



PHOT 301: Quantum Photonics

LECTURE 07

Michaël Barbier, Summer (2024-2025)

OVERVIEW OF THE COURSE

week	Topic	Reading
Week 1	Introduction & Required Mathematical Methods. Waves and Schrödinger's equation, Probability, Uncertainty and Time evolution. Infinite square well.	
Week 2	The harmonic oscillator, Creation and annihilation operators. Free particle, 1D Bound states & Scattering/Transmission, Finite well	
Week 3	Quantum mechanics formalism: Functions and operators, uncertainty. Approximation methods.	
Week 4	Angular momentum and the Hydrogen atom, Spin Magnetic fields, The Pauli equation, Minimal Coupling, Aharonov Bohm Perturbation: Fine Structure of Hydrogen, The Zeeman Effect	Ch. 4, Pert. Ch. 7
Week 5	Identical particles, Periodic table, Molecular bonds, Periodic structures, Band structure, Bloch functions Time-dependent perturbation: Absorption, spontaneous emission, and stimulated emission	
Week 6	Final exam	

3D SCHRÖDINGER EQUATION

- Remember: time-independent Schrödinger equation in 1D:

$$\underbrace{-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}}_{\text{kinetic energy } K} + U(x) \psi = E \psi$$

- First term corresponds to the kinetic energy K of the particle
- Kinetic energy K in 3D:

$$K = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad \rightarrow \quad \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} + \frac{\hbar^2 k_z^2}{2m}$$

- 3D time-independent Schrödinger equation:

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

3D Particle in a Box

3D PARTICLE IN A BOX

- Schrodinger equation:

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

- Separation of the variables to find $\psi(x, y, z)$:

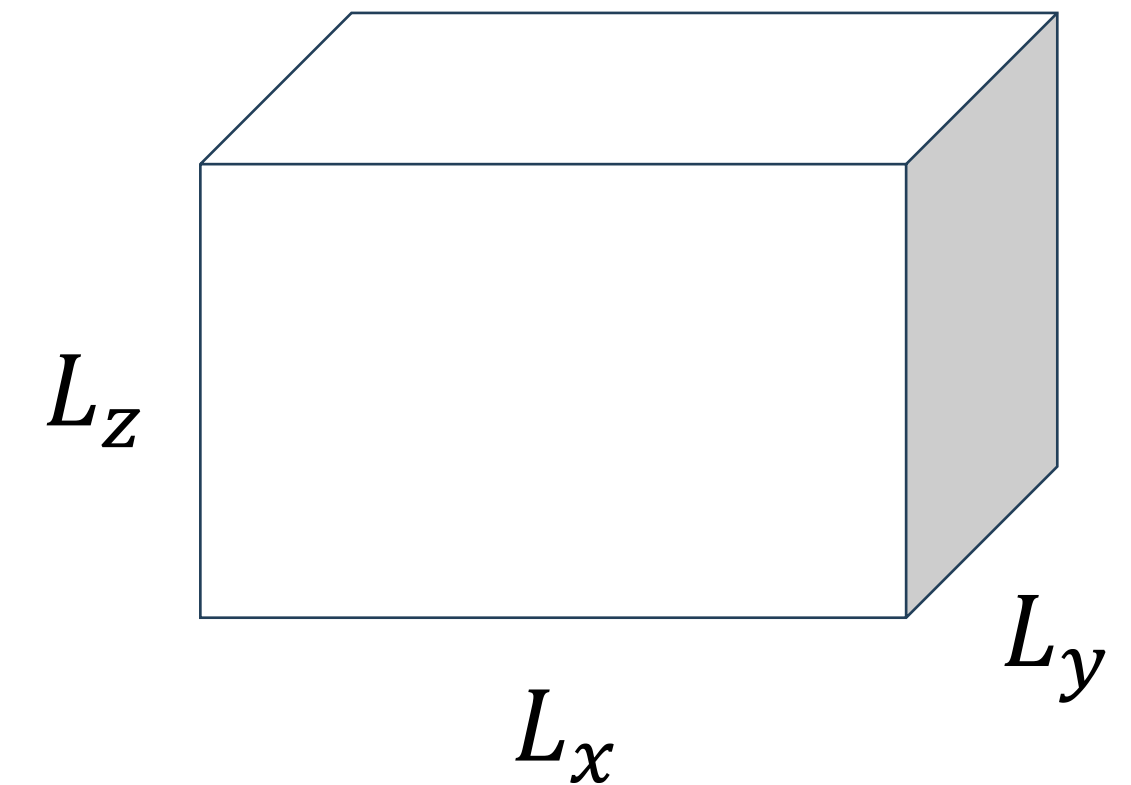
$$\psi(x, y, z) = X(x) Y(y) Z(z)$$

$$\Rightarrow -\frac{\hbar^2}{2m} \left(\frac{\partial^2 X Y Z}{\partial x^2} + \frac{\partial^2 X Y Z}{\partial y^2} + \frac{\partial^2 X Y Z}{\partial z^2} \right) = E \psi$$

Inside the box:

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

$$\begin{cases} 0 < x < L_x \\ 0 < y < L_y \\ 0 < z < L_z \end{cases}$$



3D PARTICLE IN A BOX: SEPARATION OF THE VARIABLES

- Separation of the variables to find $\psi(x, y, z)$:

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

$$\Rightarrow -\frac{\hbar^2}{2m} \left(\frac{\partial^2 XYZ}{\partial x^2} + \frac{\partial^2 XYZ}{\partial y^2} + \frac{\partial^2 XYZ}{\partial z^2} \right) = E \psi$$

