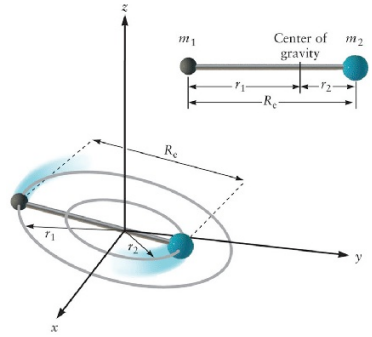
Chapter 4

Quantum mechanics in more than one-dimension

Previously, we have explored the manifestations of quantum mechanics in one spatial dimension and discussed the properties of bound and unbound states. The concepts developed there apply equally to higher dimension. However, for a general two or three-dimensional potential, without any symmetry, the solutions of the Schrödinger equation are often inaccessible. In such situations, we may develop approximation methods to address the properties of the states (see chapter 7). However, in systems where there is a high degree of symmetry, the quantum mechanics of the system can often be reduced to a tractable low-dimensional theory.



4.1 Rigid diatomic molecule

As a pilot example let us consider the quantum mechanics of a rigid diatomic molecule with nuclear masses m_1 and m_2, and (equilibrium) bond length, R_e (see figure). Since the molecule is rigid, its coordinates can be specified by its centre of mass, $\mathbf{R} = \frac{m_1\mathbf{r}_1+m_2\mathbf{r}_2}{m_1+m_2}$, and internal orientation, $\mathbf{r} = \mathbf{r}_2 - \mathbf{r_1}$ (with $|\mathbf{r}| = R_e$). Defining the total mass $M = m_1 + m_2$, and moment of inertia, $I = \mu R_e^2$, where $\mu = m_1 m_2/(m_1 + m_2)$ denotes the reduced mass, the corresponding Hamiltonian can be then separated into the kinetic energy associated with the centre of mass motion and the rotational kinetic energy,

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{L}}^2}{2I}\,, \tag{4.1}$$

where $\hat{\mathbf{P}} = -i\hbar\nabla_{\mathbf{R}}$ and $\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}}$ denotes the angular momentum associated with the internal degrees of freedom. Since the internal and centre of mass degrees of freedom separate, the wavefunction can be factorized as $\psi(\mathbf{r}, \mathbf{R}) = e^{i\mathbf{K}\cdot\mathbf{R}}Y(\mathbf{r})$, where the first factor accounts for the free particle motion of the body, and the second factor relates to the internal angular degrees of freedom.

As a result of the coordinate separation, we have reduced the problem of the rigid diatomic molecule to the study of the quantum mechanics of a particle moving on a sphere – the **rigid rotor**,

$$\hat{H}_{\text{rot}} = \frac{\hat{\mathbf{L}}^2}{2I}\,.$$

The eigenstates of this component of the Hamiltonian are simply the states of the angular momentum operator. Indeed, in *any* quantum mechanical system involving a radial potential, the angular momentum will be conserved, i.e.

$[\hat{H}, \hat{\mathbf{L}}] = 0$ meaning that the angular component of the wavefunction can be indexed by the states of the angular momentum operator. We therefore now digress to discuss the quantum mechanics of angular momentum.

4.2 Angular momentum

4.2.1 Commutation relations

Following the usual canonical quantization procedure, the angular momentum operator is defined by $\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}}$ where, as usual, $\mathbf{r}$ and $\hat{\mathbf{p}}$ obey the commutation relations, $[\hat{p}_i, r_j] = -i\hbar\delta_{ij}$.[1] Using this relation, one may then show that the angular momentum operators obey the **spin commutation relations**, (exercise)

$$\boxed{[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k\,.} \tag{4.2}$$

where, as usual, ϵ_{ijk} denotes the totally antisymmetric tensor — the Levi-Civita symbol.[2]

▷ Exercise. Show that the angular momentum operator commutes with the Hamiltonian of a particle moving in a central potential, $\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(r)$. Show that the Hamiltonian of a free particle of mass m confined to a sphere of radius R is given by $\hat{H} = \frac{\hat{\mathbf{L}}^2}{2mR^2}$.

4.2.2 Eigenvalues of angular momentum

In the following, we will construct a basis set of angular momentum states. Since the angular momentum is a *vector* quantity, it may be characterized by its magnitude and direction. For the former, let us define the operator $\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$. With the latter, since the separate components of the angular momentum are all mutually non-commuting, we cannot construct a common set of eigenstates for any two of them. They do, however, commute with $\hat{\mathbf{L}}^2$ (exercise). Therefore, in the following, we will look for an eigenbasis of $\hat{\mathbf{L}}^2$ and *one* direction, say $\hat{L}_z$,

$$\hat{\mathbf{L}}^2|a,b\rangle = a|a,b\rangle, \qquad \hat{L}_z|a,b\rangle = b|a,b\rangle\,.$$

To find $|a,b\rangle$, we could simply proceed by looking for a suitable coordinate basis to represent $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ in terms of differential operators. However, although we will undertake such a programme in due course, before getting to this formalism, we can make substantial progress without resorting to an explicit coordinate representation.

▷ Info. **Raising and lowering operators for angular momentum:** The set of eigenvalues a and b can be obtained by making use of a trick based on a "ladder operator" formalism which parallels that used in the study of the quantum harmonic oscillator in section 3.4. Specifically, let us define the raising and lowering operators,

$$\boxed{\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y\,.}$$

[1] In this chapter, we will index the angular momentum operators with a 'hat'. Later, we will become lazy and the hat may well disappear.

