Quantum Mechanics in 3D and the Hydrogen atom

vrije Universiteit *amsterdam*

Quantum Mechanics in 3D and the Hydrogen atom

- The Schrödinger equation in 2D
- Particle in a 2D box
  - Quantum numbers
  - Degeneracy
  - Splitting of energy levels
- Particle in a 3D box (cube)
- Simple treatment of the H atom

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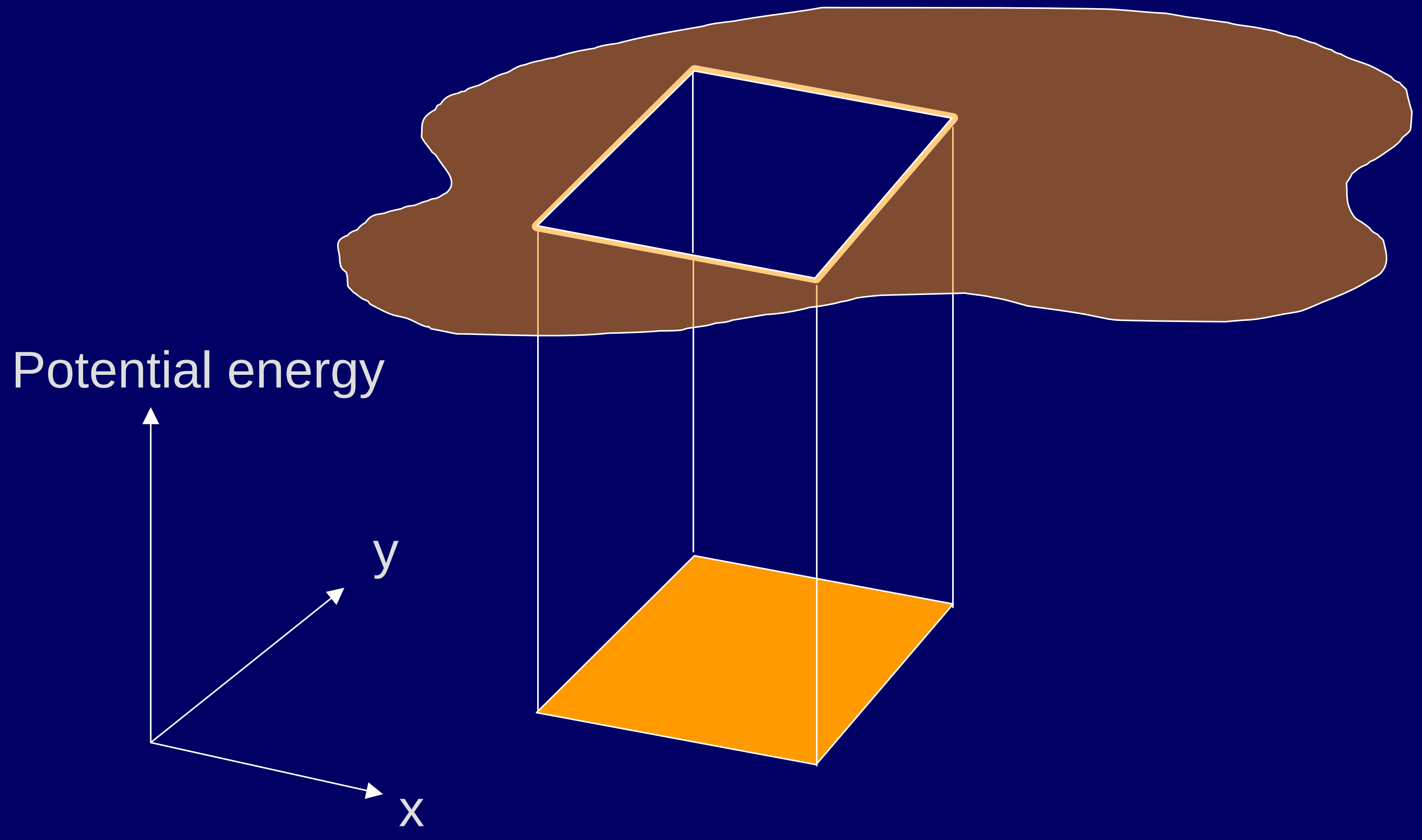
2D infinite well



Separation of x- and y-variable when U=0

We look for a solution of

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}-\frac{\hbar^2}{2m}\frac{d^2\psi}{dy^2}=E\psi$$

in the form $\psi(x,y)=X(x)Y(y)$

We find $\psi(x,y)=A\sin\left(\frac{n_1\pi}{L}x\right)\sin\left(\frac{n_2\pi}{L}y\right)$

and

$$E=\frac{\hbar^2\pi^2}{2mL^2}\left(n_1^2+n_2^2\right)$$

Solutions

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = E_1 X$$

$$-\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2} = E_2 Y$$

$$X \propto \sin\left(\frac{n_1\pi}{L}x\right)$$

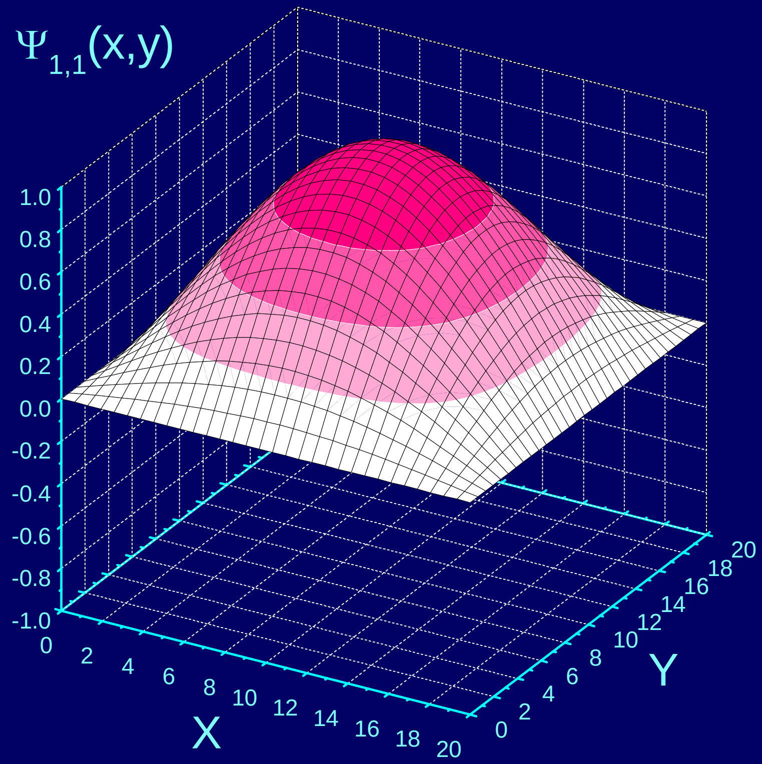
$$Y \propto \sin\left(\frac{n_2\pi}{L}y\right)$$

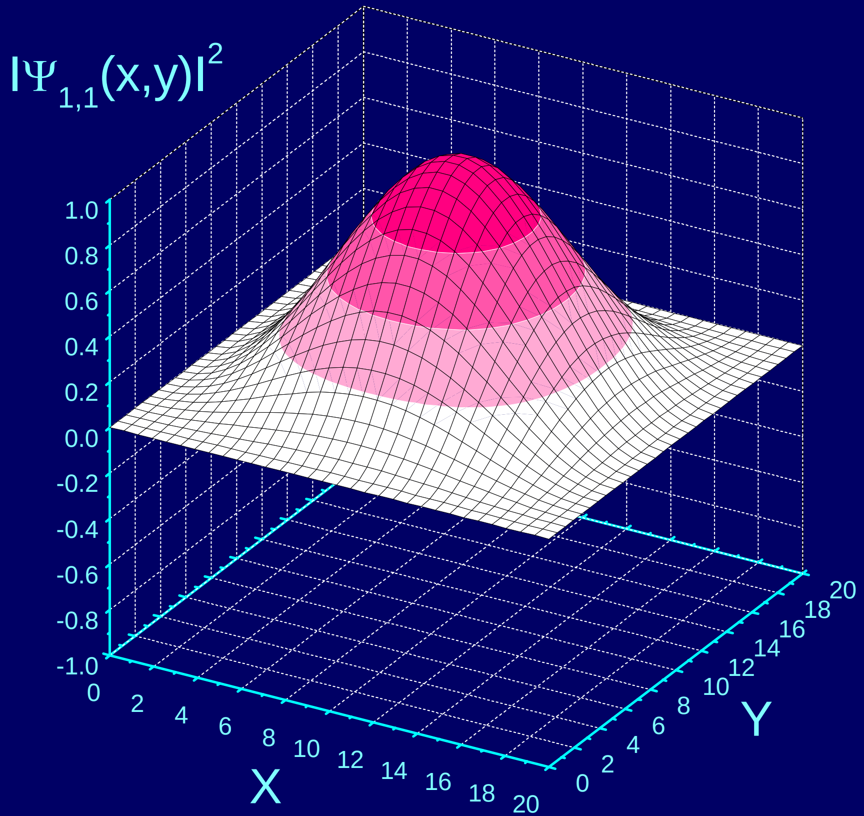
$$E_1 = \frac{\hbar^2\pi^2}{2mL^2}n_1^2$$

$$E_2 = \frac{\hbar^2\pi^2}{2mL^2}n_2^2$$

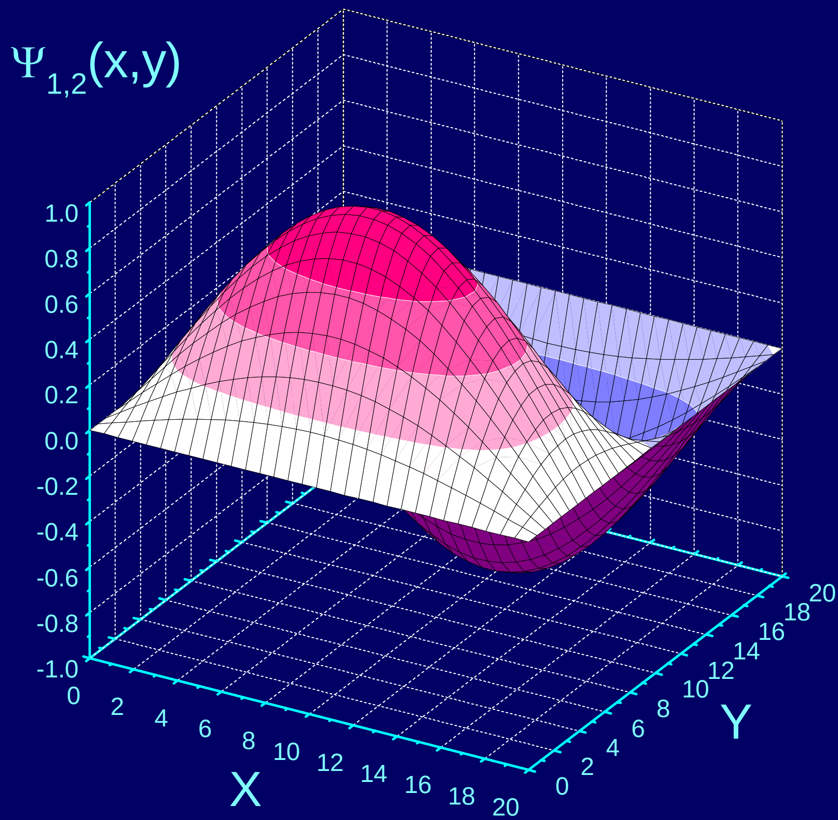
$$E = E_1 + E_2 = \frac{\hbar^2\pi^2}{2mL^2}\left(n_1^2 + n_2^2\right)$$

