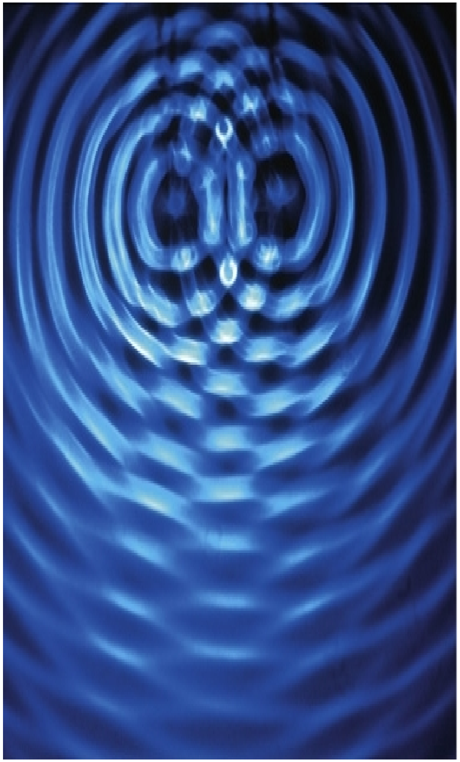
Useful quantum models in Chemistry



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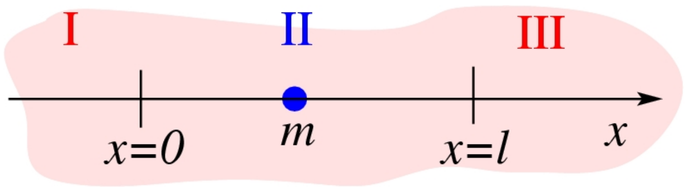
I.A. Schrödinger's equation



$$V(x) = \begin{cases} +\infty & x \leqslant 0 & \text{(I)} \\ 0 & 0 < x < l & \text{(II)} \\ +\infty & l \leqslant x & \text{(III)} \end{cases}$$

- Zones (I) and (III) $\Rightarrow |\psi(x)|^2 = 0 \rightarrow \psi_{\mathrm{I}}(x) = \psi_{\mathrm{III}}(x) = 0$
- Zone (II)

$$\hat{H}\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \underbrace{V(x)\psi(x)}_{0} = E\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x)$$

- Independent solutions

$$\psi_1(x) = \text{sen}(kx) \qquad \psi_2(x) = \cos(kx)$$

$$\frac{d^2\psi_1(x)}{dx^2} = -k^2\,\text{sen}(kx) \qquad \frac{d^2\psi_2(x)}{dx^2} = -k^2\cos(kx)$$

$$k = \frac{\sqrt{2mE}}{\hbar}$$

$$\psi(x) = A\,\psi_1(x) + B\,\psi_2(x) = A\,\text{sen}\left(\frac{\sqrt{2mE}}{\hbar}x\right) + B\cos\left(\frac{\sqrt{2mE}}{\hbar}x\right)$$

$$\psi(x) = A\,\mathrm{sen}\left(\frac{\sqrt{2mE}}{\hbar}x\right) + B\cos\left(\frac{\sqrt{2mE}}{\hbar}x\right)$$

- Continuity $x = 0 \Rightarrow \psi_{\mathrm{I}}(x=0) = \psi_{\mathrm{II}}(x=0)$

$$A\,\mathrm{sen}\left(\frac{\sqrt{2mE}}{\hbar}0\right) + B\cos\left(\frac{\sqrt{2mE}}{\hbar}0\right) = 0$$

$$A\cdot 0 + B\cdot 1 = 0$$

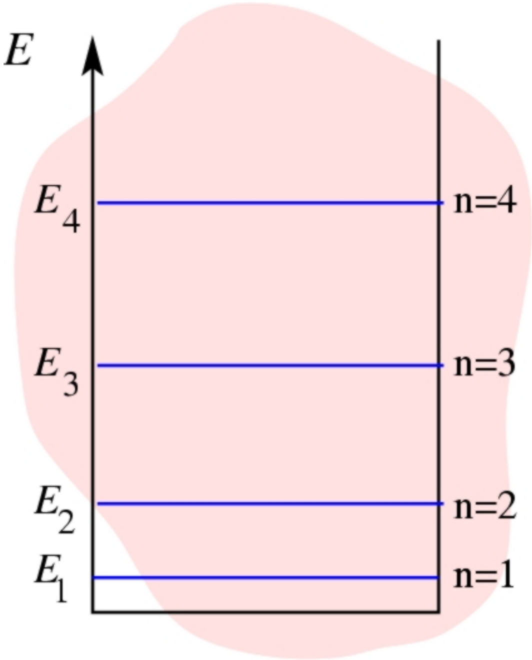
$$B = 0$$

- Continuity $x = l \Rightarrow \psi_{\mathrm{II}}(x=l) = \psi_{\mathrm{III}}(x=l)$

