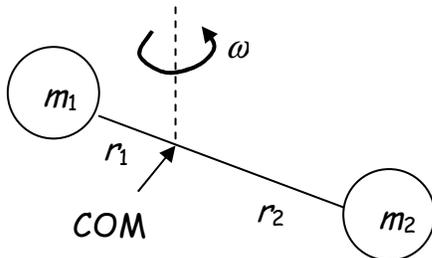


Rigid Rotations

Consider the rotation of two particles at a fixed distance R from one another:



$$r_1 + r_2 \equiv R$$

$$m_1 r_1 = m_2 r_2 \quad \text{center of mass (COM)}$$

These two particles could be an electron and a proton (in which case we'd be looking at a hydrogen atom) or two nuclei (in which case we'd be looking at a diatomic molecule). Classically, each of these rotating bodies has an angular momentum $L_i = I_i \omega$ where ω is the angular velocity and I_i is the moment of inertia $I_i = m_i r_i^2$ for the particle. Note that, in the COM, the two bodies must have the same angular frequency. The classical Hamiltonian for the particles is:

$$H = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} = \frac{1}{2} m_1 r_1^2 \omega^2 + \frac{1}{2} m_2 r_2^2 \omega^2 = \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) \omega^2$$

Instead of thinking of this as two rotating particles, it would be really nice if we could think of it as one **effective particle** rotating around the origin. We can do this if we define the effective moment of inertia as:

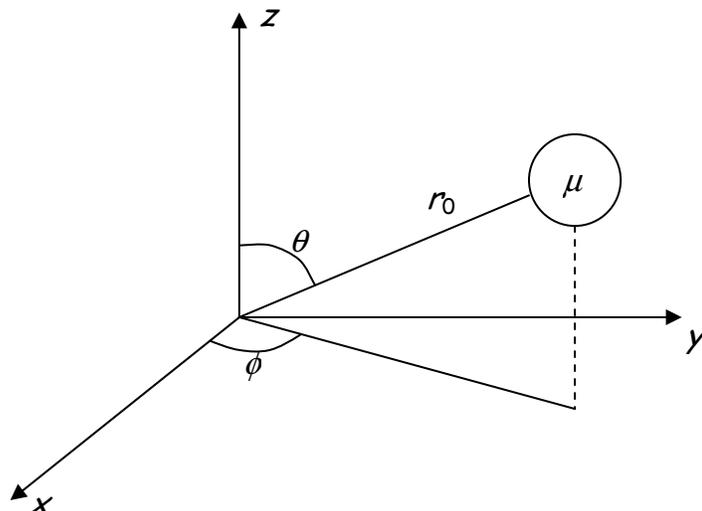
$$I = m_1 r_1^2 + m_2 r_2^2 = \mu r_0^2 \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

where, in the second equality, we have noted that this two particle system behaves as a single particle with a **reduced mass** μ rotating at a distance R from the origin. Thus we have