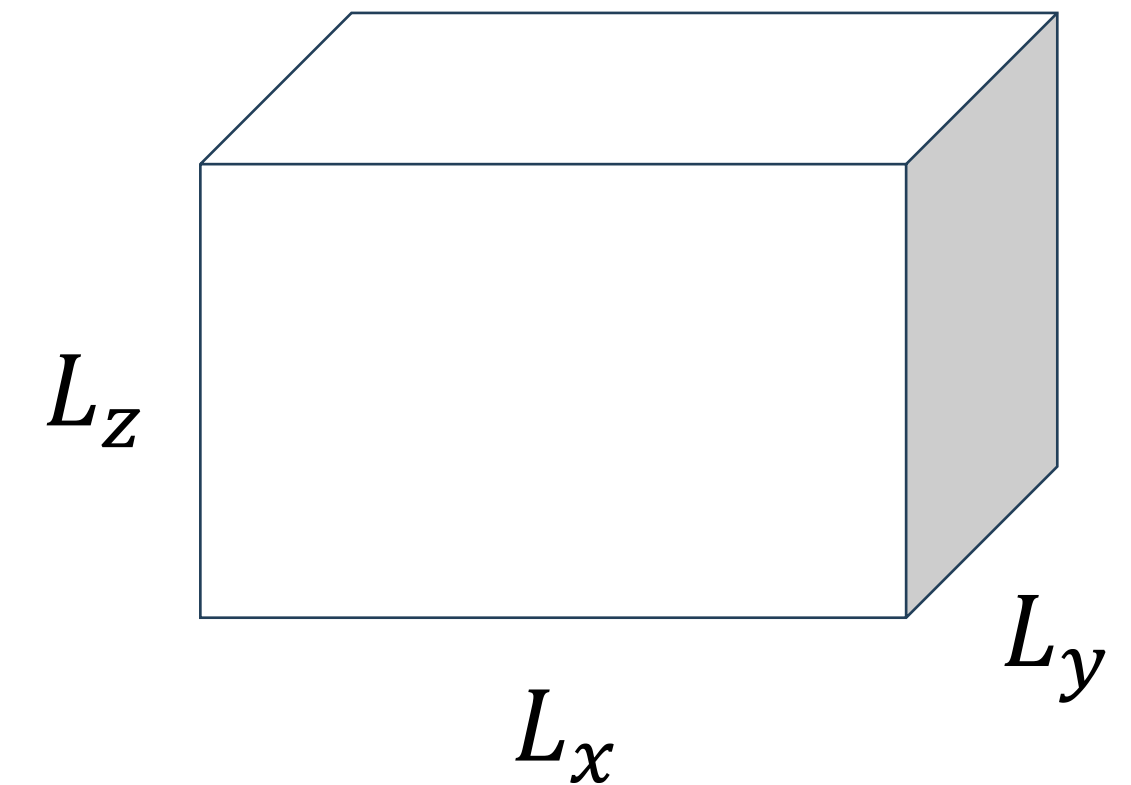
$$\Rightarrow -\frac{\hbar^2}{2m} \left(YZ \frac{\partial^2 X}{\partial x^2} + XZ \frac{\partial^2 Y}{\partial y^2} + XY \frac{\partial^2 Z}{\partial z^2} \right) = E \psi$$

$$\Rightarrow -\frac{\hbar^2}{2m} \left(\frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} \right) = E$$

Inside the box:

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3D PARTICLE IN A BOX: SEPARATION OF THE VARIABLES

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$$\Rightarrow -\frac{\hbar^2}{2m} \left(\frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} \right) = E$$

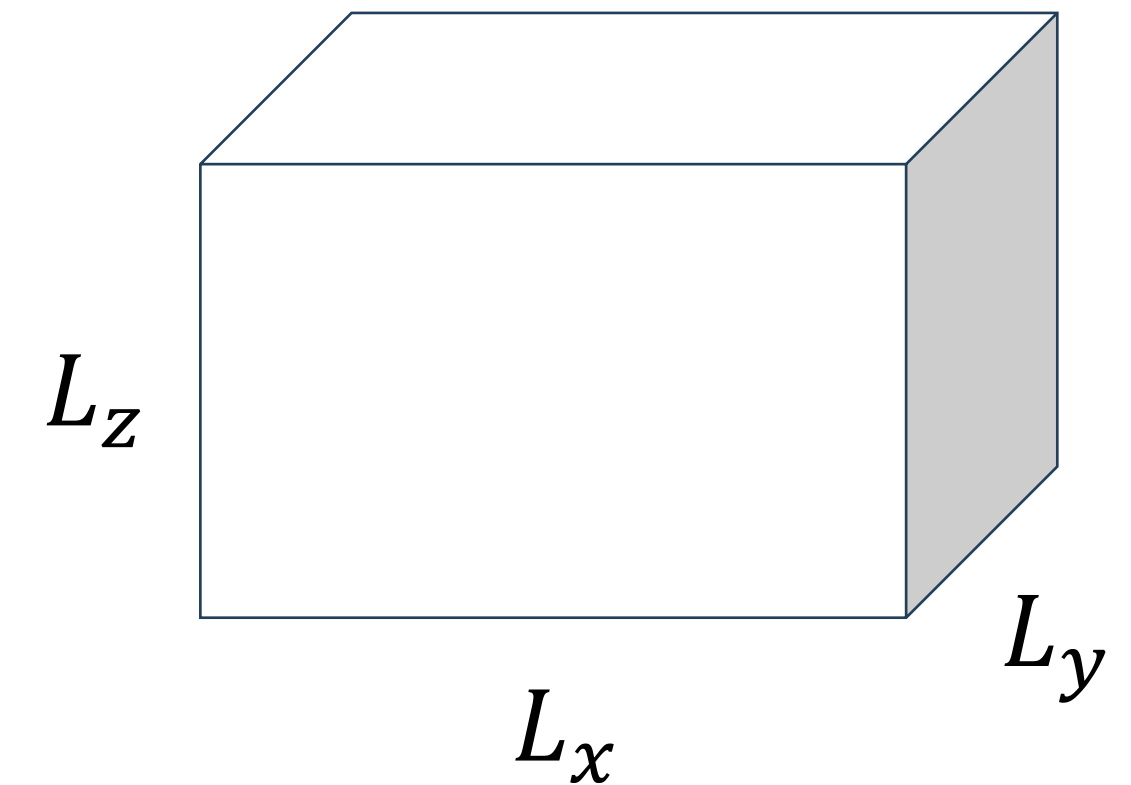
System of equations:

$$\Rightarrow \begin{cases} -\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} = E_x X \\ -\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} = E_y Y \\ -\frac{\hbar^2}{2m} \frac{d^2 Z}{dz^2} = E_z Z \end{cases}, \quad E = E_x + E_y + E_z$$

Inside the box:

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

$$\begin{cases} 0 < x < L_x \\ 0 < y < L_y \\ 0 < z < L_z \end{cases}$$



3D PARTICLE IN A BOX: SOLUTIONS

- Each equation is similar to the 1D particle in a box

$$-\frac{\hbar^2}{2m} \frac{\partial^2 X}{\partial x^2} = E_x X, \quad X(x) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x \pi x}{L_x}\right), \quad E_x = \frac{\hbar^2 \pi^2 n_x^2}{2m L_x^2}$$

