Teoria quantistica Sistemi semplici risolvibili esattamente

Particella su una sfera

ROTAZIONE in 3D

Chimica Fisica 2

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Particella su una sfera
Riassunto

Le energie di una particella costretta a muoversi in una regione finita di spazio sono quantizzate.

1. **La funzione d'onda di una particella su una sfera deve soddisfare contemporaneamente a due condizioni cicliche al contorno, quindi due numeri quantici: l ed m_l ;**

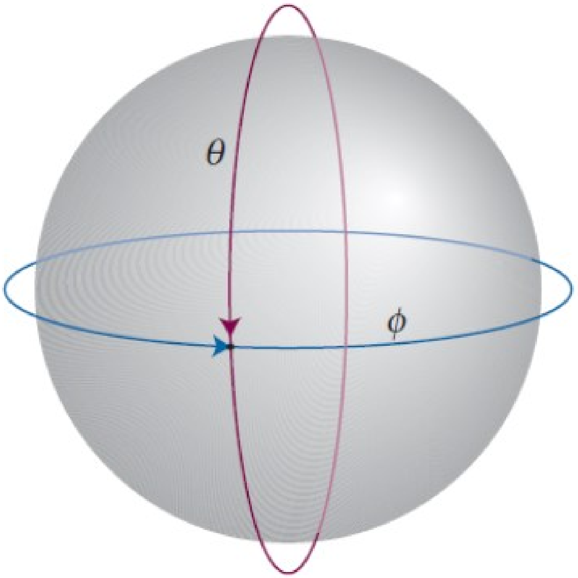
2. **L'Energia e il momento angolare della particella sulla sfera sono quantizzati;**

3. **La quantizzazione spaziale e' la restrizione della componente z del momento angolare a certi valori;**

4. **Il modello vettoriale del momento angolare usa dei diagrammi (rappresentazioni grafiche) per rappresentare lo stato del momento angolare di una particella rotante nello spazio.**

Particella su una sfera
Introduzione

We now consider a particle of mass *m* that is free to move anywhere on the surface of a sphere of radius *r*. We shall need the results of this calculation when we come to describe rotating molecules and the states of electrons in atoms. The requirement that the wavefunction should match as a path is traced over the poles as well as around the equator of the sphere surrounding the central point, introduces a second cyclic boundary condition and therefore a second quantum number.



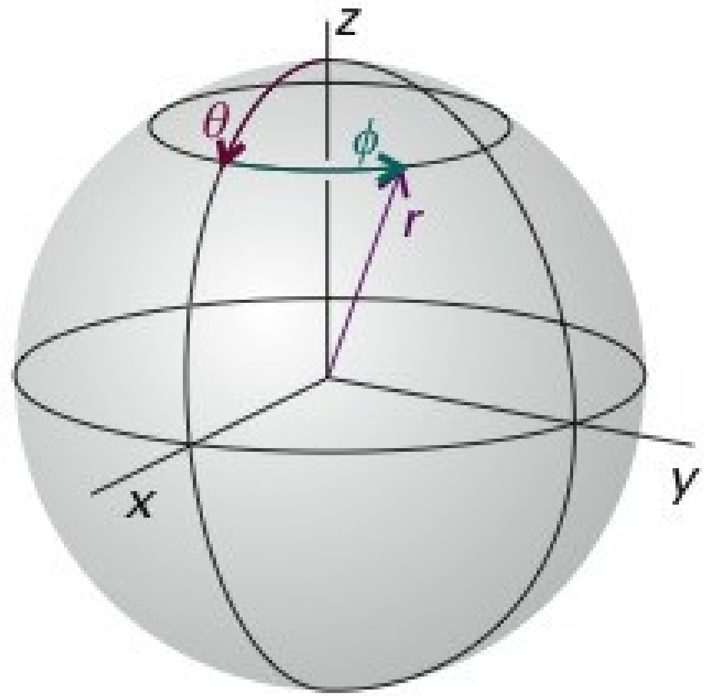
Rotation in 3 dimensions: the particle on a sphere

The Schrödinger equation

The hamiltonian for motion in three dimensions is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V \qquad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The symbol ∇^2 is a convenient abbreviation for the sum of the three second derivatives; it is called the **laplacian**, and read either 'del squared' or 'nabla squared'. For the particle confined to a spherical surface, $V = 0$ wherever it is free to travel, and the radius r is a constant. The wavefunction is therefore a function of the **colatitude**, θ, and the **azimuth**,ϕ (see the Figure), and so we write it as ψ(θ,ϕ).



Spherical polar coordinates. For a particle confined to the surface of a sphere, only the colatitude, θ and the azimuth, ϕ, can change.