[2] Recall that $\epsilon_{ijk} = 1$ if (i,j,k) is an even permutation of (1,2,3), -1 if it is an odd permutation, and 0 if any index is repeated.

With this definition, one may then show that (exercise)

$$[\hat{L}_z, \hat{L}_\pm] = \pm\hbar\hat{L}_\pm \,.$$

Since each component of the angular momentum commutes with $\hat{\mathbf{L}}^2$, we can deduce that the action of $\hat{L}_\pm$ on $|a,b\rangle$ cannot affect the value of a relating to the magnitude of the angular momentum. However, they do effect the projection:

$$\hat{L}_z\hat{L}_\pm|a,b\rangle = \hat{L}_\pm\hat{L}_z|a,b\rangle + [\hat{L}_z,\hat{L}_\pm]|a,b\rangle = (b\pm\hbar)\hat{L}_\pm|a,b\rangle \,.$$

Therefore, if $|a,b\rangle$ is an eigenstate of $\hat{L}_z$ with eigenvalue b, $\hat{L}_\pm|a,b\rangle$ is either zero, or an eigenstate of $\hat{L}_z$ with eigenvalue $b\pm\hbar$, i.e. $\hat{L}_\pm|a,b\rangle = C_\pm(a,b)|a,b\pm\hbar\rangle$ where $C_\pm(a,b)$ is a normalisation constant.

To fix the normalisation, we may note that the norm,

$$\left|\left|\hat{L}_\pm|a,b\rangle\right|\right|^2 = \langle a,b|\hat{L}_\pm^\dagger\hat{L}_\pm|a,b\rangle = \langle a,b|\hat{L}_\mp\hat{L}_\pm|a,b\rangle \,,$$

where we have used the identity $\hat{L}_\pm^\dagger = \hat{L}_\mp$. Then, making use of the relation $\hat{L}_\mp\hat{L}_\pm = \hat{L}_x^2 + \hat{L}_y^2 \pm i[\hat{L}_x\hat{L}_y] = \hat{\mathbf{L}}^2 - \hat{L}_z^2 \pm \hbar\hat{L}_z$, and the presumed normalisation, $\langle a,b|a,b\rangle = 1$, one finds

$$\left|\left|\hat{L}_\pm|a,b\rangle\right|\right|^2 = \langle a,b|\left(\hat{\mathbf{L}}^2 - \hat{L}_z^2 \pm \hbar\hat{L}_z\right)|a,b\rangle = a - b^2 \mp \hbar b \,. \tag{4.3}$$

As a represents the eigenvalue of a sum of squares of Hermitian operators, it is necessarily non-negative. Moreover, b is real. Therefore, for a given a, b must be bounded: there must be a $b_{\max}$ and a (negative or zero) $b_{\min}$. In particular,

$$\left|\left|\hat{L}_+|a,b_{\max}\rangle\right|\right|^2 = a - b_{\max}^2 - \hbar b_{\max}$$
$$\left|\left|\hat{L}_-|a,b_{\min}\rangle\right|\right|^2 = a - b_{\min}^2 + \hbar b_{\min} \,,$$

For a given a, $b_{\max}$ and $b_{\min}$ are determined uniquely — there cannot be two states with the same a but different b annihilated by $\hat{L}_+$. It also follows immediately that $a = b_{\max}(b_{\max}+\hbar)$ and $b_{\min} = -b_{\max}$. Furthermore, we know that if we keep operating on $|a,b_{\min}\rangle$ with $\hat{L}_+$, we generate a sequence of states with $\hat{L}_z$ eigenvalues $b_{\min}+\hbar$, $b_{\min}+2\hbar$, $b_{\min}+3\hbar$, $\cdots$. This series must terminate, and the only possible way for that to happen is for $b_{\max}$ to be equal to $b_{\min}+n\hbar$ with n integer, from which it follows that $b_{\max}$ is either an integer or half an odd integer times $\hbar$

At this point, we switch to the standard notation. We have established that the eigenvalues of $\hat{L}_z$ form a finite ladder, with spacing $\hbar$. We write them as $m\hbar$, and ℓ is used to denote the maximum value of m, so the eigenvalue of $\hat{\mathbf{L}}^2$, $a = \ell(\ell+1)\hbar^2$. Both ℓ and m will be integers or half odd integers, but the spacing of the ladder of m values is always unity. Although we have been writing $|a,b\rangle$ with $a = \ell(\ell+1)\hbar^2$, $b = m\hbar$ we shall henceforth follow convention and write $|\ell,m\rangle$.

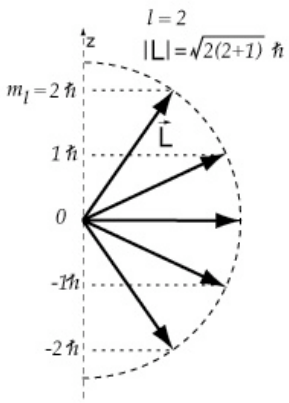


Figure 4.1: The following is a schematic showing the angular momentum scheme for $\ell = 2$ with $\mathbf{L}^2 = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$ and the five possible values for the L_z projection.