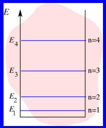
$$A\cdot\mathrm{sen}\left(\frac{\sqrt{2mE}}{\hbar}l\right) = 0 \Rightarrow \frac{\sqrt{2mE}}{\hbar}l = n\pi;\ n = 0, \pm 1, \pm 2, \ldots$$

I.B. Eigenfunctions and eigenvalues: quantization

$$\psi_{\mathrm{II}}(x) = A\,\mathrm{sen}\left(\frac{n\pi x}{l}\right);\ n = 1, 2, \ldots \begin{cases} n = 0 & \text{no normalizable} \\ n < 0 & \text{phase factor} \end{cases}$$



- Quantization $E_n = \frac{h^2}{8ml^2} n^2$
  $n = 1, 2, \ldots$
- Ground state $\Rightarrow$ E_1
- Spacing $\Rightarrow$ $E_n = n^2 E_1$



I.B. Eigenfunctions and eigenvalues: normalization

- Normalization

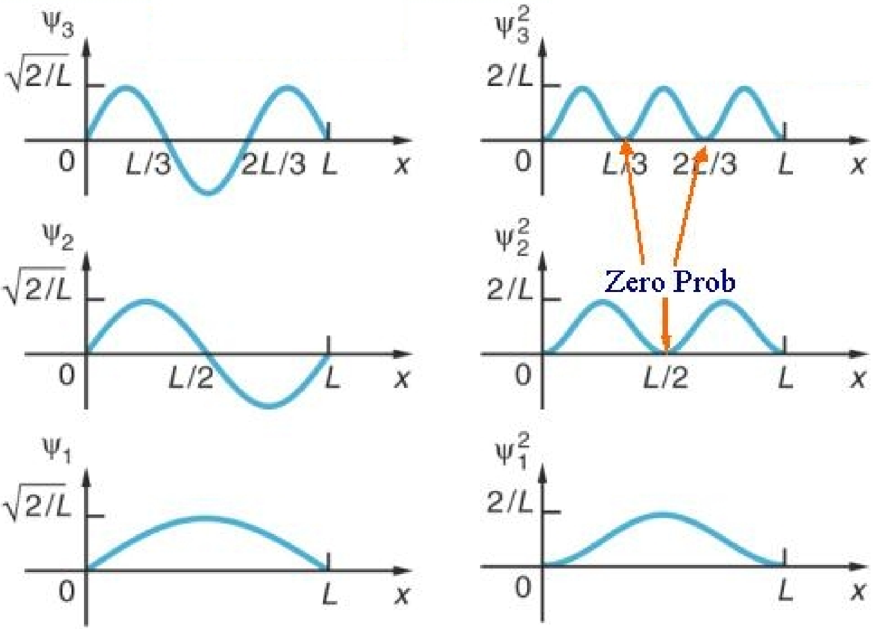
$$\int_{-\infty}^{+\infty} |\psi(x)|^2\, dx = 1$$

$$\underbrace{\int_{-\infty}^{0} |\psi_{\mathrm{I}}(x)|^2\, dx}_{0} + \int_{0}^{l} |\psi_{\mathrm{II}}(x)|^2\, dx + \underbrace{\int_{l}^{+\infty} |\psi_{\mathrm{III}}(x)|^2\, dx}_{0} = 1$$

$$|A|^2 \int_0^l \mathrm{sen}^2\left(\frac{n\pi x}{l}\right) dx = 1 \quad \Rightarrow \quad |A| = \sqrt{\frac{2}{l}}$$

$$\psi_{\mathrm{II}}(x) = \sqrt{\frac{2}{l}}\, \mathrm{sen}\left(\frac{n\pi x}{l}\right)$$