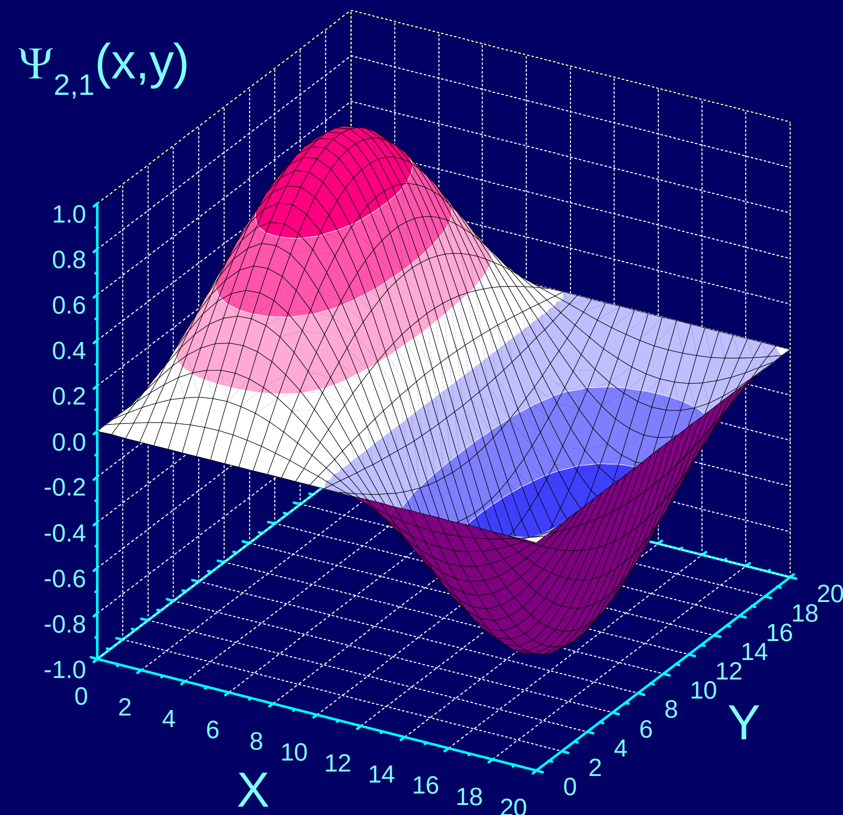
The ground state (1,1)



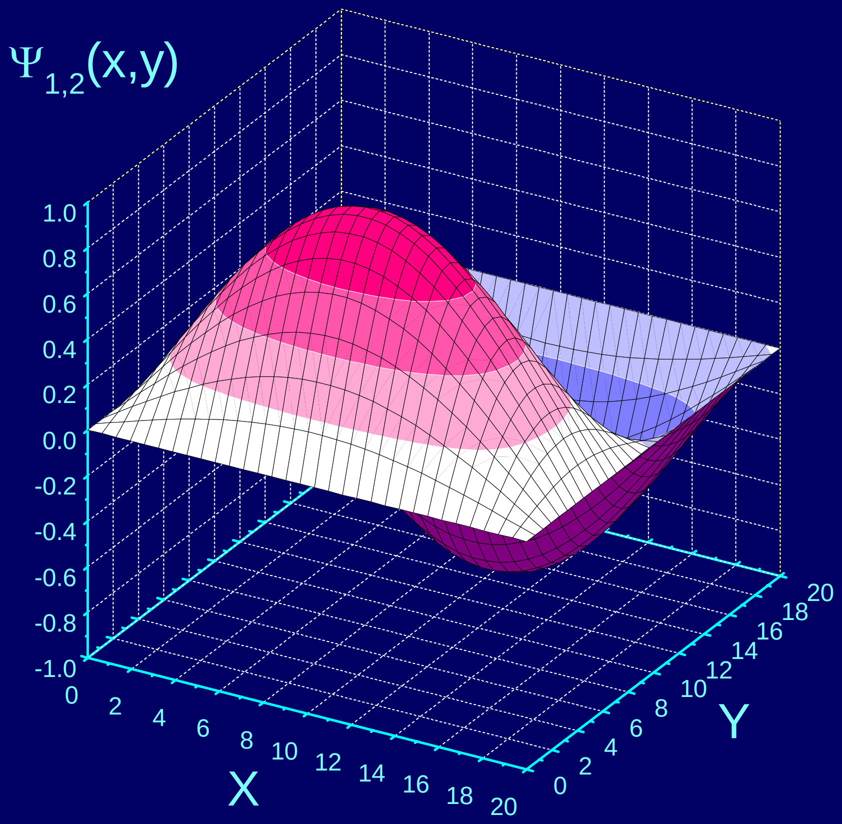


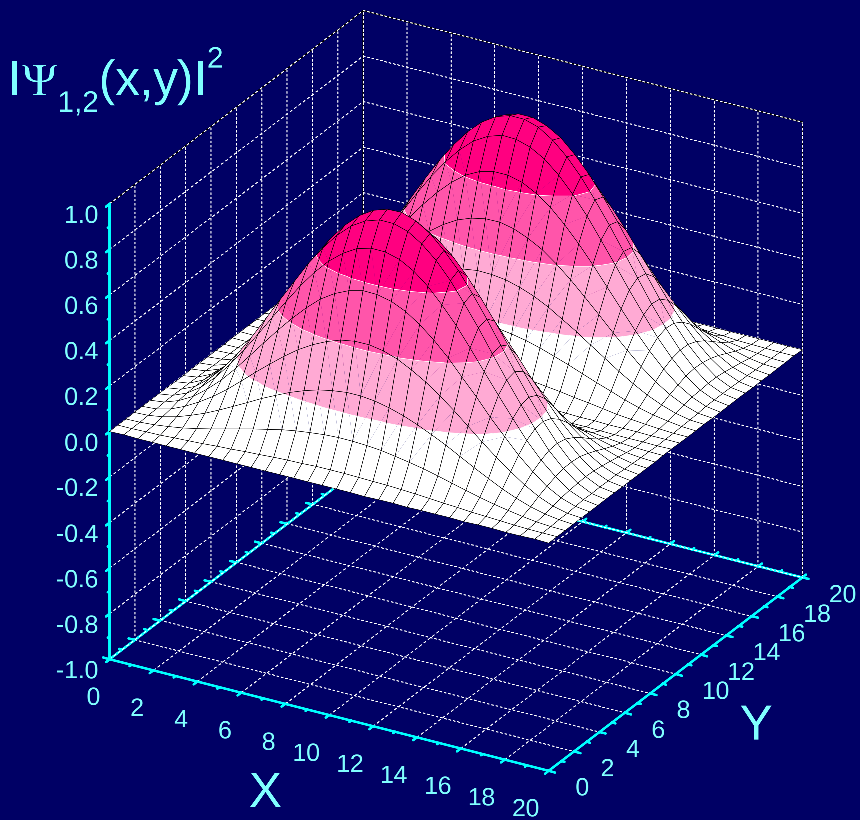
Degenerate first excited states (1,2) and (2,1)



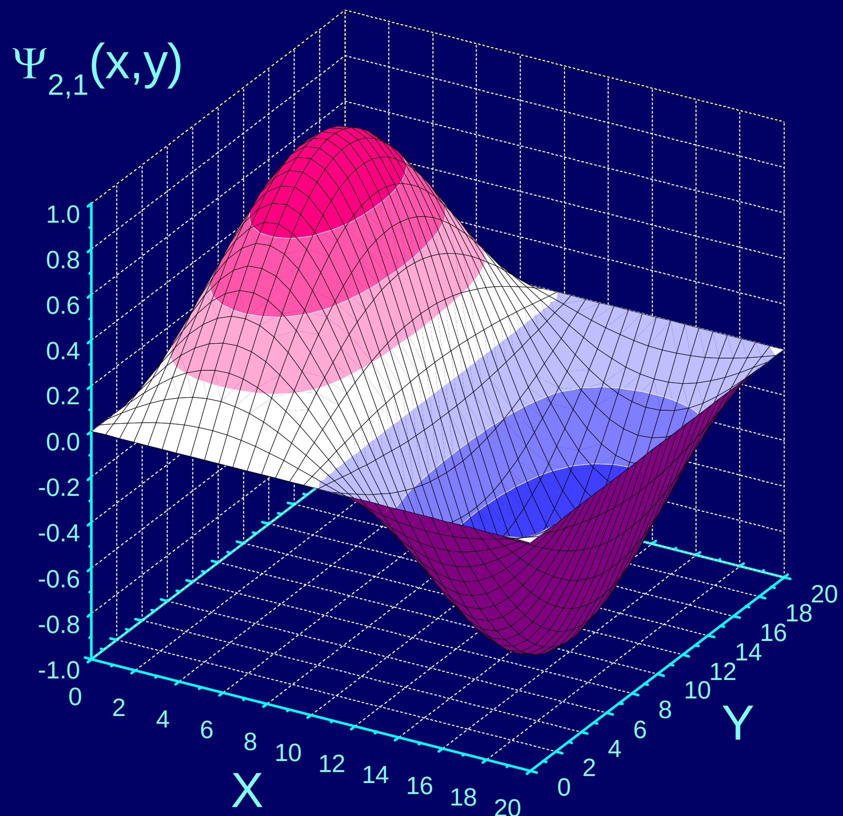


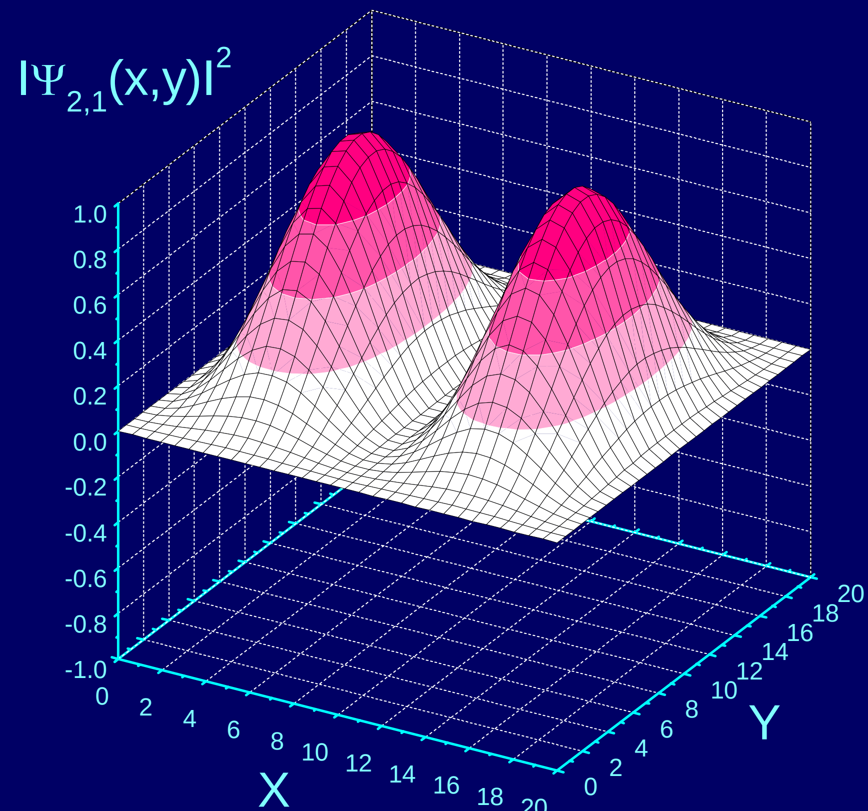
Wave function and probability density (1,2)



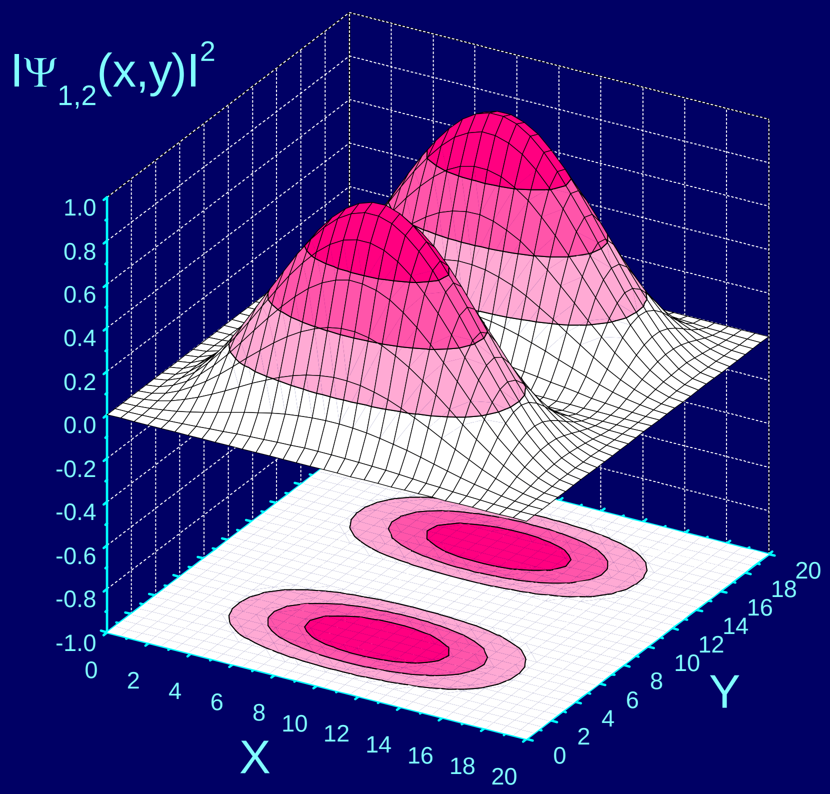


Wave function and probability density for (2,1)

