

INTRODUCTION TO QUANTUM MECHANICS

PART-III THE HAMILTONIAN OPERATOR and the SCHRODINGER EQUATION

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References:

"Introduction to Quantum Mechanics" by David Griffiths; Chapter 4

CHAPTER-10

SCHRODINGER EQUATION in 3D

Description of two interacting particles' motion

One particle motion

In the case in which a particle of mass m moves in 1-D and inside a potential $V(x,t)$, the Schrodinger Eq. is,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x,t) \psi, \text{ where } \Psi = \Psi(x, t) \quad (1)$$

When the particle moves in the 3-D space, the equation adopts the form,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V(\vec{r}, t) \psi, \text{ where } \Psi = \Psi(\vec{r}, t) \quad (2)$$

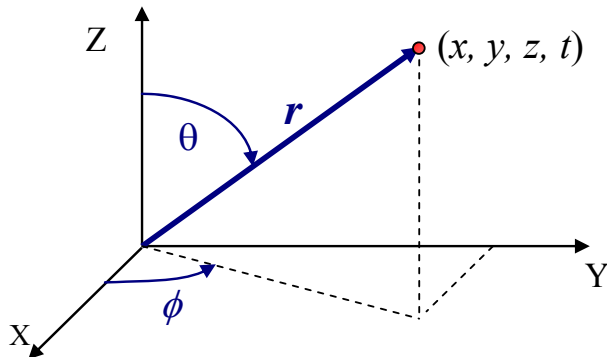
here ∇^2 stands for the Laplacian operator

In Cartesian coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

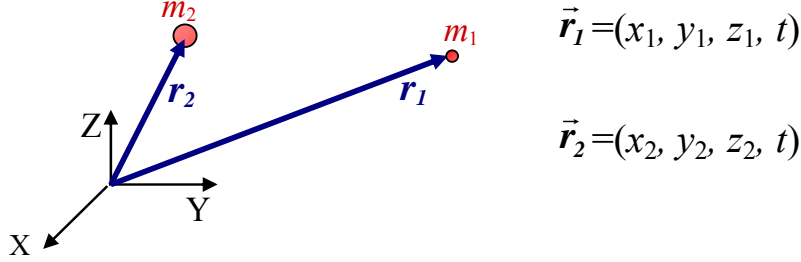
In spherical coordinates:

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



10.1 General case of an arbitrary interaction potential

Two particles motion



The mutual interaction between the two particles is specified through the potential $V(\vec{r}_1, \vec{r}_2, t)$ and the corresponding Schrodinger Eq. is

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m_1} \nabla_{\vec{r}_1}^2 \psi - \frac{\hbar^2}{2m_2} \nabla_{\vec{r}_2}^2 \psi + V(\vec{r}_1, \vec{r}_2, t) \psi, \quad (3)$$

where $\Psi = \Psi(\vec{r}_1, \vec{r}_2, t)$

In the expression above the following notation is being used,

$$\nabla_{\vec{r}_1} \equiv \left(\frac{\partial \psi}{\partial x_1}, \frac{\partial \psi}{\partial y_1}, \frac{\partial \psi}{\partial z_1} \right) ; \quad \nabla_{\vec{r}_1}^2 \equiv \frac{\partial^2 \psi}{\partial x_1^2} + \frac{\partial^2 \psi}{\partial y_1^2} + \frac{\partial^2 \psi}{\partial z_1^2} ; \text{ etc}$$

10.2 Case when the potential depends only on the relative position of the particles

Here we consider that the potential $V(\vec{r}_1, \vec{r}_2, t)$ depends only on the relative position,

$$V(\vec{r}_1, \vec{r}_2, t) = U(\vec{r}_1 - \vec{r}_2, t) \quad (4)$$

Decoupling the Center of Mass motion and the Relative Motion

For this particular case it can be shown that the motion of the two particles can be decoupled into

- the motion of the center of mass, and
- the motion relative to each other.

The CM and the relative-position variables

Such decoupling can be achieved through the following change of variables: $(\vec{r}_1, \vec{r}_2) \rightarrow (\vec{R}, \vec{r})$, where

$$\vec{R} \equiv \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}, \quad \vec{r} \equiv \vec{r}_1 - \vec{r}_2 \quad (5)$$

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \Phi(\vec{R}, \vec{r}, t)$$

Notice, by calling

$$\vec{R} = (R_x, R_y, R_z) \quad \text{and} \quad \vec{r} = (x, y, z)$$

the definitions in (5) can be re-written more explicitly as,

$$R_x \equiv \frac{m_1 x_1 + m_2 x_2}{M}, \quad R_y \equiv \frac{m_1 y_1 + m_2 y_2}{M}, \quad R_z \equiv \frac{m_1 z_1 + m_2 z_2}{M}$$

$$x = (x_1 - x_2), \quad y = (y_1 - y_2), \quad z = (z_1 - z_2) \quad (6)$$

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \Phi(\vec{R}, \vec{r}, t)$$

where we are using $M = m_1 + m_2$

You may want to jump to expression (10), which gives the form in which Eq. (3) is transformed upon the application of the change of variables defined in (5).

$\Psi(\vec{r}_1, \vec{r}_2, t) = \Phi(\vec{R}, \vec{r}, t)$ implies,

$$\begin{aligned} \frac{\partial \Psi}{\partial x_1} &= \frac{\partial \Phi}{\partial R_x} \frac{\partial R_x}{\partial x_1} + \frac{\partial \Phi}{\partial x} \frac{\partial x}{\partial x_1} = \frac{\partial \Phi}{\partial R_x} \frac{m_1}{M} + \frac{\partial \Phi}{\partial x} \\ \frac{\partial^2 \Psi}{\partial x_1^2} &= \left(\left(\frac{\partial}{\partial R_x} \frac{\partial \Phi}{\partial R_x} \right) \frac{\partial R_x}{\partial x_1} + \left(\frac{\partial}{\partial x} \frac{\partial \Phi}{\partial R_x} \right) \frac{\partial x}{\partial x_1} \right) \frac{m_1}{M} + \left(\left(\frac{\partial}{\partial R_x} \frac{\partial \Phi}{\partial x} \right) \frac{\partial R_x}{\partial x_1} + \left(\frac{\partial}{\partial x} \frac{\partial \Phi}{\partial x} \right) \frac{\partial x}{\partial x_1} \right) \\ &= \left(\frac{\partial^2 \Phi}{\partial R_x^2} \frac{m_1}{M} + \left(\frac{\partial}{\partial x} \frac{\partial \Phi}{\partial R_x} \right) \frac{m_1}{M} \right) + \left(\left(\frac{\partial}{\partial R_x} \frac{\partial \Phi}{\partial x} \right) \frac{m_1}{M} + \left(\frac{\partial^2 \Phi}{\partial x^2} \right) \right) \\ &= \frac{\partial^2 \Phi}{\partial R_x^2} \left(\frac{m_1}{M} \right)^2 + 2 \frac{m_1}{M} \left(\frac{\partial}{\partial x} \frac{\partial \Phi}{\partial R_x} \right) + \frac{\partial^2 \Phi}{\partial x^2} \end{aligned}$$

$$\frac{\partial^2 \Psi}{\partial y_1^2} = \frac{\partial^2 \Phi}{\partial R_y^2} \left(\frac{m_1}{M}\right)^2 + 2 \frac{m_1}{M} \left(\frac{\partial}{\partial y} \frac{\partial \Phi}{\partial R_y}\right) + \frac{\partial^2 \Phi}{\partial y^2}$$

$$\frac{\partial^2 \Psi}{\partial z_1^2} = \frac{\partial^2 \Phi}{\partial R_z^2} \left(\frac{m_1}{M}\right)^2 + 2 \frac{m_1}{M} \left(\frac{\partial}{\partial z} \frac{\partial \Phi}{\partial R_z}\right) + \frac{\partial^2 \Phi}{\partial z^2}$$