I.B. Eigenfunctions and eigenvalues: gráficas



- Nodes

  $\psi(x_i) = 0$

I.C. Classical limit

Ex. electron vs melon

- Electron in a box

$$m = 9.1 \cdot 10^{-31}\ \mathrm{kg}$$
$$l = 10\,\mathrm{\AA}$$
$$E_n = 6 \cdot 10^{-20} n^2\ \mathrm{J}$$
$$\Delta E \sim 10^{-20}\ \mathrm{J}$$

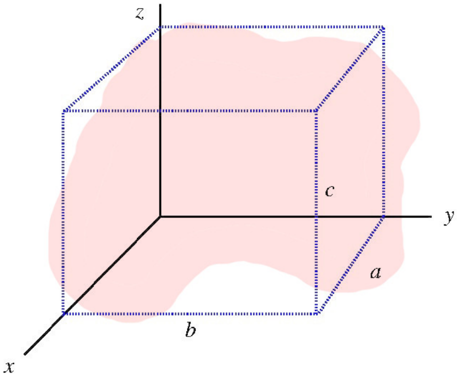
- Melon in a box

$$m = 1\ \mathrm{kg}$$
$$l = 1\ m$$
$$E_n = 4 \cdot 10^{-68} n^2\ \mathrm{J}$$
$$\Delta E \sim 10^{-68}\ \mathrm{J}$$

$$v = 1\ \mathrm{m/s} \Rightarrow\ E = 0.5\ \mathrm{J}$$
$$n = \sqrt{\frac{8ml^2E}{h^2}} \sim 10^{33}$$

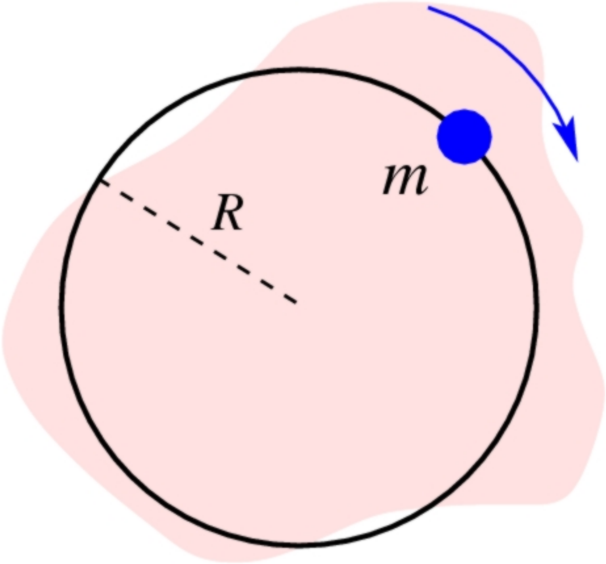
3D box

$$\hat{H}_{\text{3D}}(x,y,z) = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}\right)\begin{cases} 0 \le x \le a \\ 0 \le y \le b \\ 0 \le z \le c \end{cases}$$



- $\hat{H}_{\text{3D}}\Psi_{\text{3D}} = E_{\text{3D}}\Psi_{\text{3D}}$
- $\hat{H}_{\text{3D}}(x,y,z) = \hat{H}_{\text{1D}}(x) + \hat{H}_{\text{1D}}(y) + \hat{H}_{\text{1D}}(z)$
- $\Psi_{\text{3D}}(x,y,z) = \Psi_{\text{1D}}(x)\Psi_{\text{1D}}(y)\Psi_{\text{1D}}(z)$

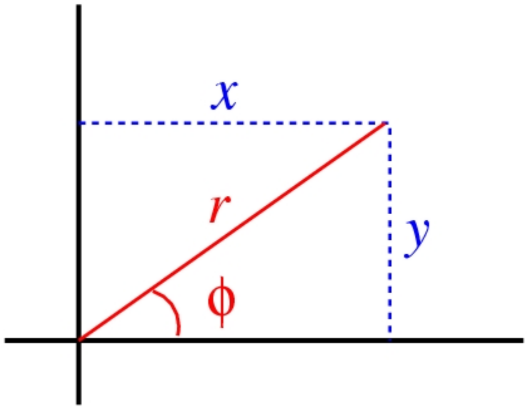
- $\hat{H}_{\text{1D}}(\alpha)\Psi_{\text{1D}}(\alpha) = E_{\text{1D}}\Psi_{\text{1D}}(\alpha)$ $(\alpha = x,y,z)$
- $E_{\text{3D}} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2} \quad n_x, n_y, n_z = 1, 2, \ldots$



