

Chapter 4

Orbital angular momentum and the hydrogen atom

If I have understood correctly your point of view then you would gladly sacrifice the simplicity [of quantum mechanics] to the principle of causality. Perhaps we could comfort ourselves that the dear Lord could go beyond [quantum mechanics] and maintain causality.

-Werner Heisenberg responds to Einstein

In quantum mechanics degenerations of energy eigenvalues typically are due to symmetries. The symmetries, in turn, can be used to simplify the Schrödinger equation, for example, by a separation ansatz in appropriate coordinates. In the present chapter we will study rotationally symmetric potentials and use the angular momentum operator to compute the energy spectrum of hydrogen-like atoms.

4.1 The orbital angular momentum

According to Emmy Noether's first theorem continuous symmetries of dynamical systems imply conservation laws. In turn, the conserved quantities (called charges in general, or energy and momentum for time and space translations, respectively) can be shown to generate the respective symmetry transformations via the Poisson brackets. These properties are inherited by quantum mechanics, where Poisson brackets of phase space functions are replaced by commutators. According to the Schrödinger equation $i\hbar\partial_t\psi = H\psi$, for example, time evolution is generated by the Hamiltonian. Similarly, the momentum operator $\vec{P} = \frac{\hbar}{i}\vec{\nabla}$ generates (spatial) translations. A (Hermitian) charge operator Q is conserved if it commutes with the Hamiltonian $[H, Q] = 0$. This equation can also be interpreted as invariance of the Hamiltonian

$H = U_\lambda^{-1} H U_\lambda$ under the unitary 1-parameter transformation group of finite transformations $U_\lambda = \exp(i\lambda Q)$ that is generated by the infinitesimal transformation Q .

The constant of motion of classical mechanics that corresponds to rotations about the origin is the (orbital) angular momentum $\vec{L} = \vec{x} \times \vec{p}$. The corresponding operator $\vec{\mathcal{L}}$ in quantum mechanics is

$$\vec{\mathcal{L}} = \vec{X} \times \vec{P} = \frac{\hbar}{i} (\vec{x} \times \vec{\nabla}) = \frac{\hbar}{i} \begin{pmatrix} y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \\ z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \\ x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \end{pmatrix}, \quad (4.1)$$

or

$$\mathcal{L}_i = \epsilon_{ijk} X_j P_k = \frac{\hbar}{i} \epsilon_{ijk} x_j \frac{\partial}{\partial x_k}. \quad (4.2)$$

There is no ordering ambiguity because X_j and P_k commute for $j \neq k$. In addition to the *orbital angular momentum* $\vec{\mathcal{L}}$, which is familiar from classical mechanics, quantum mechanical point particles can have an intrinsic angular momentum, the *spin* $\vec{\mathcal{S}}$, which will be the subject of the next chapter. The sum of all spins and orbital angular momenta of a system will be called the *total angular momentum* $\vec{\mathcal{J}}$.

4.1.1 Commutation relations

The canonical commutation relation $[X_i, P_j] = i\hbar\delta_{ij}$ implies

$$[\mathcal{L}_i, X_j] = \epsilon_{ikl} [X_k P_l, X_j] = i\hbar\epsilon_{ijk} X_k \quad (4.3)$$

and

$$[\mathcal{L}_i, P_j] = \epsilon_{ikl} [X_k P_l, P_j] = i\hbar\epsilon_{ijk} P_k \quad (4.4)$$

The form of these results suggests that all vector operators V_j (i.e. operators with a vector index) should transform in the same way. Indeed, we will find that the (axial) vector \mathcal{L}_j transforms as

$$[\mathcal{L}_i, \mathcal{L}_j] = i\hbar\epsilon_{ijk} \mathcal{L}_k. \quad (4.5)$$

To show this we use the identity

$$\epsilon_{ikl}\epsilon_{imn} = \delta_{km}\delta_{ln} - \delta_{kn}\delta_{lm}, \quad (4.6)$$

i.e. the sum over a common index i of a product of ϵ tensors is ± 1 if the free index pairs kl and mn take the same values, with the sign depending on the cyclic ordering, and vanishes otherwise. We thus find

$$[\mathcal{L}_i, \mathcal{L}_j] = \epsilon_{jlm} [\mathcal{L}_i, X_l P_m] = i\hbar\epsilon_{jlm} (\epsilon_{ilk} X_k P_m + \epsilon_{imk} X_l P_k) \quad (4.7)$$

$$= i\hbar ((\delta_{ji}\delta_{mk} - \delta_{jk}\delta_{im}) X_k P_m + (\delta_{jk}\delta_{li} - \delta_{ji}\delta_{lk}) X_l P_k). \quad (4.8)$$

Since the terms with δ_{ji} cancel this agrees with

$$i\hbar\varepsilon_{ijk}\mathcal{L}_k = i\hbar\varepsilon_{ijk}\varepsilon_{klm}X_lP_m = i\hbar(\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl})X_lP_m, \quad (4.9)$$

which completes the proof of (4.5).