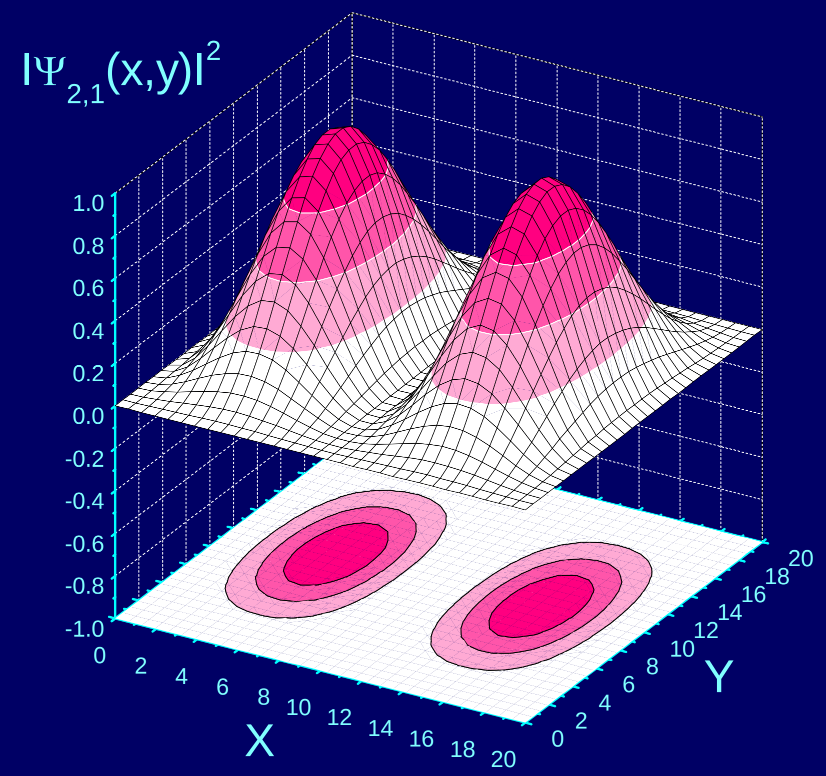




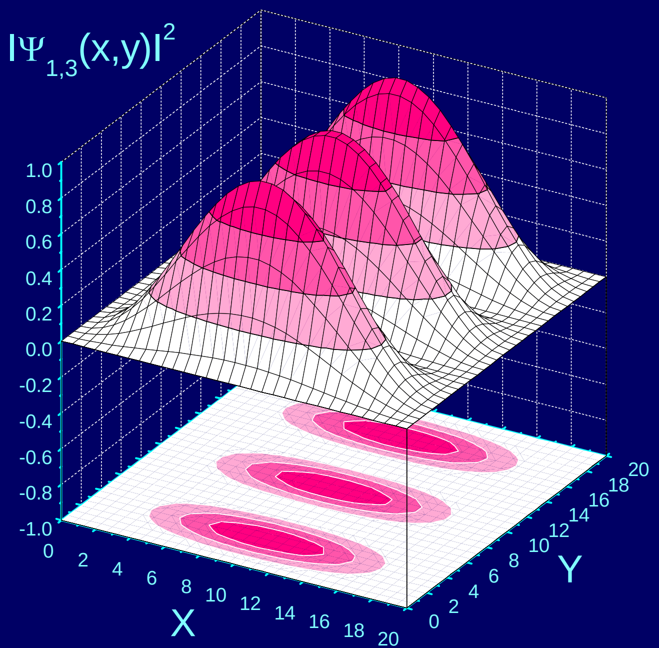
Wave function and probability densities for (1,2) and (2,1)

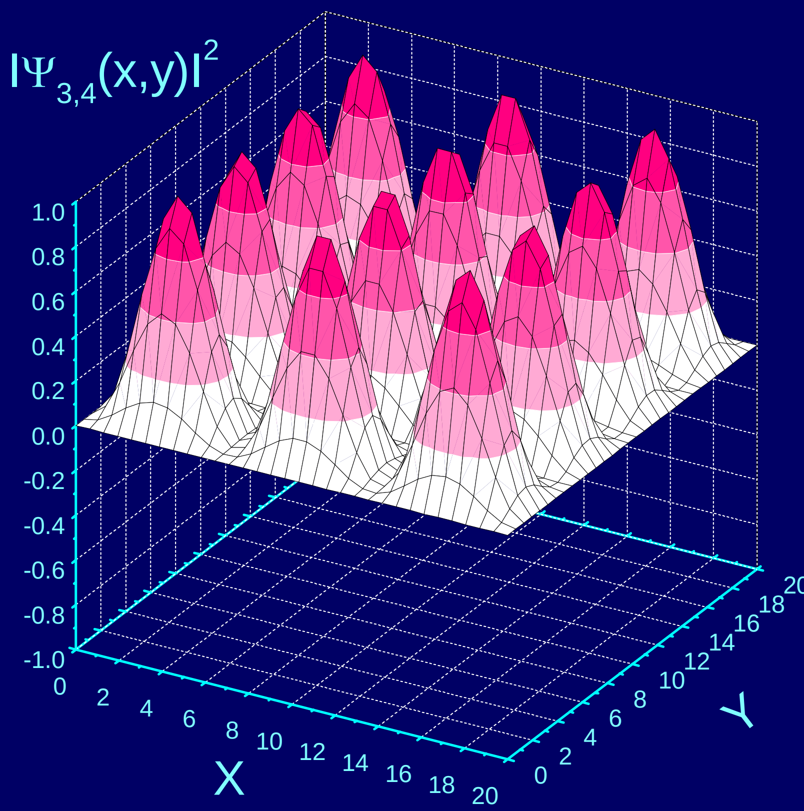


Degenerate states

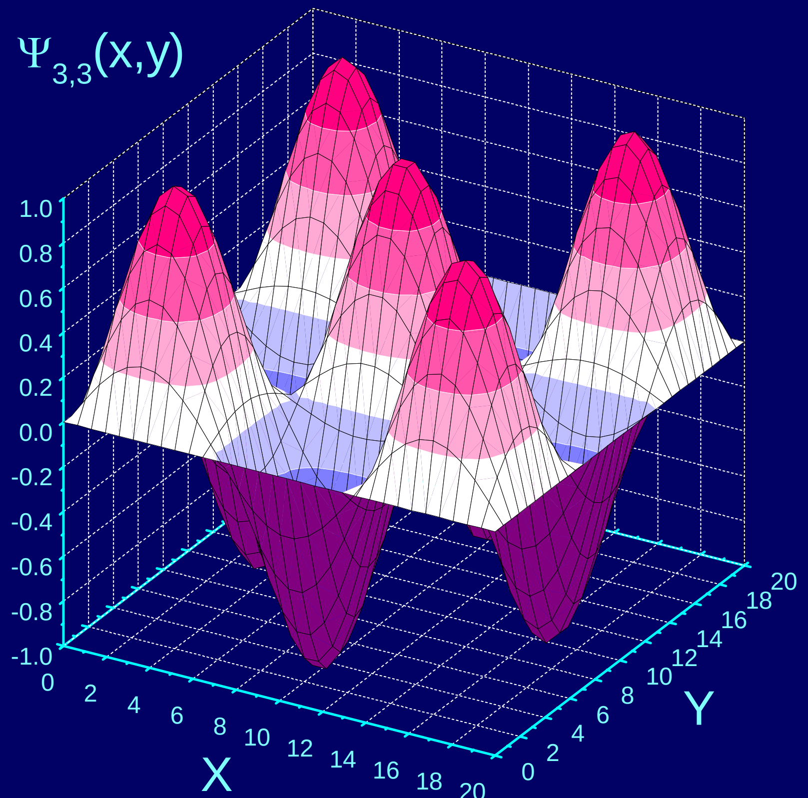


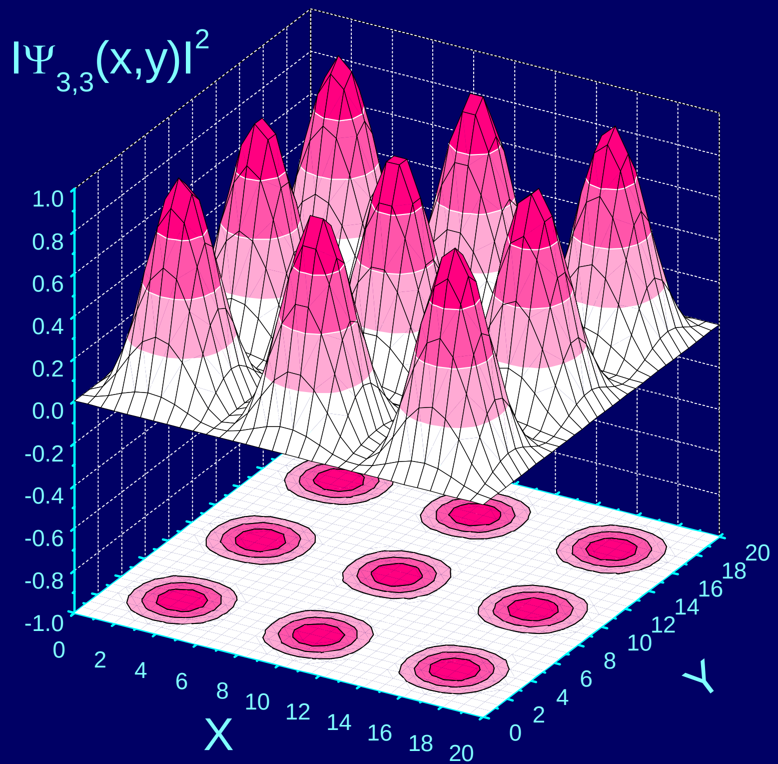
Probability density for (1,3) and (3,4) states

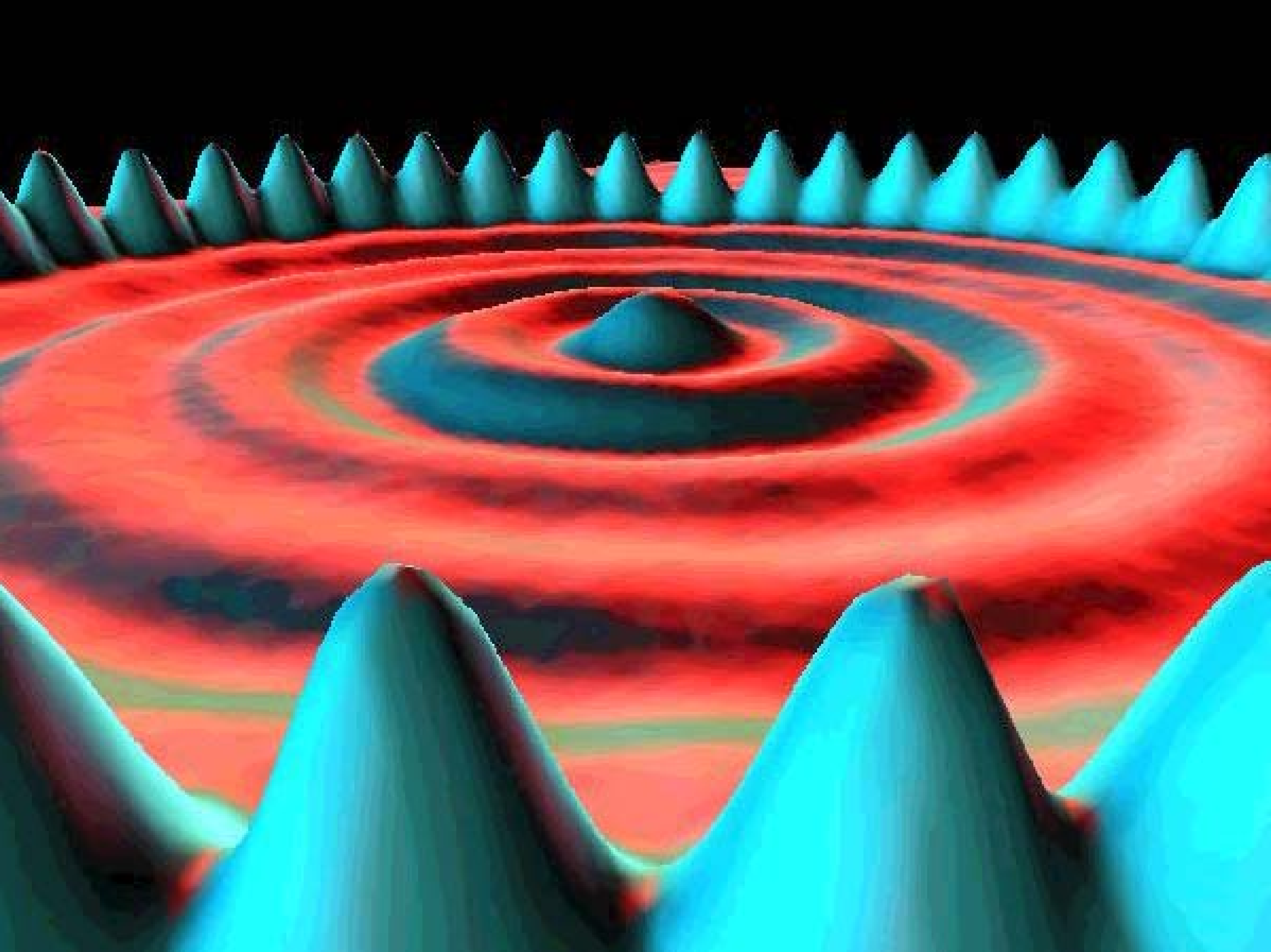




Wave function and probability density for (3,3)