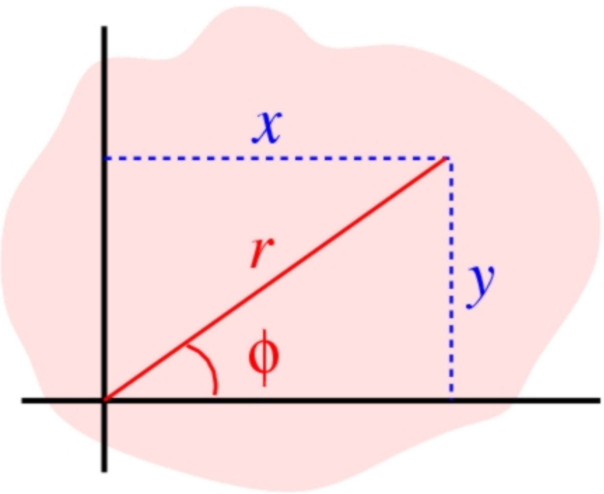
- Cartesian coord. (x, y)

$$x^2 + y^2 = R^2$$

- Polar coord. (r, ϕ)



II.A. Model: polar coordinates



- Transformations

$$r = \sqrt{x^2 + y^2} \quad \phi = \arctan\left(\frac{y}{x}\right)$$

$$y = r\,\mathrm{sen}\,\phi \qquad x = r\cos\phi$$

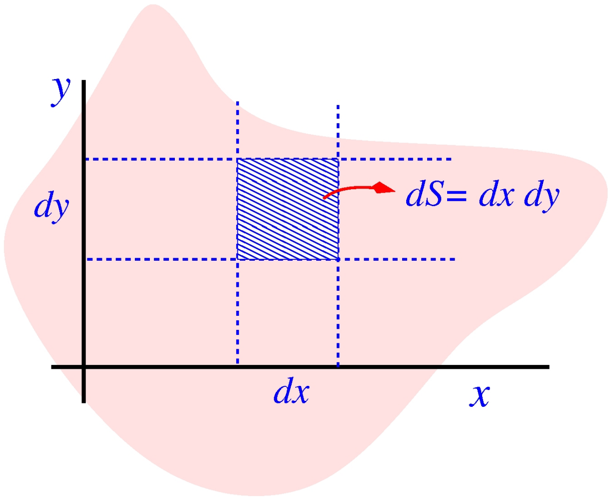
- Intervals

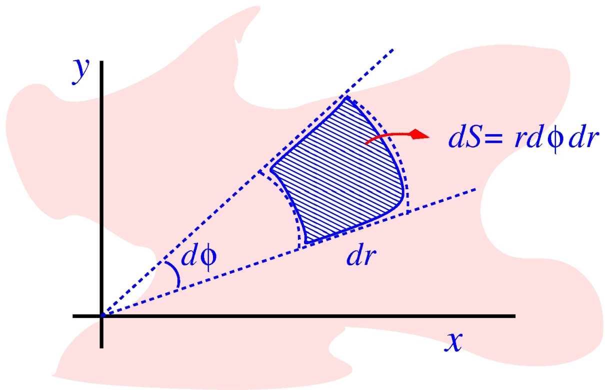
$$r \in [0, +\infty)$$

$$\phi \in [0, 2\pi)$$

II.A. Model: polar coordinates

- Differential element of surface $\Rightarrow dx\,dy = r\,dr\,d\phi$





$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} f(x,y)\,dx\,dy = \int_{0}^{+\infty}\int_{0}^{2\pi} f(r,\phi)\,r\,dr\,d\phi$$

- Hamiltonian in polar coordinates

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

$$\hat{H}(r,\phi) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right)$$

$$\hat{H}(\phi) = -\frac{\hbar^2}{2\underbrace{mR^2}_{I}}\frac{\partial^2}{\partial \phi^2}$$

- Schrödinger's equation

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

- Independent solutions

$$\psi_1(\phi) = e^{k\phi} \qquad \psi_2(\phi) = e^{-k\phi}$$

$$\frac{\partial^2\psi_1}{\partial\phi^2} = k^2\psi_1 \qquad \frac{\partial^2\psi_2}{\partial\phi^2} = k^2\psi_2$$

$$k = \sqrt{\frac{2IE}{\hbar^2}}\, i$$

$$\psi(\phi) = A\,e^{im\phi} + B\,e^{-im\phi} \qquad m = \sqrt{\frac{2IE}{\hbar^2}}$$

