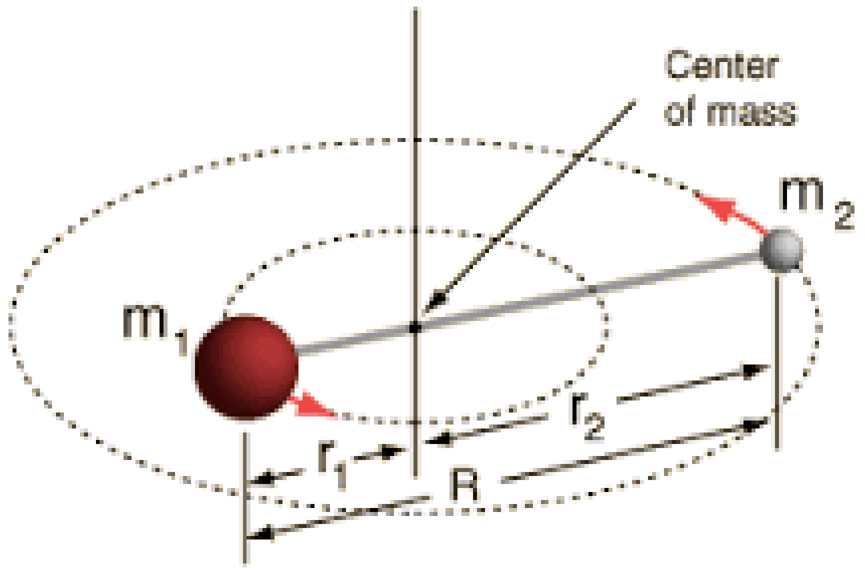
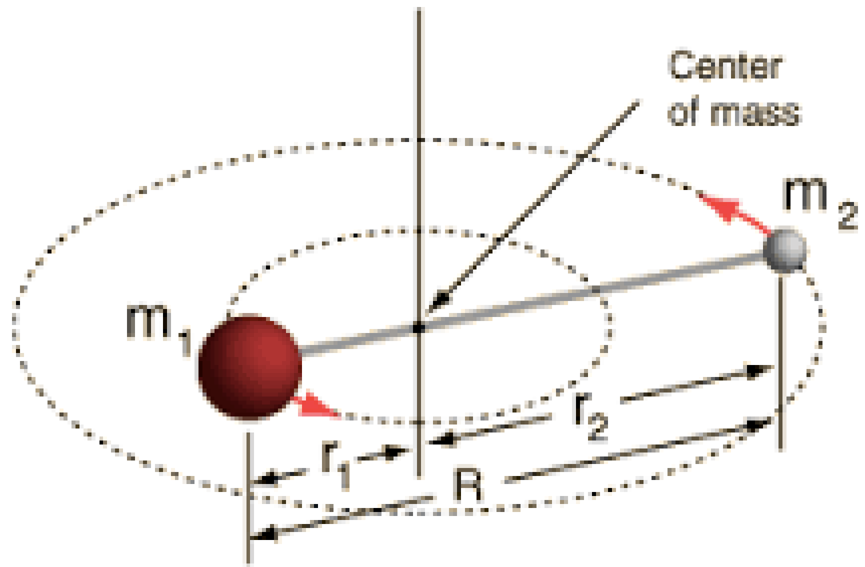
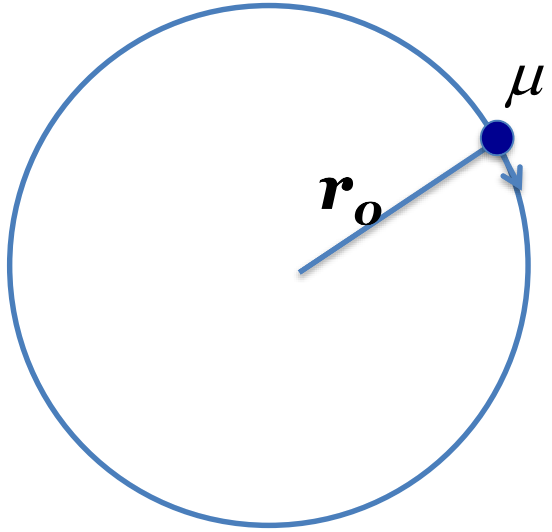
Rigid rotor