Rotation in 3 dimensions: the particle on a sphere

The wavefunctions

The Schrödinger equation

The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

As shown in the following *paragraph*, this partial differential equation can be simplified by the separation of variables procedure by expressing the wavefunction (for constant *r*) as the product

$\psi(\theta,\phi) = \Theta(\theta)\Phi(\phi)$ $\quad$ $$\psi(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$ Separation of variables

where Θ is a function only of θ and Φ is a function only of ϕ.

Rotation in 3 dimensions: the particle on a sphere

The separation of variables

The laplacian in spherical polar coordinates is

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2$$

r è costante

laplacian

where the **legendrian**, Λ^2, is

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

legendrian

Because *r* is constant, we can discard the part of the laplacian that involves differentiation with respect to *r*, and so write the Schrödinger equation as

$$\frac{1}{r^2}\Lambda^2\psi = -\frac{2mE}{\hbar^2}\psi$$

Questa era l'equazione di partenza

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

or, because $I = mr^2$, as

$$\Lambda^2\psi = -\varepsilon\psi \qquad \varepsilon = \frac{2IE}{\hbar^2}$$

Rotation in 3 dimensions: the particle on a sphere

The separation of variables

To verify that this expression is separable, we substitute ψ =ΘΦ:

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

We now use the fact that Θ and Φ are each functions of one variable, so the partial derivatives become complete derivatives:

$$\frac{\Theta}{\sin^2\theta}\frac{d^2\Phi}{d\phi^2}+\frac{\Phi}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta}=-\varepsilon\Theta\Phi$$

Division through by ΘΦ, multiplication by $\sin^2\theta$, and minor rearrangement gives

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta}+\varepsilon\sin^2\theta=0$$

The first term on the left depends only on ϕ and the remaining two terms depend only on θ.

Rotation in 3 dimensions: the particle on a sphere

The separation of variables

We met a similar situation when discussing a particle on a rectangular surface, and by the same argument, the complete equation can be separated. Thus, if we set the first term equal to the numerical constant $-m_l^2$ (using a notation chosen with an eye to the future), the separated equations are

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + \varepsilon\sin^2\theta = 0$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m_l^2 \qquad \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + \varepsilon\sin^2\theta = m_l^2$$

The first of these two equations is the same that we have seen studying the particle on a ring, so it has the same solutions

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

The second is much more complicated to solve, but the solutions are tabulated as the associated Legendre functions.

Rotation in 3 dimensions: the particle on a sphere

The separation of variables

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

eq. di Schroedinger

da: Particella su circonferenza

$$m_l = \pm\frac{(2IE)^{1/2}}{\hbar}$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + \varepsilon\sin^2\theta = 0$$

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

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + \varepsilon\sin^2\theta = m_l^2$$

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

1° NUMERO QUANTICO: m_ℓ

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Rotation in 3 dimensions: the particle on a sphere

The separation of variables

For reasons related to the behaviour of these functions, the cyclic boundary conditions on Θ arising from the need for the wavefunctions to match at θ = 0 and 2π (the North Pole) result in the introduction of a second quantum number, *l*, which identifies the acceptable solutions.

2° NUMERO QUANTICO: ℓ

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m_l^2 \qquad \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + \varepsilon\sin^2\theta = m_l^2$$

The presence of the quantum number m_l in the second equation implies, as we see below, that the range of acceptable values of m_l is restricted by the value of *l*.

$$l = 0, 1, 2, \ldots \qquad m_l = l, l-1, \ldots, -l$$

Rotation in 3 dimensions: the particle on a sphere

The separation of variables

$$\psi(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

As indicated in the previous paragraph, solution of the Schrödinger equation shows that the acceptable wavefunctions are specified by two quantum numbers l and m_l which are restricted to the values

$$l = 0, 1, 2, \ldots \qquad m_l = l, l-1, \ldots, -l$$

Note that the **orbital angular momentum quantum number *l* is non-negative** and that, for a given value of *l*, there are **2*l* + 1** permitted values of the **magnetic quantum number**, m_l.

The normalized wavefunctions are usually denoted $Y_{l,m_l}(\theta,\phi)$ and are called the **spherical harmonics** (see the Table).