Since $\nabla_{\vec{r}_1}^2 \Psi \equiv \frac{\partial^2 \Psi}{\partial x_1^2} + \frac{\partial^2 \Psi}{\partial y_1^2} + \frac{\partial^2 \Psi}{\partial z_1^2}$, adding the last three results gives,

$$\begin{aligned} \nabla_{\vec{r}_1}^2 \Psi &= \left(\frac{m_1}{M}\right)^2 \nabla_{\vec{R}}^2 \Phi + \nabla_{\vec{r}}^2 \Phi + 2 \frac{m_1}{M} \left(\frac{\partial}{\partial x} \frac{\partial \Phi}{\partial R_x} + \frac{\partial}{\partial y} \frac{\partial \Phi}{\partial R_y} + \frac{\partial}{\partial z} \frac{\partial \Phi}{\partial R_z}\right) \\ &= \left(\frac{m_1}{M}\right)^2 \nabla_{\vec{R}}^2 \Phi + \nabla_{\vec{r}}^2 \Phi + 2 \frac{m_1}{M} \nabla_{\vec{r}} \cdot \nabla_{\vec{R}} \Phi \end{aligned}$$

where we have used the notation

$$\nabla_{\vec{R}} \Psi \equiv \left(\frac{\partial \Psi}{\partial R_x}, \frac{\partial \Psi}{\partial R_y}, \frac{\partial \Psi}{\partial R_z}\right), \quad \nabla_{\vec{R}}^2 \Psi \equiv \frac{\partial^2 \Psi}{\partial R_x^2} + \frac{\partial^2 \Psi}{\partial R_y^2} + \frac{\partial^2 \Psi}{\partial R_z^2} \quad \text{and}$$

$$\nabla_{\vec{r}} \Psi \equiv \left(\frac{\partial \Psi}{\partial x}, \frac{\partial \Psi}{\partial y}, \frac{\partial \Psi}{\partial z}\right), \quad \nabla_{\vec{r}}^2 \Psi \equiv \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2}$$

Very conveniently, the previous results is expressed as,

$$\frac{1}{m_1} \nabla_{\vec{r}_1}^2 \Psi = \frac{m_1}{M^2} \nabla_{\vec{R}}^2 \Phi + \frac{1}{m_1} \nabla_{\vec{r}}^2 \Phi + 2 \frac{1}{M} \nabla_{\vec{r}} \cdot \nabla_{\vec{R}} \Phi \quad (7)$$

Similarly

$$\begin{aligned} \frac{\partial \Psi}{\partial x_2} &= \frac{\partial \Phi}{\partial R_x} \frac{\partial R_x}{\partial x_2} + \frac{\partial \Phi}{\partial x} \frac{\partial x}{\partial x_2} = \frac{\partial \Phi}{\partial R_x} \frac{m_2}{M} - \frac{\partial \Phi}{\partial x} \\ \frac{\partial^2 \Psi}{\partial x_2^2} &= \left(\left(\frac{\partial}{\partial R_x} \frac{\partial \Phi}{\partial R_x}\right) \frac{\partial R_x}{\partial x_2} + \left(\frac{\partial}{\partial x} \frac{\partial \Phi}{\partial R_x}\right) \frac{\partial x}{\partial x_2} \right) \frac{m_2}{M} - \left(\left(\frac{\partial}{\partial R_x} \frac{\partial \Phi}{\partial x}\right) \frac{\partial R_x}{\partial x_2} + \left(\frac{\partial}{\partial x} \frac{\partial \Phi}{\partial x}\right) \frac{\partial x}{\partial x_2} \right) \\ &= \left(\frac{\partial^2 \Phi}{\partial R_x^2} \frac{m_2}{M} - \left(\frac{\partial}{\partial x} \frac{\partial \Phi}{\partial R_x}\right) \right) \frac{m_2}{M} - \left(\left(\frac{\partial}{\partial R_x} \frac{\partial \Phi}{\partial x}\right) \frac{m_2}{M} - \left(\frac{\partial^2 \Phi}{\partial x^2}\right) \right) \end{aligned}$$

$$= \frac{\partial^2 \Phi}{\partial R_x^2} \left(\frac{m_2}{M}\right)^2 - 2 \frac{m_2}{M} \left(\frac{\partial}{\partial x} \frac{\partial \Phi}{\partial R_x}\right) + \frac{\partial^2 \Phi}{\partial x^2}$$

Analogous results for $\frac{\partial^2 \Psi}{\partial y_2^2}$ and $\frac{\partial^2 \Psi}{\partial z_2^2}$ lead to,

$$\frac{1}{m_2} \nabla_{\vec{r}_2}^2 \Psi = \frac{m_2}{M^2} \nabla_{\vec{R}}^2 \Phi + \frac{1}{m_2} \nabla_{\vec{r}}^2 \Phi - 2 \frac{1}{M} \nabla_{\vec{r}} \cdot \nabla_{\vec{R}} \Phi \quad (8)$$

Replacing (7) and (8) in (3) one obtains,

$$i\hbar \frac{\partial \Phi}{\partial t} = - \frac{\hbar^2}{2} \frac{m_1 + m_2}{M^2} \nabla_{\vec{R}}^2 \Phi - \frac{\hbar^2}{2} \left(\frac{1}{m_1} + \frac{1}{m_2}\right) \nabla_{\vec{r}}^2 \Phi + U(\vec{r}, t) \Phi$$

In terms the reduced mass μ

$$\frac{1}{\mu} \equiv \frac{1}{m_1} + \frac{1}{m_2} \quad (9)$$

one obtains the equation

$$i\hbar \frac{\partial \Phi}{\partial t} = - \frac{\hbar^2}{2M} \nabla_{\vec{R}}^2 \Phi - \frac{\hbar^2}{2\mu} \nabla_{\vec{r}}^2 \Phi + U(\vec{r}, t) \Phi \quad (10)$$

where $\Phi = \Phi(\vec{R}, \vec{r}, t)$

Solution by separation of variables

We will specialize in the case where the potential U does not depend explicitly on the time t . For such a case, we will be looking for solutions to Eq. (10) in the form,

$$\begin{aligned} \Phi(\vec{R}, \vec{r}, t) &\equiv \Omega(\vec{R}) F(\vec{r}) e^{-(i/\hbar)(E_{cm} + E)t} \\ &\equiv [\Omega(\vec{R}) e^{-(i/\hbar)(E_{cm})t}] [F(\vec{r}) e^{-(i/\hbar)Et}] \end{aligned} \quad (11)$$

Replacing (11) in (10)

$$(E_{CM} + E)\Omega(\vec{R})F(\vec{r}) = -\frac{\hbar^2}{2M}F(\vec{r})\nabla_{\vec{R}}^2\Omega(\vec{R}) - \frac{\hbar^2}{2\mu}\Omega(\vec{R})\nabla_{\vec{r}}^2F(\vec{r}) + U(\vec{r})\Omega(\vec{R})F(\vec{r})$$

Dividing by $\Omega(\vec{R})F(\vec{r})$

$$(E_{CM} + E) = -\frac{\hbar^2}{2M}\frac{1}{\Omega(\vec{R})}\nabla_{\vec{R}}^2\Omega(\vec{R}) - \frac{\hbar^2}{2\mu}\frac{1}{F(\vec{r})}\nabla_{\vec{r}}^2F(\vec{r}) + U(\vec{r})$$

This expression indicates that the terms on the right, although intrinsically depending on the variables \vec{r} and \vec{R} , they add up to a constant value. Selectively we choose,

$$E_{CM} = -\frac{\hbar^2}{2M}\frac{1}{\Omega(\vec{R})}\nabla_{\vec{R}}^2\Omega(\vec{R}), \quad (12)$$

and

$$E = -\frac{\hbar^2}{2\mu}\frac{1}{F(\vec{r})}\nabla_{\vec{r}}^2F(\vec{r}) + U(\vec{r}) \quad (13)$$

Equation of Motion for the Center of Mass

The first expression leads to,

$$-\frac{\hbar^2}{2M}\nabla_{\vec{R}}^2\Omega(\vec{R}) = E_{CM}\Omega(\vec{R}) \quad (14)$$

which admit solutions of the form

$$\Omega(\vec{R}) = e^{(i/\hbar)\sqrt{2ME_{CM}}\vec{n}\cdot\vec{R}} \quad (15)$$

where \vec{n} is an arbitrary constant unit vector. (That means there are many solutions of this type, one for each selected unit vector \vec{n} .)

In terms of the wavevector $\vec{k}_{CM} \equiv \frac{\sqrt{2ME_{CM}}}{\hbar}\vec{n}$, the previous expression is written as,

$$\Omega(\vec{R}) = e^{i(\vec{k}_{CM})\cdot\vec{R}} \quad (15)'$$

In short,

- if a single vector \vec{k}_{CM} were used in the separation of variables given in (11), then the motion of the CM would be described by a plane-wave that propagates in the direction of \vec{k}_{CM} ,

$$\Omega(\vec{R})e^{-(i/\hbar)(E_{CM})t} = e^{i[\vec{k}_{CM} \cdot \vec{R} - (E_{CM}/\hbar)t]} \quad (16)$$

Accordingly, the CM is likely to be anywhere in the space but has a very definite orientation of its momentum (that given by \vec{k}_{CM}).