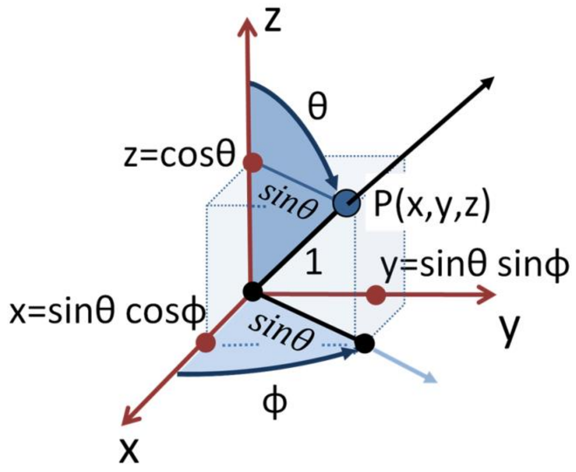
A rotating diatomic molecule





Reduced mass: From two body to one body problem

Spherical Polar Co-ordinates

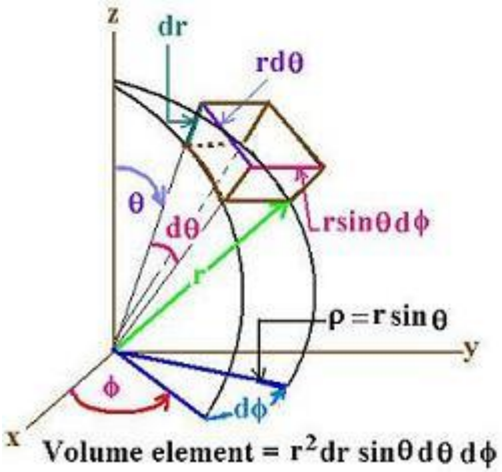


$$z = r\cos q$$
$$x = r\sin q\cos f$$
$$y = r\sin q\sin f$$

r:0 to ∞

θ: 0 to π

ϕ: 0 to 2π



$$r = \sqrt{\left(x^2 + y^2 + z^2\right)}$$
$$\theta = \cos^{-1}\left(\frac{z}{r}\right)$$
$$\phi = \tan{-1}\left(\frac{y}{x}\right)$$

$$dt = r^2 \times dr \times \sin q \times dq \times df$$

Laplacian in Spherical Coordinates

Laplacian in Spherical Coordinates

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We start with the primitive definitions

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

$$y = r\sin\theta\sin\phi$$

and

$$z = r\cos\theta$$

and their inverses

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = cos^{-1}\frac{z}{r} = cos^{-1}\frac{z}{\sqrt{x^2+y^2+z^2}}$$

and

$$\phi = tan^{-1}\frac{y}{x}$$

and attempt to write (using the chain rule)

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

and

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

and

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

Laplacian in Spherical Coordinates

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The needed (above) partial derivatives are:

$$\left(\frac{\partial r}{\partial x}\right)_{y,z} = \sin\theta\cos\phi \tag{1}$$

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

$$\left(\frac{\partial r}{\partial z}\right)_{x,y} = \cos\theta \tag{3}$$

and we have as a starting point for doing the θ terms,

$$d\cos\theta = -\sin\theta d\theta = \frac{dz}{r} - \frac{z}{r^2}\frac{1}{r}(xdx + ydy + zdz)$$

Laplacian in Spherical Coordinates

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so that, for example

$$-\sin\theta d\theta = -\frac{z}{r^2}\frac{x}{r}dx$$

which is

$$-\sin\theta d\theta = -\frac{r\cos\theta}{r^2}\sin\theta\cos\phi dx$$

so that

$$\left(\frac{\partial\theta}{\partial x}\right)_{y,z} = \frac{\cos\theta\cos\phi}{r} \tag{4}$$

$$\left(\frac{\partial\theta}{\partial y}\right)_{x,z} = \frac{\cos\theta\sin\phi}{r} \tag{5}$$

but, for the z-equation, we have

$$-\sin\theta d\theta = \frac{dz}{r} - \frac{z}{r^2}\frac{1}{r}zdz$$

which is

$$-\sin\theta d\theta = \left(\frac{1}{r} - \frac{z^2}{r^3}\right)dz = \frac{r^2 - z^2}{r^3}dz$$

$$-\sin\theta d\theta = \left(\frac{1}{r} - \frac{z^2}{r^3}\right)dz = \frac{r^2\sin^2\theta}{r^3}dz$$

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so one has

$$\left(\frac{\partial\theta}{\partial z}\right)_{x,y} = -\frac{\sin\theta}{r} \tag{6}$$

Next, we have (as an example)

$$\tan\phi = \frac{\sin\phi}{\cos\phi} = \tan^{-1}\frac{y}{x}$$

so

$$\left(1 + \frac{\sin^2\phi}{\cos^2\phi}\right)d\phi = \frac{dy}{x} - \frac{y}{x^2}dx$$

or

$$\left(\frac{1}{\cos^2\phi}\right)d\phi = \frac{dy}{x} - \frac{y}{x^2}dx$$

which leads to

$$\left(\frac{\partial\phi}{\partial y}\right)_{x,z} = \frac{\cos\phi}{r\sin\theta} \tag{7}$$

and

$$\left(\frac{\partial\phi}{\partial x}\right)_{y,z} = -\frac{\sin\phi}{r\sin\theta} \tag{8}$$