Since angular momenta in different directions do not commute they cannot be diagonalized simultaneously. If we choose \mathcal{L}_z as our first observable we expect that the combination $\mathcal{L}_x^2 + \mathcal{L}_y^2$, which is classically invariant under rotations about the z -axis, commutes with \mathcal{L}_z . This is indeed true, but it is more useful to use the completely rotation invariant $\mathcal{L}^2 = \mathcal{L}_x^2 + \mathcal{L}_y^2 + \mathcal{L}_z^2$ as the second generator of a maximal set of commuting operators. \mathcal{L}^2 is obviously Hermitian and

$$[\mathcal{L}_i, \mathcal{L}^2] = [\mathcal{L}_i, \mathcal{L}_k]\mathcal{L}_k + \mathcal{L}_k[\mathcal{L}_i, \mathcal{L}_k] = i\hbar\varepsilon_{ikr}(\mathcal{L}_r\mathcal{L}_k + \mathcal{L}_k\mathcal{L}_r) = 0. \quad (4.10)$$

A similar calculation shows that $[\mathcal{L}_i, P^2] = [\mathcal{L}_i, X^2] = 0$, so that the kinetic energy commutes with \mathcal{L}_i (and hence also with \mathcal{L}^2).

Angular momentum conservation $[\mathcal{L}_i, H]$ for rotationally symmetric Hamiltonians $H = \frac{P^2}{2m} + V(r)$ with $r = \sqrt{x^2 + y^2 + z^2}$ now already follows from the commutation of \mathcal{L}_i with any function of X^2 , but let us check this explicitly in configuration space,

$$[\mathcal{L}_j, H] = [\mathcal{L}_j, V(r)] = \frac{\hbar}{i}\varepsilon_{jkl}x_k\frac{\partial}{\partial x_l}V(r) = \frac{\hbar}{i}\varepsilon_{jkl}x_k\frac{x_l}{r}\frac{\partial}{\partial r}V(r) = 0, \quad (4.11)$$

where we used the chain rule for $V(r(x))$ with $\frac{\partial r}{\partial x_l} = \frac{x_l}{r}$ and the operator rule

$$\left[\frac{\partial}{\partial x_l}, A(x)\right]\psi(x) = \frac{\partial}{\partial x_l}(A(x)\psi(x)) - A\frac{\partial}{\partial x_l}\psi(x) = \left(\frac{\partial}{\partial x_l}A(x)\right)\psi(x), \quad (4.12)$$

or $[\partial_{x_i}, A(x)] = \partial_{x_i}A(x) + A(x)\partial_{x_i} - A(x)\partial_{x_i} = \partial_{x_i}A(x)$, i.e. commutation of ∂_{x_i} with an operator yields the partial derivative of that operator.

4.1.2 Angular momentum and spherical harmonics

We will first derive the relation

$$\Delta = \frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{r^2}\frac{\mathcal{L}^2}{\hbar^2} \quad (4.13)$$

between \mathcal{L}^2 and the Laplacian, which will help us reduce the Schrödinger equation to an ordinary radial differential equation after separation of the angular coordinates. Hence we first evaluate \mathcal{L}^2 in configuration space,

$$\begin{aligned} \mathcal{L}^2 = \mathcal{L}_i\mathcal{L}_i &= -\hbar^2\varepsilon_{ijk}x_j\partial_k\varepsilon_{ilm}x_l\partial_m = \\ &= -\hbar^2(\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl})x_j\partial_kx_l\partial_m = \\ &= -\hbar^2(x_j\partial_kx_j\partial_k - x_j\partial_kx_k\partial_j) = \\ &= -\hbar^2(x_j\partial_j + x_jx_j\partial_k\partial_k - 3x_j\partial_j - x_jx_k\partial_k\partial_j) = \\ &= -\hbar^2(x_jx_j\partial_k\partial_k - 2x_j\partial_j - x_jx_k\partial_k\partial_j). \end{aligned} \quad (4.14)$$

Next we transform to spherical coordinates $\vec{x} = (r \sin \theta \cos \varphi, r \sin \theta \sin \varphi, r \cos \theta)$, hence

$$r = \sqrt{x^2 + y^2 + z^2}, \quad \theta = \arctan \frac{\sqrt{x^2 + y^2}}{z}, \quad \varphi = \arctan \frac{y}{x}. \quad (4.15)$$

In particular

$$\frac{x_i}{r} = e_i^{(r)}, \quad x_j x_j = r^2, \quad x_j \partial_j = r \frac{\partial}{\partial r}, \quad (4.16)$$

so that we obtain

$$\mathcal{L}^2 = -\hbar^2 (r^2 \Delta - 2r \frac{\partial}{\partial r} - r^2 \frac{\partial^2}{\partial r^2}), \quad (4.17)$$

or

$$\Delta = \partial_r^2 + \frac{2}{r} \partial_r - \frac{1}{r^2} \frac{\mathcal{L}^2}{\hbar^2} = \frac{1}{r} \partial_r^2 r - \frac{1}{r^2} \frac{\mathcal{L}^2}{\hbar^2}, \quad (4.18)$$

which establishes (4.13).

