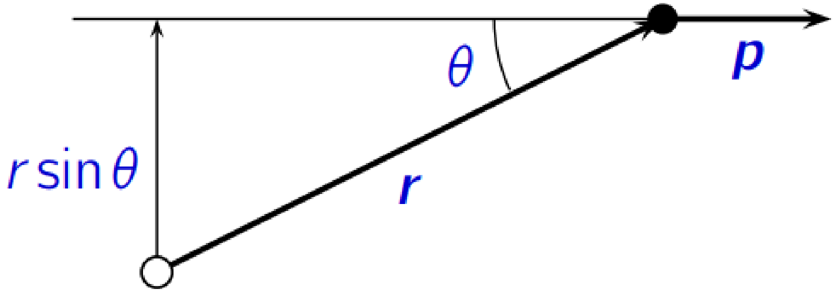
4.1 Angular Momentum

Classically, the angular momentum of an isolated system is a constant of the motion. Quantum mechanically, this means that we expect to be able to find states of definite angular momentum.



In three dimensions, the angular momentum about a point is the magnitude p of the momentum multiplied by the perpendicular distance of the momentum vector from the point ($r \sin \theta$ in the diagram).

The angular momentum describes rotation about an axis perpendicular to the plane containing $\boldsymbol{r}$ and $\boldsymbol{p}$, so in vector notation it is $\boldsymbol{J} = \boldsymbol{r} \times \boldsymbol{p}$.

4.2 Angular momentum operators

The angular momentum is the vector product $\boldsymbol{J} = \boldsymbol{r} \times \boldsymbol{p}$. That is,

$$J_x = yp_z - zp_y$$

$$J_y = zp_x - xp_z$$

$$J_z = xp_y - yp_x$$

Making the usual substitutions yields the operators

$$\hat{J}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{J}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{J}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$\hat{J}_x = -i\hbar\left(y\hat{\partial}_z - z\hat{\partial}_y\right)$$

$$\hat{J}_y = -i\hbar\left(z\hat{\partial}_x - x\hat{\partial}_z\right)$$

$$\hat{J}_z = -i\hbar\left(x\hat{\partial}_y - y\hat{\partial}_x\right)$$

Angular momentum operators don’t commute

The components of the angular momentum operator do not commute with each other. Writing $\partial/\partial x = \hat{\partial}_x$ for brevity, and remembering that $\hat{\partial}_x x = 1 + x\hat{\partial}_x$, but $\hat{\partial}_x y = y\hat{\partial}_x$ and $\hat{\partial}_x\hat{\partial}_y = \hat{\partial}_y\hat{\partial}_x$,

$$\hat{J}_x\hat{J}_y\psi = (-i\hbar)\left(y\hat{\partial}_z - z\hat{\partial}_y\right)(-i\hbar)\left(z\hat{\partial}_x - x\hat{\partial}_z\right)\psi$$

$$= -\hbar^2\left(y\hat{\partial}_z z\hat{\partial}_x - y\hat{\partial}_z x\hat{\partial}_z - z\hat{\partial}_y z\hat{\partial}_x + z\hat{\partial}_y x\hat{\partial}_z\right)\psi$$

$$= -\hbar^2\left(y\hat{\partial}_x + yz\hat{\partial}_z\hat{\partial}_x - xy\hat{\partial}_z\hat{\partial}_z - z^2\hat{\partial}_y\hat{\partial}_x + xz\hat{\partial}_y\hat{\partial}_z\right)\psi$$

$$\hat{J}_y\hat{J}_x\psi = (-i\hbar)\left(z\hat{\partial}_x - x\hat{\partial}_z\right)(-i\hbar)\left(y\hat{\partial}_z - z\hat{\partial}_y\right)\psi$$

$$= -\hbar^2\left(z\hat{\partial}_x y\hat{\partial}_z - x\hat{\partial}_z y\hat{\partial}_z - z\hat{\partial}_x z\hat{\partial}_y + x\hat{\partial}_z z\hat{\partial}_y\right)\psi$$

$$= -\hbar^2\left(yz\hat{\partial}_x\hat{\partial}_z - xy\hat{\partial}_z\hat{\partial}_z - z^2\hat{\partial}_x\hat{\partial}_y + x\hat{\partial}_y + xz\hat{\partial}_z\hat{\partial}_y\right)\psi$$

we find that

$$\boxed{\left[\hat{J}_x, \hat{J}_y\right] \equiv \hat{J}_x\hat{J}_y - \hat{J}_y\hat{J}_x = -\hbar^2\left(y\hat{\partial}_x - x\hat{\partial}_y\right) = i\hbar\hat{J}_z}$$

Commutation relations for angular momentum

We have found that

$$\left[\hat{J}_x, \hat{J}_y\right] \equiv \hat{J}_x \hat{J}_y - \hat{J}_y \hat{J}_x = -\hbar^2 \left(y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right)$$

$$\left[\hat{J}_x, \hat{J}_y\right] = i\hbar \hat{J}_z$$

Similarly,

$$\left[\hat{J}_y, \hat{J}_z\right] = i\hbar \hat{J}_x \qquad \left[\hat{J}_z, \hat{J}_x\right] = i\hbar \hat{J}_y$$

(Note that x, y and z appear in cyclic order in these equations.)