- Total wave function the **product**:

$$\psi(x, y, z) = X Y Z = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

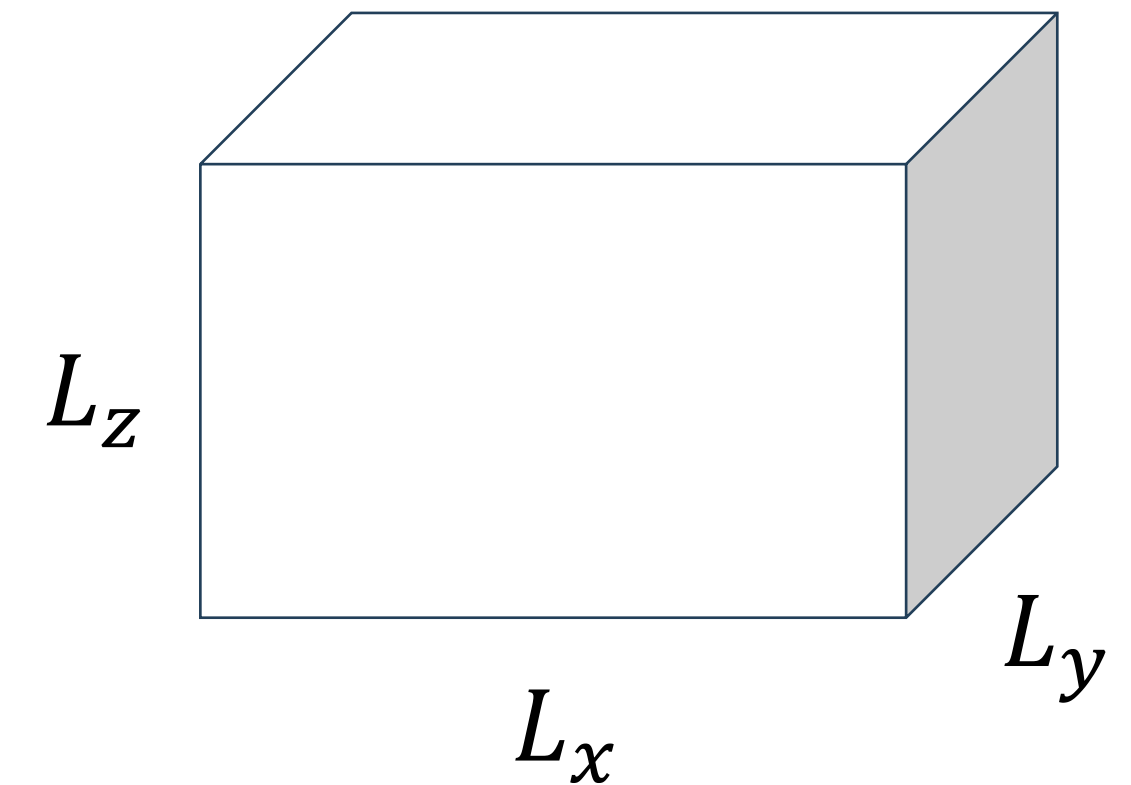
- With energy the **sum**:

$$E = E_x + E_y + E_z = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

Inside the box:

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

$$\begin{cases} 0 < x < L_x \\ 0 < y < L_y \\ 0 < z < L_z \end{cases}$$



3D PARTICLE IN A BOX: NORMALIZATION

- Normalization constant in 3D?

$$1 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\psi(x, y, z)|^2 dz dy dx$$

$$\Rightarrow 1 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |X|^2 |Y|^2 |Z|^2 dz dy dx$$

$$\Rightarrow 1 = \int_{-\infty}^{\infty} |X|^2 dx \times \int_{-\infty}^{\infty} |Y|^2 dy \times \int_{-\infty}^{\infty} |Z|^2 dz$$

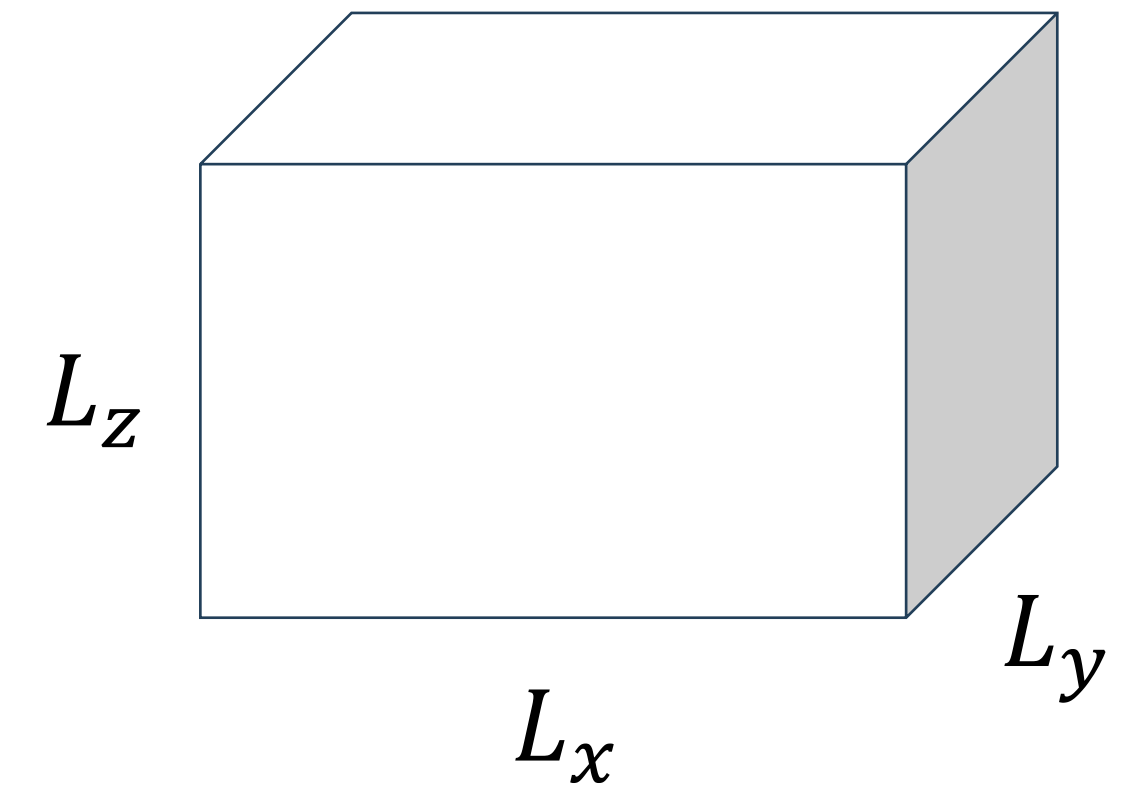
- Separation of variables: if all parts normalized then total wave function normalized

$$\psi(x, y, z) = X Y Z = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

Inside the box:

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

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3D PARTICLE IN A BOX: QUANTUM NUMBERS