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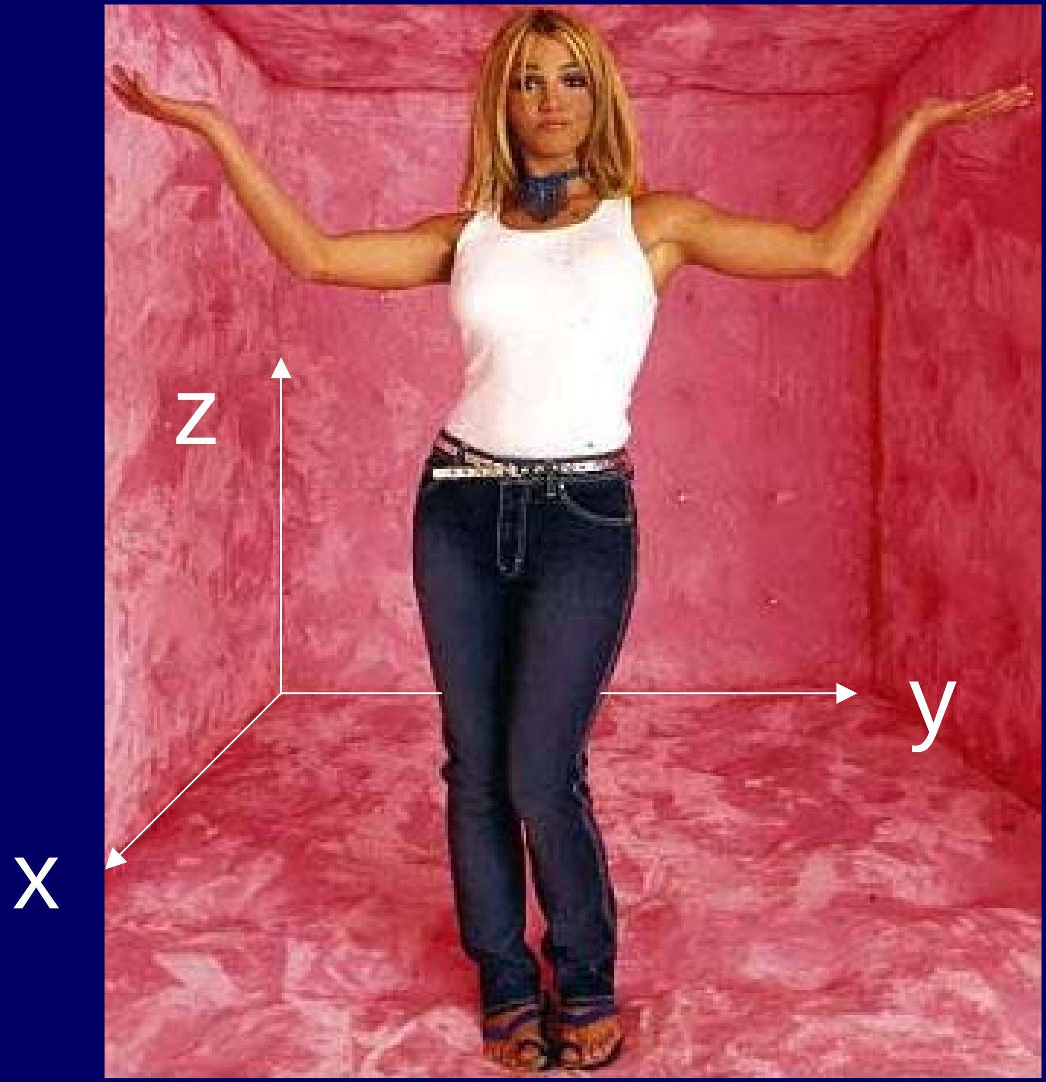
Particle in a 3D-box



http://britneyspears.ac/physics/fbarr/fbarr.html

How do we go to 3 dimensions ?

- In 3D we have kinetic energy for movements along x, y and z

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial y^2}-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial z^2}+U(x,y,z)\psi=E\psi$$

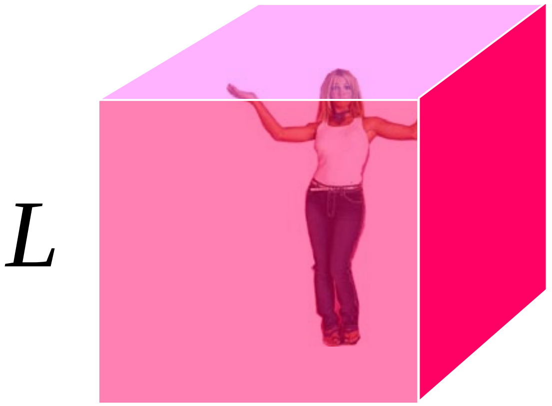
- Solutions are of the form

$$\psi(x,y,z)=X\left(x\right)Y\left(y\right)Z(z)$$

Solutions for U(x,y,z)=0

$$\psi_{n_1,n_2,n_3}(x,y,z) = A\sin\left(\frac{n_1\pi}{L}x\right)\sin\left(\frac{n_2\pi}{L}y\right)\sin\left(\frac{n_3\pi}{L}z\right)$$

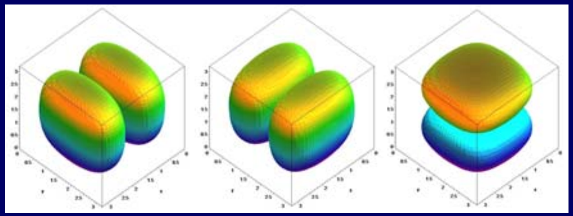
$$E_{n1,n2,n3} = \frac{\hbar^2\pi^2}{2mL^2}\left(n_1^2 + n_2^2 + n_3^2\right)$$

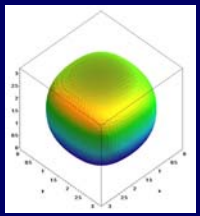


Energy levels and degeneracy

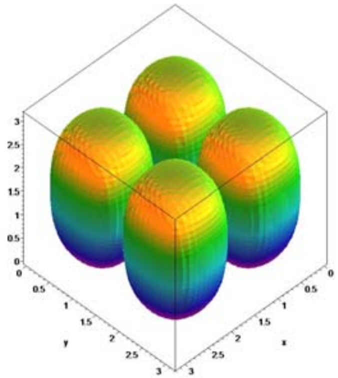
$$E_{n1,n2,n3} = \frac{\hbar^2\pi^2}{2mL^2}\left(n_1^2+n_2^2+n_3^2\right)$$

(1,3,3)	19 eV
(2,2,3)	17 eV
(1,2,3)	14 eV
(2,2,2)	12 eV
(1,1,3)	11 eV
(1,2,2)	9 eV
(1,1,2)	6 eV
(1,1,1)	3 eV
	0

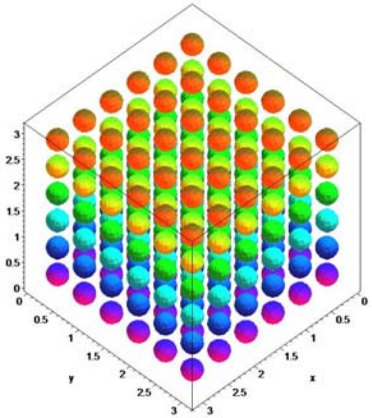




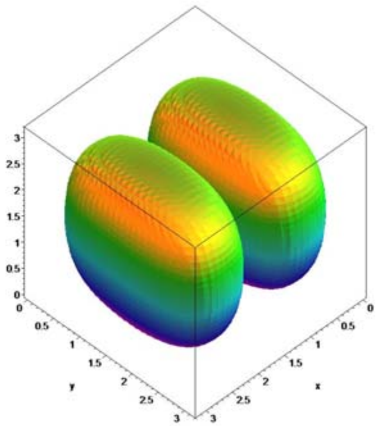
Probability density of states for the infinite 3D potential



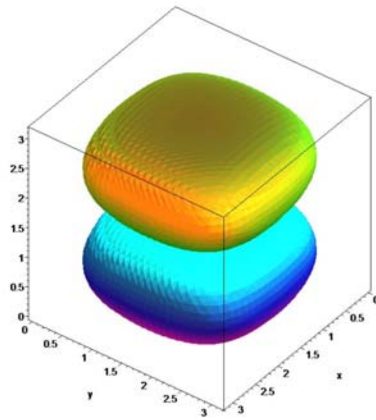
(2,2,1)



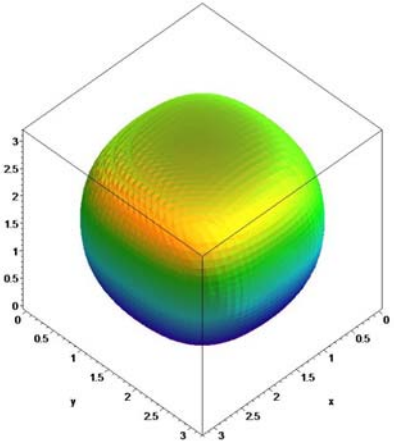
(6,6,6)



(2,1,1)



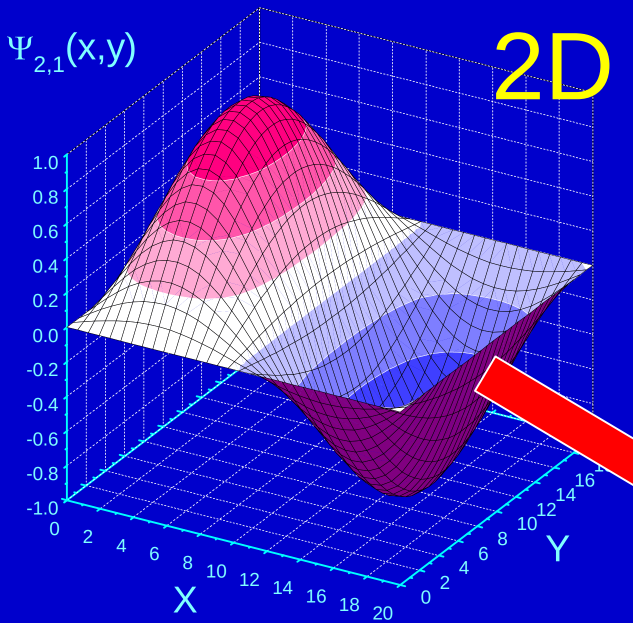
(1,1,2)