Laplacian in Spherical Coordinates

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$$\left(\frac{\partial \phi}{\partial z}\right)_{x,y} = 0 \tag{9}$$

Given these results (above) we write

$$\frac{\partial}{\partial z} = \cos\theta \frac{\partial}{\partial r} - \left(\frac{\sin\theta}{r}\right)\frac{\partial}{\partial \theta} \tag{10}$$

and

$$\frac{\partial}{\partial y} = (\sin\theta \sin\phi)\frac{\partial}{\partial r} + \left(\frac{\cos\theta \sin\phi}{r}\right)\frac{\partial}{\partial \theta} + \left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial}{\partial \phi} \tag{11}$$

and

$$\frac{\partial}{\partial x} = (\sin\theta \cos\phi)\frac{\partial}{\partial r} + \left(\frac{\cos\theta \cos\phi}{r}\right)\frac{\partial}{\partial \theta} + \left(-\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial}{\partial \phi} \tag{12}$$

From Equation 10 we form

$$\frac{\partial^2}{\partial z^2} = \cos\theta \frac{\partial\left[\cos\theta \frac{\partial}{\partial r} - \left(\frac{\sin\theta}{r}\right)\frac{\partial}{\partial \theta}\right]}{\partial r} - \left(\frac{\sin\theta}{r}\right)\frac{\partial\left(\cos\theta \frac{\partial}{\partial r} - \left(\frac{\sin\theta}{r}\right)\frac{\partial}{\partial \theta}\right]}{\partial \theta} \tag{13}$$

while from Equation 11 we obtain

$$\begin{aligned}\frac{\partial^2}{\partial y^2} &= (\sin\theta\sin\phi)\frac{\partial\left[\sin\theta\sin\phi\frac{\partial}{\partial r} + \left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial}{\partial\theta} + \left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}\partial r\right]}{\partial r} \\ &+ \left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial\left[\sin\theta\sin\phi\frac{\partial}{\partial r} + \left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial}{\partial\theta} + \left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}\right]}{\partial\theta} \\ &+ \left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial\left[\sin\theta\sin\phi\frac{\partial}{\partial r} + \left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial}{\partial\theta} + \left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}\right]}{\partial\phi}\end{aligned} \tag{14}$$

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and from Equation 12 we obtain

$$\frac{\partial^2}{\partial x^2} = (\sin\theta\cos\phi)\frac{\partial\left[\sin\theta\cos\phi\frac{\partial}{\partial r} + \left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial}{\partial\theta} - \left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}\right]}{\partial r}$$
$$+\left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial\left[\sin\theta\cos\phi\frac{\partial}{\partial r} + \left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial}{\partial\theta} - \left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}\right]}{\partial\theta}$$
$$-\left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial\left[\sin\theta\cos\phi\frac{\partial}{\partial r} + \left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial}{\partial\theta} - \left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}\right]}{\partial\phi} \tag{15}$$

Expanding, we have

$$\frac{\partial^2}{\partial z^2} = \cos^2\theta\frac{\partial^2}{\partial r^2} + \frac{\cos\theta\sin\theta}{r^2}\frac{\partial}{\partial\theta} - \frac{\sin\theta\cos\theta}{r}\frac{\partial^2}{\partial r\partial\theta}$$
$$-\left(\frac{\sin\theta}{r}\right)\left(-\sin\theta\frac{\partial}{\partial r} - \cos\theta\frac{\partial}{\partial\theta}\right) - \frac{\sin\theta\cos\theta}{r^2}\frac{\partial}{\partial\theta} + \left(\frac{\sin\theta}{r}\right)^2\frac{\partial^2}{\partial\theta^2} \tag{16}$$

while for the y-equation we have

$$\frac{\partial^2}{\partial y^2} = \sin^2\theta\sin^2\phi\frac{\partial^2}{\partial r^2} \tag{17}$$

$$+\sin\theta\sin\phi\left[+\left(\frac{\cos\theta\sin\phi}{r^2}\right)\frac{\partial}{\partial\theta} + \left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial^2}{\partial r\partial\theta}\right] \tag{18}$$

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$$+\sin\theta\sin\phi\left[\left(-\frac{\cos\phi}{r^2\sin\theta}\right)\frac{\partial}{\partial\phi}+\left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial^2}{\partial r\partial\phi}\right] \tag{19}$$

$$+\left(\frac{\cos\theta\sin\phi}{r}\right)\left[\cos\theta\sin\phi\frac{\partial}{\partial r}+\sin\theta\sin\phi\frac{\partial^2}{\partial r\partial\theta}\right] \tag{20}$$

$$+\left(\frac{\cos\theta\sin\phi}{r}\right)\left[-\left(\frac{\sin\theta\sin\phi}{r}\right)\frac{\partial}{\partial\theta}+\left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial^2}{\partial\theta^2}\right] \tag{21}$$