The uncertainty principle tells us that, for example,

$$\Delta J_x \Delta J_y \geq \frac{1}{2} \left| \left\langle \left[\hat{J}_x, \hat{J}_y\right] \right\rangle \right| = \frac{1}{2} \hbar \left| \langle J_z \rangle \right|$$

so in general we cannot find wavefunctions that are simultaneously eigenfunctions of two or more of $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$. The only exception is that it is possible to find wavefunctions for which J_x, J_y and J_z are all exactly zero.

However, $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ all commute with $\hat{\boldsymbol{J}}^2 = \hat{J}_x{}^2 + \hat{J}_y{}^2 + \hat{J}_z{}^2$. For example,

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

and similarly $\left[\hat{J}_z, \hat{J}_y{}^2\right] = -i\hbar\left(\hat{J}_y\hat{J}_x + \hat{J}_x\hat{J}_y\right)$, while $\left[\hat{J}_z, \hat{J}_z{}^2\right] = 0$.

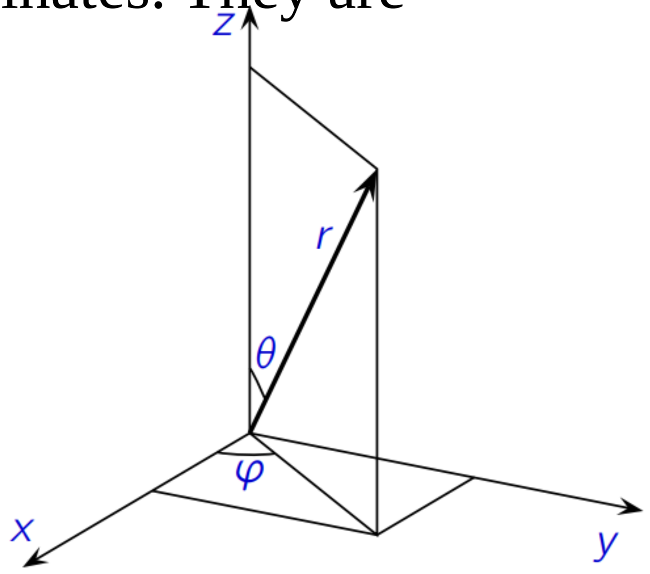
Adding these results together shows that $\left[\hat{J}_z, \hat{\boldsymbol{J}}^2\right] = 0$.

Therefore we can find wavefunctions that are eigenfunctions of both $\hat{\boldsymbol{J}}^2$ and one only of $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$. It is customary to choose $\hat{J}_z$.

Spherical polar coordinates

Before proceeding, we recall the definition of spherical polar coordinates. They are defined by

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



and conversely

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

The volume element for integration over spherical polar coordinates is

$$\mathrm{d}V = r^2 \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\varphi$$

Forgetting the $r^2\sin\theta$ is a very common source of mistakes.

$$\frac{\partial}{\partial x} = \left(\frac{\partial r}{\partial x}\right)_{y,z} \frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial x}\right)_{y,z} \frac{\partial}{\partial \theta} + \left(\frac{\partial \phi}{\partial x}\right)_{y,z} \frac{\partial}{\partial \phi}$$

$$2r\left(\frac{\partial r}{\partial x}\right) = 2x = 2r\sin\theta\cos\phi \quad , \quad \left(\frac{\partial r}{\partial x}\right)_{y,z} = \sin\theta\cos\phi$$

$$\hat{J}_x = i\hbar(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi})$$

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

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

Involved only θ and ϕ

$$\hat{J}^2 = -\hbar(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2})$$

A central force $V = V(r)$

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

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

$$= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{r^2\hbar^2}\hat{J}^2$$

$$\left[\hat{H}, \hat{J}^2\right] = 0 \qquad \left[\hat{H}, \hat{J}_z\right] = 0$$

$$\frac{d\left\langle \hat{J}_z \right\rangle}{dt} = \overline{\frac{\partial \hat{J}_z}{\partial t}} + \frac{1}{i\hbar}\overline{[\hat{J}_z, \hat{H}]} = 0 \qquad \frac{d\left\langle J^2 \right\rangle}{dt} = \overline{\frac{\partial \hat{J}^2}{\partial t}} + \frac{1}{i\hbar}\overline{[\hat{J}^2, \hat{H}]} = 0$$

4.3 Spherical harmonics

In spherical polar coordinates, $\hat{J}_z = -i\hbar\frac{\partial}{\partial\varphi}$. $\hat{J}_z$ commutes with $\hat{\boldsymbol{J}}^2$, so we can find functions that are eigenfunctions of both. Eigenfunctions of $\hat{J}_z$ satisfy the eigenvalue equation

$$\hat{J}_z\psi = -i\hbar\frac{\partial}{\partial\varphi}\psi = k\psi$$

The unnormalised solutions are of the form $\exp(ik\varphi/\hbar)$, but the value of k is restricted by the requirement that the wavefunction is single-valued — that is, $\psi(\varphi + 2\pi)$ must be the same as $\psi(\varphi)$. This means that

$$\exp\left(ik\left(\varphi+2\pi\right)/\hbar\right) = \exp\left(ik\varphi/\hbar\right)$$

Thus $k = M\hbar$, where M is an integer (positive, negative or zero), and the wavefunctions become (after normalisation)

$$\psi_M = \sqrt{\frac{1}{2\pi}}\exp\left(iM\varphi\right)$$

The eigenvalue is $M\hbar$: *the angular momentum is an integer multiple of* $\hbar$.