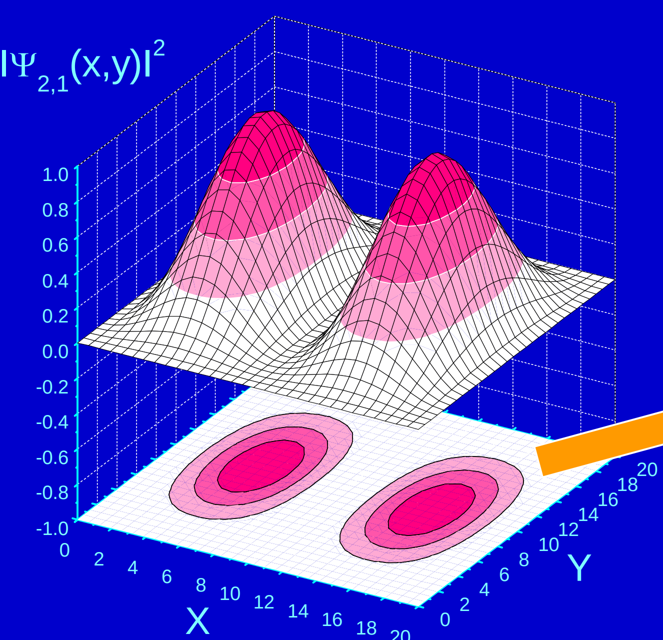


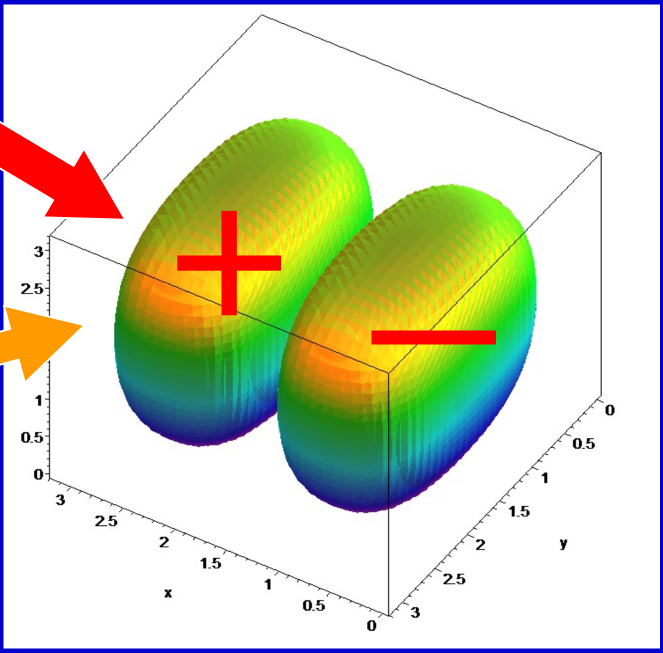
(1,1,1)

3D-Infinite potential well (2,1,1)

2D



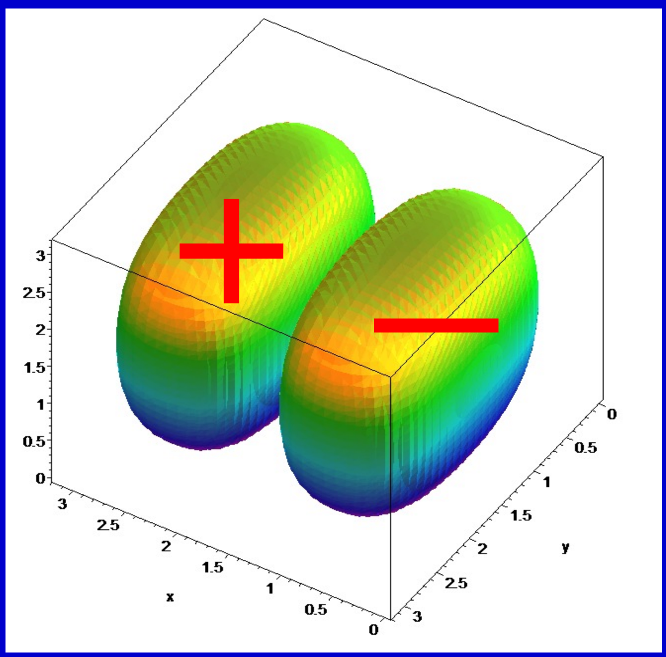


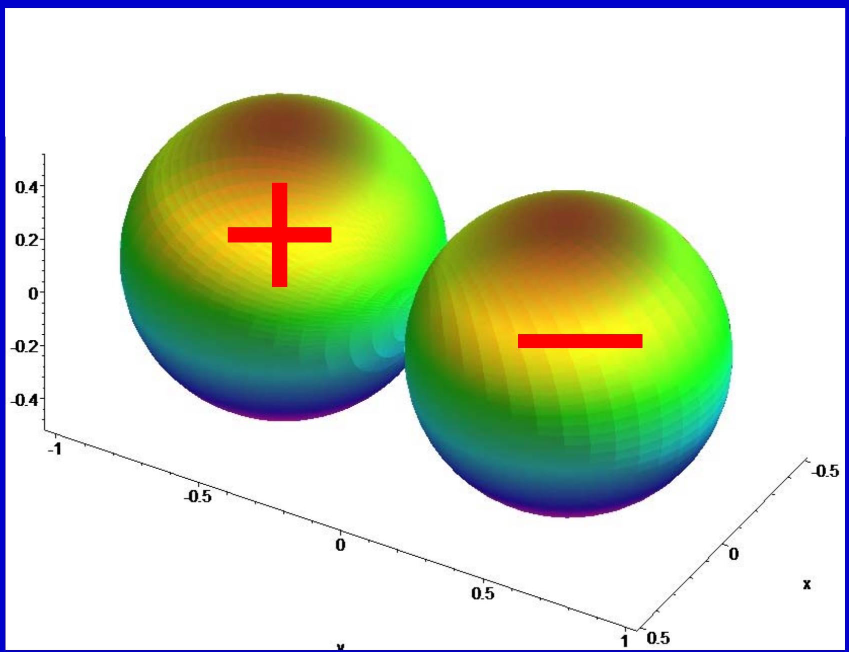


Comparison 3D-well & H-atom

3D-Infinite potential well (2,1,1)

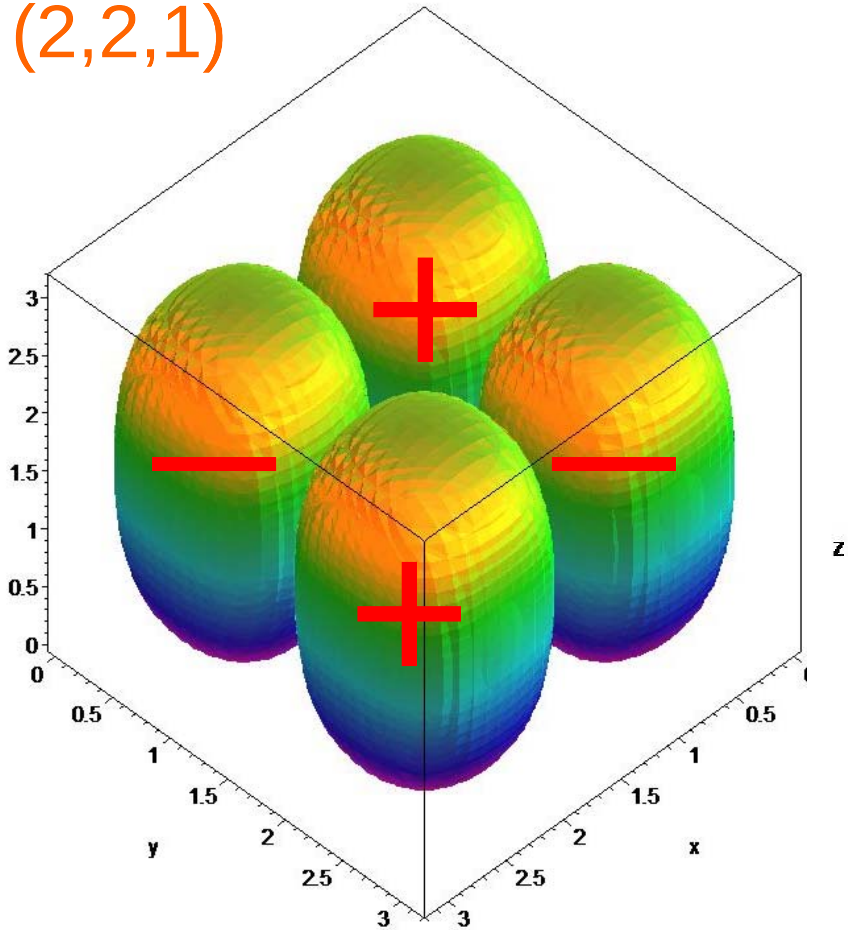
$2p_y$-states in hydrogen atom



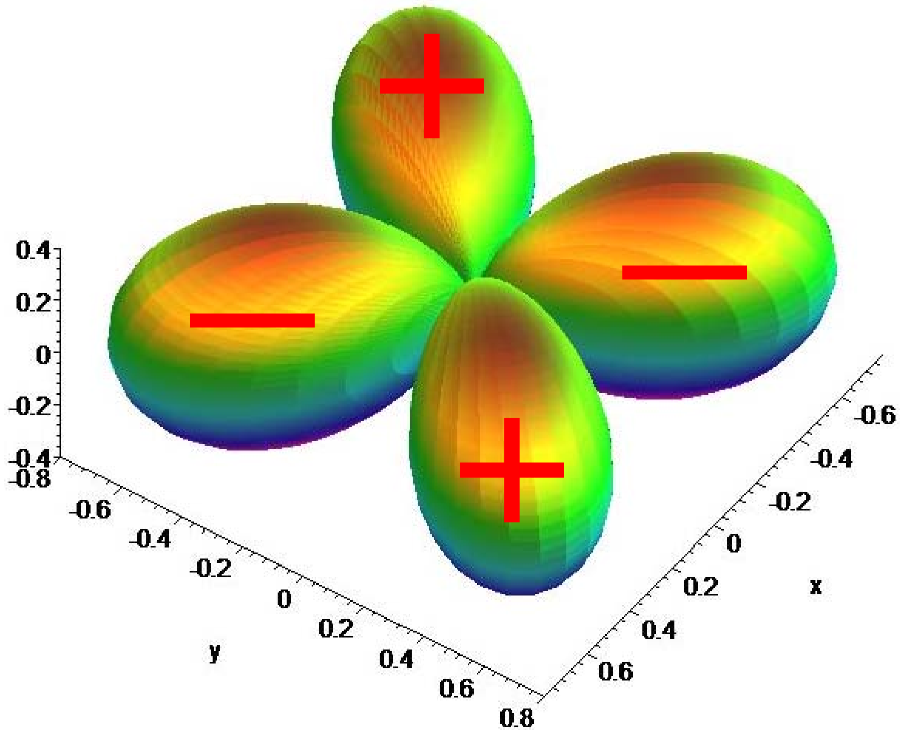


Similarity between (2,2,1) and (n=3, l =2, m=1)

3D-Infinite potential well (2,2,1)

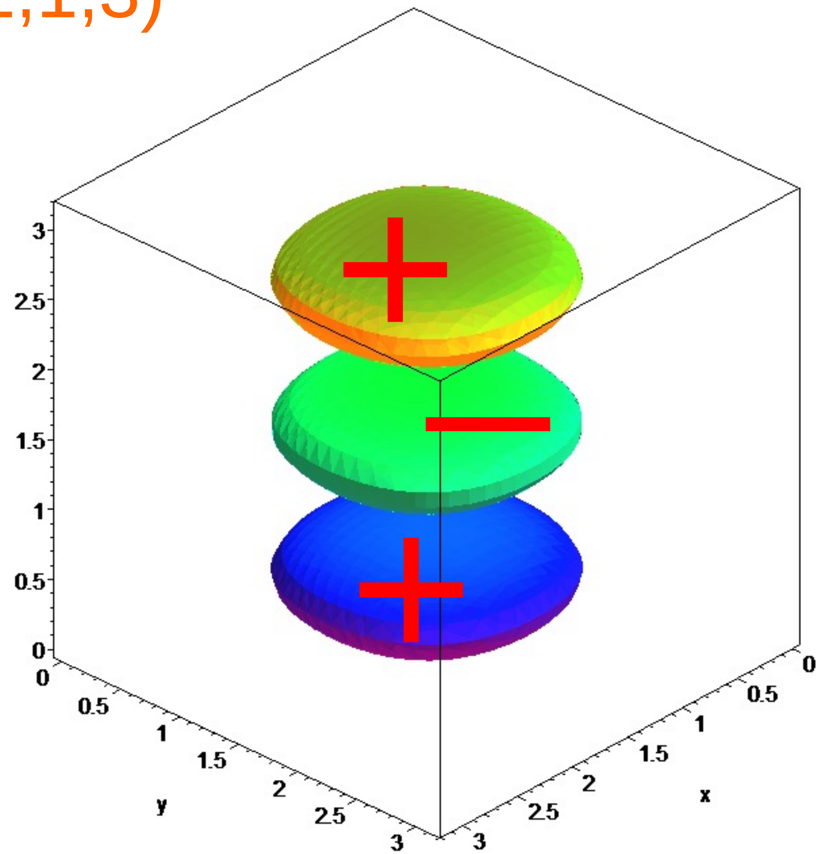


$3d_{xy}$-states in hydrogen atom

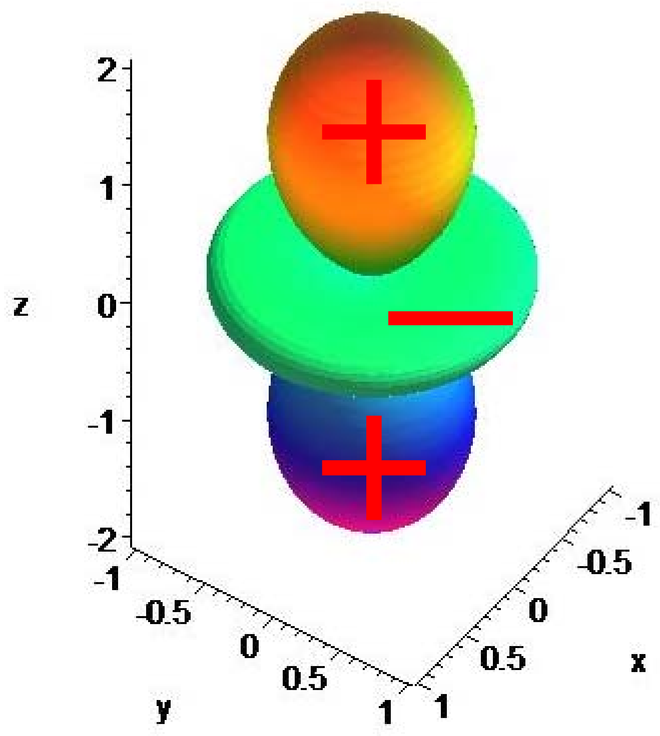


Similarity between (1,1,3) and (n=3, l =2 , m=0)

