# PHYS20302
Quantum Mechanics 2

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This unit follows PHYS20101 Introduction to Quantum Mechanics. It introduces fundamental aspects of the theory such as angular momenta and their addition, exchange symmetry in systems of identical particles, as well as time-dependent perturbation theory. These ideas are applied to the descriptions of various systems, such as hydrogen atom, multi-electron atoms, H_2^+ and hydrogen molecules, simple model of solids, and lasers. There are 7 chapters in this note and we will take about 22 lectures to cover them all in S4.
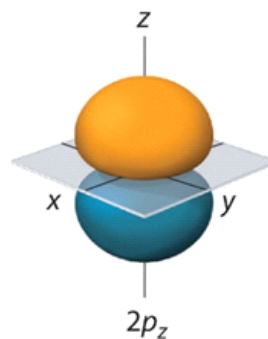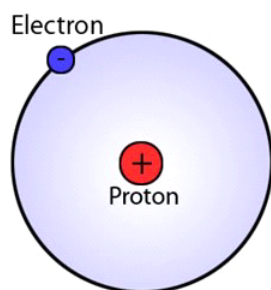
CONTENTS

References and Acknowledgements

The notes for the seven chapters are largely self-contained and sufficient for this course. However, for students seeking a more comprehensive or in-depth understanding may find the following references helpful.

1. DH McIntyre, *Quantum Mechanics, A Paradigms Appraoch*, Cambridge University Press.

2. S Gasiorowicz, *Quantum Mechanics*, Wiley.

3. F Mandl, *Quantum Mechanics*, Wiley.

4. AIM Rae, *Quantum Mechanics*, Chapman and Hall.

Special Note: As mentioned, these notes, enriched by contributions from past lecturers, are intended as teaching and learning materials for students and teaching assistants in our department. Some of the diagrams, figures, tables, and exercises are sourced from published textbooks. Please do not upload these notes to any website, whether free or paid, without the lecturer's explicit permission.

Chapter 1: Orbital Angular Momentum

1.1 Introduction: basics of QM

1.2 Particle in 2D and angular momentum I

1.3 Angular momentum II

1.4 Rotational states of diatomic molecules

1.1 Introduction: basics of QM

In PHYS20101 *Introduction to quantum mechanics*, we learned that a state of motion of a quantum system is described by a *wave function* Ψ (or a *state vector* $|\Psi\rangle$ in Dirac notation). Unlike the classical description of a particle, where motion is specified by six quantities (position and momentum vectors), the wave function $\Psi(\mathbf{r}, t)$ extends thoughout all space. Furthermore, physical quantities in classical mechanics (e.g. energy, momentum, angular momentum, etc.) are represented by *operators* in QM. The possible observed or measured values of these physical quantities correspond to the *eigenvalues* of their respective operators.

Here is a key concept you should have learned in the first semester: If a quantum particle is in a state described by a (normalized) wave function Ψ, the average value of many measurements of a physical quantity of the particle is given by the *expectation value* of the corresponding operator $\hat{A}$:

$$\langle \hat{A} \rangle = \langle \Psi | \hat{A} | \Psi \rangle = \int \Psi^* \hat{A} \Psi d\mathbf{r} \,, \quad d\mathbf{r} = dV = dxdydz \,, \quad \text{in 3D} \,. \tag{1}$$

The fundamental operators for a particle of mass m in a potential $V(\mathbf{r}, t)$ include position, momentum, angular momentum operators defined as, we use "hat" to indicate an operator,

$$
\begin{aligned}
\hat{x} &= x, \quad \hat{\mathbf{r}} = (\hat{x}, \hat{y}, \hat{z}) = (x, y, z) \\
\hat{p}_x &= -i\hbar \frac{\partial}{\partial x}, \quad \hat{\mathbf{p}} = -i\hbar \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \\
\hat{L}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \,, \quad \text{etc.}
\end{aligned}
$$

And the important Hamiltonian (or energy) operator is given by

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t), \tag{2}$$

where the Laplacian operator ∇^2 is defined as, in the Cartesian coordinates

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

The state function Ψ is obtained by solving the time-dependent Schrödinger equation (TDSE)

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \hat{H} \Psi(\mathbf{r}, t) \,. \tag{3}$$

When the potential $\hat{V}$ is independent of time, i.e. $\hat{V} = V(\mathbf{r})$ involving $\mathbf{r}$ only, the state function can be written in the *stationary* form

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \exp\left(\frac{-iEt}{\hbar}\right), \tag{4}$$

and Eq. (3) reduces to the following time-independent Schrödinger equation (TISE)

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad \text{or} \quad \hat{H}|\psi\rangle = E|\psi\rangle, \tag{5}$$

where we have used Dirac notation in the last equation. Eq. (5) is in fact an eigen equation for $\hat{H}$ with eigenfunction ψ and eigenvalue E.

In general, an eigen equation of an operator $\hat{A}$ is

$$\hat{A}\phi_i = a_i\phi_i, \quad i = 1, 2, \cdots \tag{6}$$

with index i labelling the set of eigenfunctions and eigenvalues. As previously mentioned, if we measure the physical observable A, the result will be one of its eigenvalues, a_i.