Recalling the formula for the Laplace operator in spherical coordinates

$$\Delta = \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \quad (4.19)$$

from *Mathematical Methods in Theoretical Physics* [Dirschmid, Kummer, Schweda] we conclude

$$\mathcal{L}^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right). \quad (4.20)$$

Using the chain rule

$$\partial_i = (\partial_i r) \frac{\partial}{\partial r} + (\partial_i \theta) \frac{\partial}{\partial \theta} + (\partial_i \varphi) \frac{\partial}{\partial \varphi} \quad (4.21)$$

for $\mathcal{L}_z = \frac{\hbar}{i} (x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})$ one can check that

$$\mathcal{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \varphi}. \quad (4.22)$$

The common eigenfunctions for the angle-dependent part $-\mathcal{L}^2/\hbar^2$ of the Laplace operator and for $i\mathcal{L}_z/\hbar = \partial/\partial\varphi$ are again known from the *Mathematical Methods in Theoretical Physics*.

They are the *spherical harmonics* [German: *Kugelflächenfunktionen*]

$$Y_{lm}(\theta, \varphi) = (-1)^m \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^{(m)}(\cos \theta) e^{im\varphi} = (-1)^m Y_{l,-m}^*(\theta, \varphi) \quad (4.23)$$

with the associated Legendre functions

$$P_l^{(m)}(\xi) = \frac{1}{2^l l!} (1 - \xi^2)^{\frac{m}{2}} \frac{d^{l+m}}{d\xi^{l+m}} (\xi^2 - 1)^l = (-1)^m \frac{(l+m)!}{(l-m)!} P_l^{(-m)}(\xi) \quad (4.24)$$

For $m = 0$ they reduce to the Legendre polynomials $P_l(\xi) = P_l^{(0)}(\xi)$. These results are obtained by a the separation ansatz $Y_{lm} = \Theta(\theta)\Phi(\varphi)$. The eigenvalues for the angular momenta become

$$\mathcal{L}^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm}, \quad \mathcal{L}_3 Y_{lm} = \hbar m Y_{lm}, \quad (4.25)$$

with l a nonnegative integer and $m \in \mathbb{Z}$ obeying $-l \leq m \leq l$. The quantization conditions and the ranges of the eigenvalues follow from termination conditions for the power series ansatz and from single-valuedness at $\xi = \cos \theta = \pm 1$.

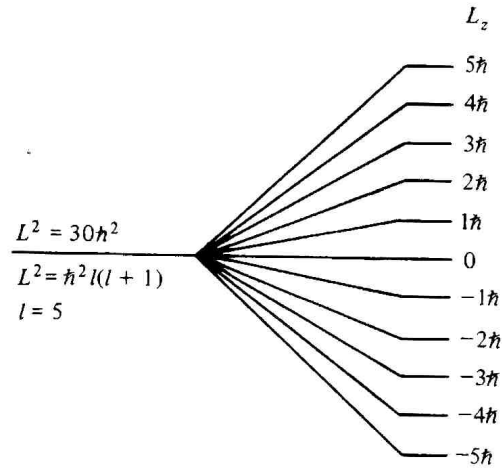


Figure 4.1: The eigenvalue $\hbar^2 l(l + 1)$ of \mathcal{L}^2 is $(2l + 1)$ -fold degenerate