- If a more precise localization of the CM were desired, then we can select a bunch of wavevectors $\vec{k}_{CM} \equiv \frac{\sqrt{2ME_{CM}}}{\hbar} \vec{n}$ within a range $\Delta\vec{k}$ and define a wavepacket

$$\Omega(\vec{R}, t) \equiv \sum_{\vec{k}_{CM}} e^{i[\vec{k}_{CM} \cdot \vec{R} - (E_{CM}/\hbar)t]} \quad (17)$$

That way the CM will be more localized (because $\Omega(\vec{R}, t)$ is more spatially localized) but, at the same time, there will be a corresponding uncertainty in its momentum.

It is worth mentioning that we have not been looking for a solution $\vec{R} = \vec{R}(t)$, as we would have been doing in a classical mechanics approach; rather we have found an amplitude probability $\Omega(\vec{R})$.

Equation governing the Relative Motion

Back to Eq. (13). This leads to,

$$-\frac{\hbar^2}{2\mu} \nabla_{\vec{r}}^2 F(\vec{r}) + U(\vec{r})F(\vec{r}) = E F(\vec{r}) \quad (18)$$

In the next section we will specialize for the case for central potentials; that is, when the potential depends only on the magnitude of the particles separation: $U(\vec{r}) = U(r)$

10.3 Central Potentials $U(\vec{r}) = U(r)$

$$-\frac{\hbar^2}{2\mu} \nabla_{\vec{r}}^2 F(\vec{r}) + U(r)F(\vec{r}) = E F(\vec{r}) \quad (19)$$

This is an equation for $F(\vec{r})$ where the energy parameter E is still to be determined. When working with central potentials, it is more convenient to use spherical coordinates to solve (19).

At the beginning of this Chapter the Laplacian operator was given in spherical coordinates. Using that expression in (19) one obtains,

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \left(\frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] F(\vec{r}) + U(r) F(\vec{r}) = E F(\vec{r}) \quad (20)$$

10.3A Separation of variables method

We will look for solutions of the form

$$F(\vec{r}) = R(r)Y(\theta, \phi) \quad (21)$$

This leads to,

$$\begin{aligned} & -\frac{\hbar^2}{2\mu} Y(\theta, \phi) \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right] R(r) + \\ & -\frac{\hbar^2}{2\mu} R(r) \left[\frac{1}{r^2 \sin \theta} \left(\frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) + \\ & + U(r) R(r)Y(\theta, \phi) = E R(r)Y(\theta, \phi) \end{aligned}$$

Dividing each term by $R(r)Y(\theta, \phi)$

$$\begin{aligned} & -\frac{\hbar^2}{2\mu} \frac{1}{R(r)} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right] R(r) + \\ & -\frac{\hbar^2}{2\mu} \frac{1}{Y(\theta, \phi)} \left[\frac{1}{r^2 \sin \theta} \left(\frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) + \\ & + U(r) = E \end{aligned}$$

$$-\frac{\hbar^2}{2\mu} \frac{1}{R(r)} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right] R(r) + r^2 [U(r) - E] +$$

$$-\frac{\hbar^2}{2\mu} \frac{1}{Y(\theta, \phi)} \left[\frac{1}{\sin \theta} \left(\frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = 0$$

$$\begin{aligned} \frac{1}{R(r)} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right] R(r) - \frac{2\mu}{\hbar^2} r^2 [U(r) - E] + \\ + \frac{1}{Y(\theta, \phi)} \left[\frac{1}{\sin \theta} \left(\frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = 0 \end{aligned}$$

The first two terms depend only on r , while the third term only on the angular variables. This means that the radial part and the angular part are each constant.

$$\begin{aligned} \frac{1}{Y(\theta, \phi)} \left[\frac{1}{\sin \theta} \left(\frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = -\lambda \\ \frac{1}{R(r)} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right] R(r) - \frac{2\mu}{\hbar^2} r^2 [U(r) - E] = \lambda \end{aligned}$$

Rearranging terms, one obtains

$$\left[\frac{1}{\sin \theta} \left(\frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = -\lambda Y(\theta, \phi) \quad \textbf{Angular Eq. (22)}$$

and

$$\left\{ -\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\lambda}{r^2} \right] + U(r) \right\} R(r) = E R(r) \quad \textbf{Radial Eq. (23)}$$

In summary, we are looking for solutions to Eq. (20) in the form

$$F(\vec{r}) = R_{E\lambda}(r) Y_{\lambda}(\theta, \phi)$$

10.3B The angular Equation

To solve the angular equation

$$\left[\frac{1}{\sin \theta} \left(\frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = -\lambda Y(\theta, \phi)$$

we will look again for solutions of the form of separated variables,

$$Y(\theta, \phi) = \Theta(\theta) \Phi(\phi) \quad (24)$$

$$\Phi(\phi) \frac{1}{\sin \theta} \left(\frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) \Theta(\theta) + \Theta(\theta) \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \Phi(\phi) = -\lambda \Theta(\theta) \Phi(\phi)$$

Dividing by $\Theta(\theta) \Phi(\phi)$ and multiplying by $\sin^2(\theta)$

$$\left[\frac{1}{\Theta(\theta)} \sin \theta \left(\frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) \Theta(\theta) + \lambda \sin^2(\theta) \right] + \frac{1}{\Phi(\phi)} \frac{\partial^2}{\partial \phi^2} \Phi(\phi) = 0$$

This means that each of the two term must be constant

$$\left[\frac{1}{\Theta(\theta)} \sin \theta \left(\frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) \Theta(\theta) + \lambda \sin^2(\theta) \right] = m^2 \quad (25)$$

$$\frac{1}{\Phi(\phi)} \frac{\partial^2}{\partial \phi^2} \Phi(\phi) = -m^2 \quad (26)$$

The value of the constant m^2 is determined by physics-based considerations.

Indeed, from the second Eq. above one obtains

$$\frac{d^2}{d\phi^2} \Phi(\phi) + m^2 \Phi(\phi) = 0$$

(where the partial derivative symbol ∂ has been dropped, since the function Φ depends only on one variable,) which has solutions of the form $\Phi(\phi) = e^{i m \phi}$. But notice that the wavefunction should take the same value whenever ϕ is incremented by 2π ; that is,

$$\Phi(\phi + 2\pi) = \Phi(\phi) \quad (\text{physics-based requirement})$$

This implies $e^{i m(\phi+2\pi)} = e^{i m \phi}$, or

$$e^{i m 2\pi} = 1$$

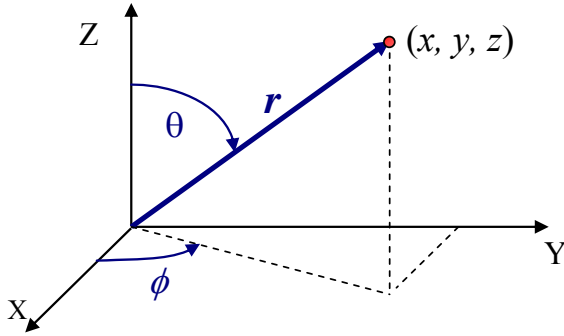
This condition can be satisfied only if m is an integer number. Thus, the dependence of the wavefunction on the ϕ variable is given by,

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}; \quad m = \dots, -2, -1, 0, 1, 2, \dots \quad (27)$$

where the factor $(1/\sqrt{2\pi})$ has been introduced to ensure the orthonormality condition of these functions in the range $0 \leq \phi \leq 2\pi$,

$$\int_0^{2\pi} \Phi_{m'}^*(\phi) \Phi_m(\phi) d\phi = \delta_{m'm} \quad (28)$$

We will see below some restrictions on the allowed range of values for m (see expression (42).)



The other angular Equation (25) has the form,

$$\left\{ \frac{1}{\sin \theta} \left(\frac{d}{d\theta} \sin \theta \frac{d}{d\theta} \right) + \left(\lambda - \frac{m^2}{\sin^2(\theta)} \right) \right\} \Theta_{\lambda m}(\theta) = 0 \quad (29)$$

where it has been emphasized that the solution depends on the parameters λ and m . The task is to find a solution over the range $0 \leq \theta \leq \pi$.