Eigenfunctions of $\hat{J}^2$

$\hat{J}^2$ is more complicated:

$$\hat{J}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

To obtain eigenfunctions of $\hat{J}^2$ we have to multiply the functions $\mathrm{e}^{iM\varphi}$ by suitable functions of θ. Write

$$Y_{JM} = \Theta_{JM}(\theta)\Phi_M(\varphi)$$

where $\Phi_M(\varphi) = \mathrm{e}^{iM\varphi}$. Then the eigenvalue equation $\hat{J}^2 Y_{JM} = \lambda Y_{JM}$ becomes

$$\hat{J}^2 Y_{JM} = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}-\frac{M^2}{\sin^2\theta}\right)\Theta_{JM}(\theta)\Phi_M(\varphi) = \lambda\Theta_{JM}(\theta)\Phi_M(\varphi)$$

We can cancel out $\Phi_M(\varphi)$ to get an eigenvalue equation in θ. The eigenvalues λ turn out to be $\hbar^2 J(J+1)$ for integer J.

The functions $Y_{JM}(\theta,\varphi)$ are *spherical harmonics*.

The Ladder-Operator Method for Angular Momentum

Raising operator $\hat{J}_+ :$ $\qquad \hat{J}_+ \equiv \hat{J}_x + i\hat{J}_y$

Lowering operator $\hat{J}_- :$ $\qquad \hat{J}_- \equiv \hat{J}_x - i\hat{J}_y$

$$\hat{J}_+\hat{J}_- = (\hat{J}_x + i\hat{J}_y)(\hat{J}_x - i\hat{J}_y)$$

$$= \hat{J}^2 - \hat{J}_z^2 + \hbar\hat{J}_z$$

Similarly $\qquad \hat{J}_-\hat{J}_+ = \hat{J}^2 - \hat{J}_z^2 - \hbar\hat{J}_z$

$$\left[\hat{J}_+, \quad \hat{J}_z\right] = [\hat{J}_x, \hat{J}_z] + i[\hat{J}_y, \hat{J}_z] \; = -i\hbar\hat{J}_y - \hbar\hat{J}_x = -\hbar\hat{J}_+$$

$$[\hat{J}_-, \hat{J}_z] = \hbar\hat{J}_-$$

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The angular momentum operators 99

$$J^2 Y = cY$$

$$\hat{J}_z Y = bY$$

$$\boxed{\hat{J}_+ \hat{J}_z Y = \hat{J}_+ bY}$$

$$(\hat{J}_z \hat{J}_+ - \hbar \hat{J}_+) Y = b \hat{J}_+ Y$$

$$\hat{J}_z (\hat{J}_+ Y) = (b + \hbar)(\hat{J}_+ Y)$$

$\hat{J}_+ Y$: an eigenfunction of $\hat{J}_z$ with $b + \hbar$ (eigenvalue)

$$\hat{J}_z (\hat{J}_+^2 Y) = (b + 2\hbar)(\hat{J}_+^2 Y)$$

$$\boxed{\hat{J}_z (\hat{J}_+^k Y) = (b + k\hbar)(\hat{J}_+^k Y)}$$

$$\hat{J}_z (\hat{J}_- Y) = (b - \hbar)(\hat{J}_- Y)$$

$$\boxed{\hat{J}_z (\hat{J}_-^k Y) = (b - k\hbar)(\hat{J}_-^k Y)}$$

$$\boxed{\hat{J}_z(\hat{J}_\pm^k Y) = (b \pm k\hbar)(\hat{J}_\pm^k Y)}$$

$\hat{J}_\pm^k Y$ is an eigenfunction of $\hat{J}_z$

Is it an eigenfunction of J^2?

