

**Lecture 4:**  
**Angular Momentum;**  
**The Hydrogen Atom**

Recall from the previous lecture:

In classical mechanics one defines the angular momentum by

$$\vec{L} = \vec{r} \times \vec{p} = (y p_z - z p_y, z p_x - x p_z, x p_y - y p_x) \quad (1)$$

We get the angular momentum operator by replacing the vector  $\vec{r}$  by the vector operator  $\hat{r} = (\hat{x}, \hat{y}, \hat{z})$  and the momentum vector by the momentum vector operator

$$\hat{p} = -i\hbar\nabla = -i\hbar(\partial_x, \partial_y, \partial_z)$$

where  $\partial_x = \partial/\partial x$  etc.

The fundamental commutation relations (FCR) are:

$$[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij} \quad \text{where} \quad \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases} \quad (2)$$

We have found the commutation relations for the components of  $\hat{L}$  with the coordinate operators  $\hat{x}$ ,  $\hat{y}$  and  $\hat{z}$ :

$$[\hat{x}, \hat{L}_x] = 0, \quad [\hat{x}, \hat{L}_y] = i\hbar\hat{z}, \quad [\hat{x}, \hat{L}_z] = -i\hbar\hat{y}$$

etc, which can be summarized by

$$[\hat{x}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{x}_k$$

where summation over the repeated index  $k$  is implied, and

$$\varepsilon_{ijk} = \begin{cases} 1 & \text{if } (ijk) = (1, 2, 3) \text{ or } (2, 3, 1) \text{ or } (3, 1, 2) \\ -1 & \text{if } (ijk) = (1, 3, 2) \text{ or } (3, 2, 1) \text{ or } (2, 1, 3) \\ 0 & \text{if } i = j \text{ or } i = k \text{ or } j = k \end{cases}$$

Similarly it is shown that

$$[\hat{p}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{p}_k$$

and hence

$$[\hat{L}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{L}_k \quad (3)$$

An important conclusion from this result is that the components of angular momentum have no common eigenfunctions.

The proof of the hermiticity of the angular momentum operators is a straight forward consequence of the hermiticity of the position and momentum operators.

We have constructed one more operator that commutes with all components of  $\hat{L}$ , namely the square of  $\hat{L}$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

and we have seen that  $\hat{L}^2$  commutes with the components of  $\hat{L}$ :

$$[\hat{L}_x, \hat{L}^2] = [\hat{L}_y, \hat{L}^2] = [\hat{L}_z, \hat{L}^2] = 0 \quad (4)$$

Finally one can also show that the components of  $\hat{L}$  and  $\hat{L}^2$  commute with  $\hat{p}^2$ , and therefore also with the K.E. operator  $\hat{T}$ , and that they commute with  $r$  and hence with any function of  $r$ .

Indeed, working in spherical polar coordinates  $(r, \theta, \varphi)$ , with the polar axis along the cartesian  $z$  direction we get

$$\begin{aligned} \hat{L}_x &= i\hbar \left( \sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \\ \hat{L}_y &= i\hbar \left( -\cos \varphi \frac{\partial}{\partial \theta} + \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \\ \hat{L}_z &= -i\hbar \frac{\partial}{\partial \varphi} \end{aligned} \quad (5)$$

We can therefore conclude that the angular momentum operators commute with the Hamiltonian of a particle in a central field, for example a Coulomb field, hence  $\hat{L}^2$  and  $\hat{L}_z$ , say, can be chosen to have common eigenfunctions with the Hamiltonian.

Detailed calculation of the transformation to  
spherical polar coordinates.