II.B. Eigenfunctions and eigenvalues: degeneracy

- Single valued function $\Rightarrow \psi(\phi) = \psi(\phi + 2\pi)$

$$A\,e^{im\phi} + B\,e^{-im\phi} = A\,e^{im(\phi+2\pi)} + B\,e^{-im(\phi+2\pi)}$$

$$A\,e^{im\phi}\left(1 - e^{2\pi m i}\right) + B\,e^{-m\phi i}\left(1 - e^{-2\pi m i}\right) = 0$$

$$\Rightarrow\; 1 - e^{-2\pi m i} = e^{-2\pi m i}\left(e^{2\pi m i} - 1\right) = -e^{-2\pi m i}\left(1 - e^{2\pi m i}\right)$$

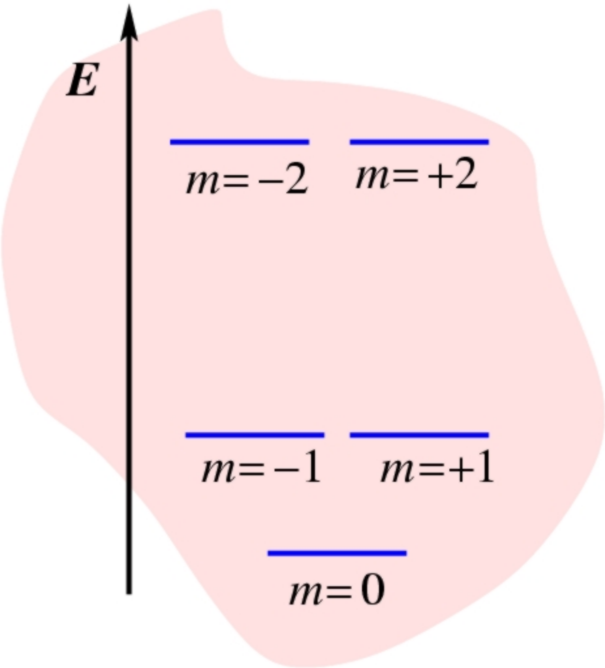
$$A\,e^{im\phi}\left(1 - e^{2\pi m i}\right) - B\,e^{-im\phi}e^{-2\pi m i}\left(1 - e^{2\pi m i}\right) = 0$$

$$\underbrace{\left(1 - e^{2\pi m i}\right)}_{0}\left(A\,e^{im\phi} - B\,e^{-im\phi}e^{-2\pi m i}\right) = 0$$

$$\cos(2m\pi) + i\,\mathrm{sen}(2m\pi) = 1 \Rightarrow\; m = 0, \pm 1, \pm 2, \ldots$$

II.B. Eigenfunctions and eigenvalues: degeneracy

- Energy quantization $\Rightarrow E_m = \frac{\hbar^2 m^2}{2I}$



- Degeneracy

$$E_{-1} = E_1$$

$$E_{-2} = E_2$$

$$\ldots\ldots$$

II.C. Angular momentum

- Angular momentum operator $\Rightarrow$ If particle moves in the xy plane then $L = l_z$

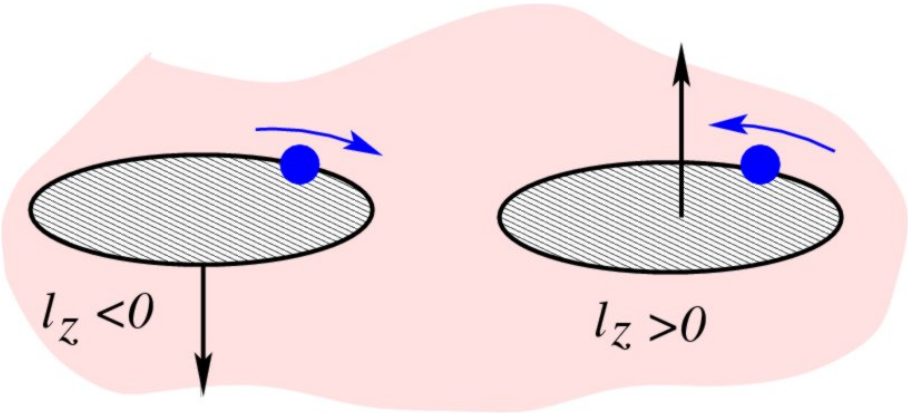
$$l_z = x p_y - y p_x \rightarrow \hat{l}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = \rightarrow \hat{l}_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$$

