Teoria quantistica
Sistemi semplici risolvibili esattamente

Particella su circonferenza

Chimica Fisica 2
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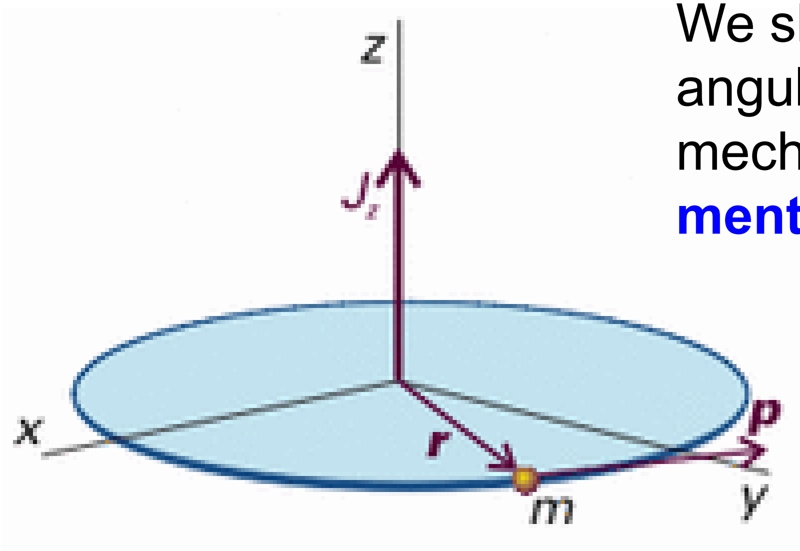
Rotational motion
2 dimensions

We consider a particle of mass m constrained to move in a circular path of radius r in the xy-plane. The total energy is equal to the kinetic energy, because V = 0 everywhere. We can therefore write $E = p^2/2m$.

According to classical mechanics, the angular momentum, J_z around the z-axis (which lies perpendicular to the xy-plane) is $J_z = \pm pr$, so the energy can be expressed as $J_z^2/2mr^2$. Because mr^2 is the moment of inertia, I, of the mass on its path, it follows that

$$E = \frac{J_z^{\,2}}{2I}$$

We shall now see that not all the values of the angular momentum are permitted in quantum mechanics, and therefore that both **angular momentum** and **rotational energy** are **quantized**.



The angular momentum of a particle of mass m on a circular path of radius r in the xy-plane is represented by a vector of magnitude pr perpendicular to the plane.