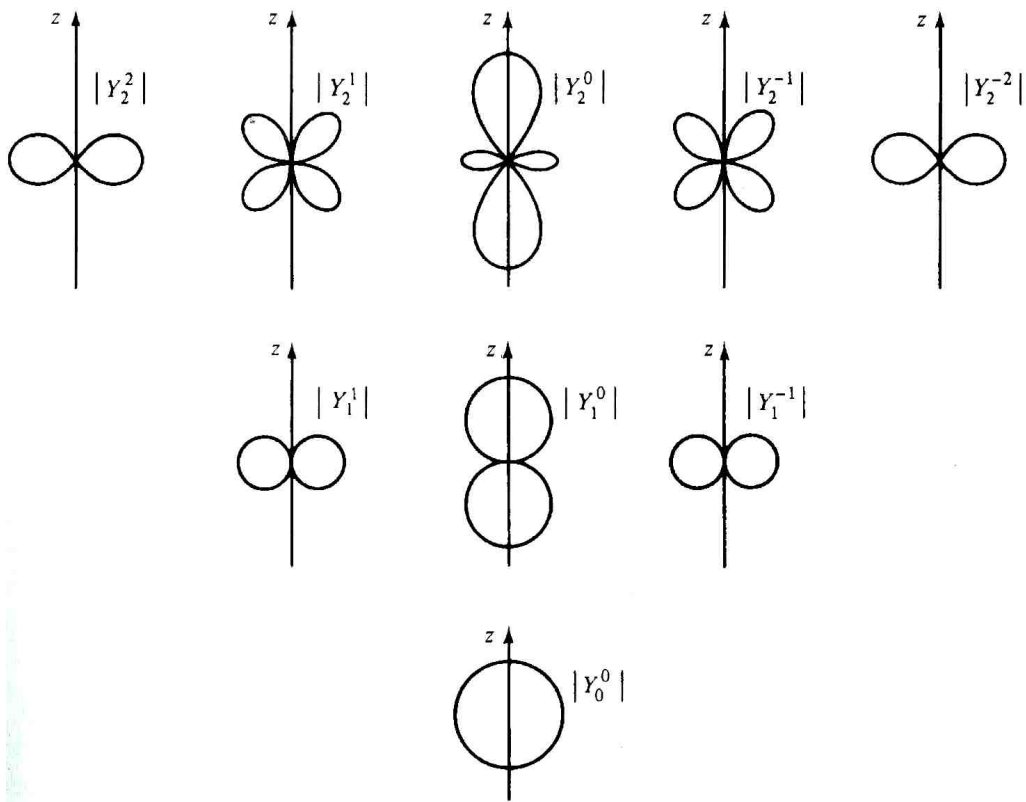


Figure 4.2: Polar plots of $|Y_l^m|$ versus Θ in any plane through the z -axis for $l = 0, 1, 2$. Note the equality $|Y_l^m| = |Y_l^{-m}|$, which follows from $Y_{l,m}^* = (-1)^m Y_{l,-m}$.

The completeness of the spherical harmonics enables us to solve the stationary Schrödinger equation for rotation invariant potentials by a separation ansatz $u(\vec{x}) = R_\lambda(r)Y_{lm}(\theta, \varphi)$ with

$$H_l R_\lambda(r) = \lambda R_\lambda(r), \quad \text{with} \quad H_l = -\frac{\hbar^2}{2m} \frac{1}{r} \partial_r^2 r + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r). \quad (4.26)$$

The energy eigenvalues λ are $(2l+1)$ -fold degenerate due to the *magnetic* quantum number m . Note that we need the *two* observables \mathcal{L}^2 and \mathcal{L}_z to characterize the wave function dependence on the *two* angle coordinates θ and φ .

4.2 The hydrogen atom

4.2.1 The two particle problem

Consider a system of two particles of the masses m_1 and m_2 and positions \vec{x}_1 and \vec{x}_2 , respectively. If there are no forces from outside translation invariance implies that the potential energy $V(\vec{x}_1, \vec{x}_2)$ only depends on the difference vector $\vec{x} = \vec{x}_1 - \vec{x}_2$. In classical mechanics this system is hence described by the Lagrangian

$$L(\vec{x}_1, \dot{\vec{x}}_1; \vec{x}_2, \dot{\vec{x}}_2) = T - V = \frac{1}{2}(m_1 \dot{\vec{x}}_1^2 + m_2 \dot{\vec{x}}_2^2) - V(\vec{x}_1 - \vec{x}_2). \quad (4.27)$$

The description can be simplified by using the relative coordinates

$$\vec{x} = \vec{x}_1 - \vec{x}_2 \quad (4.28)$$

and the center of mass coordinates

$$\vec{x}_g = \frac{m_1 \vec{x}_1 + m_2 \vec{x}_2}{m_1 + m_2} \quad (4.29)$$

as new variables, so that $\vec{x}_1 = \vec{x}_g + \frac{m_2}{m_1+m_2} \vec{x}$ and $\vec{x}_2 = \vec{x}_g - \frac{m_1}{m_1+m_2} \vec{x}$. In terms of the total mass M and the reduced mass μ ,

$$M = m_1 + m_2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}, \quad (4.30)$$

the total momentum \vec{p}_g and the relative momentum \vec{p} are

$$\vec{p}_g = M \dot{\vec{x}}_g = m_1 \dot{\vec{x}}_1 + m_2 \dot{\vec{x}}_2 = \vec{p}_1 + \vec{p}_2 \quad (4.31)$$

$$\vec{p} = \mu \dot{\vec{x}} = \frac{m_2 \vec{p}_1 - m_1 \vec{p}_2}{m_1 + m_2} \quad (4.32)$$

and the Hamiltonian becomes

$$H(\vec{x}_g, \vec{p}_g; \vec{x}, \vec{p}) = H_g(\vec{x}_g, \vec{p}_g) + H_r(\vec{x}, \vec{p}) = \frac{\vec{p}_g^2}{2M} + \frac{\vec{p}^2}{2\mu} + V(\vec{x}). \quad (4.33)$$

$H_g = \frac{\vec{p}_g^2}{2M}$ describes the uniform free motion $\dot{\vec{p}}_g = M\ddot{\vec{x}}_g = 0$ of the center of mass, while the reduced Hamiltonian

$$H_r = \frac{\vec{p}^2}{2\mu} + V(\vec{x}) \quad (4.34)$$

described the dynamics $\dot{\vec{p}} = \mu\ddot{\vec{x}} = -\vec{\nabla}V(\vec{x})$.

