# QUANTUM MECHANICS
# Lecture 22

## The angular equation
## The radial equation

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D. J. Griffiths: paragraph 4.1

# QM in 3D



1. In the last lecture we have concluded that, in general, the **time-independent Schrödinger equation in 3$D$ reads**

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\,\psi(\vec{r}) = E\,\psi(\vec{r})$$

2. However, it happens very often that the **energy potential is central**, which means that $V$ is a function only of the **distance** $r$ from the origin.

3. **This allows to simplify quite a lot the resolution of the time-independent Schrödinger equation.**

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# QM in 3D

Let us start by observing that, in case of a central potential energy $V(r)$, it is **more convenient** to adopt the **spherical coordinates** $(r, \theta, \phi)$

$$x = r\, sin\theta\, cos\phi \qquad r = \sqrt{x^2 + y^2 + z^2}$$

$$y = r\, sin\theta\, sin\phi \qquad \theta = arccos(z/r)$$

$$z = r\, cos\theta \qquad \phi = arctg(y/x)$$

$$\Rightarrow \quad d^3r \equiv dx\, dy\, dz = r^2\, dr\, sin\theta\, d\theta\, d\phi$$

# QM in 3D

In spherical coordinates, **the laplacian operator becomes**

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

where we have introduced the two operators $\hat{J}$ and $\hat{W}$ defined as follows

$$\hat{J} = \hat{J}(\theta,\phi) \equiv \frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$\hat{W} = \hat{W}(r) \equiv \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$

# QM in 3D



To solve the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi$$

$$\Rightarrow \quad -\frac{\hbar^2}{2mr^2}\left(\hat{W}\,\psi + \hat{J}\,\psi\right) + \left(V(r) - E\right)\psi = 0$$

we start by looking for solutions that can be factorized as follows

$$\psi(r,\theta,\phi) = R(r)\cdot Y(\theta,\phi)$$

with the idea that they may form a basis.

# QM in 3D



If we multiply the equation by $-\frac{2mr^2}{\hbar^2}$ and we take into account that $\hat{J}$ operates only on the angular variables whereas $\hat{W}$ only on the radial variable, we obtain

$$R\,\left(\hat{J}Y\right) + Y\,\left(\hat{W}R\right) - \frac{2mr^2}{\hbar^2}\Big(V(r) - E\Big)R\,Y = 0$$

which, dividing by $\psi = R\,Y$, becomes

$$\left[\frac{1}{Y}\,\left(\hat{J}Y\right)\right] + \left[\frac{1}{R}\left(\hat{W}R\right) - \frac{2mr^2}{\hbar^2}\Big(V(r) - E\Big)\right] = 0$$

# QM in 3D

But the first term is a function only of the angular variables, whereas the second term depends only on $r$, therefore the equation can be satisfied only if both terms are constant, or, in other words, if

$$\frac{1}{Y}\left(\hat{J}Y\right) = -k$$

$$\frac{1}{R}\left(\hat{W}R\right) - \frac{2mr^2}{\hbar^2}\left(V(r) - E\right) = k$$

where $k$ is a suitable complex number.

# The angular equation



1. Let us start by solving the angular equation

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

2. If we multiply by $-Y\,sin^2\theta$, we obtain

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

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# The angular equation



1. This equation admits square-integrable solutions if and only if $k = l(l+1)$ with $l$ a non negative integer.
2. In this case, the solutions are the so-called **spherical harmonics** $Y_l^m(\theta,\phi)$, defined as

$$Y_l^m(\theta,\phi) \equiv \epsilon\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\,P_l^m(cos\theta)\,e^{im\phi}$$

where

- $|m| \leq l$ is an integer;
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# The angular equation



The $P_l^m(z)$ are the *associated Legendre functions*, defined in terms of the Legendre polynomials

$$P_l(z) = \frac{1}{2^l\, l!} \frac{d^l}{dz^l} (z^2 - 1)^l$$

as $(0 \leq m \leq l)$

$$\begin{aligned} P_l^m(z) &\equiv (1 - z^2)^{m/2} \frac{d^m}{dz^m} P_l(z) \\ P_l^{-m}(z) &\equiv P_l^m(z) \end{aligned}$$