Rotational motion

2 dimensions

The qualitative origin of quantized rotation

quantizzazione in modo qualitativo

$$J_z = \pm pr \qquad p = \frac{h}{\lambda}$$

Lunghezza d'onda di De Broglie

$$J_z = \pm \frac{hr}{\lambda}$$

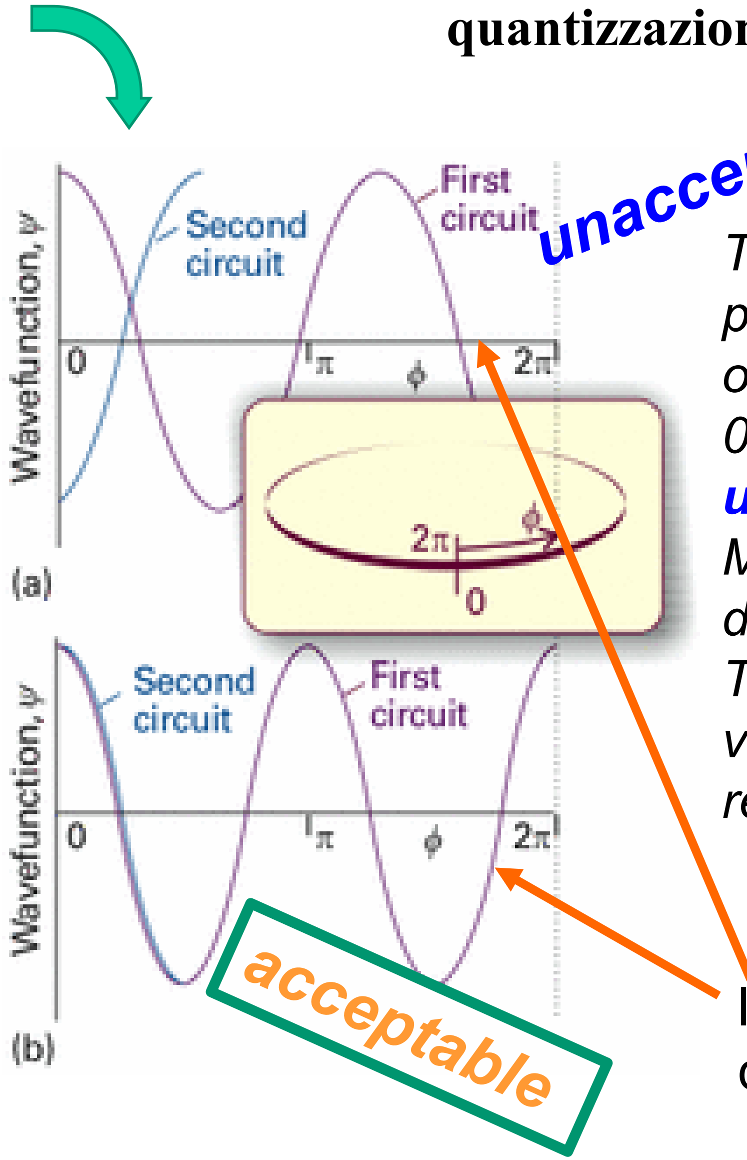
Opposite signs correspond to opposite directions of travel. This equation shows that the shorter the wavelength of the particle on a circular path of given radius, the greater the angular momentum of the particle.

It follows that, if we can see why the wavelength is restricted to discrete values, then we shall understand why the angular momentum is quantized.

Suppose for the moment that λ can take an arbitrary value. In that case, the wavefunction depends on the azimuthal angle φ as shown in Figure

Rotational motion
2 dimensions

quantizzazione in modo qualitativo

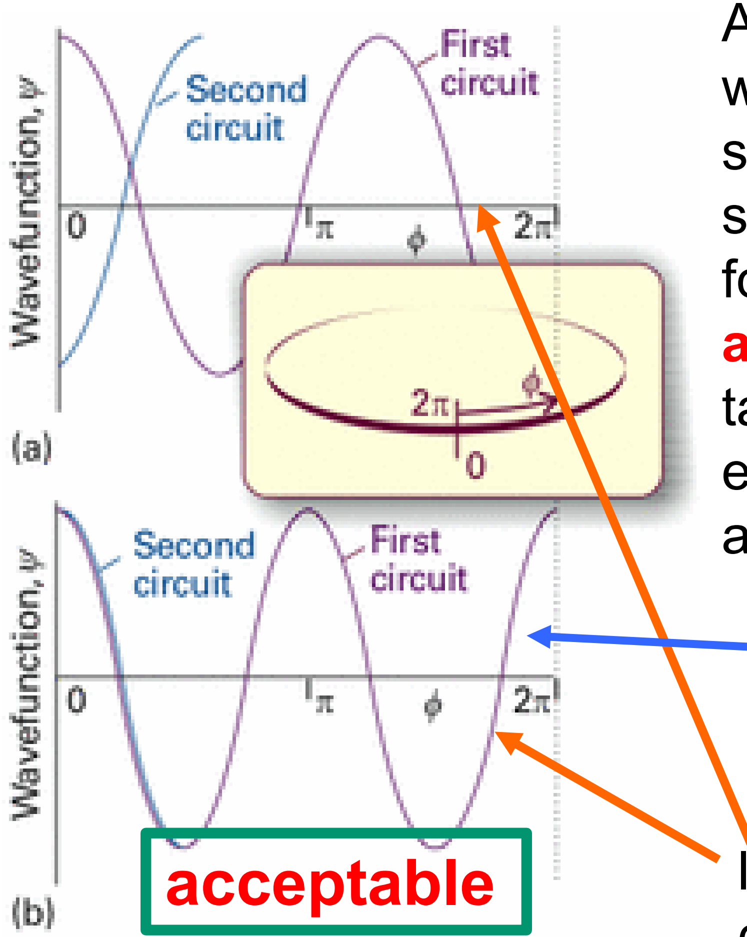


*Two solutions of the Schrödinger equation for a particle on a ring. The circumference has been opened out into a straight line; the points at ϕ = 0 and 2π are identical. The solution in (a) is **unacceptable** because it is not single-valued. Moreover, on successive circuits it interferes destructively with itself, and does not survive. The solution in (b) is **acceptable**: it is single-valued, and on successive circuits it reproduces itself.*