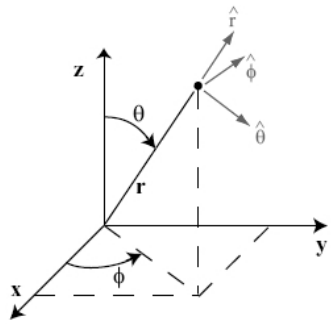
In summary, the operators $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ have a common set of orthonormal eigenstates $|\ell,m\rangle$ with

$$\boxed{\hat{\mathbf{L}}^2|\ell,m\rangle = \ell(\ell+1)\hbar^2|\ell,m\rangle, \qquad \hat{L}_z|\ell,m\rangle = m\hbar|\ell,m\rangle \,,} \tag{4.4}$$

where ℓ, m are integers or half-integers. The allowed quantum numbers m form a ladder with step spacing unity, the maximum value of m is ℓ, and the minimum value is $-\ell$. With these results, we may then return to the normalization of the raising and lowering operators. In particular, making use of Eq. (4.3), we have

$$\boxed{\begin{array}{l}\hat{L}_+|\ell,m\rangle = \sqrt{\ell(\ell+1)-m(m+1)}\hbar|l,m+1\rangle \\ \hat{L}_-|\ell,m\rangle = \sqrt{\ell(\ell+1)-m(m-1)}\hbar|l,m-1\rangle\end{array}} \,. \tag{4.5}$$

The use of m to denote the component of angular momentum in one direction came about because a Bohr-type electron in orbit is a current loop, with a magnetic moment parallel to its angular momentum. So the m measured the component of magnetic moment in a chosen direction, usually along an external magnetic field. For this reason, m is often termed the **magnetic quantum number**.



4.2.3 Representation of the angular momentum states

Having established expressions for the eigenvalues of the angular momentum operators, it is now necessary to establish coordinate representations for the corresponding eigenstates, $Y_{\ell m}(\theta,\phi) = \langle\theta,\phi|\ell,m\rangle$. Here the angles θ and ϕ denote the spherical coordinates parameterising the unit sphere (see figure). Previously, we obtained the eigenvalues of the angular momentum operator by making use of the raising and lowering operators in a manner that parallelled the study of the quantum harmonic oscillator. Similarly, to obtain explicit expressions for the eigenstates, we must make use of the coordinate representation of these operators. With $\mathbf{r} = r\hat{\mathbf{e}}_r$, the gradient operator can be written in spherical polar coordinates as

$$\nabla = \hat{\mathbf{e}}_r\partial_r + \hat{\mathbf{e}}_\theta\frac{1}{r}\partial_\theta + \hat{\mathbf{e}}_\phi\frac{1}{r\sin\theta}\partial_\phi\,.$$

From this result, we thus obtain

$$\boxed{\hat{L}_z = -i\hbar\partial_\phi, \qquad \hat{L}_\pm = \hbar e^{\pm i\phi}\left(\pm\partial_\theta + i\cot\theta\partial_\phi\right)\,,} \tag{4.6}$$

and, at least formally,

$$\boxed{\hat{\mathbf{L}}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\partial_\theta(\sin\theta\partial_\theta) + \frac{1}{\sin^2\theta}\partial_\phi^2\right]\,.}$$

Beginning with the eigenstates of $\hat{L}_z$, the eigenvalue equation (4.4), and making use of the expression above, we have

$$-i\hbar\partial_\phi Y_{\ell m}(\theta,\phi) = m\hbar Y_{\ell m}(\theta,\phi)\,.$$

Since the left hand side depends only on ϕ, the solution is separable and takes the form $Y_{\ell m}(\theta,\phi) = F(\theta)e^{im\phi}$. Note that, since m is integer, the continuity of the wavefunction, $Y_{\ell m}(\theta,\phi+2\pi) = Y_{\ell m}(\theta,\phi)$, is ensured.

To determine the second component of the eigenstates, $F(\theta)$, we could immediately turn to the eigenvalue equation involving the differential operator for $\hat{\mathbf{L}}^2$,

$$\left[\frac{1}{\sin\theta}\partial_\theta(\sin\theta\partial_\theta) - \frac{m^2}{\sin^2\theta}\partial_\phi^2\right]F(\theta) = \ell(\ell+1)F(\theta)\,.$$

However, to construct the states, it is easier to draw upon the properties of the angular momentum raising and lowering operators (much in the same way that the Hermite polynomials are generated by the action of ladder operators in the harmonic oscillator problem).

Consider then the state of maximal m, $|\ell,\ell\rangle$, for which $\hat{L}_+|\ell,\ell\rangle = 0$. Making use of the coordinate representation of the raising operator above together with the separability of the wavefunction, this relation implies that

$$0 = \langle\theta,\phi|\hat{L}_+|\ell,\ell\rangle = \hbar e^{i\phi}\left(\partial_\theta + i\cot\theta\partial_\phi\right)Y_{\ell\ell}(\theta,\phi) = \hbar e^{i(\ell+1)\phi}\left(\partial_\theta - \ell\cot\theta\right)F(\theta)\,.$$

From this result it follows that $\partial_\theta F(\theta) = \ell \cot\theta F(\theta)$ with the solution $F(\theta) = C \sin^\ell \theta$, and C a constant of normalization. States with values of m lower than ℓ can then be obtained simply by repeated application of the angular momentum lowering operator $\hat{L}_-$ to the state $|\ell, \ell\rangle$. This amounts to the relation

$$\begin{aligned} Y_{\ell m}(\theta, \phi) &= C(\hat{L}_-)^{\ell - m} \left[\sin^\ell \theta e^{i\ell\phi}\right] \\ &= C\left(-\partial_\theta + i\cot\theta\partial_\phi\right)^{\ell-m} \left[\sin^\ell \theta e^{i\ell\phi}\right] . \end{aligned}$$