It is convenient to introduce the new variable

$$w = \cos(\theta), \quad \text{for } 0 \leq \theta \leq \pi.$$

and the new function

$$G_{\lambda m}(w) = \Theta_{\lambda m}(\theta)$$

It can be shown that the Eq. for $G_{\lambda m}$ is,

$$(1-w^2) \frac{d^2 G_{\lambda m}}{dw^2} - 2w \frac{dG_{\lambda m}}{dw} + \left[\lambda - \frac{m^2}{1-w^2} \right] G_{\lambda m} = 0 \quad (30)$$

Case m=0

We will see later that the functions $G_{\lambda m}$ corresponding to $m \neq 0$ can be built upon $G_{\lambda 0}$. The latter satisfies the Eq.

$$(1-w^2) \frac{d^2 G_{\lambda 0}}{d w^2} - 2 w \frac{d G_{\lambda 0}}{d w} + \lambda G_{\lambda 0} = 0 \quad \text{Legendre Eq.} \quad (31)$$

Power series solution

$$G_{\lambda 0}(w) = \sum_{k=0}^{\infty} c_k w^k \quad (32)$$

From (31) one obtains,

$$\begin{aligned} \frac{d G_{\lambda 0}}{d w} &= \sum_{k=0}^{\infty} k c_k w^{k-1}, \quad 2 w \frac{d G_{\lambda 0}}{d w} = \sum_{k=0}^{\infty} 2 k c_k w^k, \text{ which gives,} \\ -2 w \frac{\partial G_{\lambda 0}}{\partial w} + \lambda G_{\lambda 0} &= - \sum_{k=0}^{\infty} 2 k c_k w^k + \lambda \sum_{k=0}^{\infty} c_k w^k = \\ &= \sum_{k=0}^{\infty} (-2k + \lambda) c_k w^k \end{aligned} \quad (33)$$

Also,

$$\begin{aligned} \frac{d^2 G_{\lambda 0}}{d w^2} &= \sum_{k=0}^{\infty} k(k-1) c_k w^{k-2}, \quad w^2 \frac{\partial^2 G_{\lambda 0}}{\partial w^2} = \sum_{k=0}^{\infty} k(k-1) c_k w^k \\ (1-w^2) \frac{d^2 G_{\lambda 0}}{d w^2} &= \sum_{k=0}^{\infty} k(k-1) c_k w^{k-2} - \sum_{k=0}^{\infty} k(k-1) c_k w^k \\ &= \sum_{k=2}^{\infty} k(k-1) c_k w^{k-2} - \sum_{k=0}^{\infty} k(k-1) c_k w^k \end{aligned}$$

Using $k-2 = k'$

$$= \sum_{k=0}^{\infty} (k+2)(k+1)c_{k+2}w^k - \sum_{k=0}^{\infty} k(k-1)c_k w^k$$

where we have replaced k' for k again (to avoid writing too many variables)

$$= \sum_{k=0}^{\infty} [(k+2)(k+1)c_{k+2} - k(k-1)c_k]w^k \quad (34)$$

Replacing (33) and (34) in (31), one obtains

$$\sum_{k=0}^{\infty} [(k+2)(k+1)c_{k+2} - k(k-1)c_k]w^k + \sum_{k=0}^{\infty} (-2k+\lambda)c_k w^k = 0$$

$$\sum_{k=0}^{\infty} \left\{ [(k+2)(k+1)c_{k+2} - [k(k+1) - \lambda]c_k] \right\} w^k = 0$$

This requires

$$c_{k+2} = \frac{k(k+1) - \lambda}{(k+1)(k+2)} c_k \quad \text{recursion relation} \quad (35)$$

Thus, the solution (32) can be written more explicitly as,

$$G_{\lambda 0}(w) = c_0 \left[1 + \frac{(0)(1) - \lambda}{(1)(2)} w^2 + \frac{(2)(3) - \lambda}{(3)(4)} \frac{(0)(1) - \lambda}{(1)(2)} w^4 + \dots \right] \quad (36)$$

$$+ c_1 \left[1 + \frac{(1)(2) - \lambda}{(2)(3)} w^3 + \frac{(3)(4) - \lambda}{(4)(5)} \frac{(1)(2) - \lambda}{(2)(3)} w^5 + \dots \right]$$

where c_0 and c_1 are arbitrary constants. Expression (31) provides two independent solutions. Notice, each subsequent coefficient c_{k+2} depends on the value of the previous one c_k (for example, if one coefficient were equal to zero, then all the other subsequent coefficients will be null as well.)

- **Divergence at $w=1$.** For large values of k , this series varies as $c_{k+2}/c_k \rightarrow k/(k+2)$, a behavior which is similar to the divergent series $\sum_{k=0}^{\infty} (1/k)$. This indicates that (32) diverges for $w=1$, thus

constituting an unacceptable solution, since the wavefunction has to have a definite value at $\theta=90^\circ$.

- **Polynomial solutions.** It is still possible to obtain a satisfactory solution out of (32), if λ were chosen of the form $\lambda = \ell(\ell+1)$, with ℓ being an integer value, then the coefficient series (32) would become a polynomial of degree ℓ (with the corresponding c_0 or c_1 conveniently chosen equal to zero, depending on whether ℓ is odd or even, respectively.)

Summary:

The Legendre Equation

$$(1-w^2) \frac{d^2 G_{\lambda 0}}{dw^2} - 2w \frac{dG_{\lambda 0}}{dw} + \lambda G_{\lambda 0} = 0 \quad \text{Legendre Eq.}$$

admits physically acceptable solutions provided that λ has the form of $\lambda = \ell(\ell+1)$, with ℓ being an integer. For a given ℓ , the resulting solutions is a polynomial of degree ℓ .

$$G_{\lambda 0}(w) = \sum_{k=0}^{\ell} c_k w^k \equiv P_{\ell}(w) \quad \text{Legendre Polynomial}$$

$$\text{where } c_{k+2} = \frac{k(k+1) - \ell(\ell+1)}{(k+1)(k+2)} c_k$$

Since an arbitrary multiplicative constant, c_0 or c_1 , accompany to these solutions, the Legendre polynomials are defined such that

$$P_{\ell}(1) = 1$$

From expression (36) one obtains,

$$\ell=0: P_0(w) = 1 \quad (37)$$

$$\ell=1: P_1(w) = w$$

$$\ell=2: P_2(w) = -\frac{1}{2}(1-3w^2)$$

$$\ell=3: P_3(w) = -\frac{3}{2}(w - \frac{5}{3}w^3)$$

$$\ell=4: P_4(w) = c_0(1 - 10w + \frac{7}{6}10w^4) = \frac{3}{8}(1 - 10w + \frac{35}{3}w^4)$$

...

Since P_ℓ is a polynomial of degree ℓ ,

$$P_\ell(-w) = (-1)^\ell P_\ell(w) \quad (38)$$

Without proof we state that the Legendre polynomials satisfy,

$$\int_{-1}^1 P_\ell(w) P_{\ell'}(w) dw = \frac{2}{2\ell+1} \delta_{\ell\ell'} \quad (39)$$

The general case: $m \neq 0$

We are looking for solutions to Eq. (29)

$$(1-w^2) \frac{d^2 G_{\lambda m}}{dw^2} - 2w \frac{dG_{\lambda m}}{dw} + \left[\lambda - \frac{m^2}{1-w^2} \right] G_{\lambda m} = 0$$

For that purpose, let's define the Associated Legendre functions

$$P_\ell^{|m|}(w) = (1-w^2)^{|m|/2} \frac{d^{|m|}}{dw^{|m|}} P_\ell(w) \quad (40)$$

That is, the polynomials $P_\ell^{|m|}(w)$ are obtained by taking derivatives of the already known Legendre polynomials $P_\ell(w)$ given in (37). It turns out these Associated Legendre functions satisfy Eq. (29),

$$(1-w^2) \frac{d^2 P_\ell^{|m|}}{dw^2} - 2w \frac{dP_\ell^{|m|}}{dw} + \left[\ell(\ell+1) - \frac{m^2}{1-w^2} \right] P_\ell^{|m|} = 0 \quad (41)$$

Notice that, since $P_\ell(w)$ is a polynomial of degree ℓ , $P_\ell^{|m|}(w)$ will be identically equal to zero for $|m| > \ell$. Accordingly, for a given ℓ there will be $(2\ell + 1)$ associated Legendre polynomials

$$m = -\ell, -\ell+1, \dots, \ell-1, \ell \quad (42)$$

Using the Legendre polynomials given in (37) one obtains,

$$\ell=0, \quad m=0: \quad P_0^0(w) = P_0(w) = 1 \quad (43)$$

$$\ell=1, \quad m=0: \quad P_1^0(w) = P_1(w) = w$$

$$m=1: \quad P_1^1(w) = (1-w^2)^{1/2} \frac{d}{dw} P_1(w) = (1-w^2)^{1/2}$$

$$\ell=2, \quad m=0: \quad P_2^0(w) = P_2(w) = -\frac{1}{2}(1-3w^2)$$

$$m=1: \quad P_2^1(w) = (1-w^2)^{1/2} \frac{d}{dw} P_2(w) = (1-w^2)^{1/2} 3w$$

$$m=2: \quad P_2^2(w) = (1-w^2)^{2/2} \frac{d^2}{dw^2} P_2(w) = (1-w^2)3$$

Since $\frac{d^{|m|}}{dw^{|m|}} P_\ell(w)$ is a polynomial of degree $(\ell - |m|)$ and $(1-w^2)^{|m|/2}$, is an even function, then

$$P_\ell^{|m|}(-w) = (-1)^{\ell-|m|} P_\ell^{|m|}(w) \quad (44)$$

Without proof we state that the associated Legendre polynomials satisfy,

$$\int_{-1}^1 P_\ell^{|m|}(w) P_{\ell'}^{|m|}(w) dw = \frac{2}{(2\ell+1)} \frac{(\ell+|m|)!}{(\ell-|m|)!} \delta_{\ell\ell'} \quad (45)$$

This expression will be useful for properly normalizing the wavefunction.