$$[J^2, J_\pm] = [J^2, J_x \pm iJ_y] = 0$$

$$J^2 J_\pm^k Y = cJ_\pm^k Y$$

$J_\pm^k Y$ is an eigenfunction of J^2

$$J_z Y = bY$$

$$J_z Y_k = b_k Y_k$$

where

$$Y_k = J_\pm^k Y \quad , \quad b_k = b \pm k\hbar$$

$$\boxed{J_z^2 Y_k = b_k^2 Y_k}$$

$$J^2 Y_k - J_z^2 Y_k = c Y_k - b_k^2 Y_k$$

$$(J_x^2 + J_y^2) Y_k = (c - b_k^2) Y_k$$

$$c - b_k^2 \geq 0$$

$$c^{1/2} \geq b_k \geq -c^{1/2} \quad , \quad k = 0, \pm 1, \pm 2, \cdots$$

$$J_z Y_{\max} = b_{\max} Y_{\max}$$

$$J_z Y_{\min} = b_{\min} Y_{\min}$$

$$J_+ J_z Y_{\max} = b_{\max} J_+ Y_{\max}$$

$$J_z (J_+ Y_{\max}) = (b_{\max} + \hbar)(J_+ Y_{\max})$$

$$\boxed{J_z (J_+ Y) = (b + \hbar)(J_+ Y)}$$

$$J_+ Y_{\max} = 0$$

$$J_- \longrightarrow J_+ Y_{\max} = 0$$

$$0 = J_- J_+ Y_{\max} = (J^2 - J_z^2 - \hbar J_z) Y_{\max}$$

$$= (c - b_{\max}^2 - \hbar b_{\max}) Y_{\max}$$

$$c - b_{\max}^2 - \hbar b_{\max} = 0$$

$$\boxed{c = b_{\max}^2 + \hbar b_{\max}}$$

$$J_- Y_{\min} = 0$$

$$\boxed{c = b_{\min}^2 - \hbar b_{\min}}$$

$$b_{\max}^2 + \hbar b_{\max} + (\hbar b_{\min} - b_{\min}^2) = 0$$

$$b_{\max} = -b_{\min} \quad , \quad b_{\max} = b_{\min} - \hbar$$ 🚫

$$b_{\max} - b_{\min} = n\hbar \quad , \quad n = 0, 1, 2, \cdots$$

$$b_{\max} - b_{\min} = n\hbar \quad , \quad n = 0, 1, 2, \cdots$$

$$b_{\max} = \frac{1}{2} n\hbar$$

$$b_{\max} = j\hbar \quad , \quad j = 0, \frac{1}{2}, \ 1, \frac{3}{2}, 2, \cdots$$

$$b_{\min} = -j\hbar$$

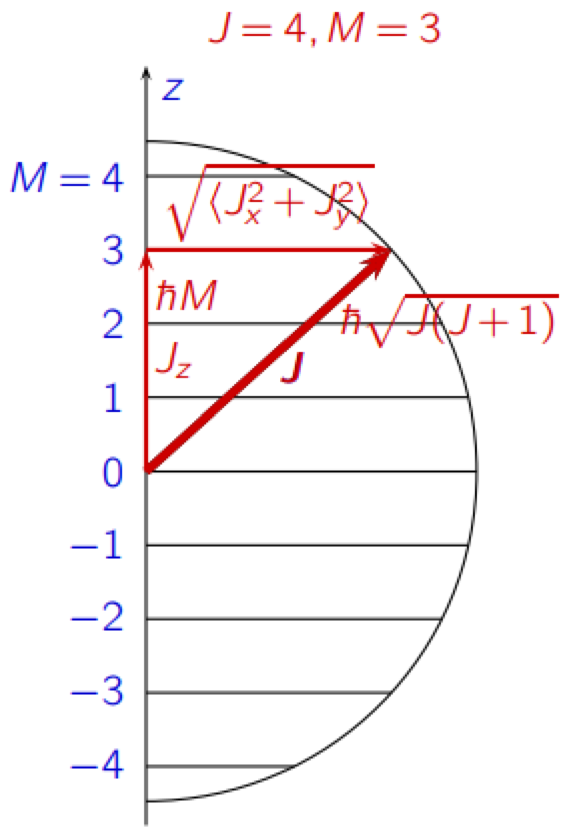
$$b = -j\hbar, (-j+1)\hbar, \cdots, (j-2)\hbar, (j-1)\hbar, j\hbar$$

$$\boxed{c = b_{\min}^2 - \hbar b_{\min} = j(j+1)\hbar^2 \quad , \quad j = 0, \frac{1}{2}, 1, \frac{3}{2}, \cdots}$$

4.4 Angular momentum eigenvalues

$$\hat{\boldsymbol{J}}^2 Y_{JM} = \hbar^2 J\left(J+1\right) Y_{JM}$$

$$\hat{J}_z Y_{JM} = \hbar M Y_{JM}$$



$\boldsymbol{J}^2$ can have definite values $\hbar^2 J(J+1)$, for integer values 0, 1, 2, . . . of J.

For a given value of J, J_z can have the definite values $M\hbar$, where M can take any of the integer values $J, J-1, \ldots, -J+1, -J$.

(For the proof, see the Mathematical Notes.)

If $\boldsymbol{J}^2$ and J_z have definite values, J_x and J_y can't, because they don't commute with J_z. All we can say about them is that

$$\left\langle J_x^{\,2} + J_y^{\,2} \right\rangle = \left\langle \boldsymbol{J}^2 - J_z^{\,2} \right\rangle = \left(J\left(J+1\right) - M^2\right)\hbar^2$$