The eigenfunctions produced by this procedure are well known and referred to as the **spherical harmonics**. In particular, one finds that the normalized eigenstates take the form,

$$\boxed{Y_{\ell m}(\theta, \phi) = (-1)^{m+|m|} \left[\frac{2\ell+1}{4\pi} \frac{(\ell - |m|)!}{(\ell + |m|)!}\right]^{1/2} P_\ell^{|m|}(\cos\theta) e^{im\phi} ,} \tag{4.7}$$

where

$$P_\ell^m(\xi) = \frac{(1-\xi^2)^{m/2}}{2^\ell \ell!} \frac{d^{m+\ell}}{d\xi^{m+\ell}} (\xi^2 - 1)^\ell ,$$

represent the **associated Legendre polynomials**. In particular, for the first few angular momentum states, we have

$$\begin{aligned} &Y_{00} = \tfrac{1}{\sqrt{4\pi}} \\ &Y_{10} = \sqrt{\tfrac{3}{4\pi}} \cos\theta, && Y_{11} = -\sqrt{\tfrac{3}{8\pi}} e^{i\phi} \sin\theta \\ &Y_{20} = \sqrt{\tfrac{5}{16\pi}} (3\cos^2\theta - 1), && Y_{21} = -\sqrt{\tfrac{15}{8\pi}} e^{i\phi} \sin\theta\cos\theta, \quad Y_{22} = \sqrt{\tfrac{15}{32\pi}} e^{2i\phi} \sin^2\theta \end{aligned}$$

Figure 4.2 shows a graphical representation of the states for the lowest spherical harmonics. From the colour coding of the states, the symmetry, $Y_{\ell,-m} = (-1)^m Y^*_{\ell m}$ is manifest.

As a complete basis set, the spherical harmonics can be used as a resolution of the identity

$$\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} |\ell, m\rangle\langle\ell, m| = \mathbb{I} .$$

Equivalently, expressed in the coordinate basis, we have

$$\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} Y^*_{\ell,m}(\theta', \phi') Y_{\ell,m}(\theta, \phi) = \frac{1}{\sin\theta} \delta(\theta - \theta')\delta(\phi - \phi') ,$$

where the prefactor $\sin\theta$ derives from the measure. Similarly, we have the orthogonality condition,

$$\int_0^\pi d\theta \sin\theta \int_0^{2\pi} Y^*_{\ell,m}(\theta, \phi) Y_{\ell',m'}(\theta, \phi) = \delta_{\ell\ell'}\delta_{mm'} .$$

After this lengthy digression, we may now return to the problem of the quantum mechanical rotor Hamiltonian and the rigid diatomic molecule. From the analysis above, we have found that the eigenstates of the Hamiltonian (4.1) are given by $\psi(\mathbf{R}, \mathbf{r}) = \frac{1}{\sqrt{2\pi}} e^{i\mathbf{K}\cdot\mathbf{R}} Y_{\ell,m}(\theta, \phi)$ with eigenvalues

$$E_{\mathbf{K},\ell} = \frac{\hbar^2 \mathbf{K}^2}{2M} + \frac{\hbar^2}{2I} \ell(\ell + 1) ,$$

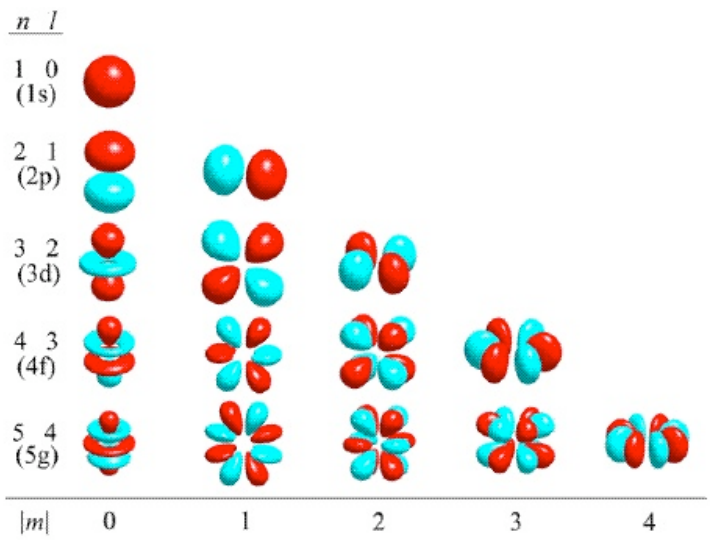


Figure 4.2: First four groups of spherical harmonics, $Y_{\ell m}(\theta, \phi)$ shown as a function of spherical angular coordinates. Specifically, the plots show the surface generated by $|\mathrm{Re}\, Y_{\ell m}(\theta, \phi)|$ to fix the radial coordinate and the colours indicate the relative sign of the real part.

where each $\mathbf{K}, \ell$ value has a $2\ell + 1$-fold degeneracy.

▷ Exercise. Using this result, determine the dependence of the heat capacity of a gas of rigid diatomic molcules on the angular degrees of freedom. How would this result change if the diatomic gas was constrained to just two spatial dimensions, i.e. the axis of rotation was always perpendicular to the plane in which the molecules can move?