$$+\left(\frac{\cos\theta\sin\phi}{r}\right)\left[-\left(\frac{\cos\phi\cos\theta}{r\sin^2\theta}\right)\frac{\partial}{\partial\phi}+\left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial^2}{\partial\phi\partial\theta}\right] \tag{22}$$

$$+\left(\frac{\cos\phi}{r\sin\theta}\right)\left[\sin\theta\cos\phi\frac{\partial}{\partial r}+\sin\theta\sin\phi\frac{\partial^2}{\partial r\partial\phi}\right] \tag{23}$$

$$+\left(\frac{\cos\phi}{r\sin\theta}\right)\left[+\left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial}{\partial\theta}+\left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial^2}{\partial\theta\partial\phi}\right] \tag{24}$$

$$+\left(\frac{\cos\phi}{r\sin\theta}\right)\left[-\left(\frac{\sin\phi\cos\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}+\left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial^2}{\partial\phi^2}\right] \tag{25}$$

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and finally

$$\frac{\partial^2}{\partial x^2} = (\sin\theta\cos\phi)\sin\theta\cos\phi\frac{\partial^2}{\partial r^2}$$

$$+(\sin\theta\cos\phi)\left[-\left(\frac{\cos\theta\cos\phi}{r^2}\right)\frac{\partial}{\partial\theta}+\left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial^2}{\partial\theta\partial r}\right] \tag{26}$$

$$-(\sin\theta\cos\phi)\left[-\left(\frac{\sin\phi}{r^2\sin\theta}\right)\frac{\partial}{\partial\phi}+\left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial^2}{\partial\phi\partial r}\right] \tag{27}$$

$$+\left(\frac{\cos\theta\cos\phi}{r}\right)\left[\cos\theta\cos\phi\frac{\partial}{\partial r}+\sin\theta\cos\phi\frac{\partial^2}{\partial r\partial\theta}\right] \tag{28}$$

$$+\left(\frac{\cos\theta\cos\phi}{r}\right)\left[-\left(\frac{\sin\theta\cos\phi}{r}\right)\frac{\partial}{\partial\theta}+\left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial^2}{\partial\theta^2}\right] \tag{29}$$

$$+\left(\frac{\cos\theta\cos\phi}{r}\right)\left[+\left(\frac{\sin\phi}{r\sin^2\theta}\right)\frac{\partial}{\partial\phi}-\left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial^2}{\partial\phi\partial\theta}\right] \tag{30}$$

$$-\left(\frac{\sin\phi}{r\sin\theta}\right)\left[\sin\theta\sin\phi\frac{\partial}{\partial r}+\sin\theta\cos\phi\frac{\partial^2}{\partial r\partial\phi}\right] \tag{31}$$

$$-\left(\frac{\sin\phi}{r\sin\theta}\right)\left[-\left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial}{\partial\theta}+\left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial^2}{\partial\theta\partial\phi}\right] \tag{32}$$

$$-\left(\frac{\sin\phi}{r\sin\theta}\right)\left[-\left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}-\left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial^2}{\partial\phi^2}\right] \tag{33}$$

Now, one by one, we expand completely each of these three terms. We have

$$\frac{\partial^2}{\partial z^2} = \cos^2\theta\frac{\partial^2}{\partial r^2} \tag{34}$$

$$+\frac{\cos\theta\sin\theta}{r^2}\frac{\partial}{\partial\theta} \tag{35}$$

$$-\frac{\sin\theta\cos\theta}{r}\frac{\partial^2}{\partial r\partial\theta} \tag{36}$$

$$+\left(\frac{\sin^2\theta}{r}\right)\frac{\partial}{\partial r} \tag{37}$$

$$-\left(\frac{\sin\theta\cos\theta}{r}\right)\frac{\partial^2}{\partial r\partial\theta} \tag{38}$$

$$+\frac{\sin\theta\cos\theta}{r^2}\frac{\partial}{\partial\theta} \tag{39}$$

$$+\left(\frac{\sin^2\theta}{r^2}\right)\frac{\partial^2}{\partial\theta^2} \tag{40}$$