In quantum mechanics the canonical commutation relations $[X_i^{(1)}, P_j^{(1)}] = [X_i^{(2)}, P_j^{(2)}] = i\hbar\delta_{ij}$ and $[X_i^{(1)}, P_j^{(2)}] = [X_i^{(2)}, P_j^{(1)}] = 0$ are, as expected, equivalent to

$$[X_i, P_j] = [X_i^{(g)}, P_j^{(g)}] = i\hbar\delta_{ij}, \quad [X_i^{(g)}, P_j] = [X_i, P_j^{(g)}] = 0 \quad (4.35)$$

(i.e. the change of variables amounts to a canonical transformation). Hence H_g and H_r commute and can be diagonalized simultaneously with a separation ansatz $u(\vec{x}_1, \vec{x}_2) = u_g(\vec{x}_g)u_r(\vec{x})$ and the total energy becomes $E = E_g + E_r$. After the separation of the center of mass motion the dynamics is hence described by a one-particle problem with effective mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ and potential $V(\vec{x})$.

4.2.2 The hydrogen atom

In this section we consider a simplified hydrogen-like atom (or ion) with a nucleus of atomic number Z and a single electron, where we neglect the spin and relativistic correction terms in the Hamiltonian, as well as the structure of the nucleus whose role is restricted to a massive point-like source for the Coulomb potential. It consists of protons with the mass m_p and elementary charge q ,

$$m_p = 1,7 \cdot 10^{-27} \text{ kg}, \quad q = 1,6 \cdot 10^{-19} \text{ Coulomb}, \quad (4.36)$$

and a number of neutrons, and the electron has charge $-q$ and mass

$$m_e = 0,91 \cdot 10^{-30} \text{ kg}. \quad (4.37)$$

The electrostatic interaction potential between the electron and the point-like nucleus thus is

$$V(r) = -\frac{q^2}{4\pi\epsilon_0} \frac{Z}{r} = -\frac{Ze^2}{r}, \quad (4.38)$$

where $r = \sqrt{(\vec{x}_e - \vec{x}_{nucleus})^2}$ denotes the distance between the electron and the nucleus and

$$e^2 = \frac{q^2}{4\pi\epsilon_0}. \quad (4.39)$$

For the hydrogen atom $Z = 1$, while $Z = 2, 3, \dots$ for the ions He^+ , Li^{++}

The quantum mechanics of this system is described by the Hamiltonian

$$H(\vec{x}, \vec{p}) = \frac{\vec{p}^2}{2\mu} + V(r) = \frac{\vec{p}^2}{2\mu} - \frac{Ze^2}{r}, \quad (4.40)$$

where the reduced mass

$$\mu = \frac{m_e m_{\text{nucleus}}}{m_e + m_{\text{nucleus}}} \approx m_e \left(1 - \frac{m_e}{m_{\text{nucleus}}}\right) \quad (4.41)$$

is very close to m_e since $m_{\text{nucleus}} \gg m_e$.

Now we recall the Laplace operator in spherical coordinates (4.19), which has a radial and a tangential part,

$$\Delta = \underbrace{\frac{1}{r} \frac{\partial^2}{\partial r^2} r}_{\text{radial component}} - \underbrace{\frac{1}{r^2} \frac{\mathcal{L}^2}{\hbar^2}}_{\text{tangential component}}. \quad (4.42)$$

The reduced Hamiltonian of a hydrogen-like atom thus becomes

$$H = -\frac{\hbar^2}{2\mu} \Delta - \frac{Ze^2}{r} = -\frac{\hbar^2}{2\mu} \left(\frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{1}{r^2} \frac{\mathcal{L}^2}{\hbar^2} \right) - \frac{Ze^2}{r} \quad (4.43)$$

or

$$H = \frac{p_r^2}{2\mu} + \frac{\mathcal{L}^2}{2\mu r^2} + V(r), \quad p_r = \frac{\hbar}{i} \frac{1}{r} \frac{\partial}{\partial r} r. \quad (4.44)$$

For bound states we expect negative energy eigenvalues $E < 0$ with

$$\left(\frac{p_r^2}{2\mu} + \frac{\mathcal{L}^2}{2\mu r^2} - \frac{Ze^2}{r} \right) u(\vec{x}) = E u(\vec{x}). \quad (4.45)$$