An important example of QM applications you learned is the 1D simple harmonic oscillator (SHO). Solving the TISE of the SHO of mass m and angular frequency ω

$$\hat{H}\psi_n(x) = E_n\psi_n(x), \quad \text{with} \quad \hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2, \tag{7}$$

we obtain the energy eigenvalues

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \cdots \tag{8}$$

and the normalized eigenfunctions

$$\psi_n(x) = \left(\frac{1}{n! 2^n a\sqrt{\pi}}\right)^{1/2} H_n(x/a) \exp\left(-\frac{x^2}{2a^2}\right), \quad a = \sqrt{\frac{\hbar}{m\omega}} \tag{9}$$

where $H_n(x/a)$ is a Hermite polynomial.

In a simple perturbation theory, we write the Hamiltonian of a quantum systems in two parts:

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{10}$$

and assume that we have solved QM of $\hat{H}_0$, namely we have obtained the eigenfunction ψ and and eigenvalue E of $\hat{H}_0$,

$$\hat{H}_0|\psi\rangle = E|\psi\rangle, \tag{11}$$

and that the effect of the time-independent perturbation potential $\hat{V}$ is small. We then use this ψ to calculate the expectation value of $\hat{H}$ as the first-order approximation of its eigenvalue

$$\langle \hat{H} \rangle = \langle \psi | (\hat{H}_0 + \hat{V}) | \psi \rangle = E + \Delta E \tag{12}$$

with $\Delta E = \langle \hat{V} \rangle = \langle \psi | \hat{V} | \psi \rangle$ as the first-order energy correction due to the perturbation potential.

Next, we begin the first topic of this course: extending the simple harmonic oscillator (SHO) to two dimensions and exploring angular momentum.

1.2 Particle in 2D and and angular momentum I

In two-dimensional (and three-dimensional) quantum mechanics, new elements come into play: multiple quantum numbers, energy level degeneracy, and, importantly, angular momentum. We will begin by exploring the two-dimensional simple harmonic oscillator (2D SHO).

1.2a The 2D SHO

For a particle of mass m moving in the xy plane in a 2D parabolic potential with spring constant k,

$$V(x, y) = \frac{1}{2}k(x^2 + y^2) = \frac{1}{2}m\omega^2(x^2 + y^2), \quad \omega = \sqrt{\frac{k}{m}} \tag{13}$$

the TISE reads

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi(x, y) + \frac{1}{2}m\omega^2\left(x^2 + y^2\right)\psi(x, y) = E\psi(x, y). \tag{14}$$

Note that $|\psi(x, y)|^2 dx dy$ is the probability to find the particle in an area element $dx dy$ around the point (x, y).

We can write the Hamiltonian operator as a sum of two independent terms

$$\hat{H} = \hat{H}_x + \hat{H}_y \tag{15}$$

where

$$\hat{H}_x = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 \,,$$
$$\hat{H}_y = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + \frac{1}{2}m\omega^2 y^2 \,.$$

Since the Hamiltonian can be written in this *separable form*, its eigenfunctions can be written as product functions of the eigenfunctions of $\hat{H}_x$ and $\hat{H}_y$. And we know what they are - they are the same as in the 1D case:

$$\hat{H}_x \psi_{n_x}(x) = \left(n_x + \frac{1}{2}\right)\hbar\omega\psi_{n_x}(x),$$

$$\hat{H}_y \psi_{n_y}(y) = \left(n_y + \frac{1}{2}\right)\hbar\omega\psi_{n_y}(y),$$

where the two quantum numbers

$$n_x, n_y = 0, 1, 2, \cdots.$$

We can show that products of these eigenfunctions of $\hat{H}_x$ and $\hat{H}_y$ are eigenfunctions of $\hat{H}$:

$$
\begin{aligned}
\hat{H}\left(\psi_{n_x}(x)\psi_{n_y}(y)\right) &= \left(\hat{H}_x + \hat{H}_y\right)\left(\psi_{n_x}(x)\psi_{n_y}(y)\right) \\
&= \left(\hat{H}_x\psi_{n_x}(x)\right)\psi_{n_y}(y) + \psi_{n_x}(x)\left(\hat{H}_y\psi_{n_y}(y)\right) \\
&= \left(n_x + \frac{1}{2}\right)\hbar\omega\psi_{n_x}(x)\psi_{n_y}(y) + \psi_{n_x}(x)\left(n_y + \frac{1}{2}\right)\hbar\omega\psi_{n_y}(y) \\
&= \left(n_x + n_y + 1\right)\hbar\omega\psi_{n_x}(x)\psi_{n_y}(y).
\end{aligned}
$$

Thus, the eigenvalues of , which are the energies of the stationary states, are

$$E_{n_x,n_y} = \left(n_x + n_y + 1\right)\hbar\omega. \tag{16}$$

And the corresponding eigenfunctions are

$$\psi_{n_x,n_y}(x,y) = \left(\frac{1}{n_x!2^n a\sqrt{\pi}\, n_y!2^n a\sqrt{\pi}}\right)^{1/2} H_{n_x}(x/a)H_{n_y}(y/a)\exp\left(-\frac{x^2+y^2}{2a^2}\right). \tag{17}$$

Degeneracy: Notice that we can now have more than one state with the same energy:

n_x	n_y	E_{n_x,n_y}
0	0	$\hbar\omega$
0	1	$2\hbar\omega$
1	0	$2\hbar\omega$
0	2	$3\hbar\omega$
1	1	$3\hbar\omega$
2	0	$3\hbar\omega$

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Two or more states that have the same energy are said to be *degenerate*. The degeneracy of an energy level is the number of states that have that energy. For example, the $3\hbar\omega$ energy level has a degeneracy of 3.