- Eigenfunctions and eigenvalues

$$\hat{l}_z \psi(\phi) = \frac{\hbar}{i}\frac{\partial}{\partial \phi}\left(A\, e^{im\phi} + B\, e^{-im\phi}\right) = m\hbar\left(A\, e^{im\phi} - B\, e^{-im\phi}\right)$$
$$= l_z\left(A\, e^{im\phi} + B\, e^{-im\phi}\right)$$

$$B = 0 \Rightarrow l_z = m\hbar$$

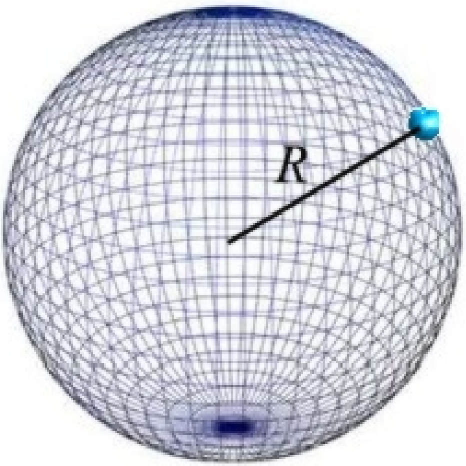
$$\psi(\phi) = A\, e^{im\phi} \qquad m = 0, \pm 1, \pm 2 \ldots$$



- Normalization $\Rightarrow \int_0^{2\pi} |\psi(\phi)|^2 d\phi = 1 \Rightarrow |A| = \frac{1}{\sqrt{2\pi}}$

- Probability density $\Rightarrow \psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \Rightarrow |\psi(\phi)|^2 = \frac{1}{2\pi}$

III.A. Model



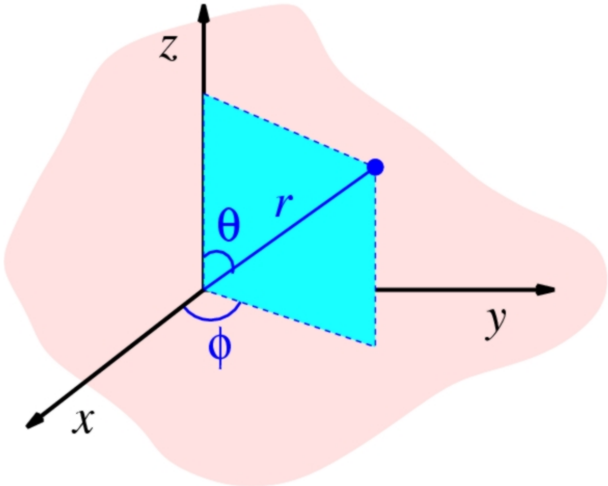
- Free motion on the surface

$$V(x, y, z) = 0$$

- Simple atomic model
- Cartesian coordinates

$$x^2 + y^2 + z^2 = R^2$$

III.A. Model: Spherical polar coordinates



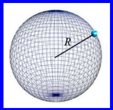
- Spherical polar coordinates

$$x = r\,\mathrm{sen}\,\theta\,\cos\phi$$
$$y = r\,\mathrm{sen}\,\theta\,\mathrm{sen}\,\phi$$
$$z = r\cos\theta$$

- Intervals $r \in [0,\infty)$, $\phi \in [0,2\pi)$, $\theta \in [0,\pi)$

- Differential element of volume $\Rightarrow d\tau = r^2\,\mathrm{sen}\,\theta\,dr\,d\theta\,d\phi$

$$\iiint_{-\infty}^{+\infty} f(x,y,z)\,dx\,dy\,dz = \int_0^{+\infty}\int_0^{\pi}\int_0^{2\pi} f(r,\theta,\phi)\,r^2\,\mathrm{sen}\,\theta\,dr\,d\theta\,d\phi$$