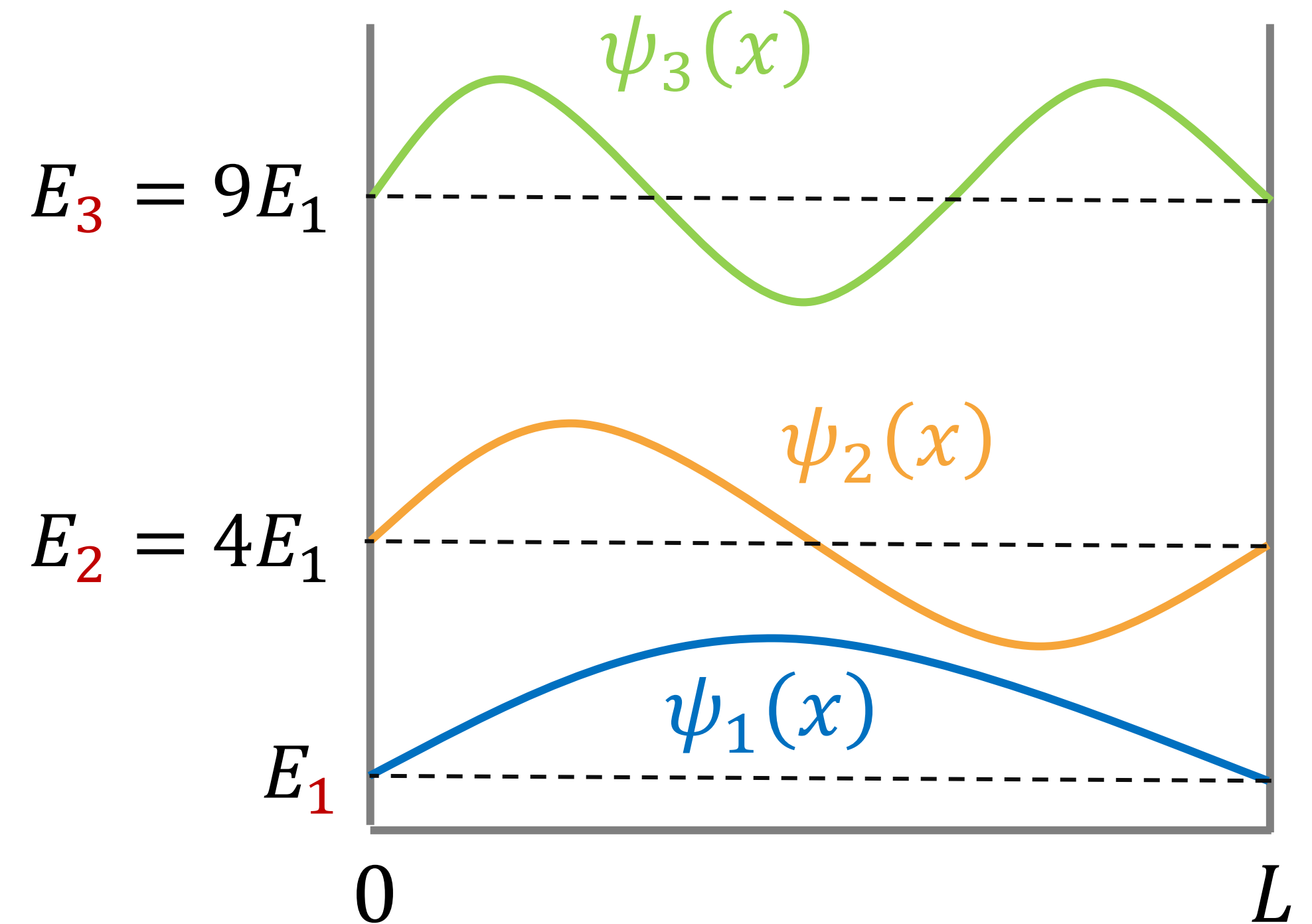
- In 1D we had quantum number n :

- Solutions for the wave function:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

- Corresponding energies:

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}$$



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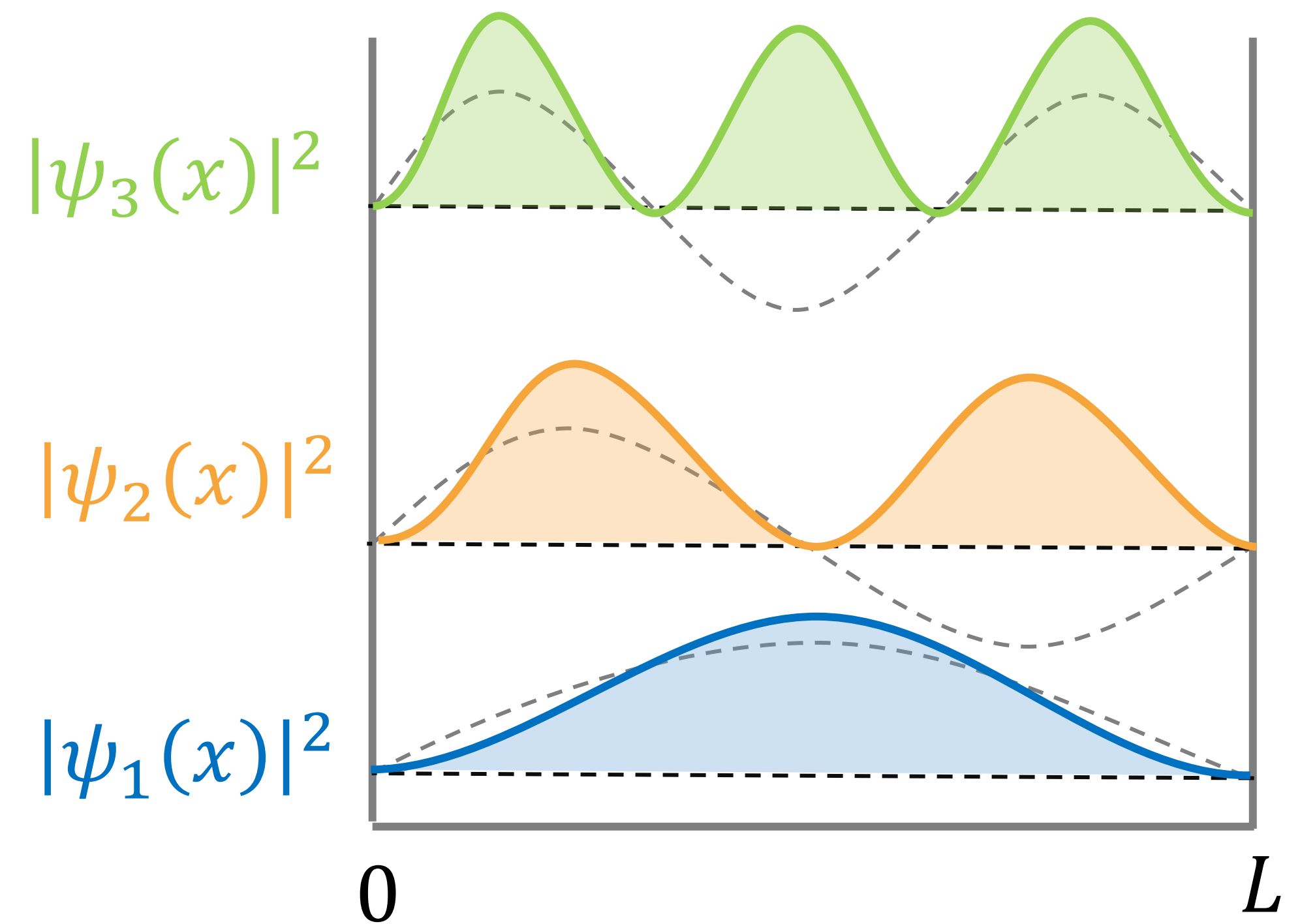
Particles “position” depending
on n : $\psi_n(x)$, E_n