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and, for the y-equation:

$$\frac{\partial^2}{\partial y^2} = \sin^2\theta \sin^2\phi \frac{\partial^2}{\partial r^2} \tag{41}$$

$$(18) \to + \left(\frac{\sin\theta\cos\theta\sin^2\phi}{r^2}\right)\frac{\partial}{\partial\theta} \tag{42}$$

$$+ \left(\frac{\cos\theta\sin\theta\sin^2\phi}{r}\right)\frac{\partial^2}{\partial r\partial\theta} \tag{43}$$

$$(19) \to - \left(\frac{\sin\phi\cos\phi}{r^2}\right)\frac{\partial}{\partial\phi} \tag{44}$$

$$+ \left(\frac{\cos\phi\sin\phi}{r}\right)\frac{\partial^2}{\partial r\partial\phi} \tag{45}$$

$$(20) \to + \left(\frac{\cos^2\theta\sin^2\phi}{r}\right)\frac{\partial}{\partial r} \tag{46}$$

$$+ \left(\frac{\cos\theta\sin\theta\sin^2\phi}{r}\right)\frac{\partial^2}{\partial r\partial\theta} \tag{47}$$

$$- \left(\frac{\sin\theta\cos\theta\sin^2\phi}{r^2}\right)\frac{\partial}{\partial\theta} \tag{48}$$

$$(21) \to + \left(\frac{\cos^2\theta\sin^2\phi}{r^2}\right)\frac{\partial^2}{\partial\theta^2} \tag{49}$$

$$- \left(\frac{\cos^2\theta\cos\phi\sin\phi}{r\sin^2\theta}\right)\frac{\partial}{\partial\phi} \tag{50}$$

$$+ \left(\frac{\cos\theta\cos\phi\sin\phi}{r^2\sin\theta}\right)\frac{\partial^2}{\partial\phi\partial\theta} \tag{51}$$

$$(22) \to + \left(\frac{\cos^2\phi}{r}\right)\frac{\partial}{\partial r} \tag{52}$$

$$+ \left(\frac{\cos\phi\sin\phi}{r}\right)\frac{\partial^2}{\partial r\partial\phi} \tag{53}$$

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$$+\left(\frac{\cos^2\phi\cos\theta}{r^2\sin\theta}\right)\frac{\partial}{\partial\theta} \quad (54)$$

$$(24)\rightarrow +\left(\frac{\cos\theta\cos\phi\sin\phi}{r^2\sin\theta}\right)\frac{\partial^2}{\partial\theta\partial\phi} \quad (55)$$

$$(25)\rightarrow -\left(\frac{\cos^2\phi\sin\phi}{r\sin^2\theta}\right)\frac{\partial}{\partial\phi} \quad (56)$$

$$+\left(\frac{\cos^2\phi}{r^2\sin^2\theta}\right)\frac{\partial^2}{\partial\phi^2} \quad (57)$$

and finally, for the x-equation, we have

$$\frac{\partial^2}{\partial x^2} = \sin^2\theta\cos^2\phi\frac{\partial^2}{\partial r^2} \quad (58)$$

$$(26)\rightarrow -\left(\frac{\sin\theta\cos\theta\cos^2\phi}{r^2}\right)\frac{\partial}{\partial\theta} \quad (59)$$

$$(26)\rightarrow +\left(\frac{\sin\theta\cos\theta\cos^2\phi}{r}\right)\frac{\partial^2}{\partial\theta\partial r} \quad (60)$$

$$\left(\frac{\cos\phi\sin\phi}{r^2}\right)\frac{\partial}{\partial\phi} \quad (61)$$

$$-\left(\frac{\sin\phi\cos\phi}{r}\right)\frac{\partial^2}{\partial\phi\partial r} \quad (62)$$

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$$
\begin{aligned}
(27) \rightarrow +\left(\frac{\cos^2\theta\cos^2\phi}{r}\right)\frac{\partial}{\partial r} && (63)\\
+\left(\frac{\sin\theta\cos\theta\cos^2\phi}{r}\right)\frac{\partial^2}{\partial r\partial\theta} && (64)\\
(27) \rightarrow -\left(\frac{\sin\theta\cos\theta\cos^2\phi}{r^2}\right)\frac{\partial}{\partial\theta} && (65)\\
+\left(\frac{\cos^2\theta\cos^2\phi}{r^2}\right)\frac{\partial^2}{\partial\theta^2} && (66)\\
(28) \rightarrow +\left(\frac{\cos\theta\cos\phi}{r}\right)\left(\frac{\cos\phi\sin\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi} && (67)\\
-\left(\frac{\sin\phi\cos\phi\cos\theta}{r^2\sin\theta}\right)\frac{\partial^2}{\partial\phi\partial\theta} && (68)\\
(29) \rightarrow -\left(\frac{\sin^2\phi}{r}\right)\frac{\partial}{\partial r} && (69)\\
-\left(\frac{\sin\phi\cos\phi}{r}\right)\frac{\partial^2}{\partial r\partial\phi} && (70)\\
(31) \rightarrow +\left(\frac{\cos\theta\sin^2\phi}{r^2\sin\theta}\right)\frac{\partial}{\partial\theta} && (71)\\
-\left(\frac{\cos\theta\sin\phi\cos\phi}{r^2\sin\theta}\right)\frac{\partial^2}{\partial\theta\partial\phi} && (72)\\
(32) \rightarrow +\left(\frac{\sin\phi\cos\phi}{r\sin^2\theta}\right)\frac{\partial}{\partial\phi} && (73)\\
+\left(\frac{\sin^2\phi}{r^2\sin^2\theta}\right)\frac{\partial^2}{\partial\phi^2} && (74)
\end{aligned}
$$