The polar coordinates are defined by

$$\begin{aligned} x &= r \sin \theta \cos \varphi, & r &= \sqrt{x^2 + y^2 + z^2} \\ y &= r \sin \theta \sin \varphi, & \theta &= \arccos(z/r) \\ z &= r \cos \theta, & \varphi &= \arctan(y/x) \end{aligned}$$

hence by the chain rule of partial differentiation

$$\begin{aligned} \frac{\partial}{\partial x} &= \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial x} \frac{\partial}{\partial \varphi} \\ \frac{\partial}{\partial y} &= \frac{\partial r}{\partial y} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y} \frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial y} \frac{\partial}{\partial \varphi} \\ \frac{\partial}{\partial z} &= \frac{\partial r}{\partial z} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z} \frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial z} \frac{\partial}{\partial \varphi} \end{aligned}$$

and we must calculate the nine coefficients

$$\frac{\partial r}{\partial x}, \frac{\partial r}{\partial y}, \dots, \frac{\partial \varphi}{\partial z}$$

We have

$$\begin{aligned} \frac{\partial r}{\partial x} &= \frac{\partial \sqrt{x^2 + y^2 + z^2}}{\partial x} = \frac{x}{\sqrt{x^2 + y^2 + z^2}} \\ &= \frac{x}{r} = \sin \theta \cos \varphi \end{aligned}$$

also

$$\frac{\partial \theta}{\partial x} = \left( \arccos \frac{z}{r} \right)' \frac{\partial}{\partial x} \left( \frac{z}{r} \right)$$

where the prime denotes differentiation w.r.t. the argument  $z/r$  of the arccos:

$$\left( \arccos \frac{z}{r} \right)' = -\frac{r}{\sqrt{x^2 + y^2}} = -\frac{1}{\sin \theta}$$

hence, after another couple of lines of calculations, the result is

$$\frac{\partial \theta}{\partial x} = \frac{1}{r} \cos \theta \cos \varphi$$

and similarly for the remaining coefficients.

Thus finally

$$\begin{aligned} \partial_x &= \sin \theta \cos \varphi \partial_r + \frac{1}{r} \cos \theta \cos \varphi \partial_\theta - \frac{1}{r} \frac{\sin \varphi}{\sin \theta} \partial_\varphi \\ \partial_y &= \sin \theta \sin \varphi \partial_r + \frac{1}{r} \cos \theta \sin \varphi \partial_\theta + \frac{1}{r} \frac{\cos \varphi}{\sin \theta} \partial_\varphi \\ \partial_z &= \cos \theta \partial_r - \frac{\sin \theta}{r} \partial_\theta \end{aligned}$$

where

$$\partial_r = \frac{\partial}{\partial r}, \quad \partial_\theta = \frac{\partial}{\partial \theta}, \quad \text{and} \quad \partial_\varphi = \frac{\partial}{\partial \varphi}$$

hence

$$\begin{aligned} \hat{L}_x &= -i\hbar (y\partial_z - z\partial_y) \\ &= i\hbar (\sin \varphi \partial_\theta + \cot \theta \cos \varphi \partial_\varphi) \\ \hat{L}_y &= -i\hbar (z\partial_x - x\partial_z) \\ &= i\hbar (-\cos \varphi \partial_\theta + \cos \theta \sin \varphi \partial_\varphi) \\ \hat{L}_z &= -i\hbar (x\partial_y - y\partial_x) \\ &= -i\hbar \partial_\varphi \\ \hat{L}^2 &= -\hbar^2 \left[ \frac{1}{\sin \theta} \partial_\theta (\sin \theta \partial_\theta) + \frac{1}{\sin^2 \theta} \partial_\varphi^2 \right] \end{aligned}$$

Since the angular momentum operators contain no operators of differentiation w.r. to  $r$ , we conclude that

$$[\hat{L}_i, r] = 0 \quad \text{for } i = 1, 2, 3, \quad \text{and} \quad [\hat{L}^2, r] = 0$$

and therefore  $\hat{L}_i$  and  $\hat{L}^2$  also commute with any function of  $r$ .