If two or more states are eigenstates of the same energy, then any linear superposition of them is also an eigenstate of the same energy. (Note that a linear superposition of eigenstates of different energies is not an eigenstate). So there is more than one way to write degenerate solutions.

Example: $\psi_{10}(x,y)$ and $\psi_{01}(x,y)$ have the same energy $2\hbar\omega$, so any linear combination of them, $a\psi_{10} + b\psi_{01}$ also has the same energy:

$$\hat{H}\left(\psi_{10} + \psi_{01}\right) = 2\hbar\omega\left(\psi_{10} + \psi_{01}\right).$$

In particular, if ψ_{10} and ψ_{01} are normalized. then the combinations

$$\psi_{\pm} = \frac{1}{\sqrt{2}}\left(\psi_{10} \pm \psi_{01}\right)$$

are also normalized.

Exercise: draw the pattern of nodes and antinodes corresponding to the solutions ψ_{10}, ψ_{01}, ψ_+ and ψ_-.

1.2b The z-component of angular momentum

Most of the potentials we are interested are 'central':

$$V(r, \theta, \phi) = V(r). \tag{18}$$

Equivalently, the corresponding force is always directed towards (or away from) the origin. The 2D SHO we have been discussing is of this type, and so are the 3D SHO and hydrogen atom, which we will come to.

In classical physics, motion in a central potential conserves angular momentum $\mathbf{L}$, because

$$\frac{d\mathbf{L}}{dt} = \mathbf{r} \times \mathbf{F}$$

and if $\mathbf{F}$ is parallel to $\mathbf{r}$ this is zero. Thus $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ is a constant. We might therefore expect that in quantum mechanics, angular momentum and energy would be compatible measurements, so that the stationary states have fixed angular momentum. We will find, however, in 3D, that the situation is more complicated than this, but let us start by studying the 2D case relevant to our 2D SHO.

The angular momentum operator $\hat{\mathbf{L}}$ can be obtained from the classical definition $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, simply by promoting $\mathbf{r}$ and $\mathbf{p}$ to operators:

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}. \tag{19}$$

For motion in the xy plane, only L_z is non-zero, and

$$\hat{L}_z = \hat{x}\hat{p}_x - \hat{y}\hat{p}_x = (-i\hbar)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \tag{20}$$

When working with a central potential, it is most convenient to work in polar variables. In plane polar coordinates, we have

$$x = r\cos\phi, \quad y = r\sin\phi.$$

Therefore

$$\frac{\partial}{\partial\phi} = \frac{\partial x}{\partial\phi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\phi}\frac{\partial}{\partial y} = -r\sin\phi\frac{\partial}{\partial x} + r\cos\phi\frac{\partial}{\partial y} = -y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y}.$$

So we have simply

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}. \tag{21}$$

Using plane polar coordinates, we write the wave function as $\psi(r,\phi)$. Let us suppose that we can find solutions that are separable:

$$\psi(r,\phi) = R(r)\Phi(\phi),$$

(we have not yet shown that this is the case, but let us suppose that it is) then, as far as the operator $\hat{L}_z$ is concerned, $R(r)$ is just a constant, and ψ is an eigenfunction of $\hat{L}_z$ if and only if Φ is. Since they are independent of r, they are independent of the choice of potential: all central potentials will have the same angular momentum eigenfunctions, so it is worth studying them in abstracto.

Eigenfunction and eigenvalue of $\hat{L}_z$ The eigen equation of $\hat{L}_z$ is

$$\hat{L}_z\Phi(\phi) = L_z\Phi(\phi), \quad \text{or} \quad -i\hbar\frac{d\Phi(\phi)}{d\phi} = L_z\Phi(\phi), \tag{22}$$

with L_z the eigenvalue. This equation is easily solved with the solution

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{iL_z\phi/\hbar} \tag{23}$$

where the prefactor is the normalization constant (can you show it?). We must also make sure it obeys any boundary conditions. But what are the boundary conditions on Φ?

Well, we said that wave functions should be single-valued functions of position. Thus, if we start from some point (r,ϕ) and move around the origin, by keeping r

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fixed and increasing ϕ, then by the time we have increased ϕ by 2π, we will have ended up back where we started and therefore Φ must be unchanged. Therefore

$$\Phi(\phi + 2\pi) = \Phi(\phi) \quad \rightarrow \quad \frac{1}{\sqrt{2\pi}} \; e^{iL_z(\phi+2\pi)/\hbar} = \frac{1}{\sqrt{2\pi}} e^{iL_z\phi/\hbar}$$

so we have, after cancelling out the same factor on both sides of the equation

$$e^{2\pi i L_z/\hbar} = 1 \quad \rightarrow \quad L_z = m\hbar, \quad m = 0, \pm 1, \pm 2, \cdots.$$

Therefore we have obtained, in a very general way, the fact that angular momentum *is quantized* in units of $\hbar$. This was assumed by Bohr in his model of the atom, but is here seen to be a result of wave mechanics. It is valid for any central potential.