lunghezze d'onda diverse

Rotational motion
2 dimensions

quantizzazione in modo qualitativo



An acceptable solution is obtained only if the wavefunction reproduces itself on successive circuits, as in Fig. (b). Because only some wavefunctions have this property, it follows that only some angular momenta are **acceptable**, and therefore that only certain rotational energies exist. Hence, the energy of the particle is **quantized**. Specifically, the only allowed wavelengths are

$$\lambda = \frac{2\pi r}{m_l}$$

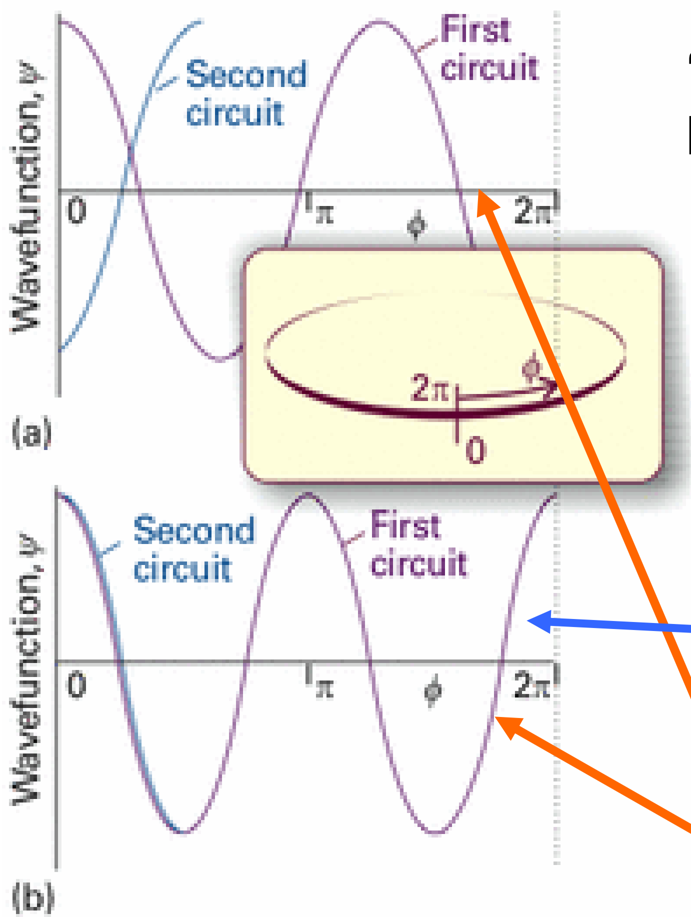
lunghezze d'onda diverse

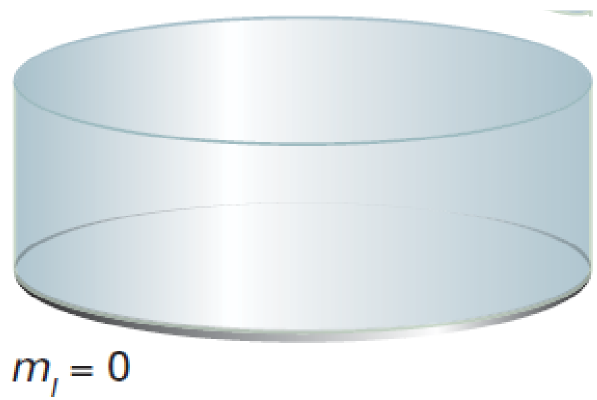
m_l = 0,1,2, …
NUMERO QUANTICO

Rotational motion
2 dimensions

quantizzazione in modo qualitativo

The value $m_\ell = 0$ corresponds to $\lambda = \infty$; a 'wave' of infinite wavelength has a constant height at all values of φ.