The first few normalized spherical harmonics are

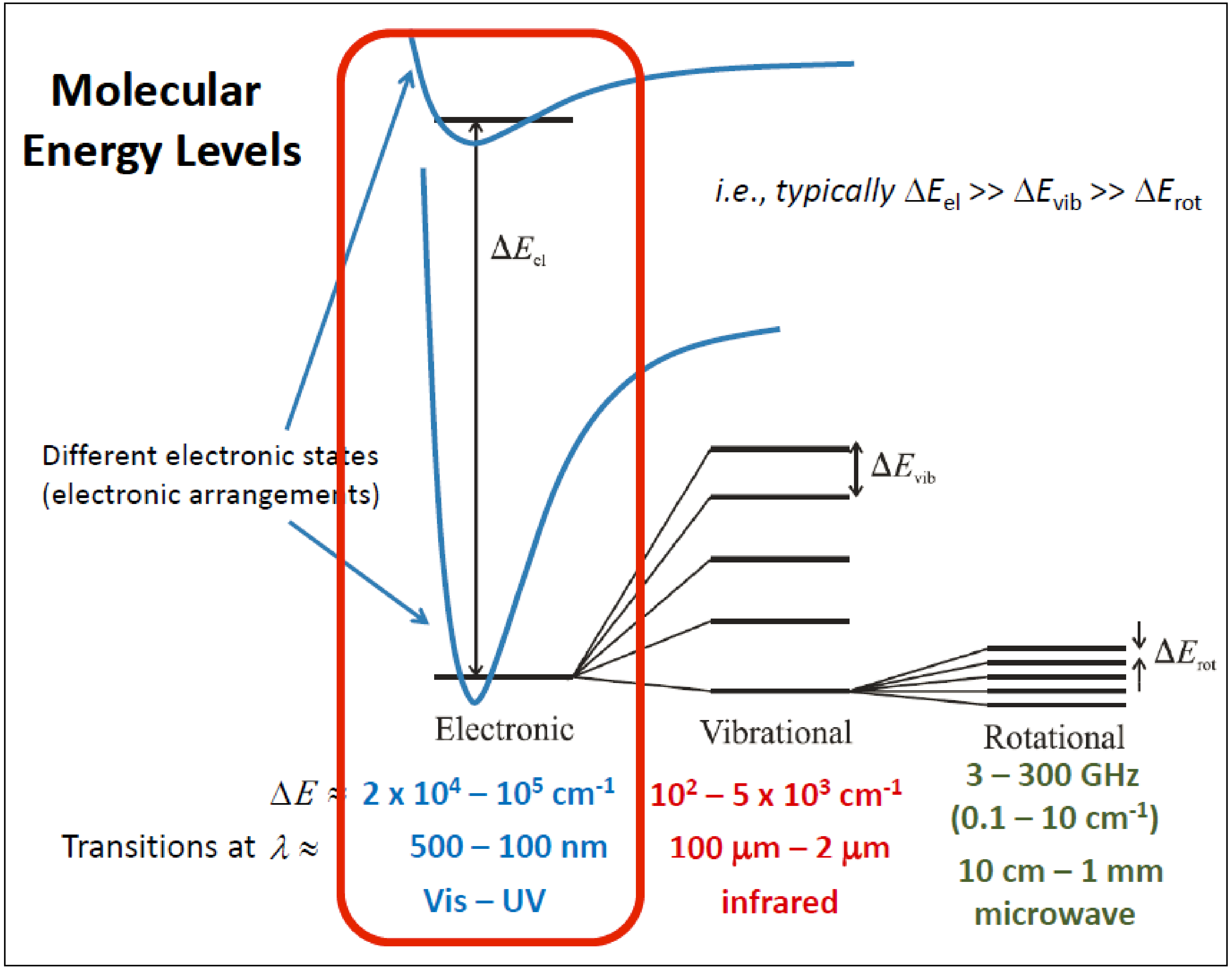
J	M	
0	0	$Y_{00}=\sqrt{\frac{1}{4\pi}}$
1	0	$Y_{10}=\sqrt{\frac{3}{4\pi}}\cos\theta$
1	± 1	$Y_{1,\pm1}=\mp\sqrt{\frac{3}{8\pi}}\sin\theta \mathrm{e}^{\pm i\varphi}$
2	0	$Y_{20}=\sqrt{\frac{5}{4\pi}}\frac{1}{2}\left(3\cos^2\theta-1\right)$
2	± 1	$Y_{2,\pm1}=\mp\sqrt{\frac{5}{4\pi}}\sqrt{\frac{3}{2}}\cos\theta\sin\theta \mathrm{e}^{\pm i\varphi}$
2	± 2	$Y_{2,\pm2}=\sqrt{\frac{5}{4\pi}}\sqrt{\frac{3}{8}}\sin^2\theta \mathrm{e}^{\pm 2i\varphi}$

A note on notation

So far we have been using $\hat{\boldsymbol{J}}^2$ and $\hat{J}_z$ for the angular momentum operators, and J and M for the quantum numbers. There are many different angular momenta that we may have to deal with, and several of them may be present in the same system. There is a fairly standard notation for these different angular momenta.

Operators	Quantum numbers	
$\boldsymbol{l}^2, l_z$	l, m_l	Orbital angular momentum of a single electron
$\boldsymbol{s}^2, s_z$	s, m_s	Spin angular momentum of a single electron
$\boldsymbol{j}^2, j_z$	j, m_j	Total angular momentum of a single electron
$\boldsymbol{L}^2, L_z$	L, M_L	Total orbital angular momentum
$\boldsymbol{S}^2, S_z$	S, M_s	Total spin
$\boldsymbol{J}^2, J_z$	J, M_J	Total angular momentum of an atom; also angular momentum of molecular rotation and general angular momentum
$\boldsymbol{I}^2, I_z$	I, m_I	Nuclear spin
$\boldsymbol{F}^2, F_z$	F, M_F	Total angular momentum including nuclear spin

$$E \approx E_{tr} + E_{ele} + E_{rot} + E_{vib}$$



Molecular Energy Levels

i.e., typically $\Delta E_{el} >> \Delta E_{vib} >> \Delta E_{rot}$

Different electronic states
(electronic arrangements)

	Electronic	Vibrational	Rotational
$\Delta E \approx$	$2 \times 10^4 - 10^5$ cm^{-1}	$10^2 - 5 \times 10^3$ cm^{-1}	3 – 300 GHz (0.1 – 10 cm^{-1})
Transitions at $\lambda \approx$	500 – 100 nm	100 μm – 2 μm	10 cm – 1 mm
	Vis – UV	infrared	microwave

4.5 The Rigid Rotor

We consider diatomic molecules. If the nuclei have masses m_1 and m_2, the rotational behaviour (classically as well as quantum mechanically) is the same as that of a particle of mass $\mu = m_1 m_2/(m_1 + m_2)$ (the *reduced mass*) moving on the surface of a sphere of radius d equal to the bond length.