Before closing this section, let me just mention that we are here talking only about the angular momentum due to the external motion of a particle about the origin, which we call the orbital angular momentum. We will come back later in Chapter 3 to discuss the possibility that the orbiting particle might also have some internal motion, that we call the *spin angular momentum.*

1.2c Angular momentum for the 2D SHO

In the last section we found the eigenfunctions and eigenvalues of the angular momentum operator. Now we explore their application to the 2D SHO by asking ourselves a series of questions:

Q1: Are the SHO solutions ψ_{n_x,n_y} eigenfunctions of $\hat{L}_z$?

The best way to find out is to try it! Starting with the ground state $\psi_{0,0}$:

$$\psi_{0,0} = A\,e^{-x^2/2a^2}\,e^{-y^2/2a^2} = A\,e^{-(x^2+y^2)/2a^2} = A\,e^{-r^2/2a^2}.$$

Since $\psi_{0,0}$ is independent of ϕ, it is trivially true that it is an eigenfunction of $\hat{L}_z$, with eigenvalue 0:

$$\hat{L}_z\psi_{0,0} = -i\hbar\frac{\partial}{\partial\phi}\left(A\,e^{-r^2/2a^2}\right) = 0 = 0\psi_{0,0}.$$

Now we try $\psi_{1,0}$ and $\psi_{0,1}$ with $E = 2\hbar\omega$:

$$\psi_{1,0} = A\,x e^{-x^2/2a^2}\,e^{-y^2/2a^2} = A\,r\cos\phi\,e^{-r^2/2a^2}.$$

$$\hat{L}_z\psi_{1,0} = -i\hbar\frac{\partial}{\partial\phi}\left(A\,r\cos\phi\,e^{-r^2/2a^2}\right) = +i\hbar\left(A\,r\sin\phi\,e^{-r^2/2a^2}\right) = +i\hbar\psi_{0,1} \not\propto \psi_{1,0}.$$

i.e., NO: $\psi_{1,0}$ is not an eigenfunction of $\hat{L}_z$. Similarly

$$\hat{L}_z\psi_{0,1} = -i\hbar\psi_{1,0} \not\propto \psi_{0,1}.$$

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Q2: Can we find SHO solutions that are eigenfunctions of $\hat{L}_z$?

Recall that $\psi_{1,0}$ and $\psi_{0,1}$ are degenerate eigenstates: they have the same energy and any linear combination of them is also an eigenfunction of energy, see **Example** on Page 9. So we try to see if we can find an arbitrary linear combination that is an eigenfunction of $\hat{L}_z$:

$$\psi \equiv a\psi_{0,1} + b\psi_{1,0}\,.$$

$$
\begin{aligned}
\hat{L}_z\psi &= -i\hbar\frac{\partial}{\partial\phi}\left(a\,A\,r\sin\phi\,e^{-r^2/2a^2} + b\,A\,r\cos\phi\,e^{-r^2/2a^2}\right) \\
&= \left(-i\hbar\,a\cos\phi + i\hbar\,b\sin\phi\right)A\,r\,e^{-r^2/2a^2}
\end{aligned}
$$

which we want to be proportional to ψ:

$$\hat{L}_z\psi \equiv L_z\left(b\cos\phi + a\sin\phi\right)A\,r\,e^{-r^2/2a^2}\,.$$

We must therefore have

$$
\begin{aligned}
L_z a &= i\hbar\,b \\
L_z b &= -i\hbar\,a \quad = \hbar^2\,b/L_z &&\Rightarrow L_z^2 = \hbar^2 \\
&&&\Rightarrow L_z = \pm\hbar \\
&&&\text{and } a = \pm ib.
\end{aligned}
$$

i.e.

$$\psi_{1,0} + i\psi_{0,1} = A\,r\left(\cos\phi + i\sin\phi\right)e^{-r^2/2a^2} = A\,r\,e^{i\phi}\,e^{-r^2/2a^2}$$

is an eigenfunction of $\hat{L}_z$ with $L_z = \hbar$, or $m = +1$, and

$$\psi_{1,0} - i\psi_{0,1} = A\,r\,e^{-i\phi}\,e^{-r^2/2a^2}$$

is an eigenfunction of $\hat{L}_z$ with $L_z = -\hbar$, or $m = -1$.

Continuing our analysis for higher energy states shows that three linear combinations of the $\psi_{2,0}$, $\psi_{1,1}$ and $\psi_{0,2}$ states can be constructed with $E = 3\hbar\omega$ and definite $L_z = 2$, 0 and -2, four combinations with $E = 4\hbar\omega$ and $L_z = 3$, 1, -1 and -3 and so on.

Q3: Can E and L_z be measured simultaneously?

That is, do $\hat{H}$ and $\hat{L}_z$ commute? We first rewrite the Hamiltonian in terms of polar coordinates, using the textbook result for ∇^2:

$$
\begin{aligned}
\hat{H} &= -\frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}m\omega^2\,r^2 \\
&= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\right) + \frac{1}{2}m\omega^2\,r^2\,.
\end{aligned}
$$

Compare this with the expression for $\hat{L}_z$:

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}.$$

The derivatives themselves all commute and, since the coefficients in $\hat{H}$ are all ϕ-independent and the coefficient in $\hat{L}_z$ is both ϕ- and r-independent, the whole expressions commute:

$$[\hat{L}_z, \hat{H}] = 0. \tag{24}$$

Therefore orbital angular momentum is conserved (it is possible to construct definite states of (the z-component of) orbital angular momentum that are stationary states).