$$\lambda = \frac{2\pi r}{\mathbf{m_l}}$$

lunghezze d'onda diverse

$\mathbf{m_l}$ = 0,1,2, …

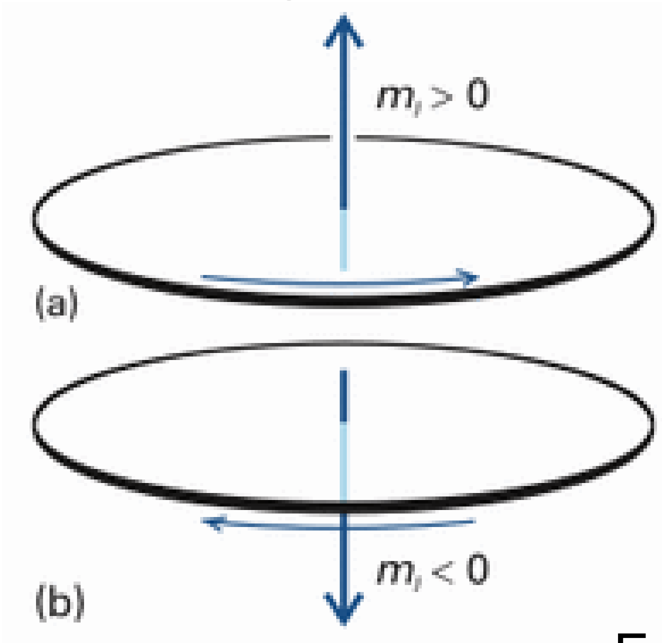
NUMERO QUANTICO

Rotational motion

2 dimensions

uquantizzazione in modo qualitativo

The angular momentum is therefore limited to the values



$$J_z = \pm\frac{hr}{\lambda} = \frac{m_l hr}{2\pi r} = \frac{m_l h}{2\pi}$$

$$\lambda = \frac{2\pi r}{\mathbf{m_l}}$$

where we have allowed m_l to have positive or negative values.

$$J_z = m_l\hbar \qquad m_l = 0, \pm1, \pm2, \ldots$$

Energie possibili

$$E = \frac{J_z^2}{2I} = \frac{m_l^2\hbar^2}{2I}$$

Vedremo ora le funzioni d'onda corrispondenti

$$\psi_{m_l}(\phi) = \frac{e^{im_l\phi}}{(2\pi)^{1/2}}$$

Rotational motion
2 dimensions
uquantizzazione in modo qualitativo

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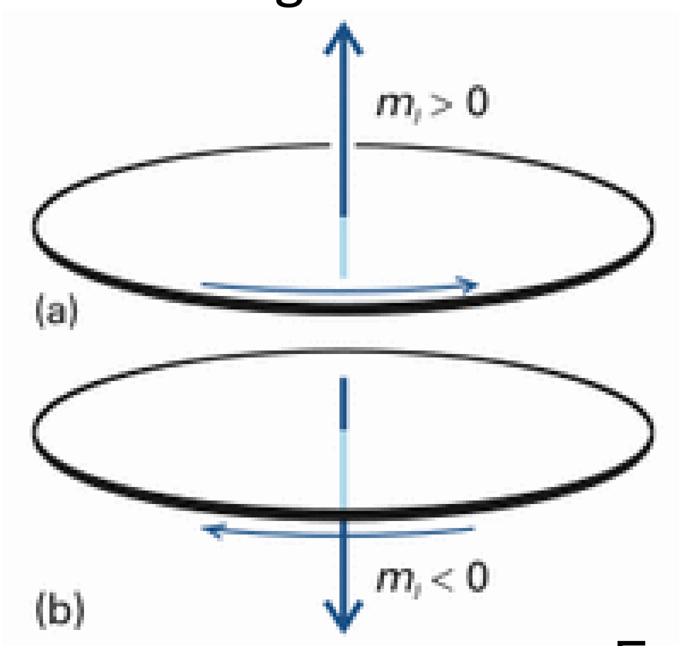