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3D PARTICLE IN A BOX: STATIONARY SOLUTIONS

- Stationary solutions : $\psi_n(x) e^{\frac{iE_n t}{\hbar}}$
- Probability density does not change in time

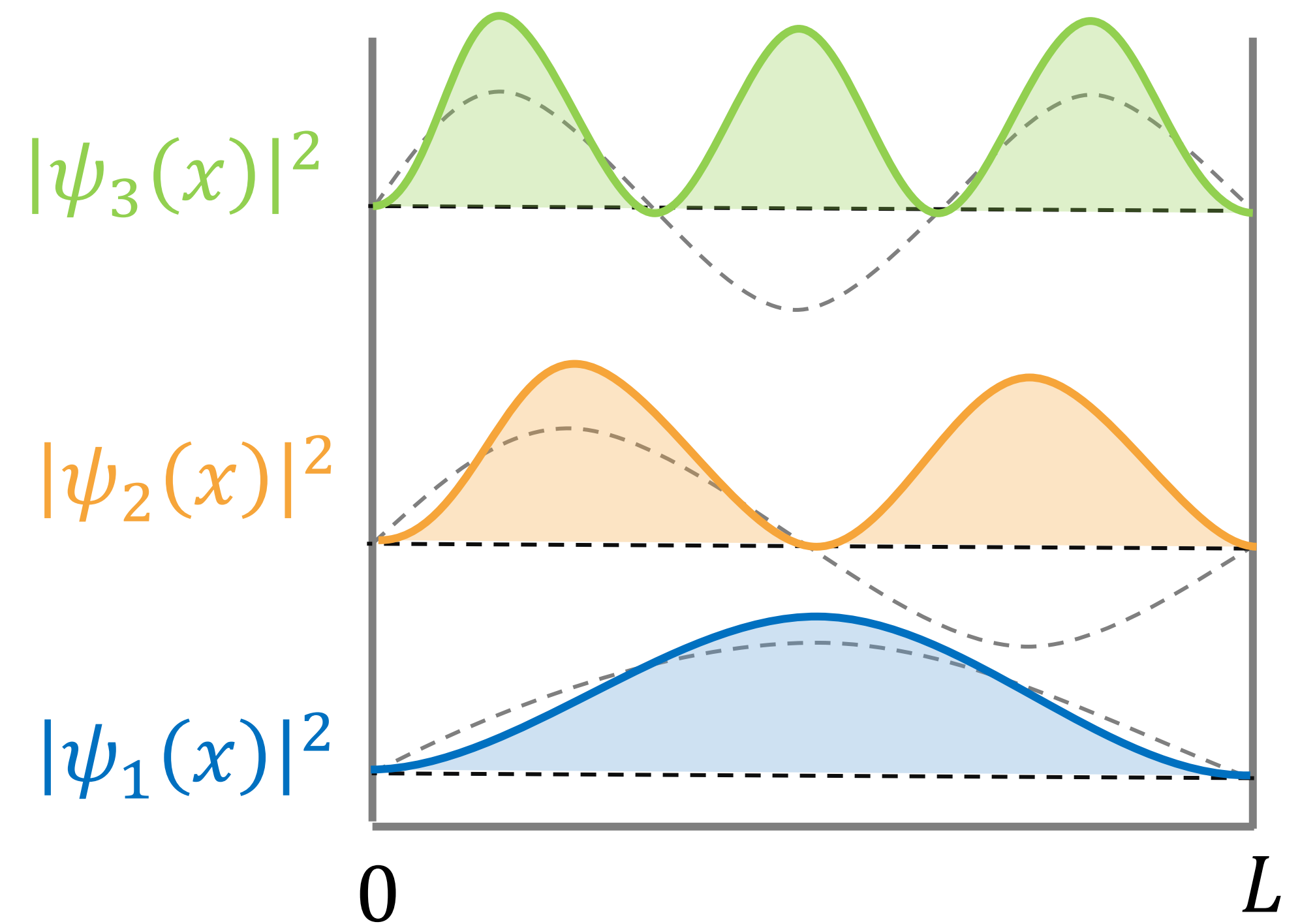
$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right),$$

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}$$

- But superpositions not stationary:

$$\psi(x) = \psi_1(x) e^{\frac{iE_1 t}{\hbar}} + \psi_2(x) e^{\frac{iE_2 t}{\hbar}}$$

Particles “position” depending
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3D PARTICLE IN A BOX: STATIONARY SOLUTIONS