III.B. Energy and angular momentum

- Angular momentum

$$\hat{L}^2(\theta,\phi) = -\hbar^2\left(\frac{1}{\operatorname{sen}^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\operatorname{sen}\theta}\frac{\partial}{\partial\theta}\operatorname{sen}\theta\frac{\partial}{\partial\theta}\right)$$

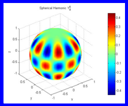
$$\hat{L}^2 Y_l^m(\theta,\phi) = L^2 Y_l^m(\theta,\phi) \rightarrow\ L^2 = l(l+1)\hbar^2 \rightarrow\ l = 0,1,2,\ldots$$

- Energy $\Rightarrow \hat{H} = \frac{\hat{L}^2}{2\underbrace{mR^2}_{I}} \Rightarrow E = l(l+1)\frac{\hbar^2}{2I}$

- z component angular momentum

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi} \rightarrow\ \hat{L}_z Y_l^m(\theta,\phi) = L_z Y_l^m(\theta,\phi)$$

$$L_z = m\hbar \qquad m = -l, -l+1, \ldots, 0, \ldots, l-1, l$$



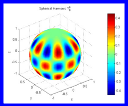
III.C. Spherical Harmonics

- Spherical Harmonics $\Rightarrow Y_l^m(\theta,\phi) = \Theta_{l,m}(\theta)\Phi_m(\phi)$

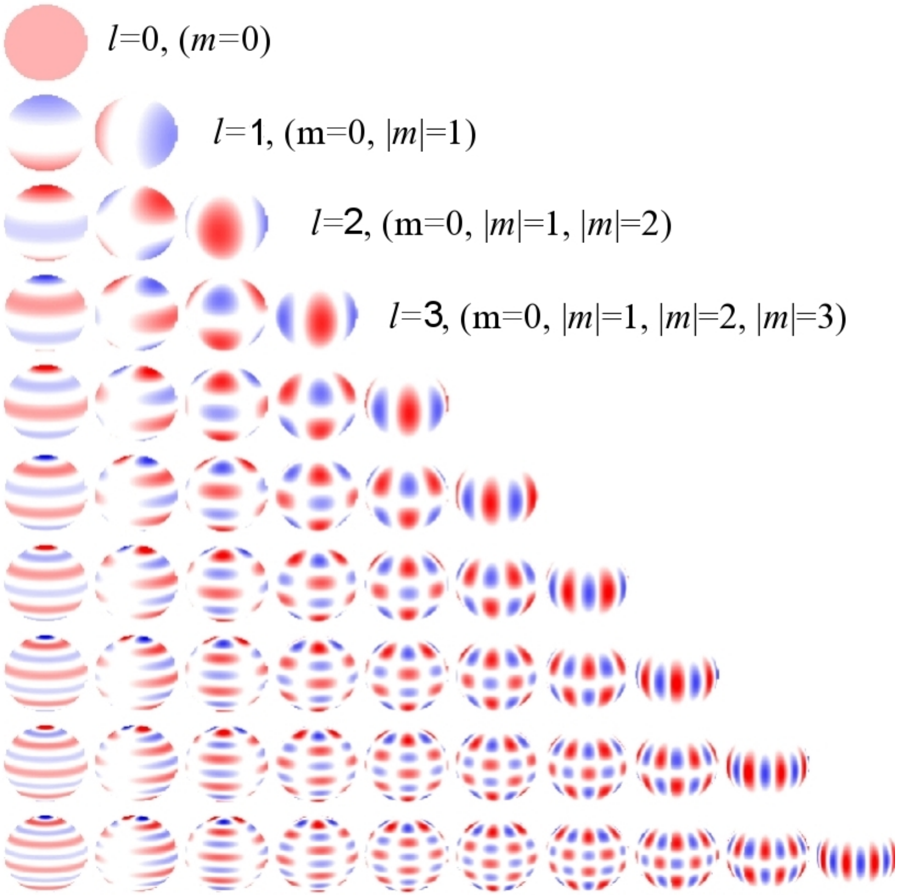
$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$\Theta_{l,m}(\theta) \Rightarrow$ Associated Legendre's functions