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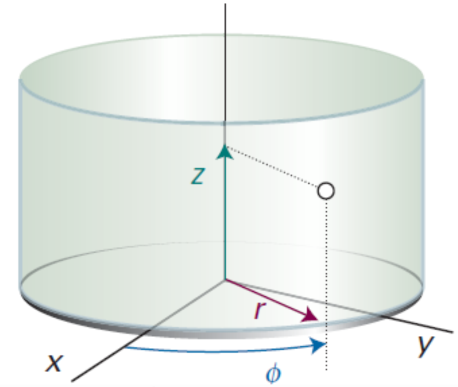
Rotational motion

2 dimensions

Metodo formale

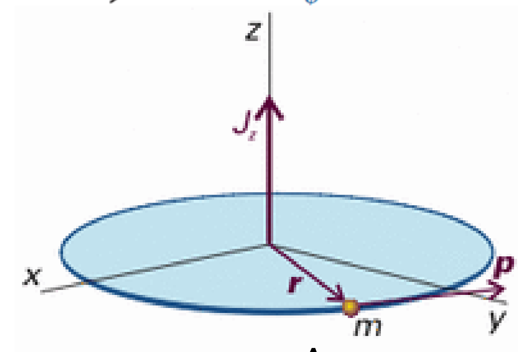
$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

coordinate cilindriche z, r, ϕ



Sufficienti r e $\boldsymbol{\phi}$

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



$$\varphi = \widehat{x\,r}$$

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}$$

r è costante

$$\hat{H} = -\frac{\hbar^2}{2mr^2}\frac{d^2}{d\phi^2}$$

$$I = mr^2$$

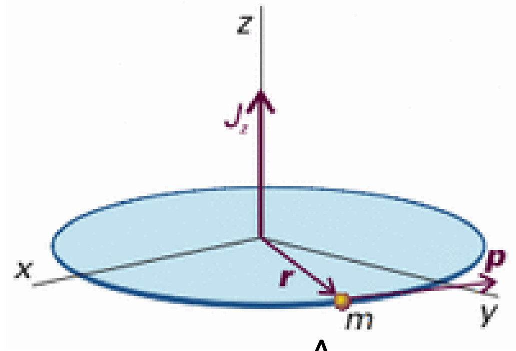
$$\hat{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$$

Rotational motion

2 dimensions

Metodo formale

$$\hat{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$$



$$\varphi = \hat{x\,r}$$

$$-\frac{\hbar^2}{2I}\frac{d^2\psi(\phi)}{d\phi^2} = E\psi(\phi)$$

$$\frac{d^2\psi}{d\phi^2} = -\frac{2IE}{\hbar^2}\psi$$

eq. di Schroedinger

$$\psi_{m_l}(\phi) = \frac{e^{im_l\phi}}{(2\pi)^{1/2}} \qquad m_l = \pm\frac{(2IE)^{1/2}}{\hbar}$$

soluzioni generali normalizzate

Numero reale

consistente con quanto già trovato in modo qualitativo

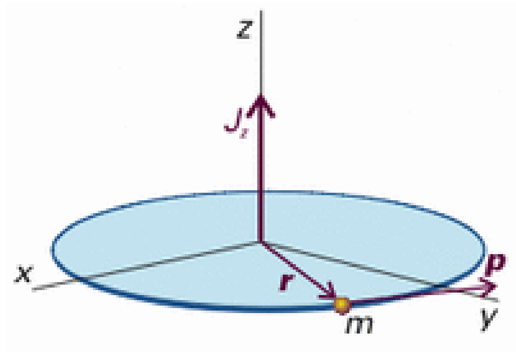
$$E = \frac{J_z^2}{2I} = \frac{m_l^2\hbar^2}{2I}$$

Rotational motion

2 dimensions

Metodo formale

Per avere una Ψ a un sol valore



cyclic boundary condition

$$\psi(\phi + 2\pi) = \psi(\phi).$$

$$\psi_{m_l}(\phi + 2\pi) = \frac{e^{im_l(\phi+2\pi)}}{(2\pi)^{1/2}} = \frac{e^{im_l\phi}e^{2\pi im_l}}{(2\pi)^{1/2}} = \psi_{m_l}(\phi)e^{2\pi im_l}$$