Summary:

The angular equation (22)

$$\left[\frac{1}{\sin \theta} \left(\frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = -\lambda Y(\theta, \phi)$$

admits solutions of the form:

$$Y(\theta, \phi) = \Theta_{\ell m}(\theta) \Phi_m(\phi)$$

$$\Theta_{\ell m}(\theta) = P_{\ell}^{|m|}(\cos \theta) = P_{\ell}^{|m|}(\cos \theta), \quad \ell = 0, 1, 2, 3, \dots$$

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}; \quad m = -\ell, \dots, -1, 0, 1, \dots, \ell$$

A proper constant in front of $\Theta(\theta) \Phi(\phi)$ is selected so that the solutions are normalized. The resultant functions are called the spherical harmonics.

Spherical Harmonics

$$Y_{\ell, m}(\theta, \phi) \equiv (-1)^m \left[\frac{(2\ell+1)(\ell-m)!}{2(\ell+m)!} \right]^{1/2} P_{\ell}^m(\cos \theta) \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad \text{for } m \geq 0 \quad (46)$$

$$Y_{\ell, m}(\theta, \phi) \equiv (-1)^m Y_{\ell, -m}^*(\theta, \phi), \quad \text{for } m < 0$$

The factor $(-1)^m$ is chosen for convenience (other authors' notation differ by a factor of $(i)^{\ell}$.)

The spherical harmonics $Y_{\ell, m}(\theta, \phi)$ constitute an orthonormal set of functions,

$$\int_{\text{angular space}} d\Omega Y_{\ell' m'}^*(\theta, \phi) Y_{\ell m}(\theta, \phi) = \delta_{\ell \ell'} \delta_{m m'}$$

Using $d\Omega = d\phi d\theta \sin \theta$,

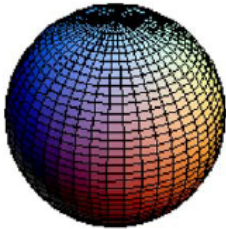
$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin \theta Y_{\ell' m'}^*(\theta, \phi) Y_{\ell m}(\theta, \phi) = \delta_{\ell \ell'} \delta_{m m'} \quad (47)$$

The following website is very helpful for visualizing the spherical harmonic functions:

http://www.vis.uni-stuttgart.de/~kraus/LiveGraphics3D/java_script/SphericalHarmonics.html

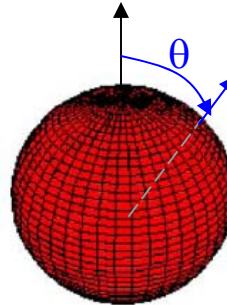
$\ell = 0, m=0$

$$Y_{0,0}(\theta, \phi) = \frac{1}{(4\pi)^{1/2}}$$



$\ell=0, m=0$

Absolute value of real part

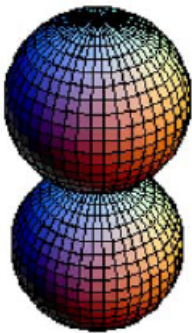


$\ell=0, m=0$

Absolute value,
colored by complex phase

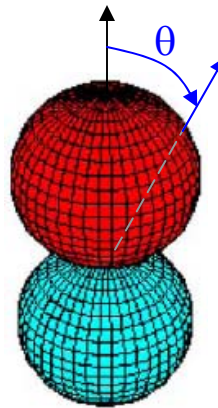
$\ell = 1, m=0$

$$Y_{1,0}(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$



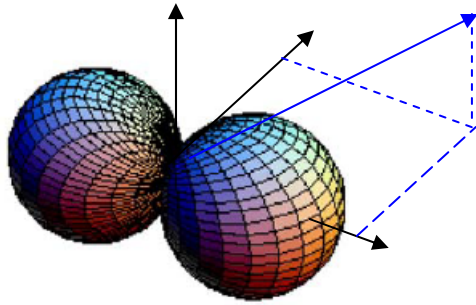
$\ell = 1, m=0$

Absolute value



Absolute value,
The two different colors indicate
the different sign taken by the
wavefunction

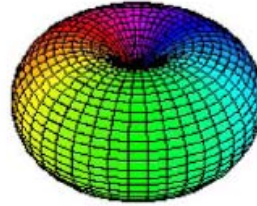
$$\ell = 1, \quad m = \pm 1 \quad Y_{1,\pm 1}(\theta, \phi) = \mp \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{\pm i\phi}$$



$$\ell = 1, \quad m = 1$$

Absolute value of real part

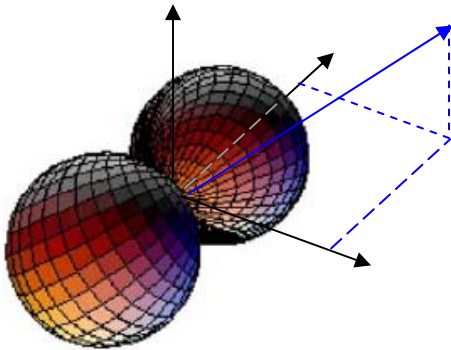
$$\left(\frac{3}{8\pi} \right)^{1/2} \sin \theta \cos \phi$$



$$\ell = 1, \quad m = 1$$

Absolute value,

colored by complex phase ϕ



$$\ell = 1, \quad m = -1$$

Absolute value of complex part

$$\left(\frac{3}{8\pi} \right)^{1/2} \sin \theta \sin \phi$$

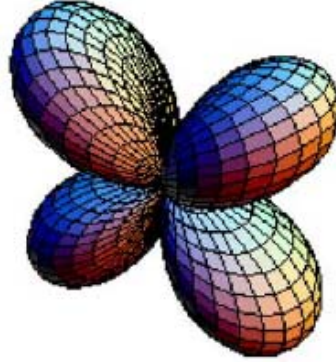
$$Y_{2,0}(\theta, \phi) = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2 \theta - 1)$$

$$Y_{2,\pm 1}(\theta, \phi) = \mp \left(\frac{5}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{\pm i\phi}$$

$$Y_{2,\pm 2}(\theta, \phi) = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta \cos \theta e^{\pm i2\phi}$$



$\ell = 2, m = 0$

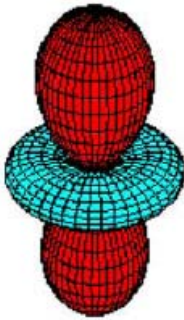


$\ell = 2, m = 1$

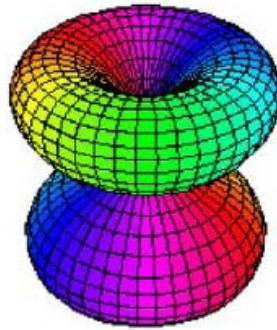


$\ell = 2, m = 2$

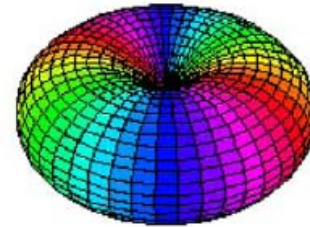
Absolute value of real part (illuminated by light.)



$\ell = 2, m = 0$



$\ell = 2, m = 1$



$\ell = 2, m = 2$

Absolute value, colored by complex phase

The spherical harmonic functions, given in (46) constitute a complete set of solution of the angular equation (22). We are now left with the task of solving the radial equation (23).

10.3B The Radial Equation

We have found that in Eq. (23) that the radial equation must satisfy

$$\left\{ -\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\ell(\ell+1)}{r^2} \right] + U(r) \right\} R_{E\ell}(r) = E R_{E\ell}(r)$$

where ℓ takes integer values $\ell = 0, 1, 2, \dots$ (this condition comes from the solutions required for the angular component of the wavefunction), and the values for E need to be determined.

