads to a radial function not normalizable. Thus we have the condition

$$\lambda \equiv n, \ \text{with } n \geqslant l + 1 \tag{4.118}$$

and in total

$$w(\rho) = L_{n-l+1}^{2l+1}(\rho) \tag{4.119}$$

with the Laguerre Polynomials

$$L_s^r(x) = \sum_{q=0}^{s} (-1)^q \frac{(s+r)!^2}{(s-q)!\ (r+q)!}\ \frac{x^q}{q!}. \tag{4.120}$$

The lowest order Laguerre Polynomials are summarized in Table 4.2 The radial wave function is then a Laguerre function

$$F_{n1}(\rho) = \rho^1\ L_{n-l=1}^{2l+1}(\rho)\ e^{-\rho/2}, \tag{4.121}$$

$$L_0^1(x) = 1 \quad , \quad L_1^1(x) = 4 - 2x \quad , \quad L_2^1(x) = 18 - 18x + 3x^2 \quad ,$$

$$L_3^1(x) = 96 - 144x + 48x^2 - 4x^3 \quad , \quad L_0^2(x) = 2 \quad ,$$

$$L_1^2(x) = 18 - 6x \quad , \quad L_2^2(x) = 144 - 96 + 12x^2 \quad ,$$

$$L_3^3(x) = 6 \quad , \quad L_1^3(x) = 96 - 24x \quad ,$$

$$L_0^4(x) = 24 \quad .$$

Table 4.2: Lowest order Laguerre Polynomials

and they again form an orthogonal system of functions

$$\int_0^\infty F_{nl}(\rho) \, F_{n'l}(\rho) \, \rho^2 d\rho = \frac{2n \, [(n+l)!]^3}{(n-l-1)!} \, \delta_{nn'} \quad . \tag{4.122}$$

We now reverse the normalization of the radial coordinate and from Eqs.(4.109,4.110) and (4.113) we find

$$\rho = \frac{2r}{na_0} \tag{4.123}$$

with the Bohr radius

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{e_0^2 m_0}, \tag{4.124}$$

which we found already in the Bohr-Sommerfeld model, see section 3.4. The radial wave function is then

$$R_{n1}(r) = N_{nl} \, F_{nl}(\rho) \quad . \tag{4.125}$$

And the normalization factor is determined by

$$\int_0^\infty R_{nl}(r) \, R_{n'l}(r) \, r^2 \, dr = \delta_{n,n'}, \tag{4.126}$$

which gives

$$N_{nl} = \frac{2}{n^2} \sqrt{\frac{(n-l-1)!}{[(n+l)!]^3}} \, a_0^{-3/2} \, . \tag{4.127}$$

The radial wave functions of the hydrogen atom are listed in Table 4.3 and plots of the lowest order radial wave functions are presented in Figure 4.10

$$R_{10}(r) = \frac{2}{\sqrt{a_0^3}}e^{-r/a_0}, \qquad R_{20}(r). = \frac{1}{2\sqrt{2}\sqrt{a_0^3}}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}\sqrt{a_0^3}}\frac{r}{a_0}e^{-r/2a_0}$$

$$R_{30}(r) = \frac{1}{81\sqrt{3}\sqrt{a_0^3}}\left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$$

$$R_{31}(r) = \frac{4}{81\sqrt{6}\sqrt{a_0^3}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}, \quad R_{32}(r) = \frac{4}{81\sqrt{30}\sqrt{a_0^3}}\frac{r^2}{a_0^2}e^{-r/3a_0}$$
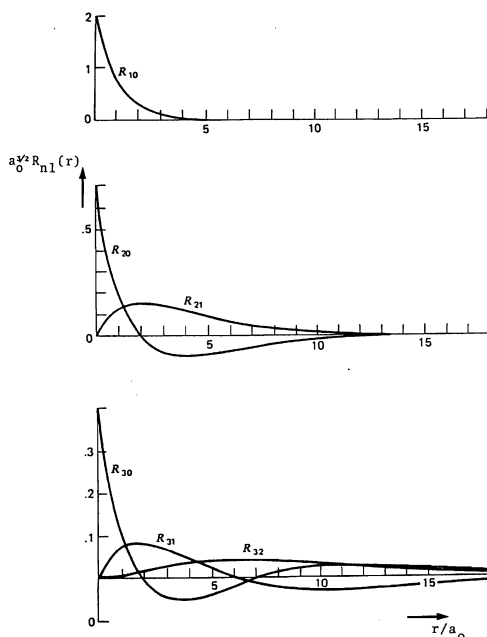
Table 4.3: Lowest order radial wavefunctions $R_{n,l}(r)$.

Figure 4.10: Radial wavefunctions $R_{nl}(r)$ of the hydrogen atom.