Rotation in 3 dimensions: the particle on a sphere

The separation of variables

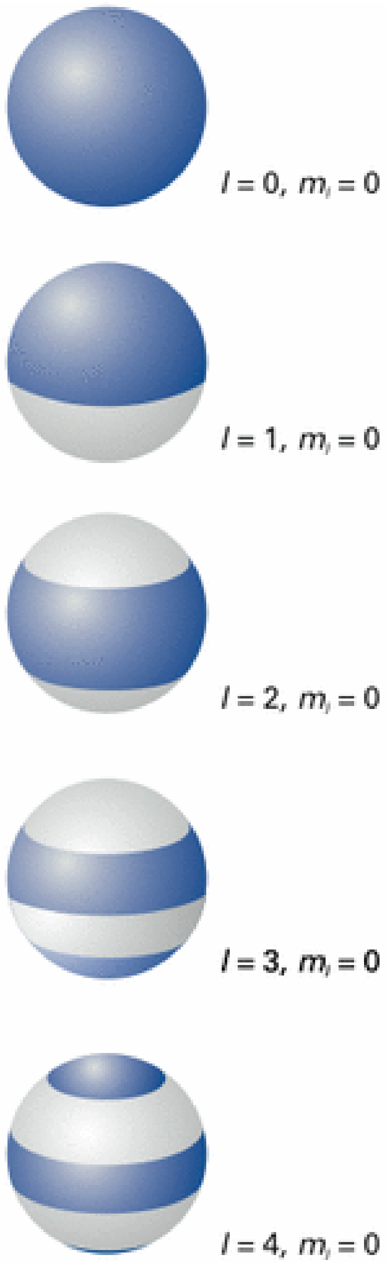
The normalized wavefunctions are usually denoted $Y_{l,m_l}(\theta,\phi)$ and are called the **spherical harmonics** (see the Table).

le funzioni
Armoniche sferiche

l	m_l	$Y_{l,m_l}(\theta,\varphi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\, e^{\pm i\phi}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\, e^{\pm i\phi}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\, e^{\pm 3i\phi}$

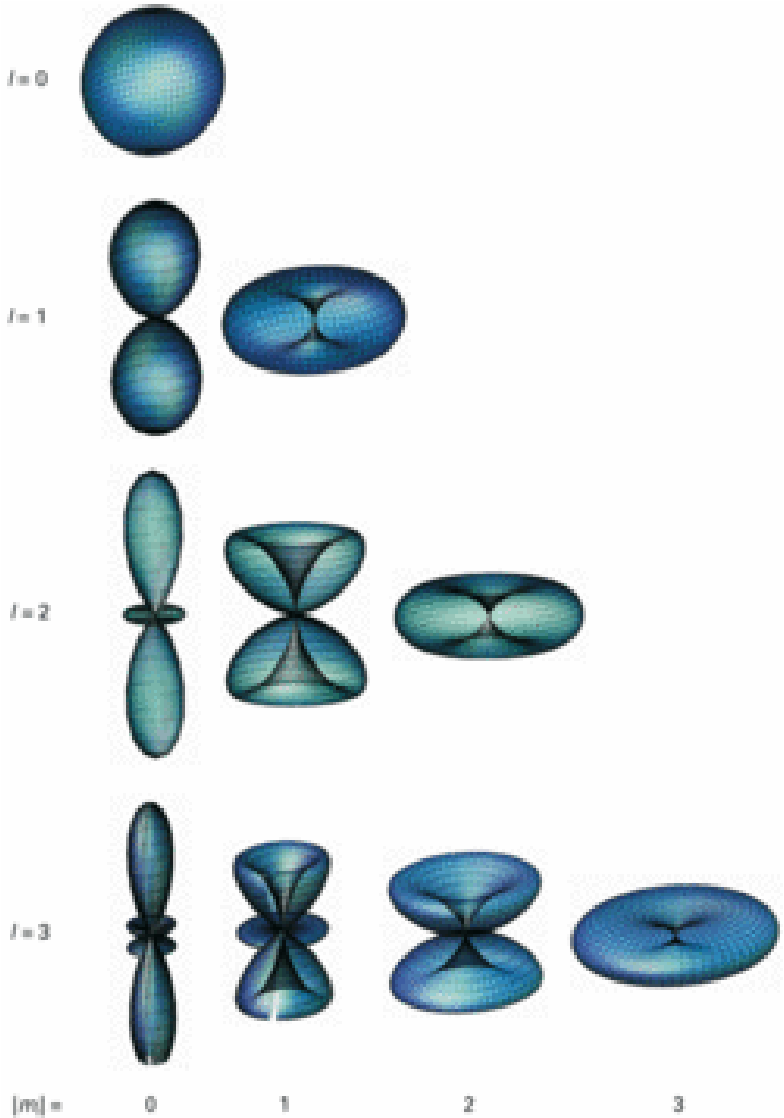
Rotational motion

3 dimensions



A representation of the wavefunctions of a particle on the surface of a sphere which emphasizes the location of angular nodes: dark and light shading correspond to different signs of the wavefunction.
Note that the number of nodes increases as the value of l increases. All these wavefunctions correspond to ml = 0; a path around the vertical z-axis of the sphere does not cut through any nodes.

Rotational motion
3 dimensions



A more complete representation of the wavefunctions for $l = 0, 1, 2$, and 3. The distance of a point on the surface from the origin is proportional to the square modulus of the amplitude of the wavefunction at that point.