For the case of a Coulomb field

$$U(r) = -\frac{\beta}{r}$$

where $\beta = \frac{Ze^2}{4\pi\epsilon_0}$, Z is the atomic number (number of protons in the nucleus) and e is the elementary charge,

we have,

$$\left\{ -\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\ell(\ell+1)}{r^2} \right] - \frac{\beta}{r} \right\} R(r) = E R(r) \quad (48)$$

Using unit-less variables r' , E'

When considering the case of a Coulomb field, it is convenient to use

$$m_e, \quad \frac{\hbar^2}{m_e \beta}, \quad \frac{\hbar^3}{m_e \beta^2} \quad (49)$$

as the units of mass, length and time, respectively. Notice that the unit of energy is $m_e \frac{\beta^2}{\hbar^2}$. For our purpose, instead of m_e we will use

the reduced mass μ instead. Thus, since $\frac{\hbar^2}{\mu \beta}$ has units of distance,

and $\mu \frac{\beta^2}{\hbar^2}$ has units of energy, the equation above can be expressed in terms of unit-less parameters r' and E' instead of the variables r and E , where

$$r \equiv r' \frac{\hbar^2}{\mu \beta}, \quad E \equiv E' \mu \frac{\beta^2}{\hbar^2}. \quad (50)$$

Indeed, using in addition $R(r) = R(r')$, $\frac{\partial R}{\partial r'} = \frac{\partial R}{\partial r} \frac{\partial r}{\partial r'} = \frac{\partial R}{\partial r} \frac{\hbar^2}{m_e \beta}$, ... etc., one obtains,

$$\left\{ \left[\frac{\partial^2}{\partial r'^2} + \frac{2}{r'} \frac{\partial}{\partial r'} - \frac{\ell(\ell+1)}{r'^2} \right] + 2 \left(E' + \frac{1}{r'} \right) \right\} R(r') = 0 \quad (51)$$

Let

$$R(r') = \frac{u(r')}{r'} \quad (52)$$

The purpose of this change of variable is to obtain an equation the resembles the one dimensional case (as we will verify below.)

$$\frac{\partial R}{\partial r'} = \frac{1}{r'} \frac{\partial u}{\partial r'} - \frac{1}{r'^2} u$$

$$\frac{2}{r'} \frac{\partial R}{\partial r'} = \frac{2}{r'^2} \frac{\partial u}{\partial r'} - \frac{2}{r'^3} u$$

$$\frac{\partial^2 R}{\partial r'^2} = \frac{1}{r'} \frac{\partial^2 u}{\partial r'^2} - \frac{1}{r'^2} \frac{\partial u}{\partial r'} + \frac{2}{r'^3} u - \frac{1}{r'^2} \frac{\partial u}{\partial r'} = \frac{1}{r'} \frac{\partial^2 u}{\partial r'^2} - \frac{2}{r'^2} \frac{\partial u}{\partial r'} + \frac{2}{r'^3} u$$

Adding the last two expressions,

$$\frac{\partial^2 R}{\partial r'^2} + \frac{2}{r'} \frac{\partial R}{\partial r'} = \frac{1}{r'} \frac{\partial^2 u}{\partial r'^2}$$

$$\left[\frac{1}{r'} \frac{\partial^2 u}{\partial r'^2} - \frac{\ell(\ell+1)}{r'^2} \frac{u(r')}{r'} \right] + 2 \left(E' + \frac{1}{r'} \right) \frac{u(r')}{r'} = 0$$

$$\frac{\partial^2 u}{\partial r'^2} - \frac{\ell(\ell+1)}{r'^2} u(r') + 2 \left(E' + \frac{1}{r'} \right) u(r') = 0$$

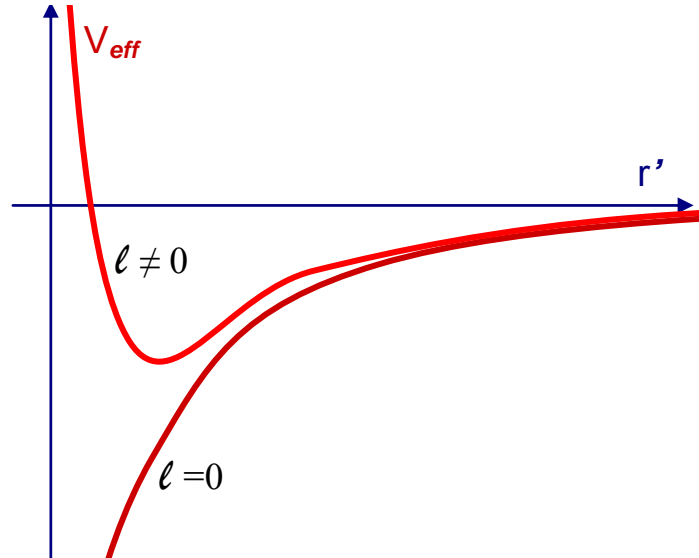
$$\frac{\partial^2 u}{\partial r'^2} + 2 \left(E' - \frac{\ell(\ell+1)}{2r'^2} + \frac{1}{r'} \right) u(r') = 0$$

This Eq. can be expressed as,

$$\frac{\partial^2 u}{\partial r'^2} + 2 \left[E' - V_{\text{eff}}(r') \right] u(r') = 0 \quad (53)$$

where an effective potential has been defined as,

$$V_{\text{eff}}(r') = \frac{\ell(\ell+1)}{2r'^2} - \frac{1}{r'}$$



Notice, Eq. (53) resembles the case for a one dimensional problem. However,

- It has significance only for $r > 0$, and
- Must be supplemented by boundary conditions at $r = 0$.

We will require that the radial function $R_{\ell E}(r)$ remain finite at the origin. Since $R_{\ell E}(r) = \frac{u(r')}{r'}$, we must require that

$$u(0) = 0 \quad (54)$$

Notice, in the region $r' \rightarrow \infty$ the equation (53) becomes,

$$\frac{\partial^2 u}{\partial r'^2} + 2E' u(r') = 0$$

- For $E' > 0$, the behavior of $u(r')$ in this region would be oscillatory.

$$u(r') \rightarrow e^{i\sqrt{2E'} r'}$$

- If our interest is to find bound states, we can ensure that the wavefunction vanishes when $r' \rightarrow \infty$ if we require that $E' < 0$

$$u(r') \rightarrow e^{-\sqrt{-2E'} r'}$$

Looking for bound states ($E' < 0$)

Bound states will be obtained with negative values for E' .

Let's define,

$$\rho = \xi r'$$

where ξ is a parameter to be chosen conveniently later.

$$u(r') = v(\rho),$$

$$\frac{\partial u}{\partial r'} = \frac{\partial v}{\partial \rho} \frac{\partial \rho}{\partial r'} = \frac{\partial v}{\partial \rho} \xi, \quad \frac{\partial^2 u}{\partial r'^2} = \xi^2 \frac{\partial^2 v}{\partial \rho^2}$$

$$\xi^2 \frac{\partial^2 v}{\partial \rho^2} + 2 \left(E' - \xi^2 \frac{\ell(\ell+1)}{2\rho^2} + \frac{\xi}{\rho} \right) v(\rho) = 0$$

$$\frac{\partial^2 v}{\partial \rho^2} + \left(-\frac{2E'}{\xi^2} - \frac{\ell(\ell+1)}{\rho^2} + \frac{2}{\xi\rho} \right) v(\rho) = 0$$

Choosing $\xi = 2\sqrt{-2E'}$

$$\frac{\partial^2 v}{\partial \rho^2} + \left(-\frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2} + \frac{1}{\sqrt{-2E'}\rho} \right) v(\rho) = 0$$

Let, $k \equiv \frac{1}{\sqrt{-2E'}}$

$$\frac{\partial^2 v}{\partial \rho^2} + \left(-\frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2} + \frac{k}{\rho} \right) v(\rho) = 0$$

Summary

- $\left\{ -\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\ell(\ell+1)}{r^2} \right] - \frac{\beta}{r} \right\} R_{\ell E}(r) = E R_{\ell E}(r)$

where $\beta = \frac{Ze^2}{4\pi\epsilon_0}$

- $R(r) = R(r') = \frac{u(r')}{r'}$, with $r \equiv r' \frac{\hbar^2}{\mu\beta}$ and $E \equiv E' \mu \frac{\beta^2}{\hbar^2}$, gives

$$\frac{\partial^2 u}{\partial r'^2} + 2 \left(E' - \frac{\ell(\ell+1)}{2r'^2} + \frac{1}{r'} \right) u(r') = 0$$

- $u(r') = v(\rho)$, $\rho = 2\sqrt{-2E'} r'$ and $k \equiv \frac{1}{\sqrt{-2E'}}$ gives,

$$\frac{\partial^2}{\partial \rho^2} V_{\ell k} + \left(-\frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2} + \frac{k}{\rho} \right) V_{\ell k} = 0 \quad (55)$$

with the condition

$$V_{\ell k}(0) = 0$$

The function $V_{\ell k}$ and the values of the parameter k (associated to the energy E) need to be determined.