Good quantum numbers We define $n = n_x + n_y$ and state that "n and m are good quantum numbers for the 2D SHO". By "good" we mean that (a) they can be known simultaneously (they correspond to operators that commute), and (b) they fully specify the state of the system: an (n, m) pair uniquely describes a state of definite energy $E = (n+1)\hbar\omega$ and orbital angular momentum $L_z = m\hbar$.

Summary of Week 1

- The two-dimensional simple harmonic oscillator has potential energy $\frac{1}{2}k(x^2 + y^2) = \frac{1}{2}kr^2$.

- It has separable solutions $\psi_{n_x,n_y}(x, y) = \psi_{n_x}(x)\psi_{n_y}(y)$ with energy $E = (n_x + n_y + 1)\hbar\omega$.

- The ground state is non-degenerate and the nth excited state has degeneracy $n + 1$.

- The operator for the z-component of orbital angular momentum is $\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$. It has eigenfunctions $\mathrm{e}^{im\phi}$ and eigenvalues $m\hbar$, where m is an integer.

- Linear combinations of the SHO separable solutions can be obtained that have definite values of E and L_z.

- The corresponding quantum numbers n and m are called "good", because they can be known simultaneously and uniquely specify the state of the system.

1.3 Angular momentum II

1.3a Angular momentum in 3D

We know that classically, $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, so we can write a vector-valued quantum operator $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$:

$$\hat{\mathbf{L}} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix}, \tag{25}$$

so $\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$ as we have seen, and

$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$,

$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$.

We will be able to construct eigenstates of the orbital angular momentum vector only if its components commute. e.g.

$$\begin{aligned} \left[\hat{L}_z, \hat{L}_x\right] \psi &= \left(\hat{L}_z\,\hat{L}_x - \hat{L}_x\,\hat{L}_z\right)\psi \\ &= -\hbar^2 \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\left(y\frac{\partial\psi}{\partial z} - z\frac{\partial\psi}{\partial y}\right) + \hbar^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(x\frac{\partial\psi}{\partial y} - y\frac{\partial\psi}{\partial x}\right) \\ &= \hbar^2\left(z\frac{\partial\psi}{\partial x} - x\frac{\partial\psi}{\partial z}\right) = i\hbar\hat{L}_y\psi\,. \end{aligned}$$

And we can find the others by cyclic symmetry:

$$\begin{aligned} \left[\hat{L}_x, \hat{L}_y\right] &= i\hbar\hat{L}_z, \\ \left[\hat{L}_y, \hat{L}_z\right] &= i\hbar\hat{L}_x, \\ \left[\hat{L}_z, \hat{L}_x\right] &= i\hbar\hat{L}_y. \end{aligned} \tag{26}$$

Because these are non-zero we cannot know two components of $\mathbf{L}$ simultaneously.

We can only fix one component of $\mathbf{L}$ precisely. Usually define this to be the z component (arbitrarily).

However, the magnitude-squared of orbital angular momentum, $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ does commute with the individual components, e.g. $\hat{L}_z$:

$$\begin{aligned} \left[\hat{L}^2, \hat{L}_z\right] &= \left[\hat{L}_x^2, \hat{L}_z\right] + \left[\hat{L}_y^2, \hat{L}_z\right] + \left[\hat{L}_z^2, \hat{L}_z\right] \\ &= \hat{L}_x\left[\hat{L}_x, \hat{L}_z\right] + \left[\hat{L}_x, \hat{L}_z\right]\hat{L}_x + \hat{L}_y\left[\hat{L}_y, \hat{L}_z\right] + \left[\hat{L}_y, \hat{L}_z\right]\hat{L}_y \\ &= -i\hbar\left(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x\right) + i\hbar\left(\hat{L}_y\hat{L}_x + \hat{L}_x\hat{L}_y\right) \\ &= 0\,. \end{aligned}$$

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Therefore we can know $|\mathbf{L}|$ and L_z simultaneously, but not $\mathbf{L}$.

1.3b The Total Angular Momentum Operator $\hat{L}^2$

Most of the potentials we are interested in are central,

$$V(x, y, z) = V(r),$$

so it is useful to express their wavefunctions, and hence the operators that act on them, in spherical polar co-ordinates:

$$
\begin{aligned}
z &= r\cos\theta, \\
y &= r\sin\theta\,\sin\phi, \\
x &= r\sin\theta\,\cos\phi.
\end{aligned}
$$