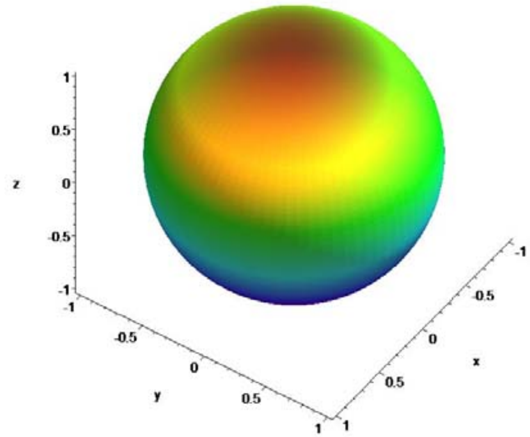
3D-Infinite potential well (1,1,3)

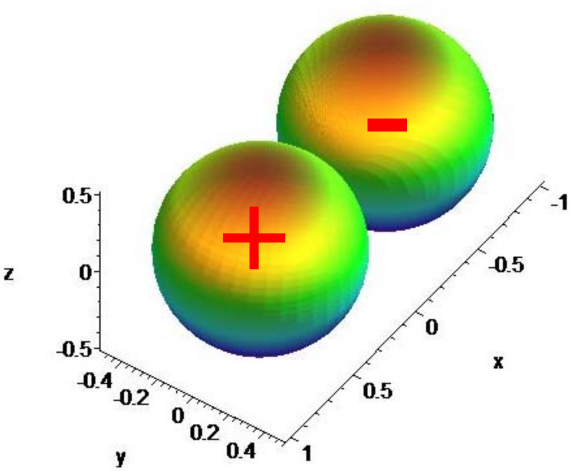


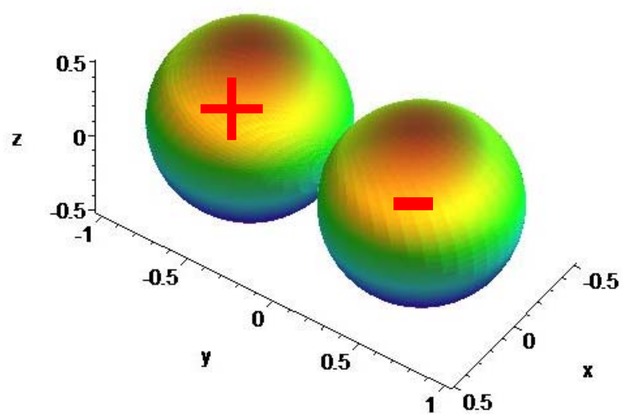
$3d_{3z^2-r^2}$-states in hydrogen atom

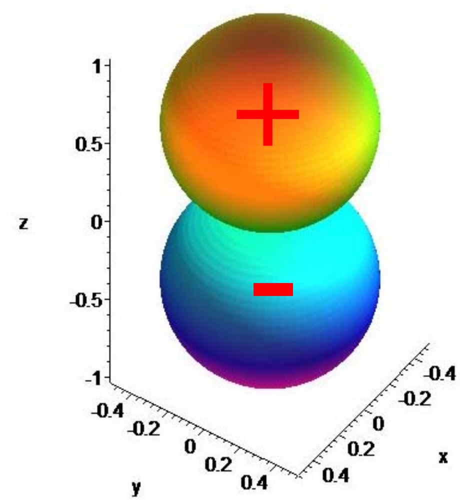


The s-wave (l =0) and p-waves (l =1) of the H-atom

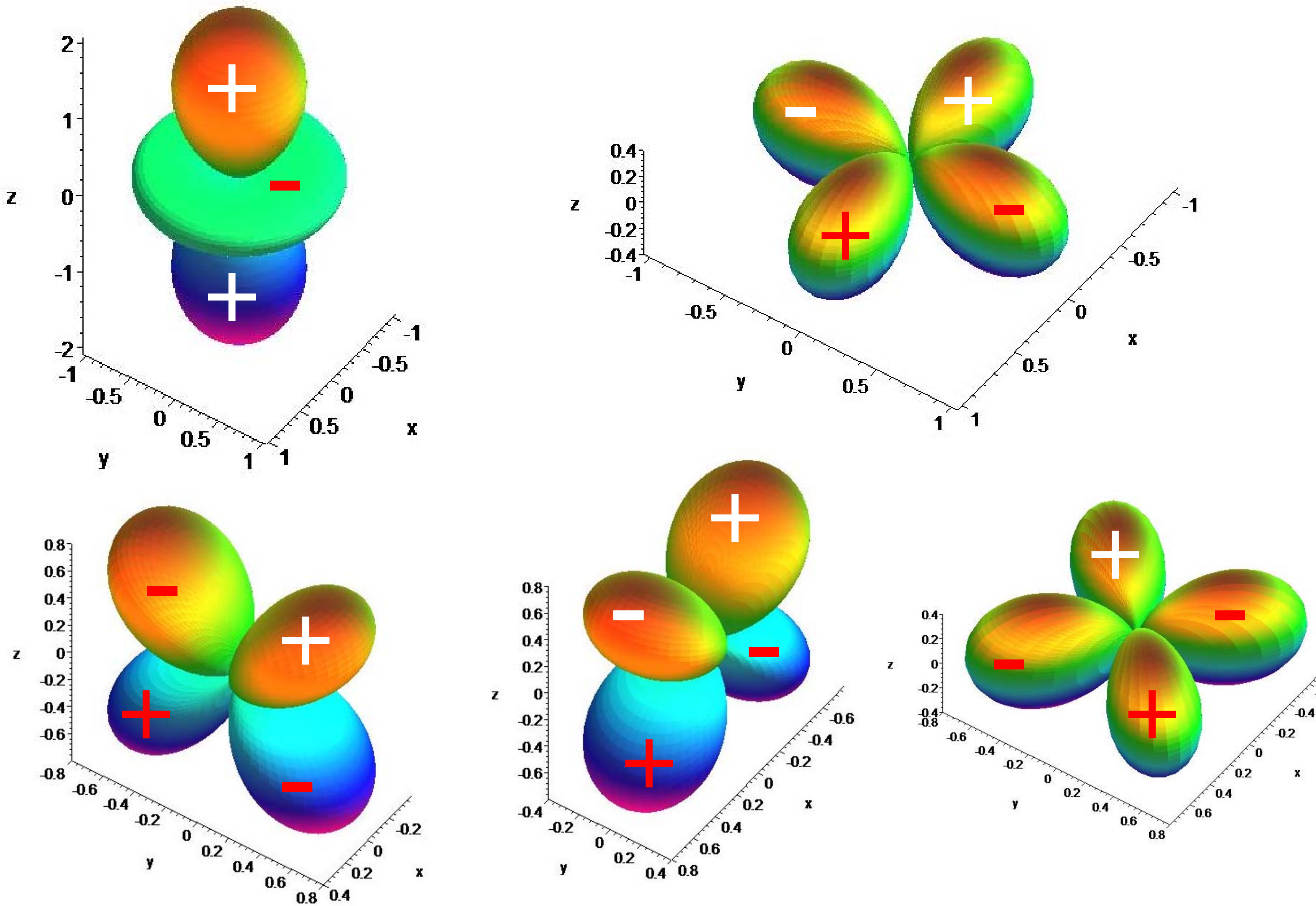








The d-waves (l =2) of the H atom



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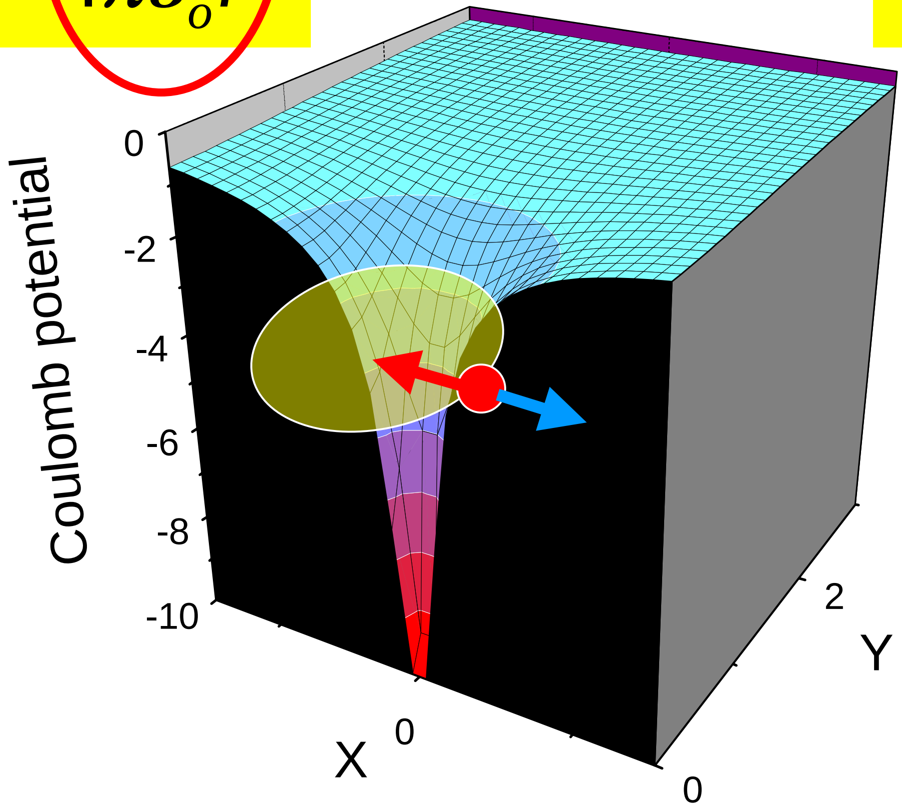
- Particle in a 3D box (cube)
- Simple treatment of the H atom: the energy levels