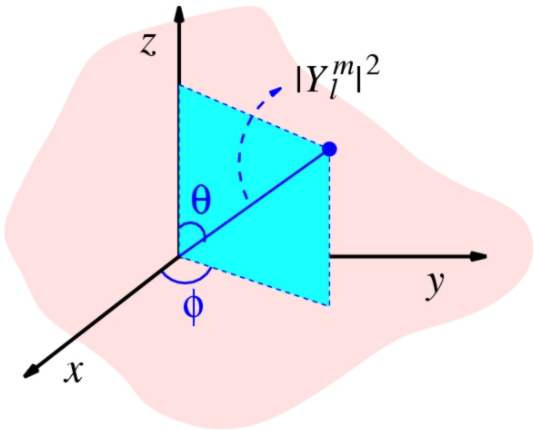
l	m	$Y_l^m(\theta,\phi)$
0	0	$1/\sqrt{4\pi}$
1	0	$\sqrt{3/4\pi}\cos\theta$
	± 1	$\pm\sqrt{3/8\pi}\,\mathrm{sen}\,\theta\, e^{\pm i\phi}$

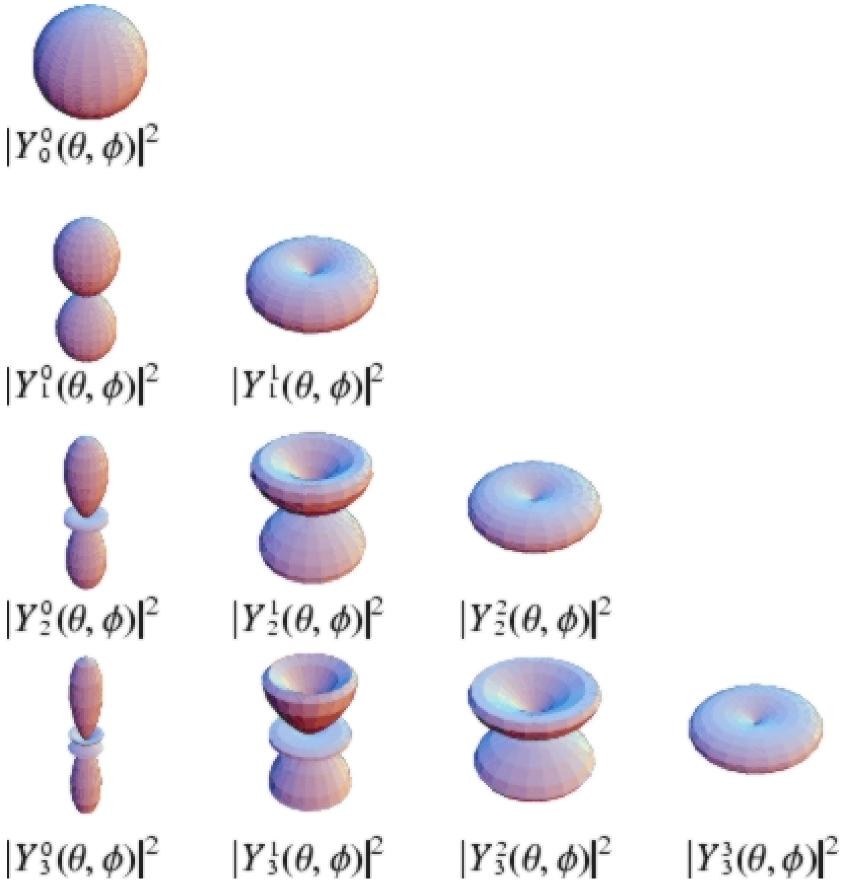


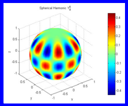
III.C. Spherical Harmonics: Probability density



III.C. Spherical Harmonics: polar representations







III.C. Spherical Harmonics: notation

l	Symbol	
0	s	sharp
1	p	principal
2	d	diffuse
3	f	fundamental
4	g	alphabetical order
$\vdots$	$\vdots$	$\vdots$

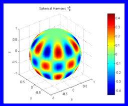
$m \Rightarrow$ subscript if $l \neq 0$

- Examples

$$Y_0^0 \to s \qquad Y_1^0 \to p_0$$

$$Y_1^1 \to p_1 \qquad Y_1^{-1} \to p_{-1}$$

$$Y_2^0 \to d_0 \qquad Y_2^2 \to d_2$$



III.C. Spherical Harmonics: ¿$\hat{L}_x, \hat{L}_y$?

- $[\hat{L}_x, \hat{L}_z] \neq 0$, $[\hat{L}_y, \hat{L}_z] \neq 0$