4.3 The central potential

In a system where the central force field is entirely radial, the potential energy depends only on $r \equiv |\mathbf{r}|$. In this case, a general non-relativistic Hamiltonian for a single particle is given by

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(r)\,.$$

In the classical system, $\mathbf{L}^2 = (\mathbf{r} \times \mathbf{p})^2 = r^2 p^2 - (\mathbf{r} \cdot \mathbf{p})^2$. As a result, we can set $\mathbf{p}^2 = \frac{\mathbf{L}^2}{r^2} + p_r^2$, where $p_r \equiv \mathbf{e}_r \cdot \mathbf{p}$ denotes the radial component of the momentum. In the quantum system, since the space and position coordinates do not commute, we have (exercise)

$$\hat{\mathbf{L}}^2 = r^2 \hat{\mathbf{p}}^2 - (\mathbf{r} \cdot \hat{\mathbf{p}})^2 + i\hbar \mathbf{r} \cdot \hat{\mathbf{p}}\,.$$

In spherical coordinates, since $\mathbf{r} \cdot \hat{\mathbf{p}} = -i\hbar \mathbf{r} \cdot \nabla = -i\hbar r \partial_r$, it follows that $\hat{\mathbf{p}}^2 = \frac{\hat{\mathbf{L}}^2}{r^2} - \frac{\hbar^2}{r^2}[(r\partial_r)^2 + r\partial_r]$. Equivalently, noting that $(r\partial_r)^2 + r\partial_r = \partial_r^2 + \frac{2}{r}\partial_r$, we can set

$$\hat{\mathbf{p}}^2 = \frac{\hat{\mathbf{L}}^2}{r^2} - \hbar^2 \left[\partial_r^2 + \frac{2}{r}\partial_r\right]\,.$$

Finally, substituted into the Schrödinger equation, we obtain the eigenvalue equation

$$\boxed{\left[-\frac{\hbar^2}{2m}\left(\partial_r^2+\frac{2}{r}\partial_r\right)+\frac{\hat{\mathbf{L}}^2}{2mr^2}+V(r)\right]\psi(\mathbf{r})=E\psi(\mathbf{r})\,.} \tag{4.8}$$

Since we already know the eigenstates of $\hat{\mathbf{L}}^2$, we can immediately take advantage of the separability of the Hamiltonian to find that $\psi(\mathbf{r}) = R(r)Y_{\ell,m}(\theta,\phi)$, where the radial part of the wavefunction is set by

$$\left[-\frac{\hbar^2}{2m}\left(\partial_r^2+\frac{2}{r}\partial_r\right)+\frac{\hbar^2}{2mr^2}\ell(\ell+1)+V(r)\right]R(r)=ER(r)\,.$$

Finally, we can further simplify this expression by setting $R(r) = u(r)/r$, whereupon we obtain the "one-dimensional" equation

$$\left[-\frac{\hbar^2\partial_r^2}{2m}+V_{\text{eff}}(r)\right]u(r)=u(r)\,, \tag{4.9}$$

where the effective potential, $V_{\text{eff}}(r) = \frac{\hbar^2}{2mr^2}\ell(\ell+1)+V(r)$, acquires an additional component due to the centrifugal component of the force. Here the equation must be solved subject to the boundary condition $u(0) = 0$. From the normalization condition,

$$\int d^3r\,|\psi(\mathbf{r})|^2=\int_0^\infty dr r^2\frac{1}{r^2}|u(r)|^2=1\,,$$

for a bound state to exist, $\lim_{r\to\infty}|u(r)|\le a/r^{1/2+\epsilon}$ with $\epsilon>0$.

From this one-dimensional form of the Hamiltonian, the question of the existence of bound states in higher dimension becomes clear. Since the wavefunction $u(r)$ vanishes at the origin, we may map the Hamiltonian from the half-line to the full line with the condition that we admit only antisymmetric wavefunctions. The question of bound states can then be related back to the one-dimensional case. Previously, we have seen that a symmetric attractive potential always leads to a bound state in one-dimension. However, odd parity states become bound only at a critical strength of the interaction.

4.4 Atomic hydrogen

The Hydrogen atom consists of an electron bound to a proton by the Coulomb potential,

$$V(r)=-\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}\,.$$

We can generalize the potential to a nucleus of charge Ze without complication of the problem. Since we are interested in finding bound states of the proton-electron system, we are looking for solutions with E negative. At large separations, the wave equation (4.9) simplifies to

$$-\frac{\hbar^2\partial_r^2}{2m}u(r)\simeq Eu(r)\,,$$

having approximate solutions $e^{\kappa r}$ and $e^{-\kappa r}$, where $\hbar\kappa=\sqrt{-2mE}$. (Here, strictly speaking, m should denote the reduced mass of electron-proton system.) The bound states we are looking for, of course, have exponentially decreasing wavefunctions at large distances.