Reduction of the Two-particle Problem to a One-Particle Problem

Two-particle

$$T = \frac{1}{2} m_1 |\dot{r}_1|^2 + \frac{1}{2} m_2 |\dot{r}_2|^2 = \frac{1}{2} M |\dot{R}|^2 + \frac{1}{2} \mu |\dot{r}|^2$$

$$M = m_1 + m_2, \qquad \mu = \frac{m_1 m_2}{m_1 + m_2},$$

$$\vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}, \qquad \vec{r} = \vec{r}_2 - \vec{r}_1$$

Translational; internal (vibration; rotation)

$$H = \frac{\hat{p}_M^2}{2M} + \left[\frac{\hat{p}_\mu^2}{2\mu} + V(x,y,z) \right]$$

$$\frac{\hat{p}_M^2}{2M}\psi_M = E_M \psi_M$$

Free particle

$$\left[\frac{p_\mu^2}{2\mu} + V(x,y,z) \right] \psi_\mu(x,y,z) = E_\mu \psi_\mu(x,y,z)$$

Suppose that the rigid rotor not affected by external force, the potential energy is zero, and the kinetic energy is $\frac{1}{2}I\boldsymbol{\omega}^2 = \hat{\boldsymbol{J}}^2/2I$, where $I = \mu d^2$ is the moment of inertia, $\boldsymbol{\omega}$ is the angular velocity vector and $\hat{\boldsymbol{J}} = I\boldsymbol{\omega}$ is the angular momentum. The Hamiltonian for the rigid rotor is therefore

$$H = \frac{\hat{\boldsymbol{J}}^2}{2I} = \frac{\hat{\boldsymbol{J}}^2}{2\mu d^2}$$

Since the Hamiltonian is just a multiple of $\hat{\boldsymbol{J}}^2$, its eigenfunctions are the spherical harmonics and its eigenvalues are $\hbar^2 J(J+1)/2I$.

The rotational constant B

Conventionally we define a *rotational constant* $B = \hbar^2/2I$, and the energies for the rigid rotor are then just $BJ(J+1)$. For each of these energy levels, the quantum number M can take the $2J+1$ values from J to $-J$, *so* each level has *degeneracy* $2J+1$.

The rotational constant B is an energy, as is the vibrational spacing $\hbar\omega$, and both can be expressed in any convenient energy unit. However, the SI units of joules or kJ mol^{-1} are not very convenient.

For a photon with frequency ν and wavelength λ, $E = h\nu = hc/\lambda = hc\lambda^{-1}$, where λ^{-1} is the *wavenumber,* i.e. the number of waves per unit length. Evidently wavenumber is proportional to energy, and it is widely used as a measure of energy.

In SI the unit of length is the metre, but the wavenumber is always expressed in *reciprocal centimetres,* cm^{-1}. This is the number of waves per centimetre, so we have to divide by 100:

$$\lambda^{-1}/\mathrm{cm}^{-1} = \frac{E/\mathrm{J}}{100\left(h/\mathrm{Js}\right)\left(c/\mathrm{ms}^{-1}\right)}$$

4.6 Rotation-vibration energy levels

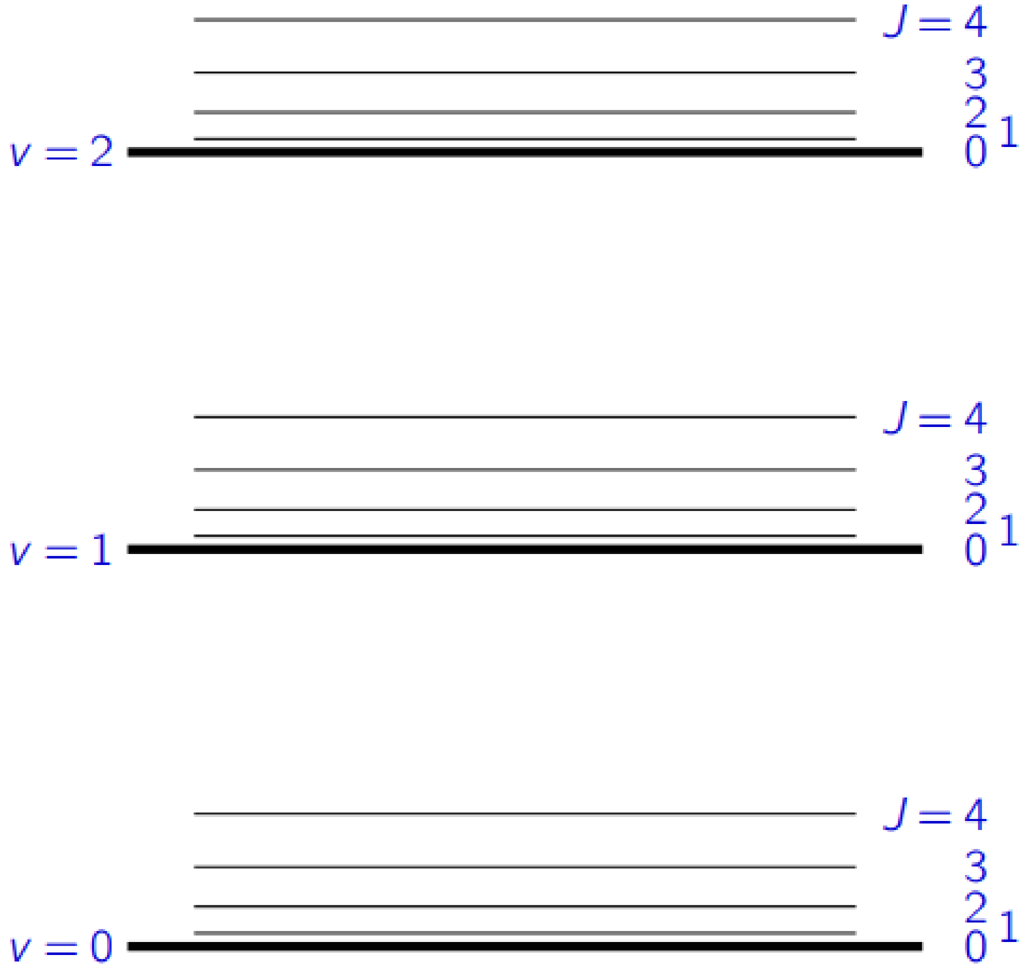
Real molecules rotate *and* vibrate. The Hamiltonian for both motions considered together is just the sum of the vibration and rotation Hamiltonians:

$$H = H_{\text{vib}} + H_{\text{rot}}$$

and these two refer to different degrees of freedom — the vibrational coordinate $r - r_e$ and the spherical polar angles θ and φ respectively. Consequently H_{vib} does not affect the rotational wavefunction and H_{rot} does not affect the vibrational one. An overall wavefunction of the form $\Psi = \psi_v^{\text{vib}}\psi_{JM}^{\text{rot}}$ is an eigenfunction of the complete Hamiltonian:

$$\begin{aligned} H\Psi &= \left(H_{\text{vib}} + H_{\text{rot}}\right)\psi_v^{\text{vib}}\psi_{JM}^{\text{rot}} \\ &= \left(H_{\text{vib}}\psi_v^{\text{vib}}\right)\psi_{JM}^{\text{rot}} + \psi_v^{\text{vib}}\left(H_{\text{rot}}\psi_{JM}^{\text{rot}}\right) \\ &= \left[E_v + BJ\left(J+1\right)\right]\Psi \end{aligned}$$

and the energy is just the sum of the individual vibrational and rotational energies E_v and $BJ(J+1)$. B is much smaller than the vibrational spacing $\hbar\omega$ — typically B is around $1\ \text{cm}^{-1}$ and $\hbar\omega$ is around $1000\ \text{cm}^{-1}$.



Rotation-vibration energy levels. The rotational spacings are very greatly exaggerated compared with the vibrational spacing.

4.7 Quantum theory of spectroscopy

Molecules can absorb or emit electromagnetic radiation and undergo transitions between energy levels, according to the following general principles:

(a) For a transition between states ψ_m and ψ_n the frequency ν_{mn} of the radiation must match the energy difference $|E_m - E_n|$ between the levels, according to the *Bohr condition* $h\nu_{mn} = |E_m - E_n|$,

(b) The rate at which transitions are induced by an external electromagnetic field is given by the *Einstein coefficient* for induced absorption or emission, B_{mn} :

$$B_{mn} = \frac{2\pi}{4\pi\varepsilon_0 3\hbar^2}\left|\int \psi_m{}^{*}\hat{\boldsymbol{\mu}}\psi_n \mathrm{d}\tau\right|^2$$

Where $\hat{\boldsymbol{\mu}}$ is the operator for the dipole moment of the molecule. This is *Fermi's golden rule.* For a given pair of states, the coefficients for induced absorption and induced emission are the same.

3. If a molecule is in an excited state ψ_m (i.e., not in its lowest-energy state) then it may undergo a spontaneous transition to a lower-energy state ψ_n, emitting radiation at the frequency ν_{mn} given by the Bohr condition. The rate at which this occurs is given by the Einstein coefficient for *spontaneous emission*, A_{mn}.

$$A_{mn} = \left(8\pi h\nu_{mn}^3 / c^3\right) B_{mn}$$

For many purposes, we do not need to know the actual rate of absorption or emission. It is enough to know whether it is zero (the transition is *forbidden)* or non-zero *(allowed)*. This information is summarized in *selection rules.*

For the harmonic oscillator, the selection rule is $\Delta v = \pm 1$; that is, transitions are allowed only between adjacent levels. In addition, the dipole moment must change during the course of the vibration.

For the Morse oscillator, and for real molecules, this selection rule does not apply rigorously, but transitions between non-adjacent levels are much weaker. They are called *overtones.*

Pure rotation spectrum

In pure rotational spectroscopy, transitions occur between rotational levels of a particular vibrational state, usually the ground state $v = 0$. The molecule must have a non-zero dipole moment. The selection rule is $\Delta J = \pm 1$.