### Eigenvalue problem of angular momentum:

We have seen that  $\hat{L}^2$  and one of the components of  $\hat{L}$  have common eigenfunctions. Inspection of the representations of  $\hat{L}_x$ ,  $\hat{L}_y$  and  $\hat{L}_z$  in terms of polar coordinates shows that the simplest operator is  $\hat{L}_z$ ; therefore we set up the eigenvalue eqs for  $\hat{L}^2$  and  $\hat{L}_z$ :

$$\begin{aligned} \hat{L}^2 Y(\theta, \varphi) &= \hbar^2 \lambda Y(\theta, \varphi) \\ \hat{L}_z Y(\theta, \varphi) &= \hbar m Y(\theta, \varphi) \end{aligned} \tag{6}$$

Here  $\hbar$  has been factored out of the eigenvalues to make  $\lambda$  and  $m$  dimensionless. Substitution of  $\hat{L}^2$  and  $\hat{L}_z$  in terms of polar coordinates yields the following two eigenvalue equations:

$$\begin{aligned} \partial_\varphi Y &= imY \\ \frac{1}{\sin\theta} \partial_\theta (\sin\theta \partial_\theta Y) + \frac{1}{\sin^2\theta} \partial_\varphi^2 Y + \lambda Y &= 0 \end{aligned} \quad (7)$$

From the former equation we get

$$Y(\theta, \varphi) = f(\theta) e^{im\varphi}$$

and substituting this into the second equation gives

$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left( \sin\theta \frac{df(\theta)}{d\theta} \right) + \left( \lambda - \frac{m^2}{\sin^2\theta} \right) f(\theta) = 0$$

or with  $w = \cos\theta$ :

$$\frac{d}{dw} \left[ (1-w^2) \frac{dg(w)}{dw} \right] + \left( \lambda - \frac{m^2}{1-w^2} \right) g(w) = 0 \quad (8)$$

where  $g(w) = f(\theta)$ .

The solutions of this DEqn are the **associated Legendre functions of the first and second kind**. The associated Legendre functions of the first kind are square integrable if  $\lambda = \ell(\ell + 1)$  where  $\ell = 0, 1, 2, \dots$ , and  $m = -\ell, -\ell + 1, \dots, \ell$ ; they are denoted  $P_\ell^m(w)$ .  $\ell$  is the **orbital angular momentum quantum number** and  $m$  is the **projection quantum number**.

Associated Legendre functions of the first kind with noninteger  $\lambda$  and associated Legendre functions of the second kind are not square integrable and must be rejected as solutions of the eigenvalue problem.

Instead of Eq.(6) we write the eigenvalue equation of the spherical harmonics now in the following final form:

$$\begin{aligned} \hat{L}^2 Y_{\ell m}(\theta, \varphi) &= \hbar^2 \ell(\ell + 1) Y_{\ell m}(\theta, \varphi) \\ \hat{L}_z Y_{\ell m}(\theta, \varphi) &= \hbar m Y_{\ell m}(\theta, \varphi) \end{aligned} \quad (9)$$

$$\ell = 0, 1, 2, \dots; \quad m = -\ell, -\ell + 1, -\ell + 2, \dots, \ell$$

#### Properties of associated Legendre functions:

$$P_\ell^m(w) = (1-w^2)^{|m|/2} \frac{d^{|m|}}{dw^{|m|}} P_\ell(w) \quad (10)$$

where  $P_\ell(w) = P_\ell^0(w)$  are Legendre polynomials:

$$P_\ell(w) = \frac{(-1)^\ell}{2^\ell \ell!} \frac{d^\ell (1-w^2)^\ell}{dw^\ell} \quad (11)$$

Special values:

$$P_\ell(1) = 1, \quad P_\ell(-1) = (-1)^\ell$$

Explicit expressions:

$$P_0(w) = 1, \quad P_1(w) = w, \quad P_2(w) = \frac{1}{2}(3w^2 - 1)$$

Orthogonality and normalization:

$$\int_{-1}^1 P_\ell(w) P_{\ell'}(w) dw = \frac{2\delta_{\ell\ell'}}{2\ell + 1} \quad (12)$$

The normalized eigenfunctions of  $\hat{L}^2$  and  $\hat{L}_z$  are the **spherical harmonics**:

$$Y_{\ell m}(\theta, \varphi) = \varepsilon \sqrt{\frac{2\ell + 1}{4\pi} \frac{(\ell - |m|)!}{(\ell + |m|)!}} P_\ell^m(\cos \theta) e^{im\varphi} \quad (13)$$

where

$$\varepsilon = \begin{cases} (-1)^m & \text{if } m > 0 \\ 1 & \text{if } m \leq 0 \end{cases}$$