$$e^{i\pi} = -1$$

dalle formule di Eulero

$$e^{\pm ix} = \cos x \pm i \sin x$$

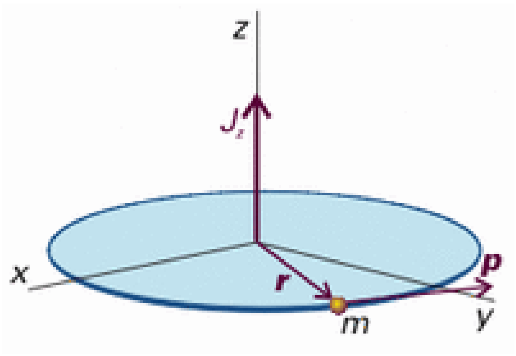
$$\psi_{m_l}(\phi + 2\pi) = (-1)^{2m_l}\psi(\phi)$$

$$(-1)^{2m_l} = 1$$

$2m_l$ must be a positive or a negative even integer

$$m_l = 0, \pm 1, \pm 2, \ldots$$

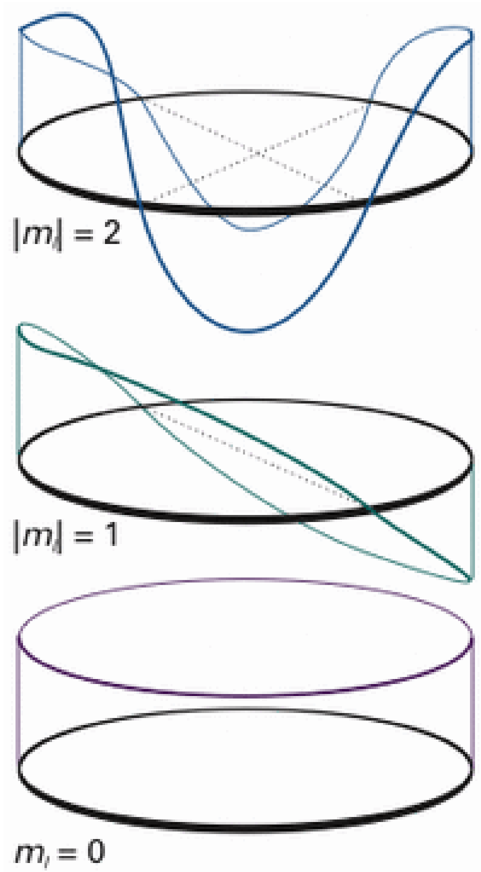
Rotational motion
2 dimensions
Metodo formale