Rotational motion
3 dimensions

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m_l^2 \qquad \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + \varepsilon\sin^2\theta = m_l^2$$

soluzioni

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

$$m_l = \pm\frac{(2IE)^{1/2}}{\hbar}$$

soluzioni

associated Legendre functions

$$l = 0, 1, 2, \ldots \qquad m_l = l, l-1, \ldots, -l$$

$$E = l(l+1)\frac{\hbar^2}{2I} \qquad l = 0, 1, 2, \ldots$$

L'ENERGIA non dipende dal numero quantico m_l

Degenerazione = $2l+1$

Rotational motion

3 dimensions

Collegamento con la struttura atomica

$$E = l(l+1)\frac{\hbar^2}{2I} \qquad l = 0, 1, 2, \ldots$$

L'ENERGIA non dipende dal numero quantico m_l

Degenerazione = $2l+1$

Per questo motivo

gli orbitali p sono 3 e sono degeneri (l=1; $2l+1$=3)
gli orbitali d sono 5 e sono degeneri (l=2; $2l+1$=5)
gli orbitali f sono 7 e sono degeneri (l=3; $2l+1$=7)
……

Rotational motion
3 dimensions

$$E = l(l+1)\frac{\hbar^2}{2I} \qquad l = 0, 1, 2, \ldots$$

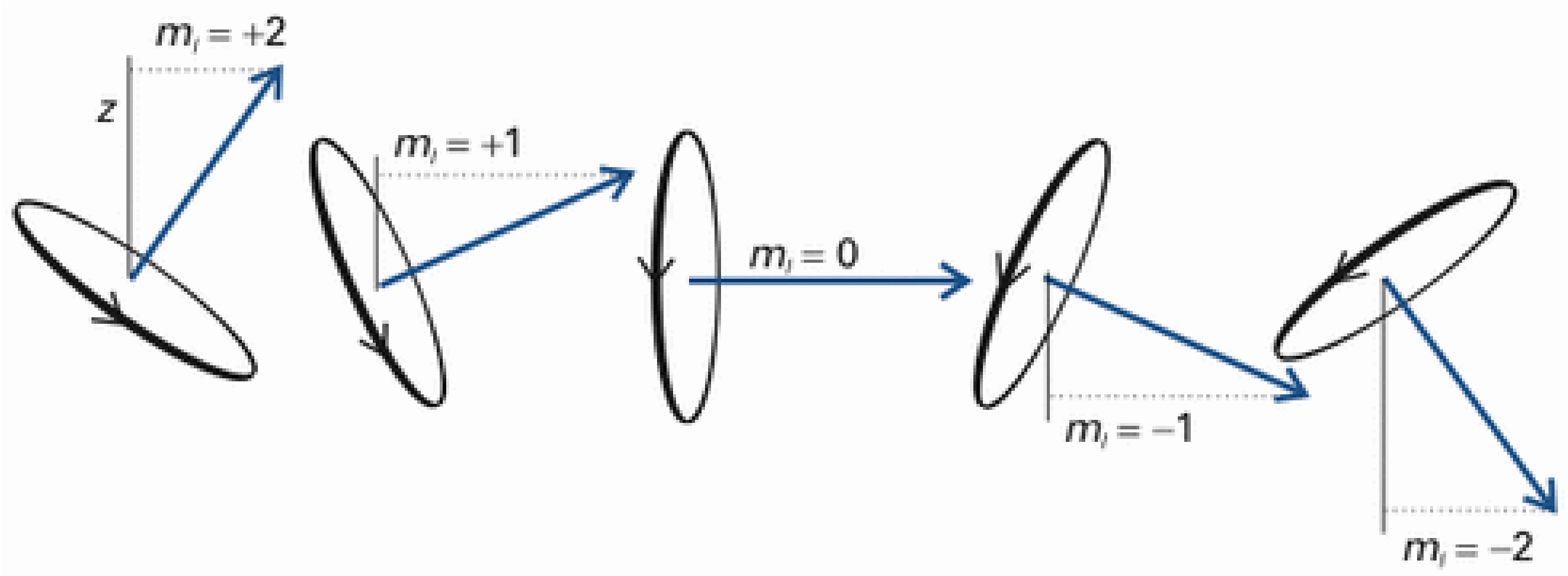
$$E = J^2/2I$$

Nella rotazione a 2 dimensioni
E = $J_z^2/2I$

$\left|\vec{J}\right|$ = Magnitude of angular momentum = $\{l(l+1)\}^{1/2}\hbar \qquad l = 0, 1, 2 \ldots$

J_z = z-Component of angular momentum = $m_l\hbar \qquad m_l = l, l-1, \ldots, -l$

Rotational motion
3 dimensions



The permitted orientations of angular momentum when l = 2. We shall see soon that this representation is too specific because the azimuthal orientation of the vector (its angle around z) is indeterminate.

QUANTIZZAZIONE SPAZIALE della ROTAZIONE di un corpo microscopico