# The angular equation



1. It turns out that

$$Y_l^{-m}(\theta, \phi) = (-1)^m \Big( Y_l^m(\theta, \phi) \Big)^*$$

and we have

$$\int_0^{2\pi} d\phi \int_0^{\pi} sin\theta \, d\theta \Big( Y_{l'}^{m'}(\theta, \phi) \Big)^* Y_l^m(\theta, \phi) = \delta_{ll'} \, \delta_{mm'}$$

2. **$\Rightarrow$ The spherical harmonics form a complete set of orthonormal functions on the surface of the unit sphere.**

3. For historical reasons, $l$ is called the **azimuthal quantum number** and $m$ is called the **magnetic quantum number**.

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# The angular equation



We have

$$l = 0 \quad : \quad Y_0^0 = \frac{1}{4\pi}$$

$$l = 1 \quad : \quad Y_1^1 = -\sqrt{\frac{3}{8\pi}}\, sin\theta\, e^{i\phi}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\, cos\theta$$

$$l = 2 \quad : \quad Y_2^2 = \sqrt{\frac{15}{32\pi}}\, sin^2\theta\, e^{2i\phi}$$

$$Y_2^1 = -\sqrt{\frac{15}{8\pi}}\, sin\theta\, cos\theta\, e^{i\phi}$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}\, \left(3cos^2\theta - 1\right)$$

.......

# The radial equation

The angular solutions $Y(\theta, \phi)$ **are the same for any spherically symmetric potential energy.**

The potential energy $V(r)$ enters only in the equation concerning $R = R(r)$:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\Big(V(r) - E\Big) = k = l(l+1)$$

which, by multiplying by $R$, becomes

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\Big(V(r) - E\Big)R - l(l+1)R = 0$$

# The radial equation

But

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = 2r\frac{dR}{dr} + r^2\frac{d^2R}{dr^2}$$

and

$$\frac{d^2}{dr^2}(rR) = \frac{d}{dr}\left(R + r\frac{dR}{dr}\right) = \frac{dR}{dr} + \frac{dR}{dr} + r\frac{d^2R}{dr^2}$$

therefore

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = r\frac{d^2}{dr^2}(rR)$$

# The radial equation

It is, now, quite useful to define a new radial function

$$u(r) \equiv r\,R(r)$$

In terms of this new function, the radial equation becomes

$$r\,\frac{d^2u}{dr^2} - \frac{2m}{\hbar^2} r \Big( V(r) - E \Big) u(r) = \frac{l(l+1)}{r}\,u(r)$$

or, equivalently

$$\frac{d^2u}{dr^2} - \frac{2m}{\hbar^2} \Big( V(r) - E \Big) u(r) - \frac{l(l+1)}{r^2}\,u(r) = 0$$

which it is called the **radial equation**.

# The radial equation



1. It is quite obvious from what we have obtained that the radial equation looks the same as the one dimensional time independent Schrödinger equation for an *effective potential*

$$\tilde{V}(r) = V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

2. The term $\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$ is the so-called *centrifugal term*: it tends to throw the particle away from the origin and this is the reason of its name.

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# The radial equation



Concerning the normalization of the function $u(r)$, let us remember that

$$
\begin{aligned}
1 &= \int d^3r \; |\psi(\vec{r})|^2 = \\
&= \int_0^\infty r^2 dr \int_0^\pi sin\theta \, d\theta \int_0^{2\pi} d\phi \, |R(r)\, Y(\theta, \phi)|^2 = \\
&= \int_0^\infty r^2 dr |R(r)|^2 \int sin\theta \, d\theta \, d\phi \, |Y(\theta, \phi)|^2 = \\
&= \int_0^\infty r^2 dr |R(r)|^2 = \int_0^\infty dr \, |u(r)|^2
\end{aligned}
$$

which means, in other words, that the wave function normalization condition requires that

$$\int_0^\infty dr \, |u(r)|^2 = 1$$