With the separation ansatz $u(\vec{x}) = R(r)Y_{lm}(\theta, \varphi)$ we obtain the radial eigenvalue equation

$$H_l R(r) = \left[-\frac{\hbar^2}{2\mu} \left(\frac{1}{r} \frac{\partial^2}{\partial r^2} r \right) + \frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{Ze^2}{r} \right] R(r) = E R(r) \quad (4.46)$$

with a Hamiltonian H_l depending on an integer parameter l . For large angular momentum l the radial Hamiltonian H_l thus has an effective repulsive contribution proportional to $1/r^2$, which is called *centrifugal barrier* (it stabilizes excited energy levels at high values of l). For fixed l (and m) we introduce a label, the *principal quantum number* n , for the different eigenvalues $E_{n,l}$ of H_l and we set

$$R(r) = \frac{1}{r} u_{n,l}(r). \quad (4.47)$$

Multiplication with $\frac{2r\mu}{\hbar^2}$ yields the differential equation

$$\left(-\frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{r^2} - \frac{2\mu Ze^2}{\hbar^2 r} - \frac{2\mu E_{n,l}}{\hbar^2} \right) u_{n,l} = 0 \quad (4.48)$$

We first consider the asymptotics of its solutions $u_{n,l}$ for $r \rightarrow 0$ and for $r \rightarrow \infty$.

- For $r \rightarrow \infty$ this equation reduces to

$$(-\partial_r^2 + \kappa^2) u_{n,l} = 0 \quad \text{with} \quad \kappa = \frac{\sqrt{-2\mu E}}{\hbar} \quad (4.49)$$

whose solution is

$$u_{n,l} \sim Ae^{-\rho} + Be^{\rho} \quad \text{with} \quad \rho = \kappa r \quad (4.50)$$

$u_{n,l}$ has to vanish at infinity, hence only $e^{-\rho}$ is acceptable for $r \rightarrow \infty$.

- For $r \rightarrow 0$ the radial equation becomes

$$\left(-\partial_r^2 + \frac{l(l+1)}{r^2}\right) u_{n,l} = 0. \quad (4.51)$$

The ansatz $u_{n,l} \sim r^q$ yields $l(l+1) - q(q-1) = 0$, hence

$$u_{n,l} \sim Ar^{-l} + Br^{l+1}. \quad (4.52)$$

Normalizability requires $u_{n,l}$ to vanish at the origin so that $u_{n,l} \sim r^{l+1}$ for $r \rightarrow 0$.

Introducing the Bohr radius a_0

$$a_0 = \frac{\hbar^2}{\mu e^2} = 0.529 \cdot 10^{-10} \text{ m}, \quad (4.53)$$

equation (4.48) takes the form

$$\left(\partial_r^2 - \frac{l(l+1)}{r^2} + \frac{2Z}{a_0} \frac{1}{r} - \kappa^2\right) u_{n,l}(r) = 0, \quad (4.54)$$

or, in terms of dimensionless variables $\rho = \kappa r$ and n ,

$$\left(\partial_\rho^2 - \frac{l(l+1)}{\rho^2} + \left(\frac{2n}{\rho} - 1\right)\right) u_{n,l} = 0, \quad n = \frac{Z}{\kappa a_0}, \quad (4.55)$$

where the *principal quantum number* n parametrizes the energy eigenvalue $E = -\mathcal{R} Z^2/n^2$ with $\mathcal{R} = \hbar^2/(2\mu a_0^2) = \mu e^4/(2\hbar^2) = 2.18 \cdot 10^{-18} \text{ J} = 13.6 \text{ eV} = 1 \text{ Rydberg}$.

In order to account for the asymptotics of the solutions we write

$$u_{n,l}(\rho) = e^{-\rho} \rho^{l+1} F(\rho), \quad (4.56)$$

where $F(\rho)$ should be nonzero at the origin and should not grow faster than polynomial at ∞ .

Since $\partial_\rho^2 u = e^{-\rho} \rho^{l+1} (F'' + 2(\frac{l+1}{\rho} - 1)F' + (1 - 2\frac{l+1}{\rho} + \frac{l(l+1)}{\rho^2})F)$ we obtain

$$\left(\rho \frac{\partial^2}{\partial \rho^2} + 2(l+1-\rho) \frac{\partial}{\partial \rho} + 2(n-l-1)\right) F_{n,l}(\rho) = 0. \quad (4.57)$$