In plane polar coordinates we showed that $\hat{L}_z = -i\hbar\partial/\partial\phi$, and it is straightforward to work through the same proof for spherical polar coordinates to find the same result:

$$\hat{L}_z = -ih\frac{\partial}{\partial\phi}.$$

For $\hat{L}_y$, we have to do a bit more work:

$$
\begin{aligned}
\hat{L}_y &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = \Big(r\cos\theta\Big)\Big(-i\hbar\Big)\left(\frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}\right) \\
&\quad - \Big(r\sin\theta\cos\phi\Big)\Big(-i\hbar\Big)\left(\frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial z}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial z}\frac{\partial}{\partial\phi}\right) \\
&= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right),
\end{aligned}
$$

and similarly for $\hat{L}_x$:

$$\hat{L}_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right).$$

Finally, after quite a bit more algebra, we can obtain

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right). \tag{27}$$

In this form, it is straightforward to see that $\hat{L}^2$ commutes with $\hat{L}_z$, because derivatives always commute with each other, $\hat{L}_z$ only takes the derivative with respect to ϕ and

none of the coefficients in $\hat{L}^2$ are ϕ-dependent, and although $\hat{L}^2$ takes derivatives with respect to both θ and ϕ, the coefficient in $\hat{L}_z$ does not depend on either,

$$\left[\hat{L}^2, \hat{L}_z\right] = 0. \tag{28}$$

Motion in a Central Potential The TISE in a central potential is given by

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + V(r)\right)\psi = E\psi. \tag{29}$$

We can either look up in a textbook, or do a pile more algebra, to express ∇^2 in spherical polar coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \tag{30}$$

Looking carefully, we notice that the part in the square brackets is identical to $-\hat{L}^2/\hbar^2$ and therefore we can write the TISE as

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\psi + \frac{\hat{L}^2}{2mr^2}\psi + V(r)\psi = E\psi. \tag{31}$$

Finally, we can notice that, since $\hat{L}^2$ depends only on θ and ϕ, while the rest of the Hamiltonian depends only on r, then it is possible to find separable solutions

$$\psi(r, \theta, \phi) = R(r)\,Y(\theta, \phi). \tag{32}$$

Moreover, if Y is chosen to be an eigenfunction of $\hat{L}^2$, then we have

$$\hat{L}^2\psi = L^2\psi$$

and two separate TISEs:

$$\left[\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{L^2}{2mr^2} + V(r)\right]R(r) = ER(r), \tag{33}$$

$$\hat{L}^2 Y(\theta, \phi) = L^2 Y(\theta, \phi). \tag{34}$$

Therefore, the eigenfunctions and eigenvalues of orbital angular momentum assume crucial importance in the solution of the Schrödinger equation for any central potential.

Classical Motion in a Central Potential The Hamiltonian above should be familiar from solving classical mechanics with a central potential, i.e. orbits. If a mass
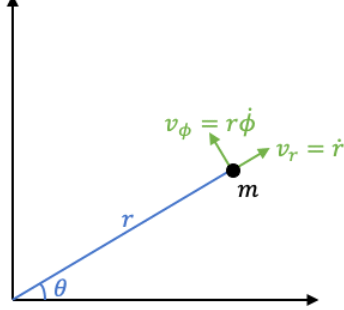
m is at some point described by r and ϕ, its velocity vector can be decomposed into components in the $\hat{r}$ and $\hat{\theta}$ directions (not operators!), v_r and v_ϕ respectively.

Since angular momentum is conserved in a central potential,

$$L = mrv_\phi,$$

we can trade v_ϕ for L in the expression for the kinetic energy, and obtain

$$T = \tfrac{1}{2}m\left(v_r^2 + v_\phi^2\right) = \tfrac{1}{2}m\dot{r}^2 + \frac{L^2}{2mr^2},$$

and the problem is effectively one-dimensional in the r direction, but with $V(r)$ replaced by

$$V_{eff}(r) = V(r) + \frac{L^2}{2mr^2},$$

known as the effective potential.

1.3c Eigenfunctions and Eigenvalues of Angular Momentum

As we have said, the eigenfunctions and eigenvalues of angular momentum are important to the solution of every problem with a central potential.

As we said in the last section, we will assume that wave functions of systems with a central potential can be written as Eq. (32), $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$. The eigenfunction equation for $\hat{L}^2$ is

$$\hat{L}^2\psi = L^2\psi$$

$$\rightarrow R(r)\hat{L}^2 Y = R(r)L^2 Y$$

$$\rightarrow -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y(\theta,\phi) = L^2 Y(\theta,\phi)$$

i.e. Eq. (34). We want Y to be an eigenfunction of $\hat{L}_z$ as well as of $\hat{L}^2$, and we know that this means that $Y \propto e^{im\phi}$, with m an integer, and $L_z = m\hbar$. Therefore

$$\frac{\partial^2 Y}{\partial\phi^2} = -m^2 Y.$$

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If we write Y in a separable form

$$Y(\theta, \phi) = P(\theta)e^{im\phi}, \tag{35}$$

then

$$-\hbar^2 \left(\frac{\partial^2}{\partial\theta^2} + \cot\theta \frac{\partial}{\partial\theta} - \frac{m^2}{\sin^2\theta} \right) P(\theta) = L^2 P(\theta).$$

Finally, on dimensional grounds, we can see that $L^2 \propto \hbar^2$, so we define

$$L^2 = \lambda\hbar^2, \qquad \lambda > 0,$$

to give

$$\frac{d^2 P}{d\theta^2} + \frac{\cos\theta}{\sin\theta} \frac{dP}{d\theta} + \left(\lambda - \frac{m^2}{\sin^2\theta} \right) P = 0, \tag{36}$$

which is known as the associated Legendre equation. In the Maths of Waves and Fields course (PHYS20171) you solve this systematically to derive the "associated Legendre polynomials" $P_l^m(\theta)$ (they are polynomials in $\cos\theta$ for even m, and $\sin\theta$ times polynomials in $\cos\theta$ for odd m, as we shall see). Here we will motivate the general expressions, by considering some trial solutions.