The transition between levels J and $J + 1$ has energy

$$\Delta E = B\left(J+1\right)\left(J+2\right) - BJ\left(J+1\right) = 2B\left(J+1\right)$$

so transitions occur at energies $2B$, $4B$, $6B$, etc. These normally fall in the microwave region of the electromagnetic spectrum.

Rotation-vibration spectrum

The selection rules for a rotating, vibrating diatomic are

- $\Delta v = \pm 1$(overtones are allowed but weak);
- $\Delta J = \pm 1$.

So the transitions between vibrational levels v and $v + 1$ fall into two groups:

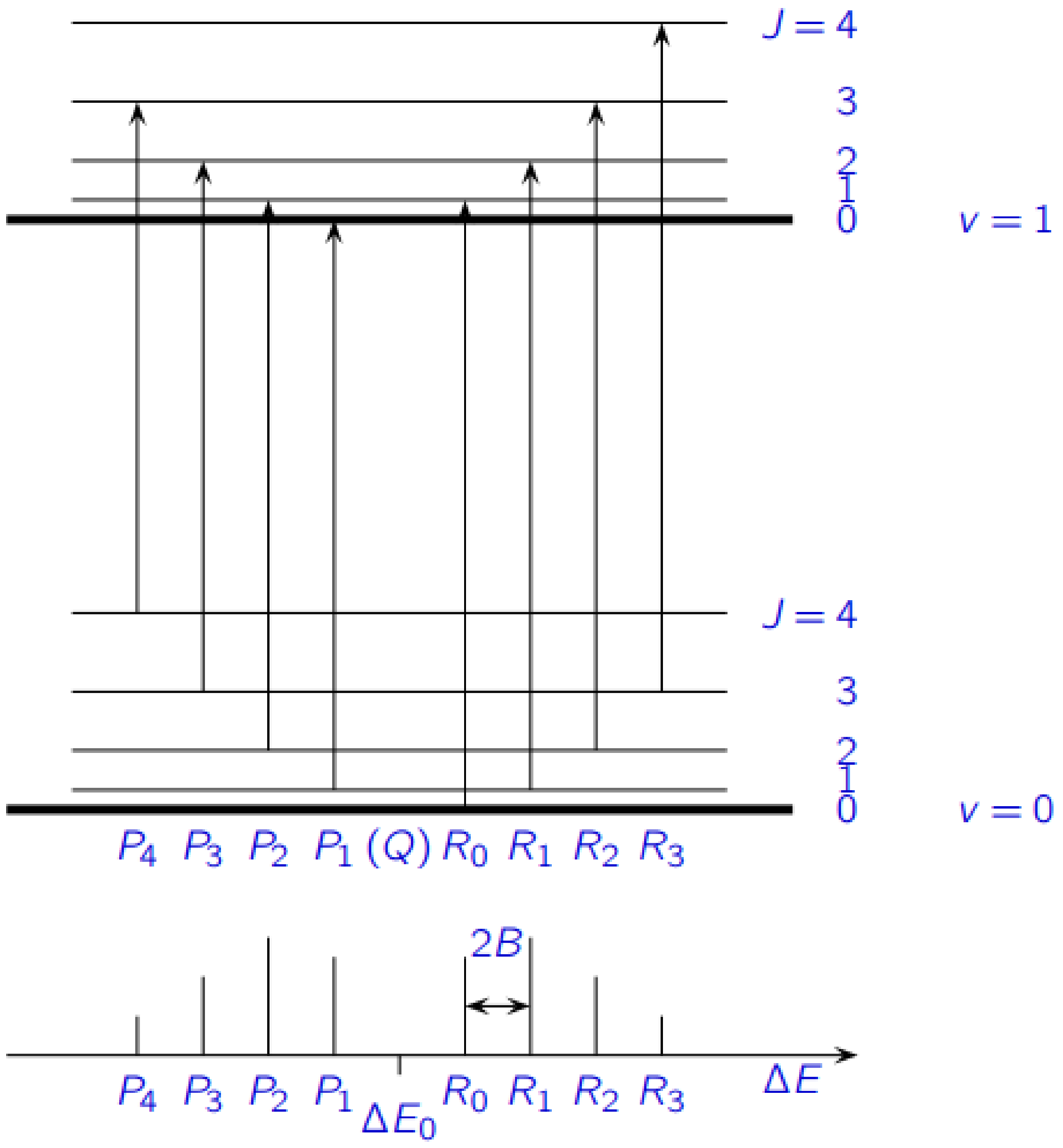
- $\Delta J = -1$ (P branch):

$$\begin{aligned}\Delta E &= E_{v+1} + B(J-1)J - E_v - BJ(J+1) \\ &= \Delta E_0 - 2BJ\end{aligned}$$

- $\Delta J = +1$ (R branch):

$$\begin{aligned}\Delta E &= E_{v+1} + B(J+1)(J+2) - E_v - BJ(J+1) \\ &= \Delta E_0 + 2B(J+1)\end{aligned}$$

where $\Delta E_0 = E_{v+1} - E_v$.


$J = 4$
3
2
1
0
$v = 1$
$J = 4$
3
2
1
0
$v = 0$
P_4 P_3 P_2 P_1 (Q) R_0 R_1 R_2 R_3
$2B$
P_4 P_3 P_2 P_1 ΔE_0 R_0 R_1 R_2 R_3
ΔE