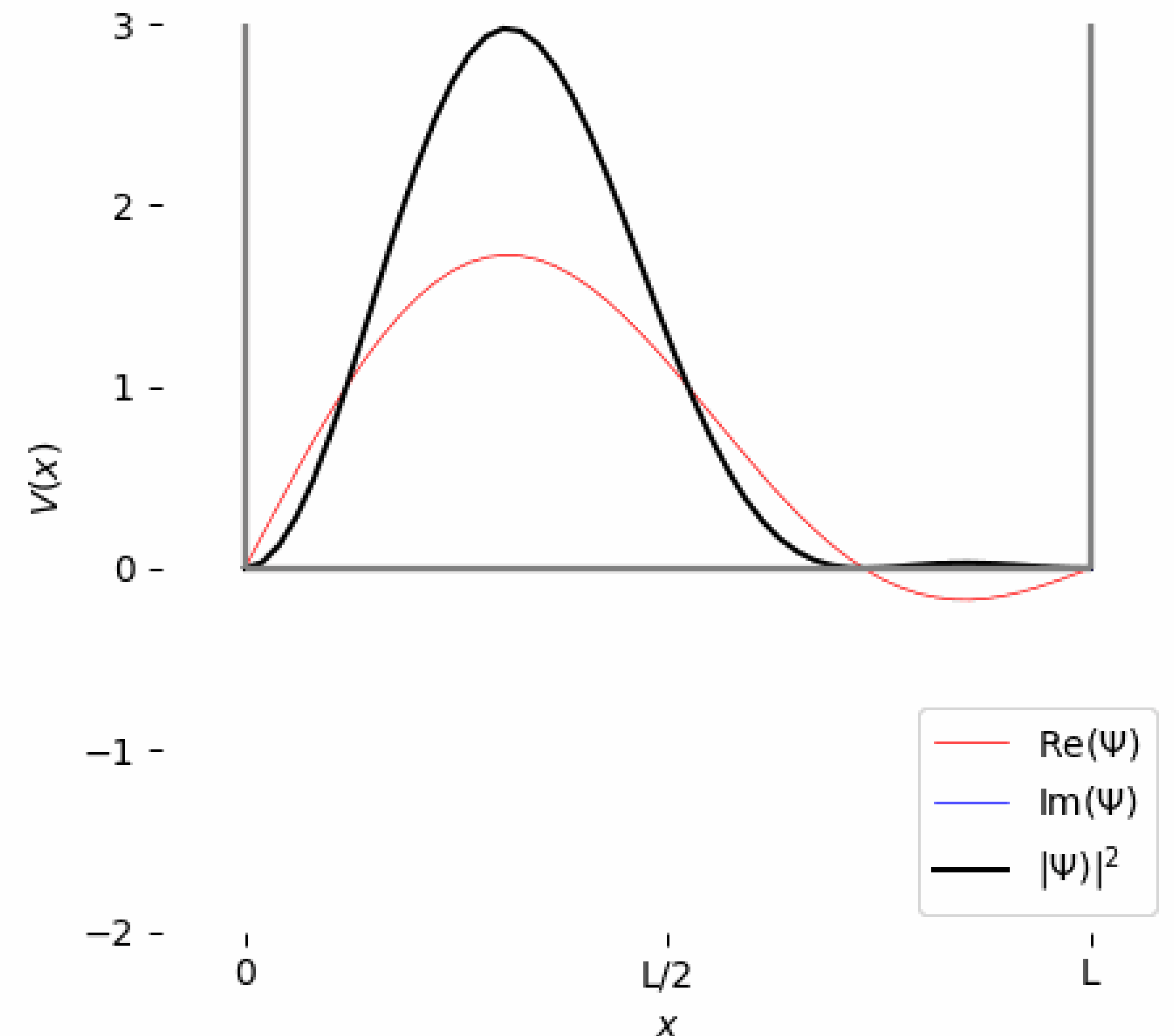
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$$\psi(x) = \psi_1(x) e^{\frac{-iE_1 t}{\hbar}} + \psi_2(x) e^{\frac{-iE_2 t}{\hbar}}$$



3D PARTICLE IN A BOX: QUANTUM NUMBERS

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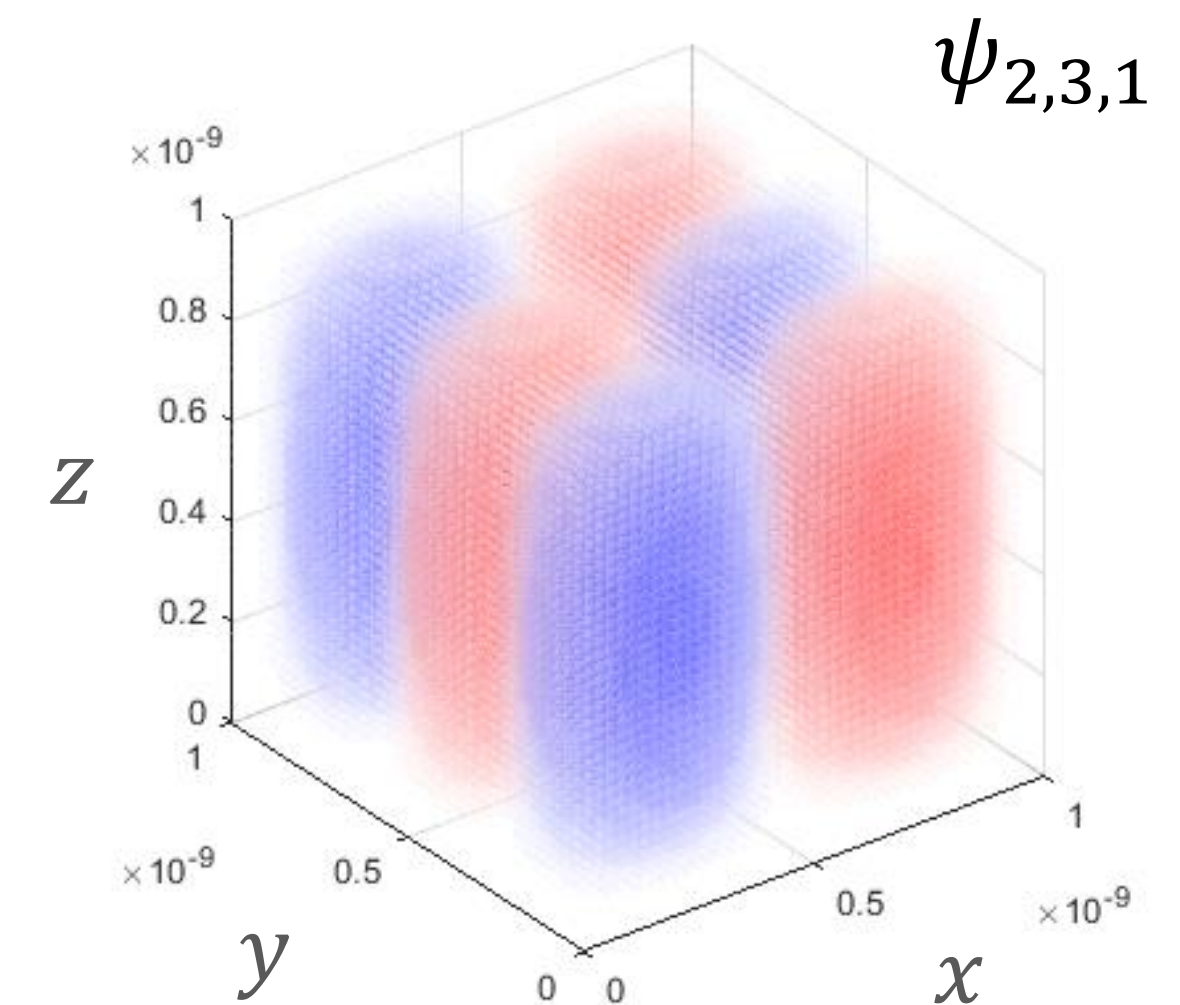
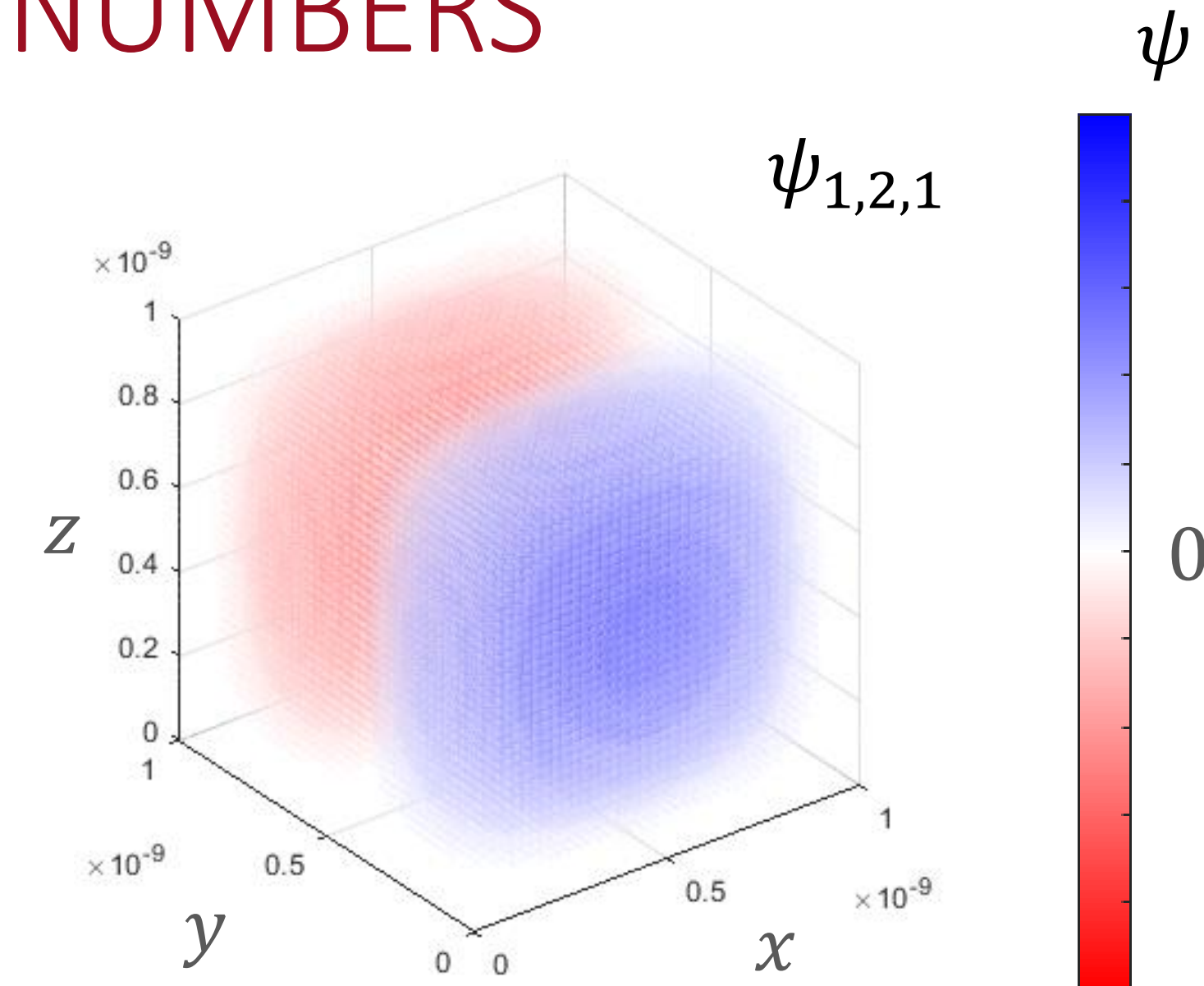
$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}$$