$$H = \frac{1}{2} I \omega^2 = \frac{L^2}{2I}$$

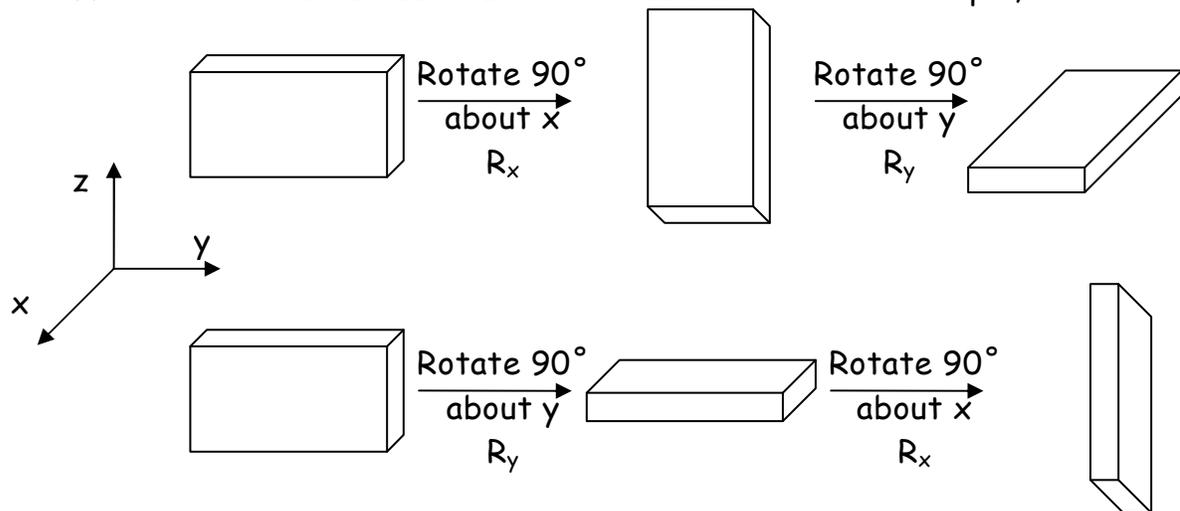
where, in the second equality, we have defined the angular momentum for this effective particle, $L = I\omega$. The problem is now completely reduced to a 1-body problem with mass μ .

Similarly, if we have a group of objects that are held in rigid



positions relative to one another - say the atoms in a crystal - and we rotate the whole assembly with an angular velocity ω , about a given axis r then by a similar method we can reduce the collective rotation of **all** of the objects to the rotation of a single "effective" object with a moment of inertia I_r . In this manner we can talk about rotations of a molecule (or a book or a pencil) without having to think about the movement of every single electron and quark individually.

It is important to realize, however, that even for a classical system, rotations about different axes **do not commute with each other**. For example,



Hence, one gets **different answers depending on what order the rotations are performed in!** Given our experience with quantum mechanics, we might define an operator \hat{R}_x (\hat{R}_y) that rotates around x (y). Then we would write the above experiment succinctly as: $\hat{R}_x \hat{R}_y \neq \hat{R}_y \hat{R}_x$. This rather profound result has nothing to do with quantum mechanics - after all there is nothing quantum mechanical about the box drawn above - but has everything to do with geometry. Thus, we will find that, while linear momentum operators commute with one another ($\hat{p}_x \hat{p}_y = \hat{p}_y \hat{p}_x$) the same will not be true for angular momenta because they relate to rotations ($\hat{L}_x \hat{L}_y \neq \hat{L}_y \hat{L}_x$).

Classically, angular momentum is given by $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. This means the corresponding quantum operator should be $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$. This vector operator has three components, which we identify as the angular momentum operators around each of the three Cartesian axes, x , y and z :

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = (\hat{x}, \hat{y}, \hat{z}) \times (\hat{p}_x, \hat{p}_y, \hat{p}_z) = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix}$$

$$= (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)\mathbf{i} + (\hat{z}\hat{p}_x - \hat{x}\hat{p}_z)\mathbf{j} + (\hat{x}\hat{p}_y - \hat{y}\hat{p}_x)\mathbf{k}$$

$$\therefore \boxed{\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \quad \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \quad \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x}$$

Now, it turns out that these angular momentum operators do not commute. For example:

$$+\hat{L}_x\hat{L}_y = +(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)(\hat{z}\hat{p}_x - \hat{x}\hat{p}_z) = +\hat{y}\hat{p}_z\hat{z}\hat{p}_x - \cancel{\hat{z}\hat{p}_y\hat{z}\hat{p}_x} - \cancel{\hat{y}\hat{p}_z\hat{x}\hat{p}_z} + \hat{z}\hat{p}_y\hat{x}\hat{p}_z$$

$$-\hat{L}_y\hat{L}_x = -(\hat{z}\hat{p}_x - \hat{x}\hat{p}_z)(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y) = -\hat{z}\hat{p}_x\hat{y}\hat{p}_z + \cancel{\hat{z}\hat{p}_x\hat{z}\hat{p}_y} + \cancel{\hat{x}\hat{p}_z\hat{y}\hat{p}_z} - \hat{x}\hat{p}_z\hat{z}\hat{p}_y$$