Orthogonality of the spherical harmonics:

$$\int Y_{\ell m}^*(\theta, \varphi) Y_{\ell' m'}(\theta, \varphi) d\Omega = \delta_{mm'} \delta_{\ell\ell'} \quad (14)$$

where  $d\Omega = \sin \theta d\theta d\varphi$ , and the integral extends over the unit sphere:

$$\theta \in [0, \pi], \quad \varphi \in [0, 2\pi]$$

## Plots of Associated Legendre Polynomials

Shown here are plots of the associated Legendre polynomials  $P_\ell^m(x)$  for  $x \in [-1, 1]$ ,  $\ell = 2, 3, 4$  and  $m = 0, 1, \dots, \ell$ . These plots were produced with **Mathematica** v. 4 which uses a convention that differs from the convention in these lectures by an overall factor of  $(-1)^m$ .

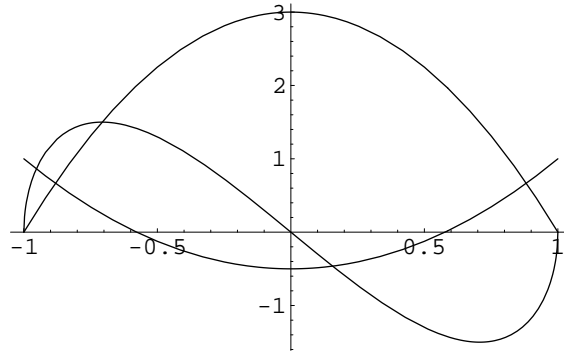


Figure 1: Associated Legendre functions  $P_2^m(x)$ ,  $m = 0, 1, 2$

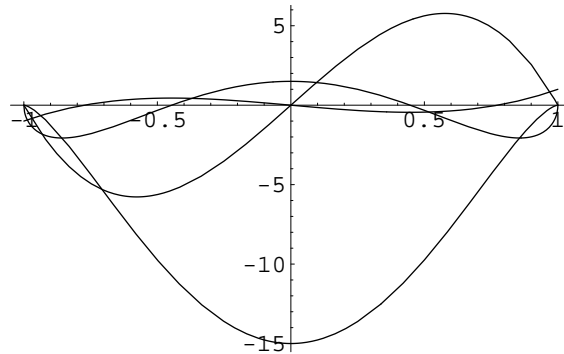


Figure 2: Associated Legendre functions  $P_3^m$ ,  $m = 0, 1, 2, 3$

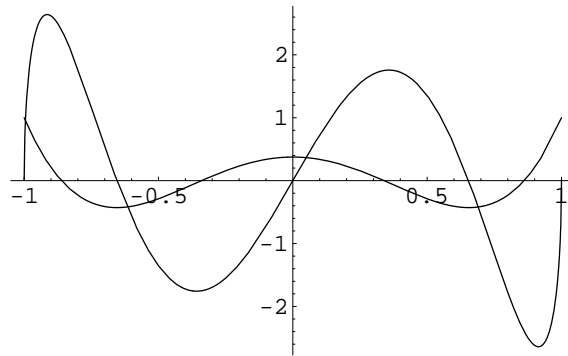


Figure 3: Associated Legendre functions  $P_4^m(x)$ ,  $m = 0, 1$

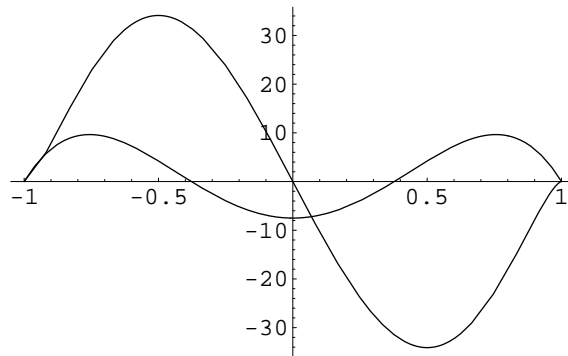


Figure 4: Associated Legendre functions  $P_4^m(x)$ ,  $m = 2, 3$