Expanding $F(\rho)$ into a power series $\sum_{j=0}^{\infty} a_j \rho^j$ the l.h.s. of (4.57) becomes a sum of three terms:

$$\rho F'' = \sum_{j=1}^{\infty} \rho^j (j(j+1)a_{j+1}), \quad (4.58)$$

$$2(l+1-\rho)F' = \sum_{j=0}^{\infty} \rho^j (2(l+1)(j+1)a_{j+1} - 2ja_j), \quad (4.59)$$

$$2(n-l-1)F = \sum_{j=0}^{\infty} \rho^j 2(n-l-1)a_j. \quad (4.60)$$

The vanishing of the coefficient of ρ^j implies the recursion relation

$$(j+1)(j+2l+2)a_{j+1} = 2(l+j+1-n)a_j. \quad (4.61)$$

For large j the ratio a_{j+1}/a_j is approximately $2/j$, which is the same as in the Taylor series of $e^{2\rho}$. The asymptotic behavior of the resulting solution would effectively invert the exponential damping in our ansatz (4.56). Normalizability therefore requires that the series terminates, which implies $l+j+1-n=0$ for some nonnegative integer j , i.e. the principal quantum number n has to be a positive integer

$$n = 1, 2, 3, \dots, \quad 0 \leq l < n \quad (4.62)$$

and the energy eigenvalues are

$$E_n = -\frac{Z^2 \mathcal{R}}{n^2} = -\frac{1}{2\mu} \left(\frac{Z\hbar}{a_0 n} \right)^2. \quad (4.63)$$

Somewhat surprisingly, the energy levels do not depend on the orbital quantum number l . For fixed principal quantum number n we therefore have an degeneracy of

$$\sum_{l=0}^{n-1} (2l+1) = n^2, \quad (4.64)$$

which is larger than what is implied by angular momentum conservation. The energy degeneracy for different values of l is a special property of the pure Coulomb interaction. It is lifted in nature by additional interaction terms that lead to the fine structure and hyperfine structure of the spectral lines. Note, however, that the degeneracy due to angular momentum conservation cannot be lifted by any corrections except in the presence of external forces, like an external magnetic field, which would break the rotation symmetry of the complete system (i.e. the atom plus its interaction with the environment). For a proper discussion of these effects we need to consider the spin of the electron. This will be the subject of the next section.

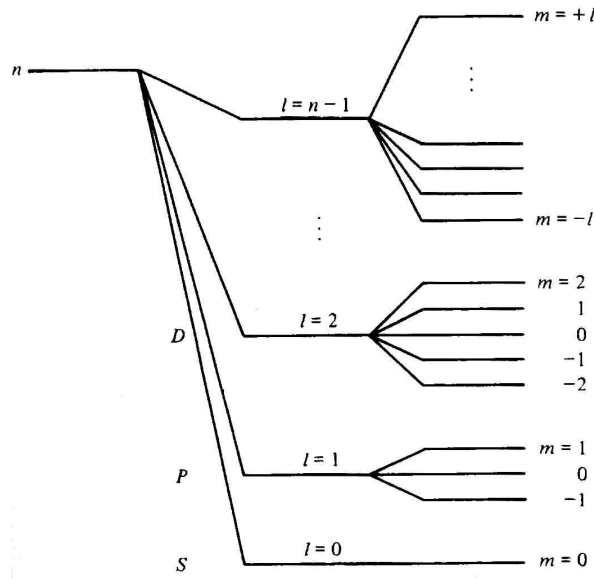


Figure 4.3: Term diagram for the hydrogen atom illustrating all n^2 degenerate states corresponding to the principal quantum number n .

The non-uniqueness of common eigenfunctions of H , L^2 and L_z for the Coulomb potential implies the existence of an independent conserved quantity that lifts this degeneracy. An appropriate observable can be constructed in terms of the Runge–Lenz vector,

$$\vec{M} = \frac{1}{2m}(\vec{P} \times \vec{L} - \vec{L} \times \vec{P}) - \alpha \frac{\vec{x}}{r} \quad \text{for} \quad V(r) = -\frac{\alpha}{r}, \quad (4.65)$$

which is well-known in the classical mechanics of planetary motion. It is straightforward to check its conservation $[H, \vec{M}] = 0$. Evaluation of the classical version $\vec{p} \times \vec{L}/m - \alpha\vec{x}/r$ at the perihelion shows that this vector points along the direction of the principal axis of the Kepler ellipse, which is a constant of non-relativistic motion in a pure $1/r$ potential. The quantum operator (4.65) is obtained by Weyl symmetrization, which is necessary for self-adjointness.¹

¹ With $[\vec{P}, \frac{1}{r}] = i\hbar \frac{\vec{x}}{r^3}$, $[P_i, \frac{x_j}{r}] = \frac{\hbar}{ir}(\delta_{ij} - \frac{x_i x_j}{r^2})$, $\vec{A} \times (\vec{B} \times \vec{C}) = A_j \vec{B} C_j - A_j B_j \vec{C}$ and $(\vec{x} \times \vec{L})^\dagger = -\vec{L} \times \vec{x}$ we can verify

$$[H, \vec{M}] = [-\frac{\alpha}{r}, \frac{\vec{P} \times \vec{L} - \vec{L} \times \vec{P}}{2m}] + [\frac{P^2}{2m}, -\alpha \frac{\vec{x}}{r}] = \frac{i\hbar\alpha}{2m} \left(\frac{\vec{x}}{r^3} \times \vec{L} - \vec{L} \times \frac{\vec{x}}{r^3} + \vec{P} \frac{1}{r} - (\vec{P} \vec{x}) \frac{\vec{x}}{r^3} + \frac{1}{r} \vec{P} - \frac{\vec{x}}{r^3} (\vec{x} \vec{P}) \right) = 0 \quad (4.66)$$