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Gathering terms as coefficients of partial derivatives, we obtain (from Equations 34, 41 and 58)

$$\frac{\partial^2}{\partial r^2}\left(\cos^2\theta+\sin^2\theta\sin^2\phi+\sin^2\theta\cos^2\phi\right)\to\frac{\partial^2}{\partial r^2}$$

and (from Equations 35, 38, 42, 48, 54, 59, 65, and 71)

$$\frac{\partial}{\partial\theta}\left(+\frac{\cos\theta\sin\theta}{r^2}+\frac{\sin\theta\cos\theta}{r^2}-\frac{\sin\theta\cos\theta\sin^2\phi}{r^2}-\frac{\sin\theta\cos\theta\sin^2\phi}{r^2}+\frac{\cos^2\phi\cos\theta}{r^2\sin\theta}\right.$$
$$\left.-\frac{\sin\theta\cos\theta\cos^2\phi}{r^2}-\frac{\sin\theta\cos\theta\cos^2\phi}{r^2}+\frac{\cos\theta\sin^2\phi}{r^2\sin\theta}\right)$$
$$\to\frac{\cos\theta}{r^2\sin\theta}\frac{\partial}{\partial\theta}\tag{75}$$

while we obtain from Equations 40, 49, and 66:

$$\frac{\partial^2}{\partial\theta^2}\left(\frac{\sin^2\theta}{r^2}+\frac{\cos^2\theta\sin^2\phi}{r^2}+\frac{\cos^2\theta\cos^2\phi}{r^2}\right)\to\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}\tag{76}$$

From Equations 37, 46, 52, 63, 69,

$$\frac{\partial}{\partial r}\left(+\frac{\sin^2\theta}{r}+\frac{\cos^2\theta\sin^2\phi}{r}+\frac{\cos^2\phi}{r}+\frac{\cos^2\theta\cos^2\phi}{r}-\frac{\sin^2\phi}{r}\right)\to\frac{2}{r}\frac{\partial}{\partial r}\tag{77}$$

From Equations 44, 50, 56, 61, 67 and 73 we obtain

$$\frac{\partial}{\partial\phi}\left(-\frac{\sin\phi\cos\phi}{r^2}-\frac{\cos^2\theta\cos\phi\sin\phi}{r\sin^2\theta}-\frac{\cos^2\theta\cos\phi\sin\phi}{r\sin^2\theta}+\frac{\cos\phi\sin\phi}{r^2}+\left(\frac{\cos\theta\cos\phi}{r}\right)\right.$$
$$\left.+\left(\frac{\cos\theta\cos^2\phi\sin\phi}{r^2\sin\theta}\right)+\frac{\sin\phi\cos\phi}{r\sin^2\theta}\right)\to 0\tag{78}$$

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$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi_e}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi_e}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi_e}{\partial\phi^2}\right]$$

Kinetic energy operator in Spherical Coordinates

$$-\frac{\hbar^2}{2\mu}\left[\qquad\qquad \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Rigid rotor

- Potential energy = 0
- KE term: entire Hamiltonaian
- *r* = constant
- Derivative with respect to *r* = 0

Hamiltonian in Spherical Coordinates

$$-\frac{\hbar^2}{2\mu}\left[\qquad \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Rigid rotor

- Potential energy = 0
- KE term: entire Hamiltonaian
- r = constant
- Derivative with respect to r = 0

Hamiltonian from square of angular momentum operator

$$\widehat{L^2} = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$$

Hamiltonian from square of angular momentum operator

$$\widehat{L^2} = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$\hat{H} = \frac{\widehat{L^2}}{2I} = \frac{\widehat{L^2}}{2\mu r_o^2}$$

$$= -\frac{\hbar^2}{2\mu r_0{}^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = m r_0^2 \ ,$$ where m = Reduced mass

Wavefunctions: Spherical harmonics, same as in H atom

$$Y_J^M(q,f) = Q_{J,|M|}(q)F_M(f)$$

Schrodinger equation

$$Y_J^M(q,f) = Q_{J,|M|}(q)F_M(f)$$

$$-\frac{\hbar^2}{2\mu {r_0}^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Theta\Phi = E\Theta\Phi$$

$$-\frac{\hbar^2}{2\mu {r_0}^2}\left[\frac{\Phi}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{\Theta}{sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\right] = E\Theta\Phi$$

Multiplying by $-\frac{2\mu {r_0}^2}{\hbar^2\Theta\Phi}$

$$\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2} = -\boxed{\frac{2\mu {r_0}^2}{\hbar^2}E} = -\beta$$

Multiplying by $sin^2\theta$ and rearranging

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

$$= M^2$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\beta sin^2\theta = M^2$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = -M^2$$