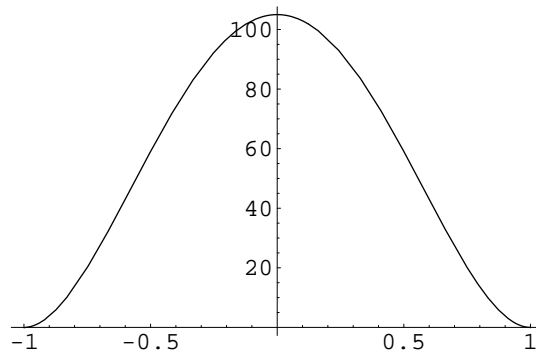


Figure 5: Associated Legendre functions  $P_4^4(x)$

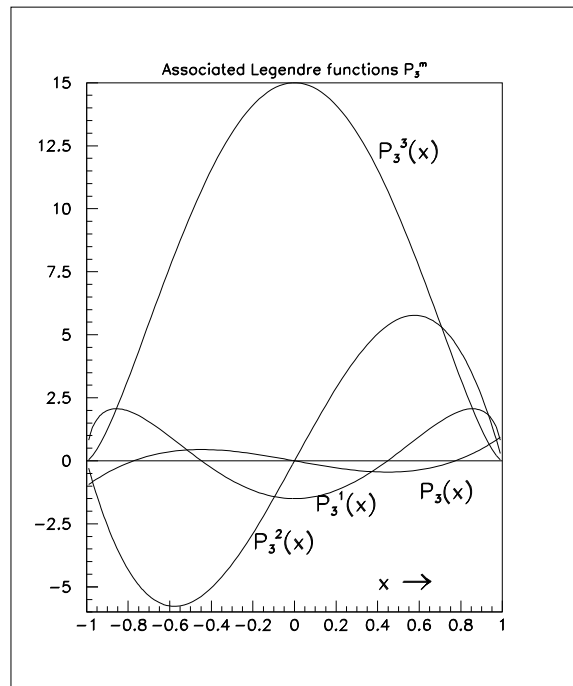
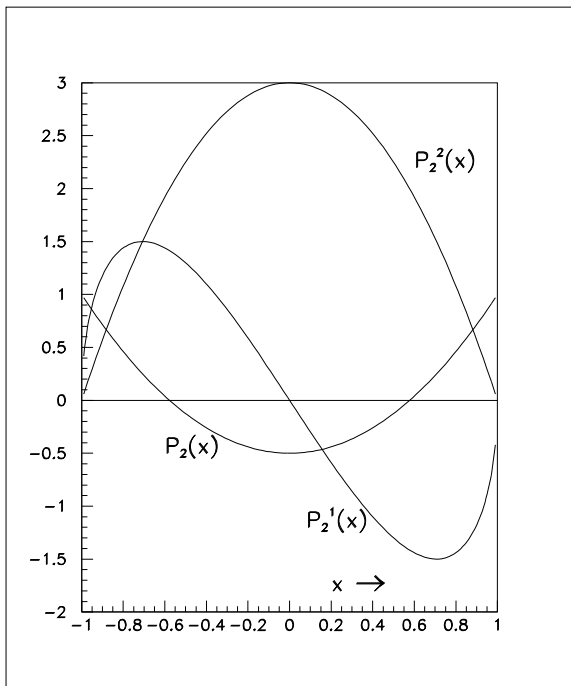


Figure 6: Associated Legendre functions



## Orthogonality of eigenfunctions of hermitian operators.

The discussion of angular momentum has led us to eigenfunctions, the spherical harmonics  $Y_{lm}(\theta, \varphi)$ , which are orthogonal to each other for different  $\ell$  and  $m$ . Here it will be shown that such orthogonality is a general property of eigenfunctions of hermitian operators.

For this discussion it will be convenient to use a shorthand notation for the scalar product of two functions (**Neumann notation**):

$$(f, g) = \int f^* g dx \quad (15)$$

where  $dx$  is the element of space of as many dimensions as required.

We will need a general property of the scalar product:

$$(f, g) = (g, f)^* \quad (16)$$

Indeed, by definition of the scalar product we have

$$(f, g) = \int f^* g dx$$

and

$$(g, f) = \int g^* f dx = \left( \int f^* g dx \right)^*$$

and hence the statement.