The Lenz vector, of course, does not commute with \mathcal{L}_z but rather transforms as a vector, $[\mathcal{L}_i, M_j] = i\hbar \varepsilon_{ijk} M_k$. Since $\vec{M} \cdot \vec{L} = \vec{L} \cdot \vec{M} = 0$ and (after a tedious calculation) $M^2 = \frac{2H}{m}(\mathcal{L}^2 + \hbar^2) + \lambda^2$ is a function of H and \mathcal{L}^2 , only M_z qualifies for the additional commuting operator that lifts the degeneracy. The algebra is completed (after further tedious calculations) by

$$[M_i, M_j] = i\hbar \frac{2H}{m} \varepsilon_{ijk} \mathcal{L}_k. \quad (4.67)$$

For fixed energy $H\psi = E\psi$ the six conserved charges \mathcal{L}_i and $\mathcal{M}_j = \sqrt{\frac{-m}{2E}} M_j$ form an angular momentum algebra $SO(4)$ in 4 dimensions, or, equivalently, two independent angular momentum algebras $SO(3)$ generated by $\frac{1}{2}(\mathcal{L}_i \pm \mathcal{M}_i)$. The properties of abstract angular momentum algebras, which will be derived in the next section, can then be used for a complete algebraic computation of the energy levels of the hydrogen atom. For more details see <http://hbar.physik.uni-oldenburg.de/vlqm/VLqm/node72.html> or [Hannabuss].

4.3 Summary

- For a Hamiltonian of the form $H = \frac{p^2}{2m} - V(r)$, which is symmetric under rotations, the angular momentum $\mathcal{L} = \vec{X} \times \vec{P}$ is conserved $[H, \mathcal{L}_i] = 0$ and the algebra $[\mathcal{L}_i, \mathcal{L}_j] = i\hbar\varepsilon_{ijk}\mathcal{L}_k$ leads to the following three commuting operators

$$[H, \mathcal{L}_z] = [H, \mathcal{L}^2] = [\mathcal{L}_z, \mathcal{L}^2] = 0. \quad (4.68)$$

- The common eigenfunctions of \mathcal{L}^2 and \mathcal{L}_z are the spherical harmonics with eigenvalues

$$\mathcal{L}^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm} \quad (4.69)$$

and

$$\mathcal{L}_z Y_{lm} = \hbar m Y_{lm} \quad (4.70)$$

with l and $|m| \leq l$ integer. The eigenvalue of \mathcal{L}^2 is $(2l+1)$ fold degenerate.

- The Schrödinger equation for the hydrogen atom can be solved by reducing the non-relativistic two-body problem to the one-body problem with reduced mass $\mu = m_1 m_2 / M$ and a free center of mass motion with total mass $M = m_1 + m_2$.

With the formula for the Laplace operator

$$\Delta = \frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{1}{r^2} \frac{\mathcal{L}^2}{\hbar^2} \quad (4.71)$$

and a separation ansatz in spherical coordinates the energy eigenvalues

$$E_n = -\frac{Z^2 \mathcal{R}}{n^2} = -2\mu \left(\frac{Z\hbar}{a_0 n} \right)^2, \quad (4.72)$$

are determined by the termination condition of the power series solution to the radial equation (4.57), which is related to the differential equation

$$xL''(x) + (2l+2-x)L'(x) - (l+1-n)L(x) = 0 \quad (4.73)$$

for the associated Laguerre polynomials

$$L_r^s(x) = \partial_x^s L_r(x) = \partial_x^s e^x \partial_x^r e^{-x} x^r, \quad \text{with } r = n+l, \quad s = 2l+1 \quad (4.74)$$

by $x = 2\rho = 2\kappa r$ with $\kappa = \sqrt{\frac{-2\mu E_n}{\hbar^2}} = \frac{Z}{na_0}$. The normalized wave functions are

$$u_{nlm} = \sqrt{\frac{(n-l-1)!(2\kappa^3)}{2n((n+1)!)^3}} (2\kappa r)^l e^{-\kappa r} L_{n+l}^{2l+1}(2\kappa r) Y_{lm}(\theta, \varphi) \quad (4.75)$$

where $n \in \mathbb{N}$ is the principal quantum number, $l < n$ the orbital quantum number and m the magnetic quantum number. Due to the approximation of a pure Coulomb interaction and electrons without spin E_n is n^2 -fold degenerate.