To further simplify the wave equation, it is convenient to introduce the dimensionless variable $\rho = \kappa r$, leading to the equation

$$\partial_\rho^2 u(\rho) = \left(1 - \frac{2\nu}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right) u(\rho)\,,$$

where (for reasons which will become apparent shortly) we have introduced the dimensionless parameter $\nu = \frac{Ze^2}{4\pi\epsilon_0}\frac{\kappa}{2E}$. Notice that in transforming from r to the dimensionless variable ρ, the scaling factor depends on energy, so will be different for different energy bound states! Consider now the behaviour of the wavefunction near the origin. The dominant term for sufficiently small ρ is the centrifugal component, so

$$\partial_\rho^2 u(\rho) \simeq \frac{\ell(\ell+1)}{\rho^2} u(\rho)\,,$$

for which the solutions are $u(\rho) \sim \rho^{-\ell}$ and $u(\rho) \sim \rho^{\ell+1}$. Since the wavefunction cannot be singular, we must choose the second solution.

We have established that the wavefunction decays as $e^{-\kappa r} = e^{-\rho}$ at large distances, and goes as $\rho^{\ell+1}$ close to the origin. Factoring out these two asymptotic behaviours, let us then define $w(\rho)$ such that $u(\rho) = e^{-\rho}\rho^{\ell+1}w(\rho)$. We leave it as a tedious but straightforward exercise to show that

$$\rho\partial_\rho^2 w(\rho) + 2(\ell+1-\rho)\partial_\rho w(\rho) + 2(\nu - (\ell+1))w(\rho) = 0\,.$$

Substituting the trial series solution, $w(\rho) = \sum_{k=0}^{\infty} w_k \rho^k$, we obtain a recurrence relation between successive coefficients:

$$\frac{w_{k+1}}{w_k} = \frac{2(k+\ell+1-\nu)}{(k+1)(k+2(\ell+1))}\,.$$

For large values of k, $w_{k+1}/w_k \to 2/k$, so $w_k \sim 2^k/k!$ and therefore $w(\rho) \sim e^{2\rho}$. This means we have found the diverging radial wavefunction, $u(\rho) \sim e^{\rho}$, which is in fact the correct behaviour for general values of the energy.

To find the bound states, we must choose energies such that the series is not an infinite one. As long as the series stops somewhere, the exponential decrease will eventually take over, and yield a finite (bound state) wavefunction. Just as for the simple harmonic oscillator, this can only happen if for some k, $w_{k+1} = 0$. Inspecting the ratio w_{k+1}/w_k, evidently the condition for a bound state is that

$$\nu = n, \qquad \text{integer}\,,$$

in which case the series for $w(\rho)$ terminates at $k = n - \ell - 1$. From now on, since we know that for the functions we're interested in ν is an integer, we replace ν by n.

Finally, making use of the definitions of ν and κ above, we obtain the bound state energies,

$$\boxed{E_n = -\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \frac{m}{2\hbar^2}\frac{1}{n^2} \equiv -\frac{Z^2}{n^2}\mathrm{Ry}\,.}$$

Remarkably, this is the very same series of bound state energies found by Bohr from his model! Of course, this had better be the case, since the series of energies Bohr found correctly accounted for the spectral lines emitted by hot hydrogen atoms. Notice, though, that there are some important differences

with the Bohr model: the energy here is determined entirely by n, called the principal quantum number, but, in contrast to Bohr's model, n is not the angular momentum. The true ground state of the hydrogen atom, $n = 1$, has zero angular momentum: since $n = k + \ell + 1$, $n = 1$ means both $l = 0$ and $k = 0$. The ground state wavefunction is therefore spherically symmetric, and the function $w(\rho) = w_0$ is just a constant. Hence $u(\rho) = \rho e^{-\rho} w_0$ and the actual radial wavefunction is this divided by r, and of course suitably normalized.

To write the wavefunction in terms of r, we need to find κ. Putting together $\rho = \kappa_n r$, $\kappa_n = \sqrt{-2mE_n/\hbar^2}$ and the expression for E_n, we find that $\kappa_n = \frac{Ze^2}{4\pi\epsilon_0}\frac{m}{\hbar^2 n} = \frac{Z}{na_0}$, where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10}\,\mathrm{m}$$

denotes the **Bohr radius** – the radius of the lowest orbit in Bohr's model. With this definition, the energy levels can then be expressed as $E_n = -\frac{1}{4\pi\epsilon_0}\frac{(Ze)^2}{2a_0}\frac{1}{n^2}$.

Moving on to the excited states: for $n = 2$, we have a choice: either the radial function $w(\rho)$ can have one term, as before, but now the angular momentum $\ell = 1$ (since $n = k+\ell+1$); or $w(\rho)$ can have two terms (so $k = 1$), and $\ell = 0$. Both options give the same energy, 0.25 Ry, since n is the same, and the energy only depends on n. In fact, there are four states at this energy, since $\ell = 1$ has states with $m = 1$, $m = 0$ and $m = 1$, and $\ell = 0$ has the one state $m = 0$. For $n = 3$, there are 9 states altogether: $\ell = 0$ gives one, $\ell = 1$ gives 3 and $\ell = 2$ gives 5 different m values. In fact, for principal quantum number n there are n^2 degenerate states (n^2 being the sum of the first n odd integers).