Now consider the hermitian operator  $\hat{A}$ . Take any two of its eigenfunctions with different eigenvalues  $a \neq b$ :

$$\hat{A}\psi_a = a\psi_a \quad (17)$$

$$\hat{A}\psi_b = b\psi_b \quad (18)$$

Take the scalar product of the former eqn with  $\psi_b$  and the scalar product of the latter eqn with  $\psi_a$ :

$$(\psi_b, \hat{A}\psi_a) = a(\psi_b, \psi_a) \quad (19)$$

$$(\psi_a, \hat{A}\psi_b) = b(\psi_a, \psi_b) \quad (20)$$

then, by hermiticity of  $\hat{A}$  we get on the left-hand side of Eq. (20)

$$(\hat{A}\psi_a, \psi_b) = (\psi_b, \hat{A}\psi_a)^*$$

where in the second step we have used Eq. (16), and on the right-hand side of Eq. (20) we get  $(\psi_b, \psi_a)^*$ , *i.e.*

$$(\psi_b, \hat{A}\psi_a)^* = b(\psi_b, \psi_a)^*$$

and taking the complex conjugate of this, remembering that the eigenvalues of hermitian operators are real, we get

$$(\psi_b, \hat{A}\psi_a) = b(\psi_b, \psi_a)$$

and upon subtraction of this from Eq. (19) we get

$$0 = (a - b)(\psi_b, \psi_a)$$

and since by assumption  $b \neq a$ , we get

$$(\psi_b, \psi_a) = 0$$

*i.e.* orthogonality of the eigenfunctions.

## The Hydrogen Atom.

The hydrogen atom consists of an electron bound to a proton. Since the proton mass is nearly 2000 times greater than the electron mass, we can to a very good approximation assume the proton to be stationary and consider the motion of the electron in the proton's Coulomb field. Then, assuming the proton to be at the origin of a coordinate system, the Hamiltonian of the problem is

$$\hat{H} = \frac{\hat{p}^2}{2m_e} + V(r) \quad (21)$$

where  $m_e$  is the electron mass and  $V(r) = -e^2/r$  is the Coulomb potential.

Alternatively we can write the Hamiltonian for the two-body problem:

$$\hat{H} = \frac{\hat{p}_p^2}{2m_p} + \frac{\hat{p}_e^2}{2m_e} + V(|\vec{r}_p - \vec{r}_e|)$$

and carry out the reduction to centre-of-mass coordinates  $\mathbf{R}$  and relative coordinates  $\vec{r}$  by a procedure familiar from the Kepler problem in classical mechanics. This leads to the Hamiltonian (21), with  $m_e$  replaced by the **reduced mass**  $\mu = m_p m_e / (m_p + m_e)$ . The difference between the electron mass and the reduced mass is small but must not be ignored when comparing theoretical results with spectroscopic data. It can also be significant when we apply the results of this derivation to other systems.

The eigenvalue problem for the Hamiltonian (21) is

$$\hat{H}\psi(r, \theta, \varphi) = E\psi(r, \theta, \varphi) \quad (22)$$

where use is made of the spherical symmetry of the Hamiltonian by introducing polar coordinates.

The Laplacian operator  $\nabla^2$  in spherical coordinates is of the following form:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]$$

and we recognise that the expression in square brackets is, up to a factor of  $-\hbar^2$ , the angular momentum operator  $\hat{L}^2$ . We can therefore write the Hamiltonian in the following form:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2\mu r^2} + V(r)$$

Since there is no angular dependence in the potential energy and no  $r$  dependence in the angular momentum, we can factorize the wave function thus:

$$\psi(r, \theta, \varphi) = R(r) Y(\theta, \varphi) \quad (23)$$

where  $R(r)$  is the **radial wave function** and  $Y(\theta, \varphi)$  is the spherical harmonic familiar from our discussion of angular momentum in quantum mechanics. Then the eigenvalue equation (22) takes on the following form:

$$-\frac{\hbar^2}{2\mu} \frac{Y(\theta, \varphi)}{r^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \frac{R(r)}{2\mu r^2} \hat{L}^2 Y(\theta, \varphi) + V(r) R(r) Y(\theta, \varphi) = E R(r) Y(\theta, \varphi)$$