$$\Rightarrow [\hat{L}_x, \hat{L}_y] = \hat{y}\hat{p}_z[\hat{p}_z, \hat{z}] + \hat{x}\hat{p}_y[\hat{z}, \hat{p}_z]$$

$$= -i\hbar\hat{y}\hat{p}_z + i\hbar\hat{x}\hat{p}_y = i\hbar\hat{L}_z \therefore$$

Now, we could proceed to work out the relationships for $[\hat{L}_y, \hat{L}_z]$ and $[\hat{L}_z, \hat{L}_x]$.

However, we note that our answer **must always be invariant to a cyclic permutation** $\mathbf{x} \rightarrow \mathbf{y}, \mathbf{y} \rightarrow \mathbf{z}, \mathbf{z} \rightarrow \mathbf{x}$. This must be the case because our labeling of the x, y and z axes is totally arbitrary: if we chose to relabel our axes so that $\mathbf{x} \rightarrow \mathbf{y}, \mathbf{y} \rightarrow \mathbf{z}, \mathbf{z} \rightarrow \mathbf{x}$, then all the mathematics would work out exactly the same, with the letters shuffled around in the corresponding manner. The only thing we must be careful of is that our relabeling preserves the right-handedness, or chirality, of our coordinates. Cyclic permutations preserve the handedness while a simple interchange of two axes (i.e. $\mathbf{x} \leftrightarrow \mathbf{y}$) will reverse the handedness of our coordinates and give us the wrong answer (try it and see). This cyclic invariance is very important because it reduces the work we need to do by a factor of 3, but we must be careful to apply it correctly. In the future, we can therefore state the result for the z axis and then infer the results for x and y by cyclic permutations. In this case, we infer:

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$$

$$\xrightarrow[\substack{x \rightarrow y \\ y \rightarrow z \\ z \rightarrow x}]{} [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$$

$$\xrightarrow{\substack{x \rightarrow y \\ y \rightarrow z \\ z \rightarrow x}} [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

Because the angular momentum operators do not commute, they do not share a common set of eigenfunctions. Thus, we arrive at the important conclusion that **a system cannot simultaneously have well-defined angular momentum around the x, y and z axes**. The best we can hope for is well-defined angular momentum around 1 axis.

Returning to the problem of rigid rotations, we are interested in the eigenstates of the Hamiltonian

$$\hat{H} = \frac{\hat{\mathbf{L}}^2}{2I} = \frac{1}{2I} (L_x^2 + L_y^2 + L_z^2).$$

It is relatively easy to show that while the x, y and z angular momentum operators do not commute with each other, they do commute with $\hat{\mathbf{L}}^2$:

$$\begin{aligned} [L_z, \mathbf{L}^2] &= [L_z, L_x^2] + [L_z, L_y^2] + [L_z, L_z^2] \\ &= [L_z, L_x^2] + [L_z, L_y^2] = [L_z, L_x]L_x + L_x[L_z, L_x] + [L_z, L_y]L_y + L_y[L_z, L_y] \\ &= (-i\hbar L_y)L_x + L_x(i\hbar L_y) + (i\hbar L_x)L_y + L_y(-i\hbar L_x) \\ &= 0 \end{aligned}$$

At this point, we make use of cyclic permutations to assert that $[\hat{L}_y, \hat{\mathbf{L}}^2] = 0$ and $[\hat{L}_x, \hat{\mathbf{L}}^2] = 0$ as well. Since \hat{L}_z commutes with $\hat{\mathbf{L}}^2$, the two operators share common eigenfunctions, so we can talk about a particle with a well-defined z-component of angular momentum (call it m) and a well-defined total angular momentum (call it l). Thus, when we are looking for the eigenfunctions of the rigid rotor Hamiltonian, we are looking for states indexed by two quantum numbers l and m . This makes sense because we started with a 3D system that would have had three quantum numbers but we've now restricted the motion to the surface of a sphere, which is two dimensional. For such a 2D system, we expect 2 quantum numbers. Based on the above analysis, we will denote the angular momentum eigenstates by Y_l^m , with m associated with the eigenvalue of \hat{L}_z and l associated with $\hat{\mathbf{L}}^2$.