Separation of variables

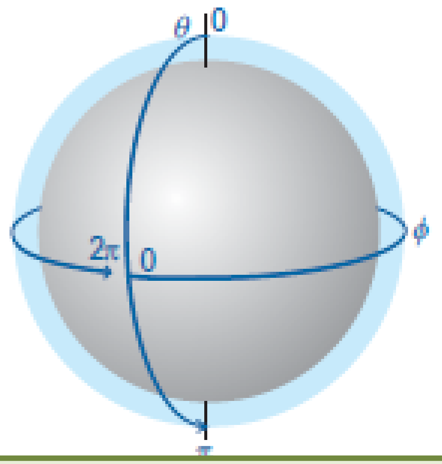
Solution to ϕ part

$$\Phi(\phi) = Ae^{\pm im\phi}$$

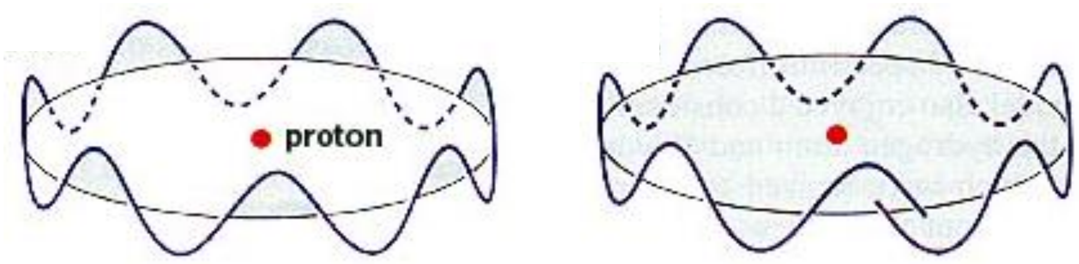
$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -M^2$$

$$\frac{d^2\Phi}{d\phi^2} = -M^2\Phi$$

Trial solution: $\Phi = A.e^{\pm iM\phi}$



‘ϕ’ ranges from 0 to 2π



Wavefunction has to be continuous

$$\Rightarrow \Phi(\phi + 2\pi) = \Phi(\phi)$$

Periodic Boundary Condition

Solution to ϕ part

⌐ F(f +2p)=F(f)

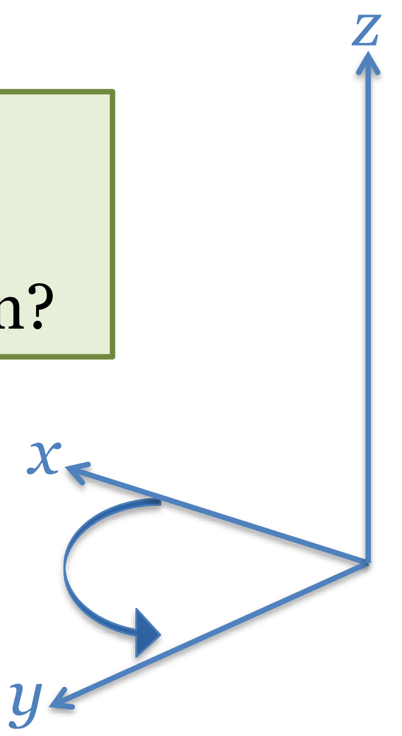
$$A.e^{\pm iM(\phi+2\pi)} = A.e^{\pm iM\phi}$$

$\cos(2\pi M$ $) = 1$

- True only if M=0, ±1, ±2, ±3, ±4,....
- What kind of information does Φ contain?

Change in ϕ: Circular motion in xy plane

z – component of angular momentum?



Angular momentum: from classical to quantum picture

$$\vec{L} = \vec{r} \times \vec{p}$$

L_z

$$\widehat{p_y} = \frac{\hbar}{i}\frac{\partial}{\partial y}; \qquad \widehat{p_x} = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$\therefore \widehat{L_z} = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \longrightarrow \longrightarrow \widehat{L_z} = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$$

Is Φ an eigenfunction?