Quantization of rotation

$$E = m_l^2 \hbar^2 / 2I$$

$$J_z = m_l \hbar \qquad m_l = 0, \pm 1, \pm 2, \ldots$$

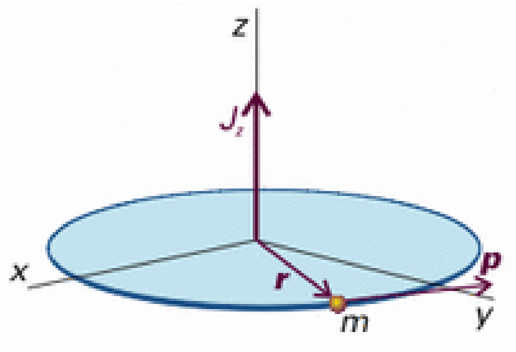


Energia indipandente dal segno di m_l

Cresce m_l , cresce il numero di nodi nella Ψ

Momento angolare QUANTIZZATO

Rotational motion
2 dimensions
Metodo formale



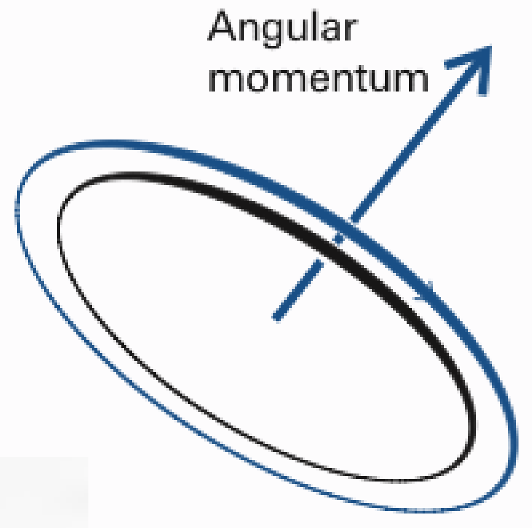
Quantization of rotation

$$(E = m_l^2\hbar^2/2I)$$

$$l_z = xp_y - yp_x$$

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

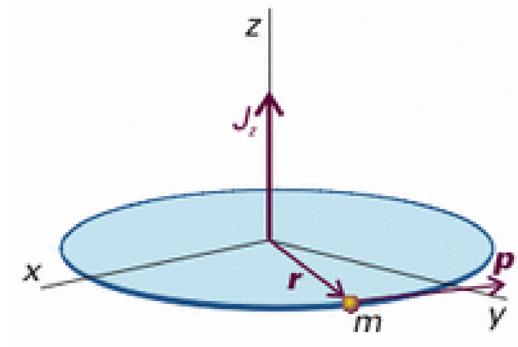
$$\hat{l}_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$$



$$\hat{l}_z\psi_{m_l} = \frac{\hbar}{i}\frac{d\psi_{m_l}}{d\phi} = im_l\frac{\hbar}{i}e^{im_l\phi} = m_l\hbar\psi_{m_l}$$

Rotational motion

2 dimensions



$$\psi^*_{m_l}\psi_{m_l} = \left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}}\right)^*\left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}}\right) = \left(\frac{e^{-im_l\phi}}{(2\pi)^{1/2}}\right)\left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}}\right) = \frac{1}{2\pi}$$

Rotational motion
2 dimensions - Metodo formale

The hamiltonian for a particle of mass m in a plane (with $V = 0$) is the same as that given in eqn 8.9:

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

and the Schrödinger equation is $\hat{H}\psi = E\psi$, with the wavefunction a function of the angle ϕ. It is always a good idea to use coordinates that reflect the full symmetry of the system, so we introduce the coordinates r and ϕ (Fig. 8.27), where $x = r\cos\phi$ and $y = r\sin\phi$. By standard manipulations we can write

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2} \qquad (8.39)$$

However, because the radius of the path is fixed, the derivatives with respect to r can be discarded. The hamiltonian then becomes

$$\hat{H} = -\frac{\hbar^2}{2mr^2}\frac{d^2}{d\phi^2}$$

The moment of inertia $I = mr^2$ has appeared automatically, so $\hat{H}$ may be written

$$\hat{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2} \qquad (8.40)$$

Rotational motion
2 dimensions - Metodo formale

and the Schrödinger equation is

$$\frac{d^2\psi}{d\phi^2} = -\frac{2IE}{\hbar^2}\psi \qquad (8.41)$$

The normalized general solutions of the equation are

$$\psi_{m_l}(\phi) = \frac{e^{im_l\phi}}{(2\pi)^{1/2}} \qquad m_l = \pm\frac{(2IE)^{1/2}}{\hbar} \qquad (8.42)$$

The quantity m_l is just a dimensionless number at this stage.

We now select the acceptable solutions from among these general solutions by imposing the condition that the wavefunction should be single-valued. That is, the wavefunction ψ must satisfy a **cyclic boundary condition**, and match at points separated by a complete revolution: $\psi(\phi + 2\pi) = \psi(\phi)$. On substituting the general wavefunction into this condition, we find

$$\psi_{m_l}(\phi + 2\pi) = \frac{e^{im_l(\phi+2\pi)}}{(2\pi)^{1/2}} = \frac{e^{im_l\phi}e^{2\pi i m_l}}{(2\pi)^{1/2}} = \psi_{m_l}(\phi)e^{2\pi i m_l}$$

As $e^{i\pi} = -1$, this relation is equivalent to

$$\psi_{m_l}(\phi + 2\pi) = (-1)^{2m_l}\psi_{m_l}(\phi) \qquad (8.43)$$

Because we require $(-1)^{2m_l} = 1$, $2m_l$ must be a positive or a negative even integer (including 0), and therefore m_l must be an integer: $m_l = 0, \pm1, \pm2, \ldots$. The corresponding energies are therefore those given by eqn 8.38a with $m_l = 0, \pm1, \pm2, \ldots$.