We are now left with the fairly difficult problem of solving for the eigenvalues, E_l , and eigenstates, Y_l^m , of the rigid rotor. Notice that the eigenvalues of the

rigid rotor Hamiltonian will only depend on l because the Hamiltonian is proportional to \hat{L}^2 . In order to fully solve this differential equation, it is most convenient to work in spherical polar coordinates. In most *math* textbooks, ϕ is defined to be the angle relative to the z axis while the vast majority of quantum mechanics texts use θ in this capacity. We will use the latter definition, but be careful that any equations taken from other sources use this same convention! Here are some useful relations in spherical polar

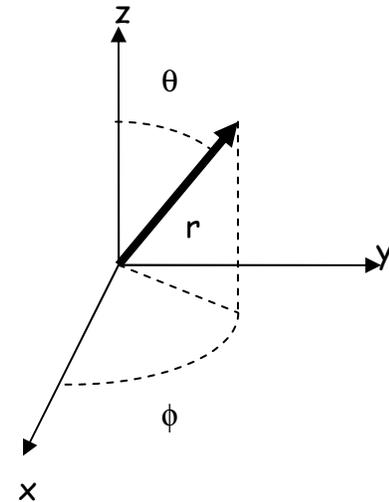
coordinates:

$$x \equiv r \cos \phi \sin \theta$$

$$y \equiv r \sin \phi \sin \theta$$

$$z \equiv r \cos \theta$$

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



In order to make progress, we need to express the angular momentum operators in spherical polar coordinates, as well. This rearrangement turns out to be a fairly tedious application of the chain rule and we will merely state the results:

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

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

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

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \Rightarrow \hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

As a result, the Schrödinger equation for the rigid rotor becomes

$$\frac{-\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y_l^m(\theta, \phi) = E_l Y_l^m(\theta, \phi)$$

where we have noted that, because the rotating particle is constrained to be on the surface of a sphere of radius R , the associated wavefunction must be a function of θ and ϕ only.

As it turns out, there are some very nice operator algebra tricks that allow us to get the eigenvalues, E_l , quickly. These tricks are analogous to the raising and lowering operator manipulations we used to solve the Harmonic oscillator, and we will use them to derive the eigenvalues in the next lecture. The result is that the energies of the rigid rotor obey:

$$E_l = \frac{\hbar^2}{2I} l(l+1) \quad l = 0, 1, 2, \dots$$

One confusing point about angular momentum is that for different kinds of angular momentum, we use different letters. So while l is the letter chosen for an electron moving around the nucleus, J is the chosen letter for the rotation of a diatomic molecule:

$$E_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, 2, \dots$$

Thus, the spacing between the energy levels increases with increasing J , unlike for the harmonic oscillator, where they were equally spaced:

$$E_{J+1} - E_J = \frac{\hbar^2}{2I} [(J+1)(J+2) - J(J+1)] = \frac{\hbar^2}{I} (J+1)$$

Further, for each J we have multiple possible values of m (also known as K in some contexts):

$$m = 0, \pm 1, \pm 2, \dots, \pm J$$

Thus, each energy level is $(2J+1)$ -fold degenerate. Physically, m reflects the component of the angular momentum along the z -direction. For fixed J , the different values of m reflect the different directions the angular momentum vector could be pointing - for large, positive m the angular momentum is mostly along $+z$; if m is zero the angular momentum is orthogonal to z . Physically, we know that the energy of the rotation doesn't depend on the direction. This is reflected in the fact that the energy depends only on J , which measures the length of the vector, not its direction.