Let's figure out the behavior of $V_{\ell k}(\rho)$ near the origin .

Assume

$$V_{\ell k}(\rho) = \rho^s \sum_{j=0}^{\infty} c_j \rho^j = c_0 \rho^s + c_1 \rho^{s+1} + \dots \quad (56)$$

The power s is unknown (i.e. we do not know yet has fast $V_{\ell k}(\rho)$ tends to zero when $\rho \rightarrow 0$.)

The value of s is determined by replacing the expansion (56) in (55) and analyzing the terms of lowest power, that is ρ^s . In effect, such procedure gives,

$$\begin{aligned} c_0 s(s-1) \rho^{s-2} + c_1 (s+1)(s) \rho^{s-1} + \dots \\ - \ell(\ell+1) c_0 \rho^{s-2} - \ell(\ell+1) c_1 \rho^{s-1} + \dots \\ + k c_0 \rho^{s-1} + k c_1 \rho^s + \dots \\ + \frac{1}{4} c_0 \rho^s + \dots = 0 \end{aligned}$$

For a given value of ℓ , this expression above imposes the following condition on s ,

$$s(s-1) - \ell(\ell+1) = 0 \quad (\text{condition on } s) \quad (57)$$

The possible choices for s are $s = \ell + 1$ and $s = -\ell$. The second option is discarded on the basis that such selection would not satisfy the condition $V_{\ell k}(0) = 0$. Thus,

$$s = \ell + 1 \quad (58)$$

$$V_{\ell k}(\rho) \xrightarrow{\rho \rightarrow 0} \rho^{\ell+1}$$

Let's figure out the behavior of $V_{\ell k}(\rho)$ when $\rho \rightarrow \infty$.

In this region Eq. (55) takes the form,

$$\frac{\partial^2}{\partial \rho^2} V_{\ell k} - \frac{1}{4} V_{\ell k} = 0,$$

which has solutions of the form

$$V_{\ell k}(\rho) \xrightarrow{\rho \rightarrow 0} e^{-\frac{1}{2}\rho} \quad (59)$$

Full solution of Eq, (55)

The results in (58) and (59) suggest looking for solutions of the form

$$V_{\ell k}(\rho) = e^{-\frac{1}{2}\rho} \rho^{\ell+1} g_{\ell k}(\rho), \quad (60)$$

$$\text{where } g_{\ell k}(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \text{ and } c_0 \neq 0$$

$$\begin{aligned} \frac{d}{d\rho} V_{\ell k}(\rho) &= e^{-\frac{1}{2}\rho} \rho^{\ell+1} \frac{dg}{d\rho} + e^{-\frac{1}{2}\rho} (\ell+1) \rho^{\ell} g - \frac{1}{2} e^{-\frac{1}{2}\rho} \rho^{\ell+1} g \\ &= e^{-\frac{1}{2}\rho} \left(\rho^{\ell+1} \frac{dg}{d\rho} + (\ell+1) \rho^{\ell} g - \frac{1}{2} \rho^{\ell+1} g \right) \end{aligned}$$

$$\begin{aligned} \frac{d^2}{d\rho^2} V_{\ell k}(\rho) &= e^{-\frac{1}{2}\rho} \left(-\frac{1}{2} \rho^{\ell+1} \frac{dg}{d\rho} - \frac{1}{2} (\ell+1) \rho^{\ell} g + \frac{1}{4} \rho^{\ell+1} g \right) + \\ &+ e^{-\frac{1}{2}\rho} \left(\rho^{\ell+1} \frac{d^2g}{d\rho^2} + 2(\ell+1) \rho^{\ell} \frac{dg}{d\rho} + \ell(\ell+1) \rho^{\ell-1} g + \right. \\ &\quad \left. - \frac{1}{2} \rho^{\ell+1} \frac{dg}{d\rho} - \frac{1}{2} (\ell+1) \rho^{\ell} g \right) \end{aligned}$$

Thus

$$\begin{aligned} \bullet \quad \frac{d^2}{d\rho^2} V_{\ell k}(\rho) &= e^{-\frac{1}{2}\rho} \left(\rho^{\ell+1} \frac{d^2g}{d\rho^2} + [2(\ell+1) \rho^{\ell} - \rho^{\ell+1}] \frac{dg}{d\rho} + \right. \\ &\quad \left. + \frac{1}{4} \rho^{\ell+1} g - (\ell+1) \rho^{\ell} g + \ell(\ell+1) \rho^{\ell-1} g \right) \end{aligned}$$

$$\bullet \left(-\frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2} + \frac{k}{\rho} \right) V_{\ell k} = e^{-\frac{1}{2}\rho} \left(-\frac{1}{4}\rho^{\ell+1} g - \ell(\ell+1)\rho^{\ell-1} g + k\rho^{\ell} g \right)$$

The addition of these last two expressions should be equal to zero,

$$\rho^{\ell+1} \frac{d^2 g}{d\rho^2} + [2(\ell+1)\rho^{\ell} - \rho^{\ell+1}] \frac{dg}{d\rho} + [k - (\ell+1)]\rho^{\ell} g = 0$$

$$\rho \frac{d^2 g_{\ell k}}{d\rho^2} + [2\ell + 2 - \rho] \frac{dg_{\ell k}}{d\rho} + [k - (\ell+1)] g_{\ell k} = 0 \quad (61)$$

According to (60), we expand the function g in a power series,

$$g_{\ell k}(\rho) = \sum_{j=0}^{\infty} c_j \rho^j, \quad \text{where } c_0 \neq 0 \quad (62)$$

$$\frac{dg_{\ell k}}{d\rho} = \sum_{j=1}^{\infty} j c_j \rho^{j-1} \xrightarrow{\text{making } j' = j-1} \sum_{j'=0}^{\infty} (j'+1) c_{j'+1} \rho^{j'}$$

$$\frac{d^2 g_{\ell k}}{d\rho^2} = \sum_{j=2}^{\infty} j(j-1) c_j \rho^{j-2} \xrightarrow{\text{making } j' = j-2} \sum_{j'=0}^{\infty} (j'+2)(j'+1) c_{j'+2} \rho^{j'}$$

$$\begin{aligned} \rho \frac{d^2 g_{\ell k}}{d\rho^2} &= \sum_{j=2}^{\infty} j(j-1) c_j \rho^{j-1} \xrightarrow{\text{making } j' = j-1} \sum_{j'=1}^{\infty} (j'+1)(j') c_{j'+1} \rho^{j'} \\ &= \sum_{j'=0}^{\infty} (j'+1)(j') c_{j'+1} \rho^{j'} \end{aligned}$$

$$\rho \frac{dg_{\ell k}}{d\rho} = \sum_{j=1}^{\infty} j c_j \rho^j \xrightarrow{\text{or}} \sum_{j'=0}^{\infty} j' c_{j'} \rho^{j'}$$

Replacing the expression on the right side in (61), and renaming j' back to j , we obtain

$$(j+1)(j) c_{j+1} + [2\ell + 2](j+1) c_{j+1} - j c_j + [k - (\ell+1)] c_j = 0$$

$$[2\ell + 2 + j](j+1)c_{j+1} + [k - (\ell + 1 + j)]c_j = 0$$

We obtain the following recurrence formula

$$c_{j+1} = \frac{(\ell + 1 + j) - k}{(2\ell + 2 + j)(j+1)} c_j \quad (63)$$

For large j , $\frac{c_{j+1}}{c_j} \rightarrow \frac{1}{j+1}$. This convergence is similar to the expansion of the function $e^\rho = \sum_j \frac{1}{j!} \rho^j$, which is not acceptable in this case, since the wavefunction should tend to zero in the region $\rho \rightarrow \infty$.

One way to obtain a useful solution is to find the conditions under which the series (62) gets truncated into a polynomial.