1. $P(\theta) = $ constant, e.g. $P(\theta) = 1$.

$$\Rightarrow \lambda - \frac{m^2}{\sin^2\theta} = 0.$$

This is only true for all θ if $\lambda = 0$, $m = 0$.

2. $P(\theta) = \cos\theta$.

$$\rightarrow -\cos\theta + \frac{\cos\theta}{\sin\theta}(-\sin\theta) + \left(\lambda - \frac{m^2}{\sin^2\theta} \right)\cos\theta = 0$$

$$\Rightarrow (\lambda - 2)\cos\theta - m^2 \frac{\cos\theta}{\sin^2\theta} = 0$$

This is only true for all θ if $\lambda = 2$, $m = 0$.

3. $P(\theta) = \sin\theta$.

$$\rightarrow -\sin\theta + \frac{\cos\theta}{\sin\theta}(\cos\theta) + \left(\lambda - \frac{m^2}{\sin^2\theta} \right)\sin\theta = 0$$

$$\Rightarrow (\lambda - 2)\sin\theta + \frac{1 - m^2}{\sin\theta} = 0$$

This is only true for all θ if $\lambda = 2$, $m^2 = 1$.

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4. $P(\theta) = 3\cos^2\theta - 1$. Why this? Either because it is orthogonal to 1 and $\cos\theta$, or because we tried a quadratic in $\cos\theta$ with arbitrary coefficients and only this combination gave a soluble equation, or just because we know the answer!

$$\cdots$$

Which gives an equation that is only true for all θ if $\lambda = 6$, $m = 0$.

5. $P(\theta) = \sin\theta\cos\theta$. This gives an equation that is only true for all θ if $\lambda = 6$, $m^2 = 1$.

6. $P(\theta) = \sin^2\theta$. This gives an equation that is only true for all θ if $\lambda = 6$, $m^2 = 4$.

The systematic approach shows that these are the only solutions, which we can summarize as:

$\lambda = 0$ with $m = 0$

$\lambda = 2$ with $m = 0, \pm 1$

$\lambda = 6$ with $m = 0, \pm 1, \pm 2$

$\lambda = 12$ with $m = 0, \pm 1, \pm 2, \pm 3$

$\vdots$

$\lambda = l(l+1)$ with $m = -l, -l+1, \ldots, +l$

Note: l is known as the orbital angular momentum quantum number. m is known as the magnetic quantum number (evident in the hydrogen energy-level splitting observed when a magnetic field is applied, see Chapter 4). They are good quantum numbers: simultaneous eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ have eigenvalues $L^2 = l(l+1)\hbar^2$ and $L_z = m\hbar$.

Note: the physical requirement that no component of a vector can be greater than its magnitude corresponds to $|L_z| \leq |\mathbf{L}|$

$$\Rightarrow L_z^2 \leq L^2 \Rightarrow m^2 \leq l(l+1) \Rightarrow |m| \leq l.$$

1.3d The Spherical Harmonic Functions
The eigenfunction $Y_{l,m}$ of angular momentum

$$Y_{l,m}(\theta, \phi) = P_{l,m}(\cos\theta)\mathrm{e}^{im\phi} \tag{37}$$

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is called a 'spherical harmonic'. This eigenstate is often written as $|l, m\rangle$ in Dirac notation. It provides a description of the shape of the wave function. The spherical harmonics represent the allowed wave functions for a particle on a sphere, where the distance to the origin (r) is fixed, but otherwise the particle is allowed free movement. We will discuss more about its properties in the last section of Chapter 2.

The complete eigenfunctions of a particle moving in a central potential have the form

$$\psi(r, \theta, \phi) = R(r)Y_{l,m}(\theta, \phi)$$

which we will study in more details later when we discuss Hydrogen in Chapter 2. The volume element in 3D spherical polar coordinates is

$$dV = r^2 dr d\Omega = r^2 dr \sin\theta d\theta d\phi$$

where the solid angle $d\Omega = \sin\theta d\theta d\phi$ is the angular part. The spherical harmonics are normalised with the angular part of the volume element,

$$\int |Y_{l,m}|^2 d\Omega = \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi |Y_{l,m}(\theta, \phi)|^2 = 1. \tag{38}$$

The lowest few spherical harmonics are shown below.

Angular Functions Corresponding to L^2 and L_z

l	m_l	Angular function
0	0	$Y_{00} = 1/\sqrt{4\pi}$
1	0	$Y_{10} = \sqrt{3/4\pi}\ \cos\theta$
	± 1	$Y_{1\pm 1} = \mp\sqrt{3/8\pi}\ \sin\theta\ e^{\pm i\phi}$
2	0	$Y_{20} = \frac{1}{2}\sqrt{5/4\pi}\ (3\cos^2\theta - 1)$
	± 1	$Y_{2\pm 1} = \mp\sqrt{15/8\pi}\ \sin\theta\cos\theta\ e^{\pm i\phi}$
	± 2	$Y_{2\pm 2} = \frac{1}{4}\sqrt{15/2\pi}\ \sin^2\theta\ e^{\pm i2\phi}$

Summary of Week 2

- The components of angular momentum do not commute with each other: $\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z$, etc.