From now on, we label the wavefunctions with the quantum numbers, $\psi_{n\ell m}(r, \theta, \phi)$, so the ground state is the spherically symmetric $\psi_{100}(r)$. For this state $R(r) = u(r)/r$, where $u(\rho) = e^{-\rho}\rho^{\ell+1}w(\rho) = e^{-\rho}\rho w_0$, with w_0 a constant and $\rho = \kappa_1 r = Zr/a_0$. So, as a function of r, $R_{10}(r) = Ne^{-Zr/a_0}$ with N the normalization constant:

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}\,.$$

For $n = 2$, $\ell = 1$ the function $w(\rho)$ is still a single term, a constant, but now $u(\rho) = e^{-\rho}\rho^{\ell+1}w(\rho) = e^{-\rho}\rho^2 w_0$, and, for $n = 2$, $\rho = \kappa_2 r = Zr/2a_0$, remembering the energy-dependence of κ. After normalization, we find

$$R_{21} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}\,.$$

The other $n = 2$ state has $\ell = 0$. So from $n = k + \ell + 1$, we have $k = 1$ and the series for w has two terms, $k = 0$ and $k = 1$, the ratio being

$$\frac{w_{k+1}}{w_k} = \frac{2(k + \ell + 1 - n)}{(k + 1)(k + 2(\ell + 1))} = -1\,,$$

for the relevant values: $k = 0$, $\ell = 0$, $n = 2$. So $w_1 = -w_0$, $w(\rho) = w_0(1 - \rho)$. For $n = 2$, $\rho = r/2a_0$, the normalized wavefunction is given by

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

Note that the zero angular momentum wavefunctions are non-zero and have non-zero slope at the origin. This means that the full three-dimensional wavefunctions have a slope discontinuity there! But this is fine - the potential is

infinite at the origin. (Actually, the proton is not a point charge, so really the kink will be smoothed out over a volume of the size of the proton - a very tiny effect.)

In practice, the first few radial functions $w(\rho)$ can be constructed fairly easily using the method presented above, but it should be noted that the differential equation for $w(\rho)$,

$$\rho\partial_\rho^2 w(\rho) + 2(\ell+1-\rho)\partial_\rho w(\rho) + 2(n-(\ell+1))w(\rho) = 0\,,$$

is in fact Laplace's equation, usually written

$$(z\partial_z^2 + (k-1-z)\partial_z + p)L_p^k(z) = 0\,,$$

where k, p are integers, and $L_p^k(z)$ is a **Laguerre polynomial**. The two equations are the same if $z = 2\rho$, and the solution to the radial equation is therefore,

$$w_{n\ell}(\rho) = L_{n-\ell-1}^{2\ell+1}(2\rho)\,.$$

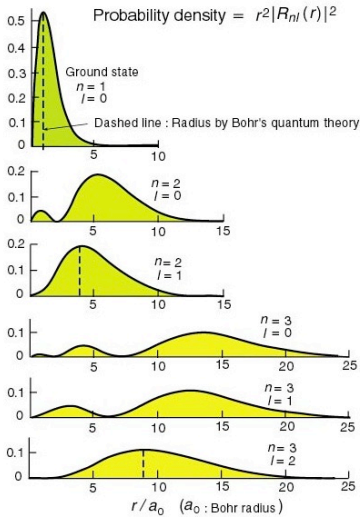
The Laguerre polynomials $L_p^0(z)$, and **associated Laguerre polynomials** $L_p^k(z)$ are given by:

$$L_p^0(z) = e^z \frac{d^p}{dz^p}(e^{-z}z^p), \qquad L_p^k(z) = (-1)^k \frac{d^p}{dz^p} L_{p+k}^0(z)\,.$$

(These representations can be found neatly by solving Laplace's equation using - surprise - a Laplace transform.) The polynomials satisfy the orthonormality relations (with the mathematicians' normalization convention)

$$\int_0^\infty e^{-z} z^k L_p^k L_q^k dz = \frac{[(p+k)!]^3}{p!}\delta_{pq}\,.$$

But what do the polynomials look like? The function $e^{-z}z^p$ is zero at the origin (apart from the trivial case $p = 0$) and zero at infinity, always positive and having non-zero slope except at its maximum value, $z = p$. The p derivatives bring in p separated zeroes, easily checked by sketching the curves generated by successive differentiation. Therefore, $L_p^0(z)$, a polynomial of degree p, has p real positive zeroes, and value at the origin $L_p^0(0) = p!$, since the only non-zero term at $z = 0$ is that generated by all p differential operators acting on z^p.



The associated Laguerre polynomial $L_p^k(z)$ is generated by differentiating $L_{p+k}^0(z)$ k times. Now $L_{p+k}^0(z)$ has $p+k$ real positive zeroes, differentiating it gives a polynomial one degree lower, with zeroes which must be one in each interval between the zeroes of $L_{p+k}^0(z)$. This argument remains valid for successive derivatives, so $L_p^k(z)$ must have p real separate zeroes.

Putting all this together, and translating back from ρ to r, the radial solutions are given by,

$$R_{n\ell}(r) = Ne^{-Zr/na_0}\left(\frac{Zr}{na_0}\right)^\ell L_{n-\ell-1}^{2\ell+1}(2Zr/na_0)\,,$$

with N the normalization constant. For a given principle quantum number n,the largest ℓ radial wavefunction is given by $R_{n,n-1} \propto r^{n-1}\, e^{-Zr/na_0}$.

▷ Info. The eigenvalues of the Hamiltonian for the hydrogen exhibit an unexpectedly high degeneracy. The fact that $E_{n\ell m}$ is independent of m is common to all central potentials – it is just a reflection of rotational invariance of the Hamiltonian.

However, the degeneracy of different ℓ values with the same principle quantum number is considered "accidental", a peculiarity of the $1/r$ potential. To understand the **origin of the degeneracy for atomic hydrogen**, it is helpful to reflect first on the classical dynamics.