Moment of truth

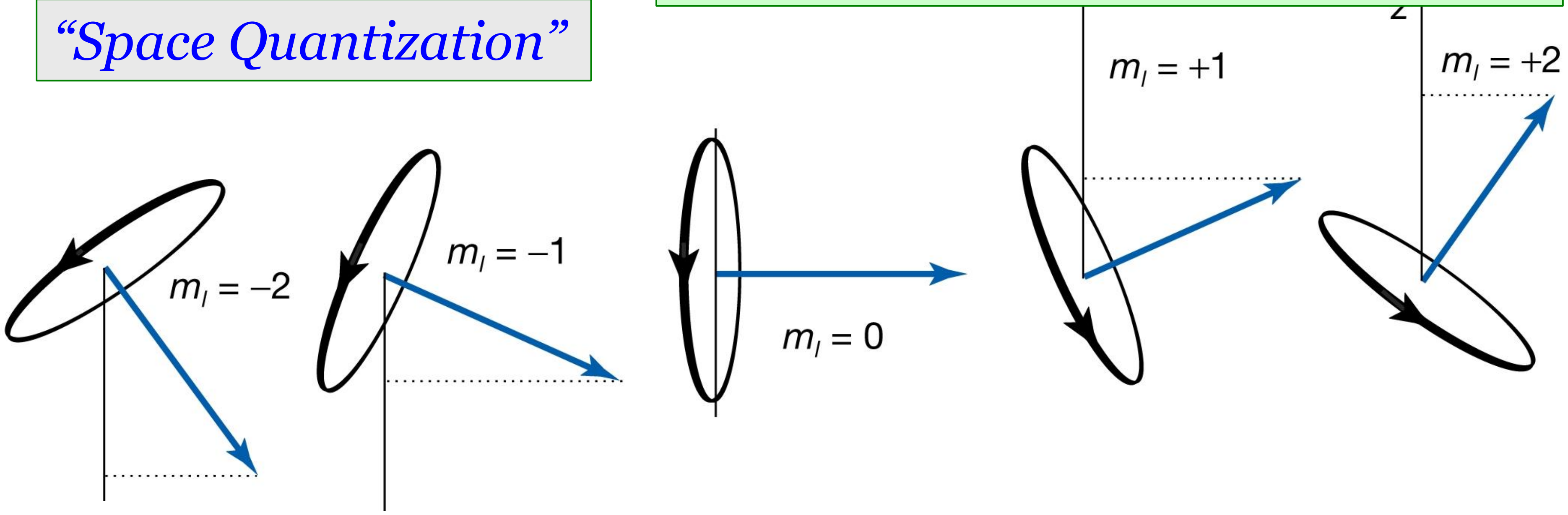
$$\widehat{L_z} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

$$\Phi = A.e^{\pm iM\phi}$$

$$\widehat{L_z}\Phi = \frac{\hbar}{i}iM\Phi = M\hbar\Phi$$

z-component of angular momentum

"Space Quantization"



Wavefunctions: Spherical harmonics, same as in H atom

$$Y_J^M(q,f) = Q_{J,|M|}(q)F_M(f)$$

$$F(f) = Ae^{iMf}$$

$$P_J^M(\cos q) = \frac{(-1)^M}{2^l l!}(1-\cos^2 q)^{M/2}\frac{d^{J+M}}{dx^{J+M}}(\cos^2 q - 1)^J$$

$\Theta(\theta) =$

$$P_J^{-M}(\cos q) = (-1)^M \frac{(l-m)!}{(l+m)!}P_J^M(\cos q)$$

$P_J^M(\cos q)$: Associated Legendre Polynomials

$$\boxed{Y_J^M(q,f) = N_J^M P_J^M(\cos q).e^{iMf}}$$

Total Angular Momentum

$$\widehat{L^2}Y(\theta,\phi) = \hbar^2 J(J+1)Y(\theta,\phi)$$

Total Angular Momentum

Energies of a rigid rotor

$$\hat{H} = \frac{\widehat{L^2}}{2I} = \frac{\widehat{L^2}}{2\mu r_o^2}$$

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$$Y_J^M(\theta,\phi) = N_J^M P_J^M(\cos\theta).e^{iM\phi}$$

$$\hat{L}^2 Y_J^M = \left(\frac{h}{2\pi}\right)^2 J(J+1) Y_J^M$$

Energies of a rigid rotor

$$\hat{H} = \frac{\hat{L}^2}{2I} = \frac{\hat{L}^2}{2\mu r_o^2} \qquad\qquad Y_J^M(\theta, \phi) = N_J^M P_J^M(\cos\theta).e^{iM\phi}$$

$$\hat{H}Y_J^M = \frac{h^2}{8\pi^2 \mu r_o^2} J(J+1)Y_J^M$$

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$$e_J = \frac{h}{8p^2 Ic}J(J+1) \text{ cm}^{-1}, \text{ where } J = 0,1,2.....$$

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E_J, in Joule, where $J = 0,1,2.....$

$$\varepsilon_J = \frac{h}{8\pi^2 Ic} J(J+1) \ \text{cm}^{-1}\text{, where } J = 0,1,2.....$$

$$\boxed{\varepsilon_J = BJ(J+1) \ \text{cm}^{-1}}, \quad \text{where} \quad \boxed{B = \frac{h}{8\pi^2 Ic}} = \text{Rotational Constant}$$

Rotational energy levels

$$e_J = BJ\left(J+1\right)\ \text{cm}^{-1},\quad \text{where}\quad B = \frac{h}{8p^2 Ic} = \text{Rotational Constant}$$

Rotational energy levels get more widely spaced with increasing *J*