Expression (63) indicates that that is possible if k (the term that determines the energy of the system) were equal to an integer number. Indeed,

$$\begin{aligned} &\text{For a given } \ell, \text{ by selecting} \\ &\quad k = n \text{ (with } n \geq \ell + 1), \\ &g_{k\ell} \text{ becomes a polynomial } g_{n\ell} \text{ of order } (n - \ell - 1) \end{aligned} \quad (64)$$

For a given n , the possible values for ℓ are

$$\ell = 0, 1, 2, 3, \dots, (n-1); \quad (65)$$

That is, different solutions will be associated to the same energy level.

From (55), $k \equiv \frac{1}{\sqrt{-2E'}}$. An integer value for $k = n$ implies that the allowed values for the energy are discrete and,

$$E'_n \equiv -\frac{1}{2n^2}$$

From (50), $E \equiv E' \mu \frac{\beta^2}{\hbar^2}$ where $\beta = \frac{Ze^2}{4\pi\epsilon_0}$. Thus,

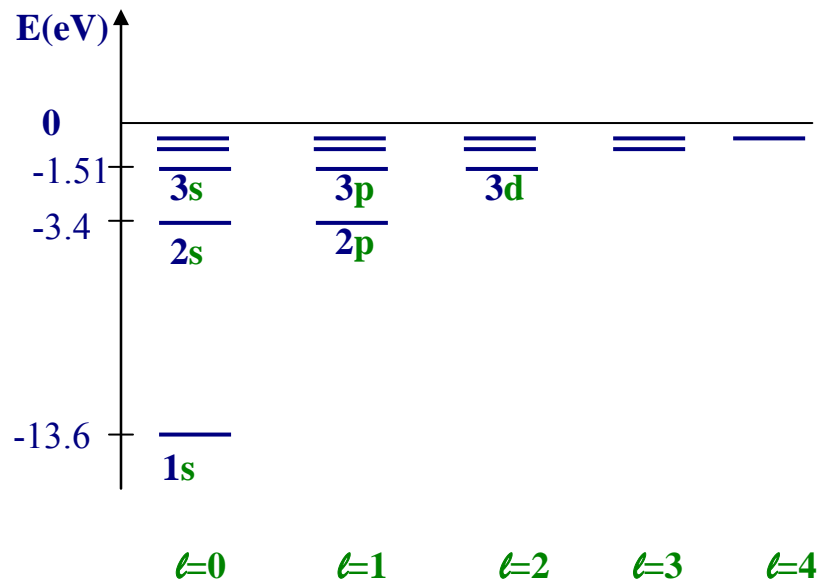
$$E_n = -\mu \frac{\beta^2}{2\hbar^2} \frac{1}{n^2} = -\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \frac{\mu}{2\hbar^2} \frac{1}{n^2}, \quad (66)$$

where $n = 1, 2, 3, \dots$

In the usual spectroscopy notation, the energy levels are specified by two symbols:

The first gives the value of the principal quantum number n .

The second is a code letter (s, p, d, \dots) that indicates the value of the orbital angular momentum ℓ (0, 1, 2, ... respectively.)



Radial wavefunctions of the bound states ($E' < 0$)

$$R(r) = R(r') = \frac{u(r')}{r'} = \frac{v(\rho)}{r'} = \frac{e^{-\frac{1}{2}\rho} \rho^{\ell+1} g_{k\ell}(\rho)}{r'}$$

$$\text{where } k \equiv \frac{1}{\sqrt{-2E'}} = n, \quad \rho = 2\sqrt{-2E'} r' = \frac{2}{n} r',$$

$$= R(r') = \frac{e^{-\frac{1}{2}\rho} \rho^{\ell+1} g_{n\ell}(\rho)}{(n/2)\rho} = \frac{2}{n} e^{-\frac{1}{2}\rho} \rho^{\ell} g_{n\ell}(\rho)$$

$$\text{where } \rho = \frac{2}{n} r', \quad r \equiv r', \frac{\hbar^2}{\mu \beta} \quad \text{and} \quad \beta = \frac{Ze^2}{4\pi\epsilon_0};$$

The expression for ρ is further expressed as

$$\rho \equiv \frac{2}{n} \frac{\mu}{\hbar^2} \frac{Ze^2}{4\pi\epsilon_0} r = \frac{2Z}{n} (r/a_0) \quad \text{where} \quad a_0 \equiv \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} = 0.529 \times 10^{-10} m$$

That is,

$$R_{n\ell}(r) = e^{-\frac{1}{2}\rho} \rho^\ell g_{n\ell}(\rho) = e^{-\frac{Z}{n}(r/a_0)} \rho^\ell g_{n\ell}(\rho) \quad (67)$$

$$\text{where } \rho \equiv \frac{2Z}{n} (r/a_0) \quad \text{and} \quad a_0 \equiv \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2}$$

$$g_{n\ell}(\rho) = \sum_{j=0}^{\infty} c_j \rho^j, \quad \text{with } c_0 \neq 0 \quad \text{and} \quad c_{j+1} = \frac{(\ell+1+j)-n}{(2\ell+2+j)(j+1)} c_j$$

We have omitted the coefficient in front of the exponential term in $R_{n\ell}$, since it will be absorbed by the coefficient c_0 from the polynomial $g_{n\ell}$.

Case $n=1$

According to (65), the only possible value for the orbital angular momentum is $\ell = 0$.

Also, from (67),

$$c_{j+1} = \frac{(\ell+1+j)-n}{(2\ell+2+j)(j+1)} c_j = \frac{(1+j)-1}{(2+j)(j+1)} c_j = \frac{j}{(2+j)(j+1)} c_j$$

For $j=0$ the recurrence formula gives $c_1=0$. Hence $c_j=0$ for any $j>0$.

Thus $g_{10}(\rho) = c_0$.

Expression (67) gives, $R_{10}(r) = e^{-\frac{1}{2}\rho} c_0 = e^{-\frac{\mu}{\hbar^2} \beta r} c_0 = e^{-\frac{\mu Z e^2}{4\pi\epsilon_0 \hbar^2} r} c_0$;

$$R_{10}(r) = c_0 e^{-Zr/a_0} \quad (68)$$

where the result has been expressed in terms of the Bohr's radius

$$a_0 \equiv \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} = 0.529 \times 10^{-10} \text{ m} \quad (69)$$

The condition of normalization requires, $\int_{r=0}^{\infty} |R_{10}(r)|^2 r^2 dr = 1$. Using

$$(68) \text{ one obtains, } (c_0)^2 \int_{r=0}^{\infty} e^{-2Zr/a_0} r^2 dr = 1; \quad (c_0)^2 \frac{1}{4} (a_0/Z)^3 = 1;$$

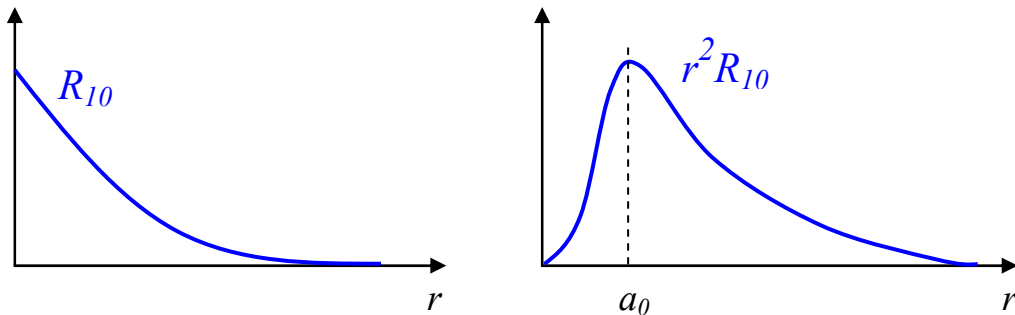
$(c_0)^2 = 4(Z/a_0)^3$; and finally $c_0 = 2(Z/a_0)^{3/2}$. Thus, (68) becomes,

$$R_{10}(r) = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \quad (70)$$

The radial distribution function D_{nl}

$$D_{10}(r) = |R_{10}(r)|^2 r^2 \quad (71)$$

gives the probability per unit length that the electron is to be found at a distance r from the nucleus.



This radial solution (71) is complemented with the spherical harmonic corresponding to $\ell = 0$ and $m=0$ (given in expression (46),

$Y_{0,0}(\theta, \phi) = \frac{1}{(4\pi)^{1/2}}$. Thus, the solution to the Schrodinger Eq. (19) is

given by, $F_{100}(r, \theta, \phi) = R_{10}(r)Y_{0,0}(\theta, \phi) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \frac{1}{(4\pi)^{1/2}}$.

$$F_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left[\frac{Z}{a_0} \right]^{3/2} e^{-Zr/a_0} \quad (72)$$

Case $n=2$

According to (65), the only possible value for the orbital angular momentum is $\ell = 0, 1$.