Centrifugal force=Coulomb attraction

We start classically

$$m\frac{v^2}{r} = \frac{e^2}{4\pi\varepsilon_o r^2}$$

$$E = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_o r}$$



$$U(r) = -\frac{e^2}{4\pi\varepsilon_o r}$$

Simple quantum physics

- We start classically

$$m\frac{v^2}{r} = \frac{e^2}{4\pi\varepsilon_o r^2}$$

$$E = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_o r}$$

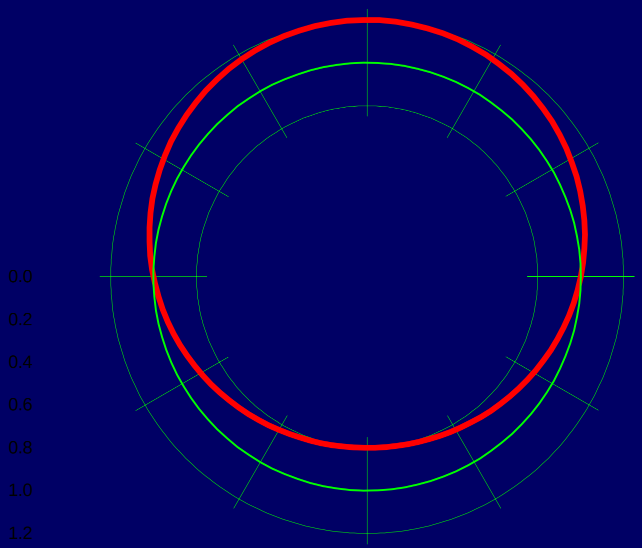
- From these relations follows

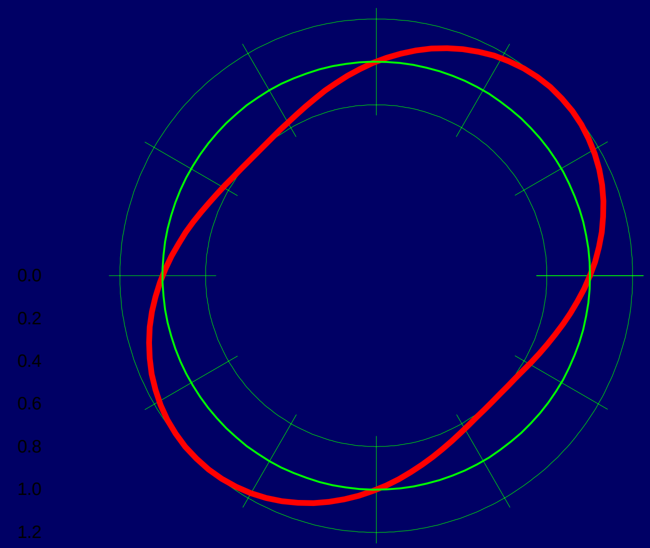
$$\frac{m^2v^2}{m} = \frac{p^2}{m} = \frac{h^2}{m\lambda^2} = \frac{e^2}{4\pi\varepsilon_o r}$$

$$2\pi r = n\lambda$$

Quantum physics

Bohr model of the atom

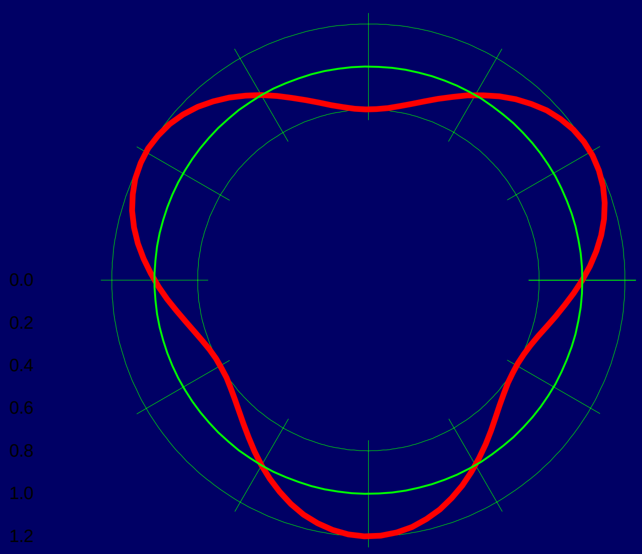


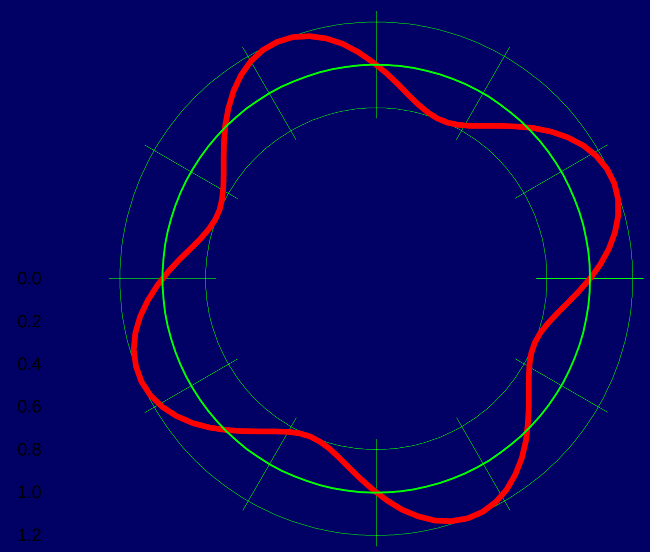


n=1

n=2

Bohr model of the atom

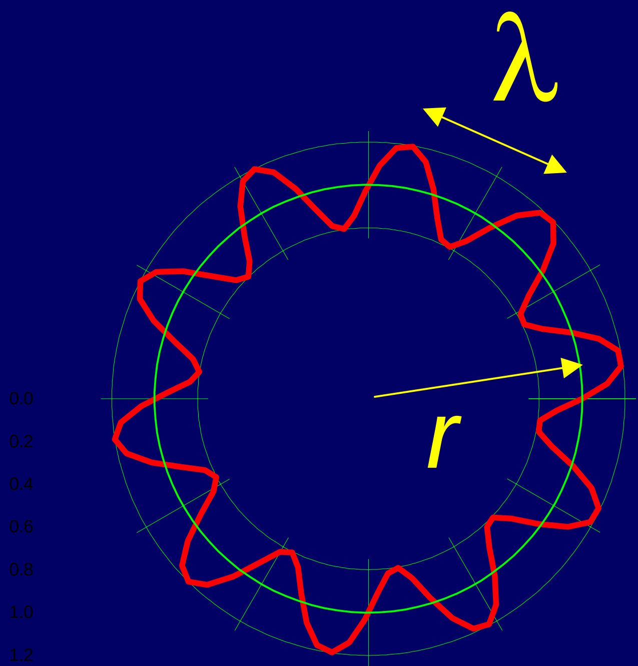




n=3

n=4

Bohr model of the atom



$$2\pi r = n\lambda$$

Quantum physics

n=10

Simple quantum physics

We start classically

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$$E = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_o r}$$

From these relations follows

$$\frac{m^2v^2}{m} = \frac{p^2}{m} = \frac{h^2}{m\lambda^2} = \frac{e^2}{4\pi\varepsilon_o r}$$

$$2\pi r = n\lambda$$

Quantum physics

$$r_n = \frac{4\pi\varepsilon_o \hbar^2}{me^2} n^2$$

Energy levels

$$m\frac{v^2}{r} = \frac{e^2}{4\pi\varepsilon_o r^2}$$

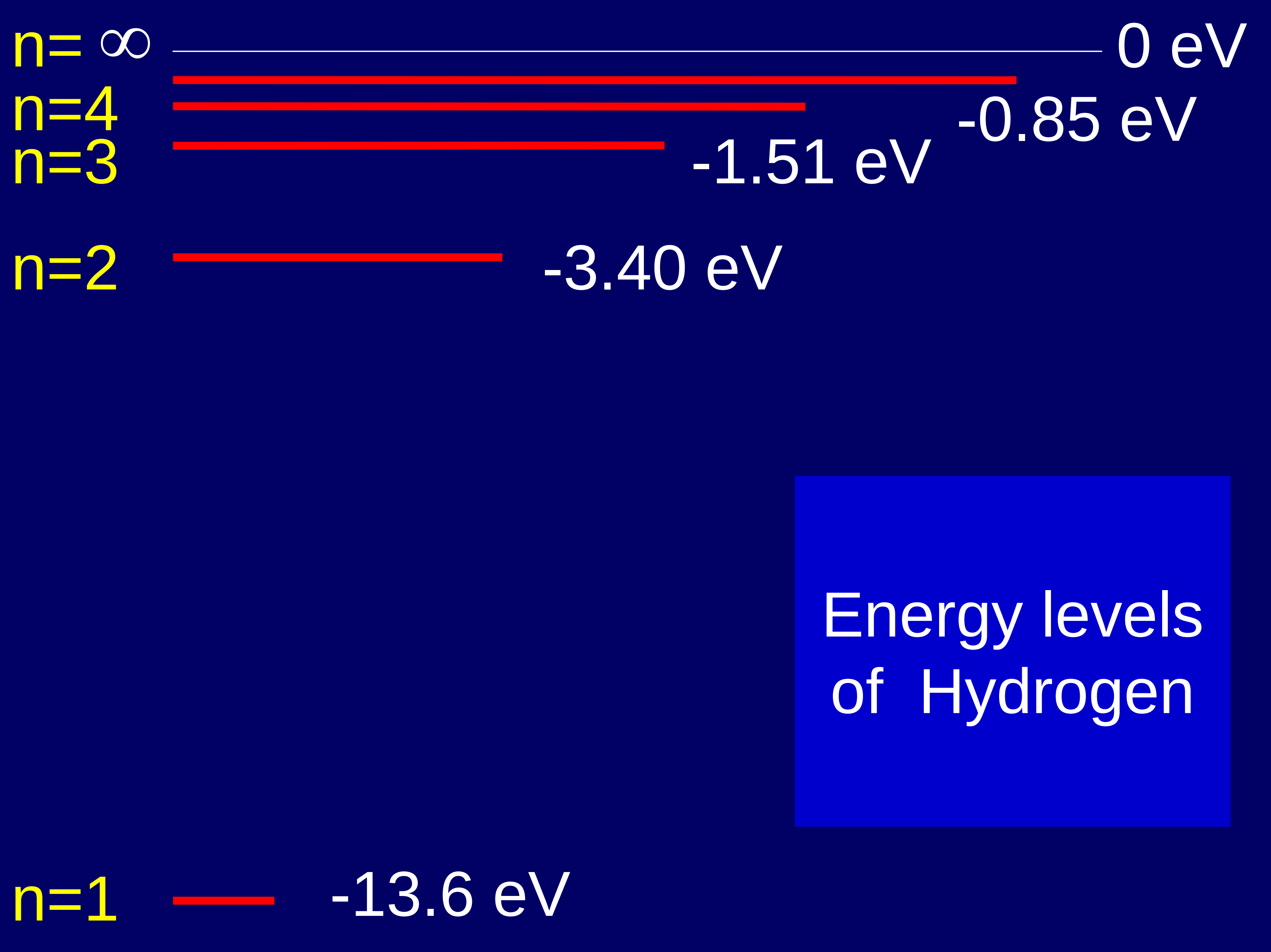
$$E = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_o r} = -\frac{e^2}{8\pi\varepsilon_o r}$$

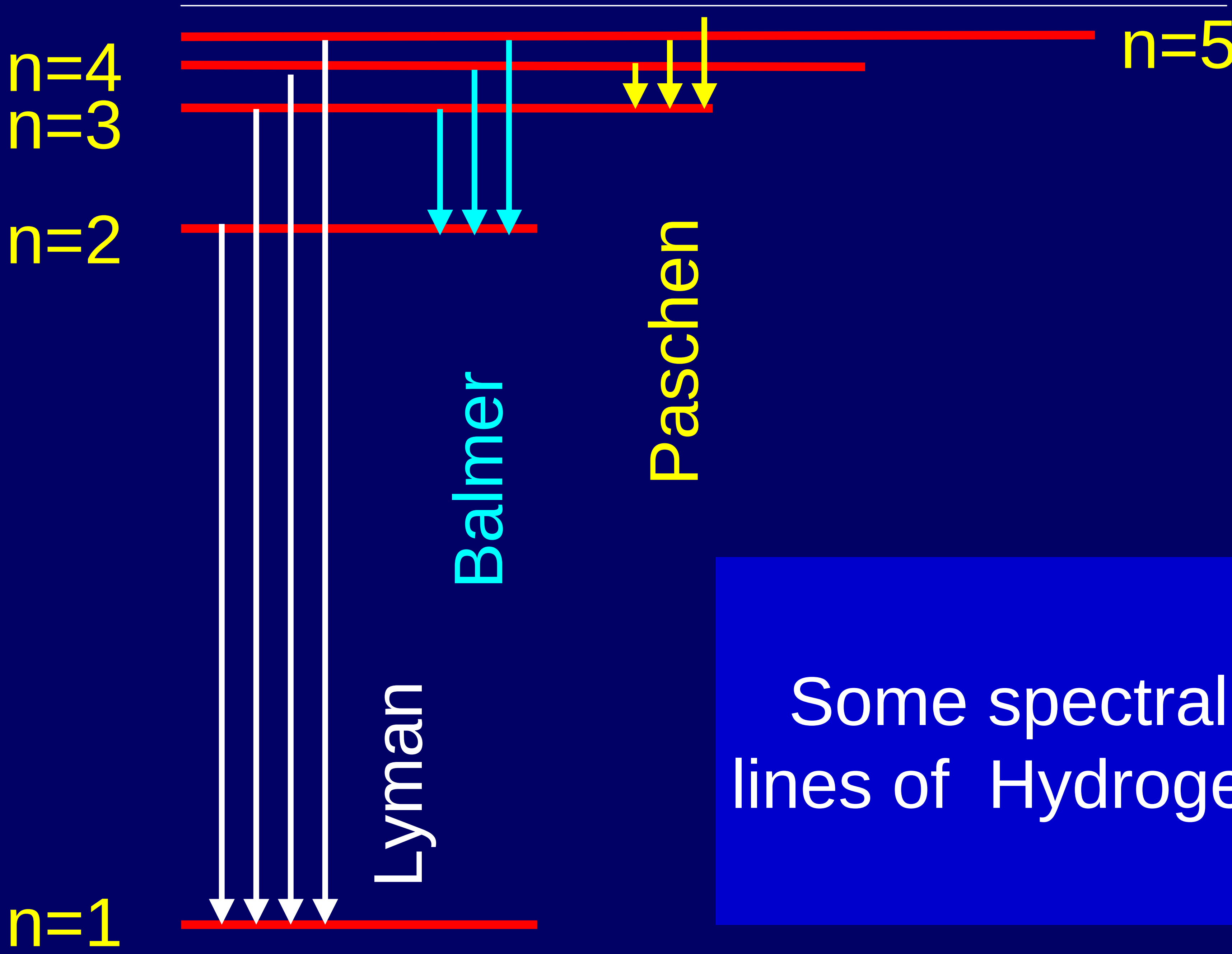
$$E_n = -\frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{1}{n^2}$$