- We can only know one component exactly at a time. We choose the z axis to be that one.

- The components of angular momentum do commute with the magnitude of angular momentum: $\left[\hat{L}^2, \hat{L}_z\right] = 0$, etc.

- $\hat{L}^2$ and $\hat{L}_z$ commute with the Hamiltonian for a central potential, so stationary states of definite L^2 and L_z can be constructed.

- $L^2 = l(l+1)\hbar^2$, where l is an integer $l \geq 0$ and $L_z = m\hbar$ where m is an integer $|m| \leq l$.

- l and m are good quantum numbers.

- The eigenfunctions are called the spherical harmonics, $Y(\theta, \phi) = P_l^m(\theta)e^{im\phi}$, where $P_l^m(\theta)$ are the associated Legendre polynomials. These eigenstates are often written as $|l, m\rangle$ in Dirac notation.

1.4 Rotational Motion of Diatomic Molecules

In this section, we approximate diatomic molecules as rigid bodies - we ignore their vibrational motion because the energy scales and time scales are completely different.
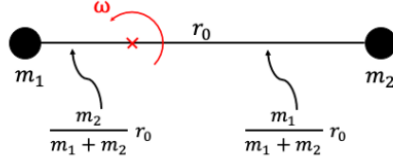
The two atoms, of masses m_1 and m_2 separated by a distance r_0, are free to rotate around their common centre of mass. The moment of inertia is given by

$$I = m_1 \left(\frac{m_2}{m_1 + m_2} r_0 \right)^2 + m_2 \left(\frac{m_1}{m_1 + m_2} r_0 \right)^2 = \frac{m_1 m_2}{m_1 + m_2} r_0^2 \equiv \mu r_0^2, \qquad (39)$$

where μ is the reduced mass, as before.

Classically, the kinetic energy is given by

$$E = \tfrac{1}{2} I \omega^2 \,,$$

and the angular momentum is given by

$$L = I \omega \,.$$

Since L is conserved. it is convenient to rewrite the kinetic energy as

$$E = \frac{L^2}{2I} \,.$$

The potential energy function is zero (i.e. constant in ϕ). Therefore we expect, in quantum mechanics,

$$\hat{H} = \frac{1}{2I} \hat{L}^2 \,. \qquad (40)$$

Since we know the eigenvalues and eigenfunctions of $\hat{L}^2$, we can immediately write down the rotational energy levels of a diatomic molecule:

$$E_l = \frac{\hbar^2}{2I} l(l+1) \,. \qquad (41)$$

e.g. for an H_2 molecule, $\mu = m/2 = 0.84 \times 10^{-27}$ kg, $r_0 = 0.74$ Å;

$$\Rightarrow \frac{\hbar^2}{2I} = 7.5 \times 10^{-3} \,\text{eV} \,.$$

This energy, via the Boltzmann constant, $E \sim k_B T$, corresponds to a temperature of $T \sim 90\,\mathrm{K}$, so rotational excited states are populated at room temperature, unlike the vibrational states with a typical energy spacing of 0.1 eV corresponding to a few thousand Kelvins.

This energy corresponds to a photon wavelength $\lambda \approx 0.16\,\mathrm{mm}$, in the far infrared, towards microwaves. Most other diatomic molecules have a similar bond length, but higher masses, and therefore smaller energy, so they give longer wavelengths, more towards microwaves. The study of molecular absorption is called microwave spectroscopy.

Experimenters in microwave spectroscopy typically quote their results in wave number, measured in cm^{-1}, $\widetilde{\nu}$,

$$\widetilde{\nu} = \frac{1}{\lambda} = \frac{f}{c} = \frac{E}{hc} = \frac{h}{8\pi^2 cI}l(l+1) \equiv Bl(l+1)\,.$$

(to give B in cm^{-1}, c should be used in $\mathrm{cm\,s}^{-1}$). The energy level diagram is shown below.
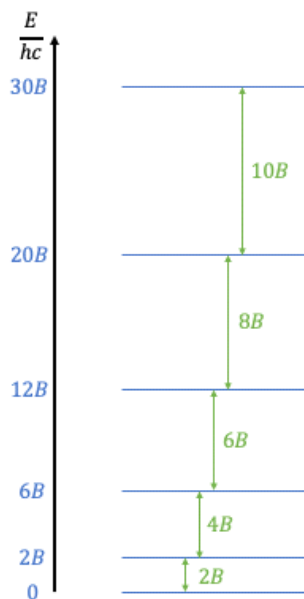
It turns out that only transitions $\Delta l = \pm 1$ are allowed by emission/absorption of one photon (more details later in Chapter 5). Therefore we get a series of absorption lines at $\widetilde{\nu} = 2B$, $4B$, $6B$, $8B$, ... From the microwave absorption spectrum, B can be measured, and hence I, and hence, since the masses are known, r_0. In practice, of course, diatomic molecules can both vibrate and rotate simultaneously. The vibrational motion is modelled by a simple harmonic oscilator (SHO) you studied in PHYS20101 last Semester.

Summary of Chapter 1

- Summary of Week 1 on Page 13

- Summary of Week 2 on Page 21

- We have applied our knowledge of the angular momentum eigenfunctions to the rotation of diatomic molecules and obtained, without further calculation, a prediction for their microwave absorption spectrum