But we know from Eq.(9) that

$$\hat{L}^2 Y(\theta, \varphi) = \hbar^2 \ell(\ell + 1) Y(\theta, \varphi)$$

After making this replacement in the eigenvalue equation we see that the spherical harmonic  $Y(\theta, \varphi)$  cancels and we are left with the **radial wave equation**:

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \left[ \frac{2\mu e^2}{\hbar^2 r} - \frac{\ell(\ell + 1)}{r^2} + \frac{2\mu E}{\hbar^2} \right] R(r) = 0 \quad (24)$$

and we note that for the bound state problem we have  $E < 0$ .

To solve this differential equation it is convenient to introduce instead of  $r$  a new dimensionless variable  $\rho$ :

$$\rho = \varepsilon r$$

where  $\varepsilon$  is defined by  $\varepsilon^2 = 8\mu|E|/\hbar^2$ . Then, if we also set  $\lambda = (e^2/\hbar) \sqrt{\mu/2|E|}$ , we get the DEq in the following form:

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left( \rho^2 \frac{dR}{d\rho} \right) + \left[ \frac{\lambda}{\rho} - \frac{\ell(\ell + 1)}{\rho^2} - \frac{1}{4} \right] R = 0 \quad (25)$$

where  $R$  is now a function of  $\rho$ . The factor of 8 in the definition of  $\varepsilon$  looks unnatural at this stage, but it will be convenient later on.

We begin solving Eq. (25) by considering its asymptotic form for  $\rho \rightarrow \infty$ :

$$\frac{d^2 R}{d\rho^2} - \frac{1}{4} R = 0$$

whose solution is  $R = C \exp(-\rho/2)$ , where  $C$  is an integration constant. The second, linearly independent solution  $\exp(+\rho/2)$  is discarded as it leads to a nonnormalizable wave function.

We shall now seek the solution of the exact equation (25) in the form of

$$R = F(\rho)e^{-\rho/2}$$

Then we get the following differential equation for  $F(\rho)$ :

$$F''(\rho) + \left( \frac{2}{\rho} - 1 \right) F'(\rho) + \left( \frac{\lambda - 1}{\rho} - \frac{\ell(\ell + 1)}{\rho^2} \right) F(\rho) = 0$$

where the primes denote differentiation with respect to  $\rho$ .

This differential equation is of the type of linear differential equations with *regular singularities*.

This equation can be solved by an ansatz of a power series about the singularity at  $\rho = 0$ :

$$F(\rho) = \rho^s L(\rho) \equiv \rho^s (a_0 + a_1\rho + a_2\rho^2 + \dots + a_n\rho^n + \dots)$$

where  $a_0 \neq 0$ . This gives us a differential equation for the function  $L(\rho)$ :

$$\rho^2 L'' + [2(s + 1)\rho - \rho^2] L' + \{(\lambda - s - 1)\rho + [s(s + 1) - \ell(\ell + 1)]\} L = 0 \quad (26)$$

Setting  $\rho = 0$  we get

$$[s(s + 1) - \ell(\ell + 1)]a_0 = 0$$

and since by assumption  $a_0 \neq 0$  we get

$$s(s+1) - \ell(\ell+1) = 0$$

which is a quadratic equation for  $s$ . (In the theory of linear differential equations this is called **indicial equation**.) The two roots are

$$s = \ell \quad \text{and} \quad s = -\ell - 1$$

The second root must be discarded as it leads to a nonnormalizable wave function. Substituting  $s = \ell$  in Eq. (26) we get, after cancellation of an overall factor of  $\rho$ :

$$\rho L'' + [2(\ell+1) - \rho] L' + (\lambda - \ell - 1)L = 0 \quad (27)$$

If we substitute the power series for  $L(\rho)$  into the DEq (27) we get after some rearrangements the following equation:

$$\sum_{k=0}^{\infty} \{a_{k+1} (k+1) (k+2\ell+2) + (\lambda - \ell - 1 - k)a_k\} \rho^{k+1} = 0$$

and by comparing powers of  $\rho$  we get the following recurrence relations for the coefficients  $a_k$ :

$$a_{k+1} = \frac{\ell+1+k-\lambda}{(k+1)(k+2\ell+2)} a_k, \quad k = 0, 1, 2, \dots \quad (28)$$