- In 3D we have **quantum numbers**: n_x, n_y, n_z :

$$\psi_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

$$\Rightarrow \psi_{2,1,1}(x, y, z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{2\pi x}{L_x}\right) \sin\left(\frac{1\pi y}{L_y}\right) \sin\left(\frac{1\pi z}{L_z}\right)$$



3D PARTICLE IN A BOX: DEGENERACY

- Assume a cubic box $L = L_x = L_y = L_z$

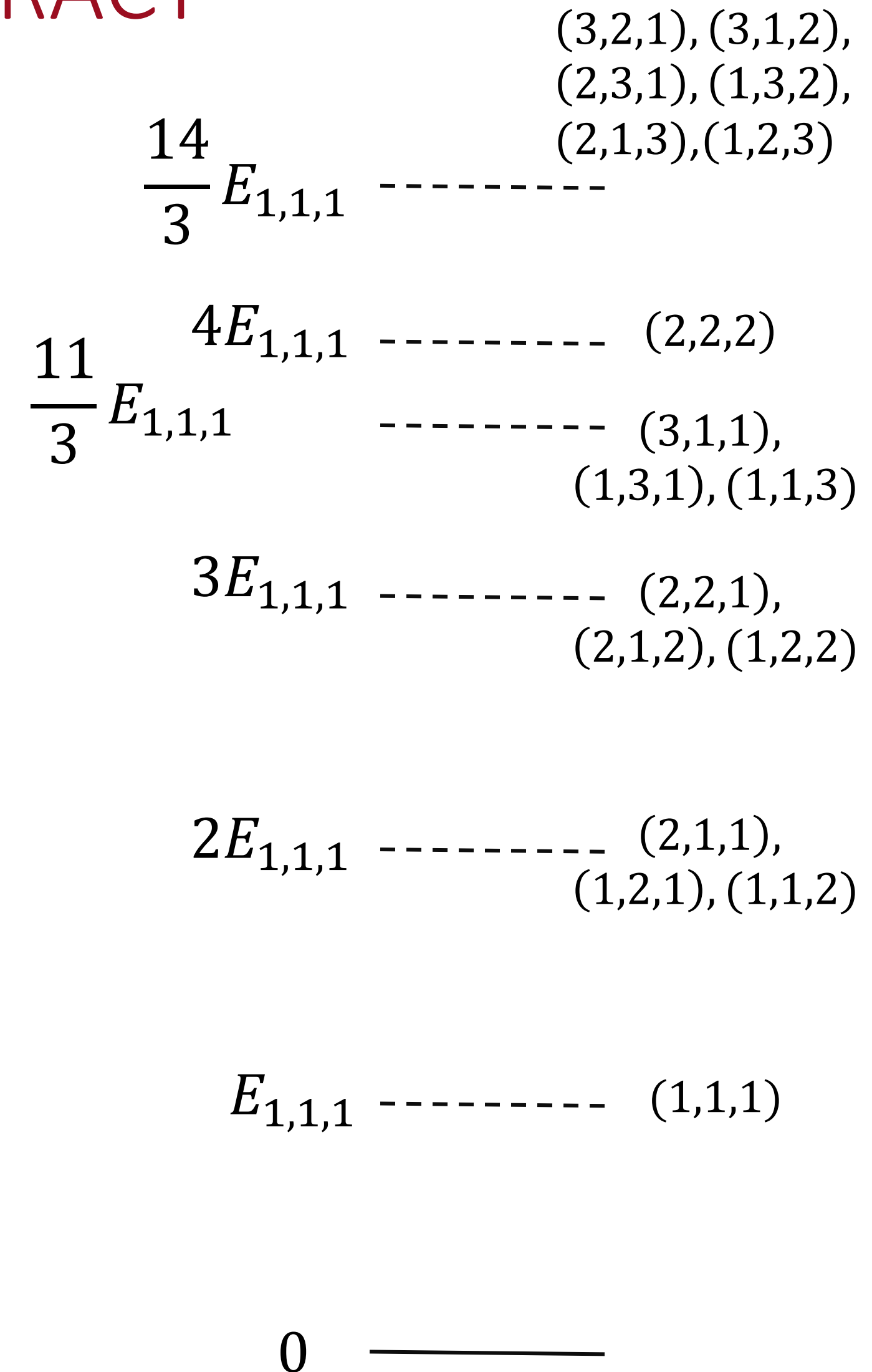
$$\psi(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