In classical mechanics, central forces also lead to conservation of angular momentum leaving orbits restricted to lie in a plane. However, for $1/r$ type potentials, these orbits are also *closed*, i.e. they do not precess. In classical mechanics, this implies that there is an additional conserved vector, since the direction of the major axis of the elliptical orbit is a constant of the motion. This direction is determined by the **Runge-Lenz vector**,

$$\mathbf{R} = \frac{1}{m}\mathbf{p}\times\mathbf{L} - \frac{e^2}{4\pi\epsilon_0}\frac{\mathbf{r}}{r}\,.$$

In quantum theory, up to an operator ordering prescription, $\mathbf{R}$ becomes an operator,

$$\hat{\mathbf{R}} = \frac{1}{2m}(\hat{\mathbf{p}}\times\hat{\mathbf{L}} - \hat{\mathbf{L}}\times\hat{\mathbf{p}}) - \frac{e^2}{4\pi\epsilon_0}\frac{\mathbf{r}}{r}\,.$$

With this definition, one may confirm that $[\hat{H},\hat{\mathbf{R}}] = 0$ (exercise).

As a vector operator, $\hat{\mathbf{R}}$ exhibits the following commutation relations, $[\hat{R}_i,\hat{L}_j] = i\hbar\epsilon_{ijk}\hat{R}_k$. Similarly, $[\hat{R}_i,\hat{N}_j] = i\hbar\frac{(-2\hat{H})}{m}\epsilon_{ijk}\hat{L}_k$ (exercise). Moreover, one may confirm that

$$\hat{\mathbf{R}}^2 = \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 + \frac{2\hat{H}}{m}(\hat{\mathbf{L}}^2+\hbar^2)\,,$$

showing that $\hat{H}$ can be written in terms of the two constants of motion, $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{R}}^2$. Focussing on the bound states, if we consider the Hermitian operator, $\hat{K} = \sqrt{\frac{-m}{2\hat{H}}}\hat{\mathbf{R}}$, which fulfil the following commutation relations, $[\hat{K}_i,\hat{K}_j] = i\hbar\epsilon_{ijk}\hat{L}_k$, $[\hat{K}_i,\hat{L}_j] = i\hbar\epsilon_{ijk}\hat{K}_k$, and $[\hat{L}_i,\hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k$, we find that

$$\hat{H} = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{m}{2(\hat{\mathbf{K}}^2+\hat{\mathbf{L}}^2+\hbar^2)}\,.$$

If we now define the "raising and lowering" operators, $\hat{\mathbf{M}} = \frac{\hat{\mathbf{L}}+\hat{\mathbf{K}}}{2}$, $\hat{\mathbf{N}} = \frac{\hat{\mathbf{L}}-\hat{\mathbf{K}}}{2}$ the following commutation relations emerge (exercise),

$$\begin{aligned}
[\hat{M}_i,\hat{M}_j] &= i\hbar\epsilon_{ijk}\hat{L}_k\\
[\hat{N}_i,\hat{N}_j] &= i\hbar\epsilon_{ijk}\hat{K}_k\\
[\hat{N}_i,\hat{M}_j] &= 0\,,
\end{aligned}$$

i.e. we have obtained two commuting angular momentum algebras(!) and

$$\hat{H} = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{m}{2(2\hat{\mathbf{M}}^2+2\hat{\mathbf{N}}^2+\hbar^2)}\,.$$

We can simultaneously diagonalize the operators, $\hat{\mathbf{M}}^2$, $\hat{M}_z$, $\hat{\mathbf{N}}^2$ and $\hat{N}_z$,

$$\begin{aligned}
\hat{\mathbf{M}}^2|m,n,\mu,\nu\rangle &= \hbar^2 m(m+1)|m,n,\mu,\nu\rangle, \qquad & \hat{M}_z|m,n,\mu,\nu\rangle &= \hbar\mu|m,n,\mu,\nu\rangle\\
\hat{\mathbf{N}}^2|m,n,\mu,\nu\rangle &= \hbar^2 m(m+1)|m,n,\mu,\nu\rangle, \qquad & \hat{N}_z|m,n,\mu,\nu\rangle &= \hbar\nu|m,n,\mu,\nu\rangle\,.
\end{aligned}$$

where $m,n = 0,1/2,1,3/2,\cdots$, $\mu = -m,-m+1,\cdots m$ and $\nu = -n,-n+1,\cdots n$. Since $\hat{\mathbf{R}}\cdot\hat{\mathbf{L}} = \hat{\mathbf{L}}\cdot\hat{\mathbf{R}} = 0$, then $\hat{\mathbf{K}}\cdot\hat{\mathbf{L}} = \hat{\mathbf{L}}\cdot\hat{\mathbf{R}} = 0$ and the only relevant states are those for which $\hat{\mathbf{M}}^2 - \hat{\mathbf{N}}^2 = 0$, i.e. $m = n$. Therefore,

$$\begin{aligned}
\hat{H}|m,m,\mu,\nu\rangle &= -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{m}{2\hbar^2(4m(m+1)+1)}|m,m,\mu,\nu\rangle\\
&= -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{m}{2\hbar^2(2m+1)^2}|m,m,\mu,\nu\rangle\,.
\end{aligned}$$

From this result, we can identify $2m+1 = 1,2,\cdots$ as the principle quantum number. For a given $(2m+1)$ value, the degeneracy of the state is $(2m+1)^2$ as expected.