For  $k \rightarrow \infty$  we find

$$\frac{a_{k+1}}{a_k} \Big|_{k \rightarrow \infty} \rightarrow \frac{1}{k}$$

and we note that this is the behaviour of the expansion coefficients of  $x^n \exp(x)$  for any  $n$ . Indeed

$$x^n e^x = \sum_{\nu=0}^{\infty} \frac{x^{\nu+n}}{\nu!} \equiv \sum_{\nu=0}^{\infty} b_\nu x^{\nu+n}$$

hence

$$\frac{b_{\nu+1}}{b_\nu} = \frac{\nu!}{(\nu+1)!} = \frac{1}{\nu+1} \xrightarrow{\nu \rightarrow \infty} \frac{1}{\nu}$$

Thus our series yields a radial wave function of the form of

$$R = \rho^\ell e^{-\rho/2} L(\rho) \Big|_{\rho \rightarrow \infty} \rightarrow \rho^\ell e^{\rho/2}$$

which is nonnormalizable.

But we have not yet adjusted the energy eigenvalue or, equivalently, the parameter  $\lambda$ . We can choose this such that for some value of  $k$  the series is terminated by setting the numerator of the recurrence relation (28) equal to zero. Then  $L(\rho)$  becomes a polynomial, and since this is multiplied by  $\exp(-\rho/2)$  the radial wave function is square integrable.

Recall the numerator of Eq. (28):

$$\ell+1+k-\lambda$$

Thus if we set  $\lambda = n = n' + \ell + 1$  where  $n$  is a positive integer,<sup>1</sup> then all the coefficients  $a_k$  up to  $a_{n'}$  will be nonzero, but  $a_{n'+1} = 0$ , and hence  $L(\rho)$  becomes a polynomial of order  $n'$ . The number  $n'$  is called the **radial quantum number** and  $n$  the **principal quantum number**.

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<sup>1</sup>with a different definition of  $\varepsilon$  we would have to set at this stage  $\lambda$  equal to a multiple of a positive integer.

Recalling the relation between  $\lambda$  and the energy  $E$  we get

$$n = \frac{e^2}{\hbar} \sqrt{\frac{\mu}{2|E|}}$$

and hence, if we label the energy eigenvalue with the principal q.n.:

$$E_n = -\frac{e^4 \mu}{2\hbar^2} \frac{1}{n^2}$$

or if we put  $\alpha = e^2/\hbar c$ :

$$E_n = -\frac{1}{2} \alpha^2 \mu c^2 \frac{1}{n^2} \quad (29)$$

The constant  $\alpha$  is the **fine structure** constant. It is dimensionless and has a numerical value of close to  $1/137$ . If we set  $\mu c^2 \simeq m_e c^2 = 0.5 \times 10^6$  eV, the approximate value of the electron rest energy, then we get  $E_1 = -13.6$  eV. This is the lowest energy level or **ground state energy**. In order to ionize the hydrogen atom we must supply an energy of at least  $|E_1|$ ; this energy is therefore called the **ionization energy** of the hydrogen atom.

As the principal q.n. increases we get to higher energy level. Transitions from lower to higher lying levels are **excitations** of the atom. They can take place as a result of absorption of electromagnetic radiation or by collisions with other atoms.

In an excited state the atom is unstable. It can make transitions to lower lying levels or to the ground state by emitting electromagnetic radiation. If the atom is initially at a level of principal q.n.  $m$  and makes a transition to a level of principal q.n.  $n < m$ , then the energy of the emitted photon is

$$E_{nm} = \frac{1}{2} \alpha^2 m_e c^2 \left( \frac{1}{n^2} - \frac{1}{m^2} \right)$$

which is the familiar Balmer formula that describes the hydrogen spectrum quantitatively.