$$2\pi r = n\lambda$$

Quantum physics

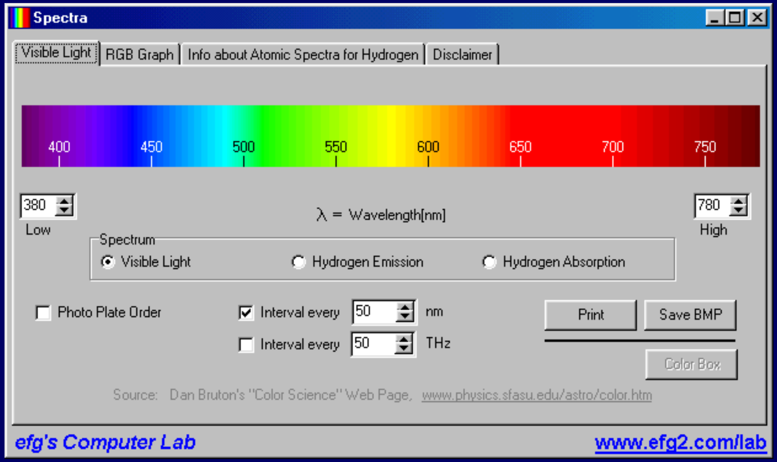
$$r_n = \frac{4\pi\varepsilon_o\hbar^2}{me^2}n^2$$


n= ∞
0 eV
n=4
-0.85 eV
n=3
-1.51 eV
n=2
-3.40 eV
Energy levels
of Hydrogen
n=1
-13.6 eV



Some spectral lines of Hydrogen

Hydrogen absorption and emission spectra



$$n = 1,2,3.......$$

$$l \le n - 1$$

$$m = l, l-1, l-2, ... -l$$

Wave functions $R_{n,l}$

$$R_{1,0}(r)=\left(\tfrac{1}{a_0}\right)^{3/2}2e^{-\frac{r}{a_0}}$$

$$R_{2,0}(r)=\left(\tfrac{1}{2a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}$$

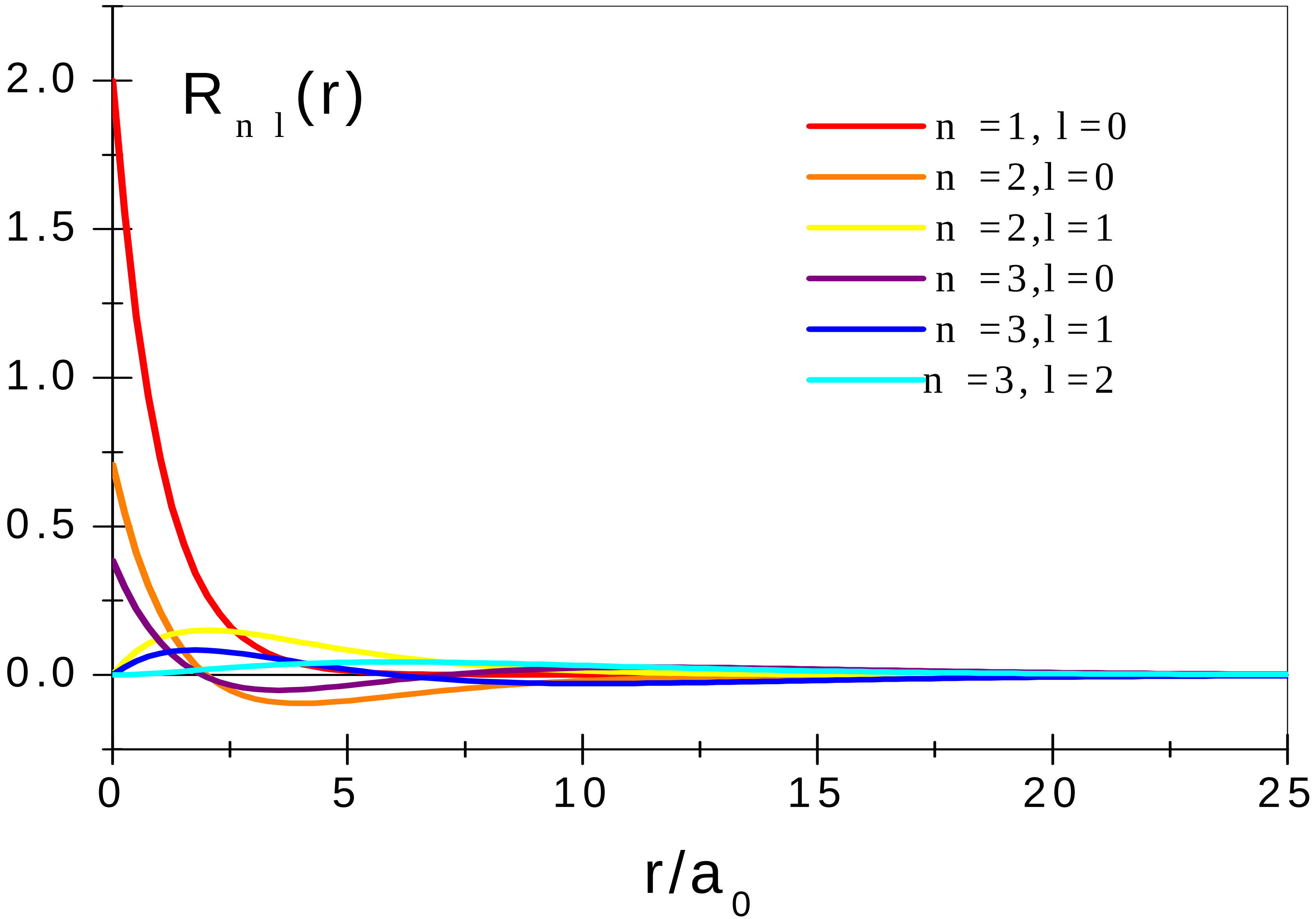
$$R_{2,1}(r)=\left(\tfrac{1}{2a_0}\right)^{3/2}\left(\frac{1}{\sqrt{3}}\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}$$

$$R_{3,0}(r)=\left(\tfrac{1}{3a_0}\right)^{3/2}2\left(1-\frac{2}{3}\frac{r}{a_0}+\frac{2}{27}\left(\frac{r}{a_0}\right)^2\right)e^{-\frac{r}{3a_0}}$$

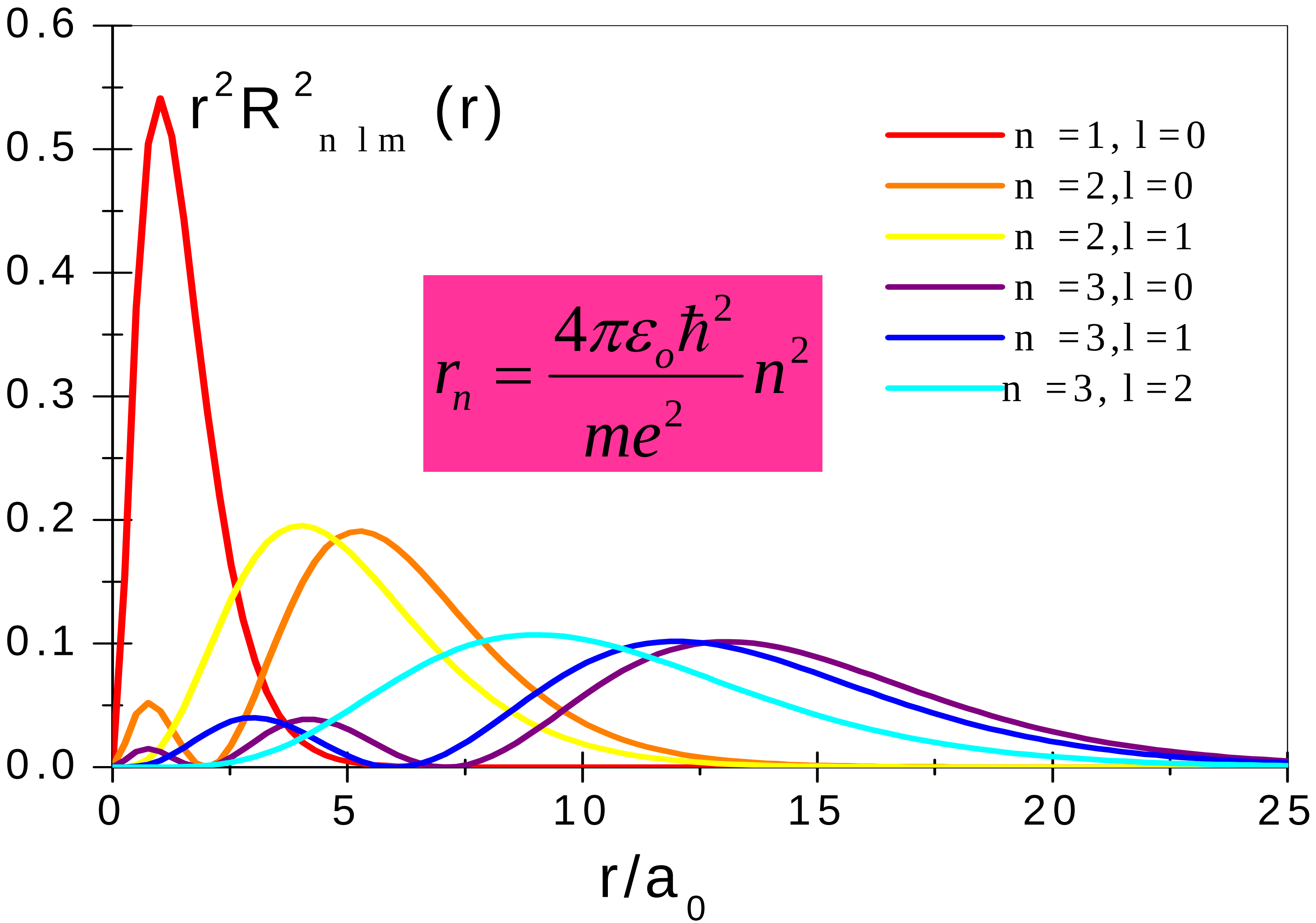
$$R_{3,1}(r)=\left(\tfrac{1}{3a_0}\right)^{3/2}\left(\frac{8}{9\sqrt{2}}\right)\left(\frac{r}{a_0}\right)\left(1-\frac{r}{6a_0}\right)e^{-\frac{r}{3a_0}}$$

$$R_{3,2}(r)=\left(\tfrac{1}{3a_0}\right)^{3/2}\left(\frac{4}{27\sqrt{10}}\right)\left(\frac{r}{a_0}\right)^2e^{-\frac{r}{3a_0}}$$

Wave functions



The radial probability distribution



$$r_n = \frac{4\pi\varepsilon_o\hbar^2}{me^2}n^2$$