4.5.3   Stationary States of Hydrogen

In total we found the stationary states, or the energy eigenfunctions, of the hydrogen atom. Those are

$$\psi_{nlm}\left(r, \vartheta, \varphi\right) = R_{nl}\left(r\right) Y_l^m\left(\vartheta, \varphi\right). \tag{4.128}$$

The lower order wave functions are listed in Table 4.4 and plots of the resulting probability densities of the lowest order energy eigenstates of the hydrogen atom are shown in Figure 4.11

$$\psi_{100}(r, \vartheta, \varphi) = \frac{1}{\sqrt{\pi}\sqrt{a_0^3}} e^{-r/a_0}$$

$$\psi_{200}(r, \vartheta, \varphi) = \frac{1}{4\sqrt{2\pi}\sqrt{a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$\psi_{210}(r, \vartheta, \varphi) = \frac{1}{4\sqrt{2\pi}\sqrt{a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \cos\vartheta$$

$$\psi_{21\pm1}(r, \vartheta, \varphi) = \frac{1}{8\sqrt{\pi}\sqrt{a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \sin\vartheta e^{\pm j\varphi},$$

$$\psi_{300}(r, \vartheta, \varphi) = \frac{1}{81\sqrt{3\pi}\sqrt{a_0^3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$$

Table 4.4: Lowest order hydrogen wavefunctions $\psi_{n,l,m}(r, \vartheta, \varphi)$.

4.5.4   Energy Spectrum of Hydrogen

We haven't yet discussed the energy eigenspectrum of hydrogen. From Eqs.(4.113) and (4.118) we find this to be

$$E = -\frac{m_0 e^4}{8\ \varepsilon_0^2 h^2} \frac{1}{n^2}, \tag{4.129}$$

which also agrees with the energy spectrum of the Bohr-Sommerfeld model, see section 3.4. The lowest energy eigenstate is

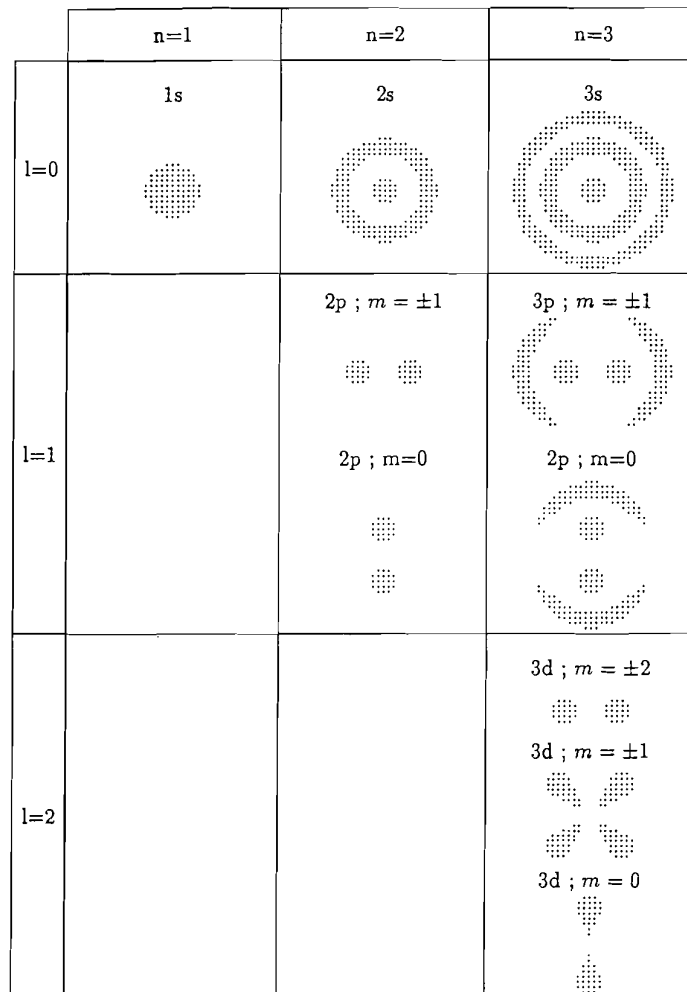$$E_1 = -\frac{m_0 e^4}{8\ \varepsilon_0^2 h^2} = -13.7\text{eV}. \tag{4.130}$$

Figure 4.11: Probability densities of the lowest order hydrogen wavefunctions. (The density is presented along the meridial plane).

$$\psi_{310}(r, \vartheta, \varphi) = \frac{1}{81\sqrt{\pi}\sqrt{a_0^3}} \left(6 - \frac{r}{a_0}\right) e^{-r/3a_0} \cos\vartheta$$

$$\psi_{31\pm1}(r, \vartheta, \varphi) = \frac{1}{81\sqrt{\pi}\sqrt{a_0^3}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin\vartheta e^{\pm j\varphi}$$

$$\psi_{320}(r, \vartheta, \varphi) = \frac{1}{81\sqrt{6\pi}\sqrt{a_0^3}} \frac{r^2}{a_0^2} e^{-r/3a_0} \left(3\cos^2\vartheta - 1\right)$$

$$\psi_{32\pm1}(r, \vartheta, \varphi) = \frac{1}{81\sqrt{\pi}\sqrt{a_0^3}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin\vartheta \cos\vartheta e^{\pm j\varphi},$$

$$\psi_{32\pm2}(r, \vartheta, \varphi) = \frac{1}{162\sqrt{3\pi}\sqrt{a_0^3}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 e^{\pm 2j\varphi}$$

Table 4.5: Lowest order hydrogen wavefunctions $\psi_{n,l,m}(r, \vartheta, \varphi)$.continued.

The energy eigenvalues constitute a sequence that converges for large $n \to \infty$ towards 0, which corresponds to removing the electron from the atom. The energy to do so is $E_{\infty 1} - E_1 = 13.7\text{eV}$.

Figure 4.12 shows the energy levels and the term diagram of the hydrogen atom and how the Lyman, Balmer, Paschen, Brackett and Pfund series arise from it. Each wavefunction is uniquely described by the set of quantum numbers (n,l,m). The first quantum number n specifies the energy eigen value E_n. As we will show in problem sets, the second quantum number l determines the eigenvalue of the squared angular momentum operator $\vec{L}^2$ with eigenvalues

$$\vec{L}^2 \, \psi_{nlm}(r, \vartheta, \varphi) = l(l+1)\hbar^2 \, \psi_{nlm}(r, \vartheta, \varphi), \qquad (4.131)$$

and the third quantum number m detemines the eigenvalue of the operator describing the z-component of the angular momentum operator

$$L_z \, \psi_{nlm}(r, \vartheta, \varphi) = m\hbar \, \psi_{nlm}(r, \vartheta, \varphi). \qquad (4.132)$$
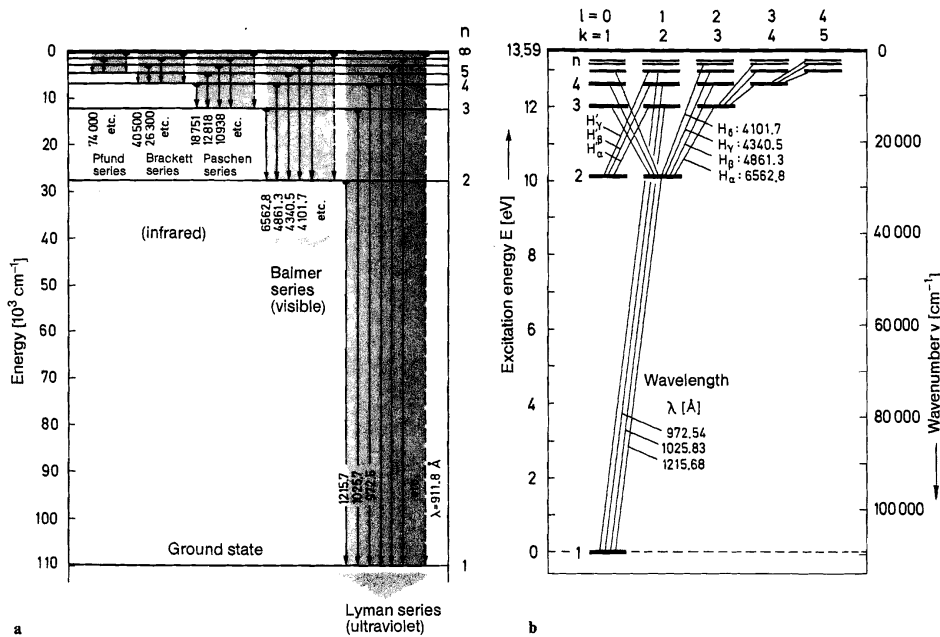
Figure 4.12: Energy levels and term diagram for the hydrogen atom [3]

In fact, the description of the electron wave functions is not yet complete, because the electron has an internal degree of freedom, that is its spin. The spin is an internal angular momentum of the electron that carries a magnetic moment with it. The Stern-Gerlach experiment shows that this degree of freedom has two eigenstates, i.e. the spin can be oriented parallel or anti-parallel to the direction of an applied magnetic field. The values of the internal angluar mometum with respect to the quantization axis defined by an external field, that shall be chosen along the z-axis, are $s = \pm \hbar/2$. Thus the energy eigenstates of an electron in hydrogen are uniquely characterized by four quantum numbers, n, l, m, and s. As Figure 4.12 shows, the energy

spectrum is degenerate, i.e. for $n > 1$, there exist to each energy eigenvalue several eigenfunctions, that are only uniquely characterized by the additional quantum numbers for angular momentum and spin. This is called degeneracy because there exist to a given energy eigenvalue several states.