- Different wave function** solutions have **same energy**

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

- If such same energies occur we call this **degeneracy**
- Wave functions: **degenerate** quantum states
- Energies: **degenerate** energy levels
- Example: the energy level $3E_{1,1,1}$ is 3-fold degenerate

with $\psi_{2,2,1}$, $\psi_{2,1,2}$, and $\psi_{1,2,2}$ having same energy



3D PARTICLE IN A BOX: SYMMETRY → DEGENERACY

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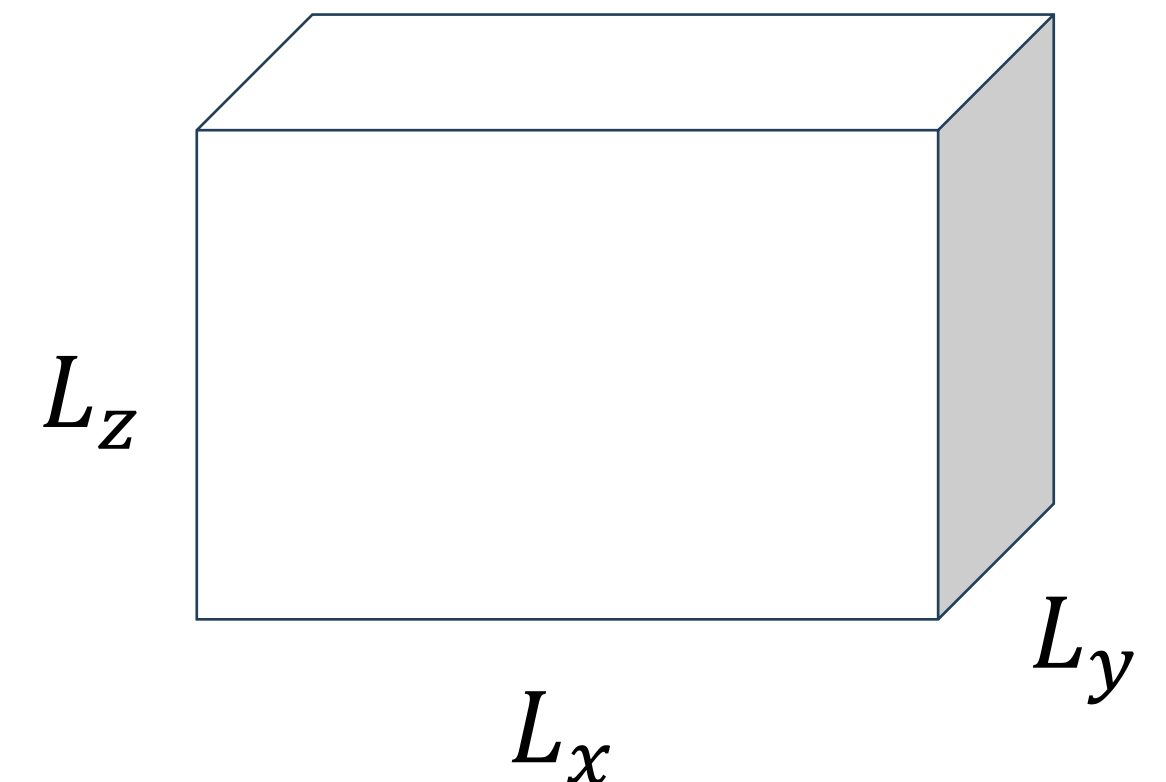
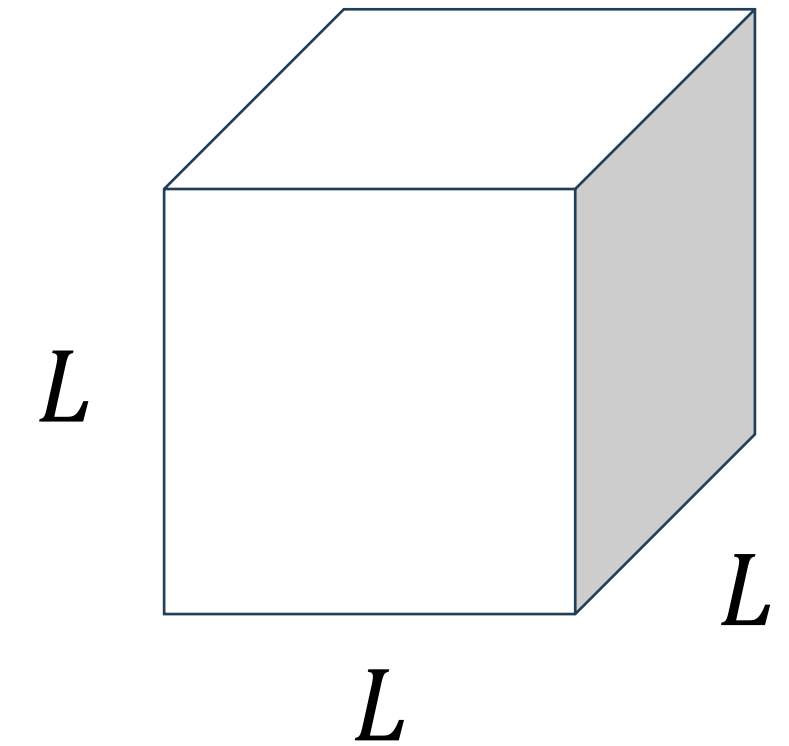
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- Different wave function solutions have **same energy**

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

- Symmetry of a cubic box** results in same situation if box is rotated over 90 degrees
- Introducing **asymmetry** lifts the degeneracy

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$



3D PARTICLE IN A BOX: SYMMETRY → DEGENERACY

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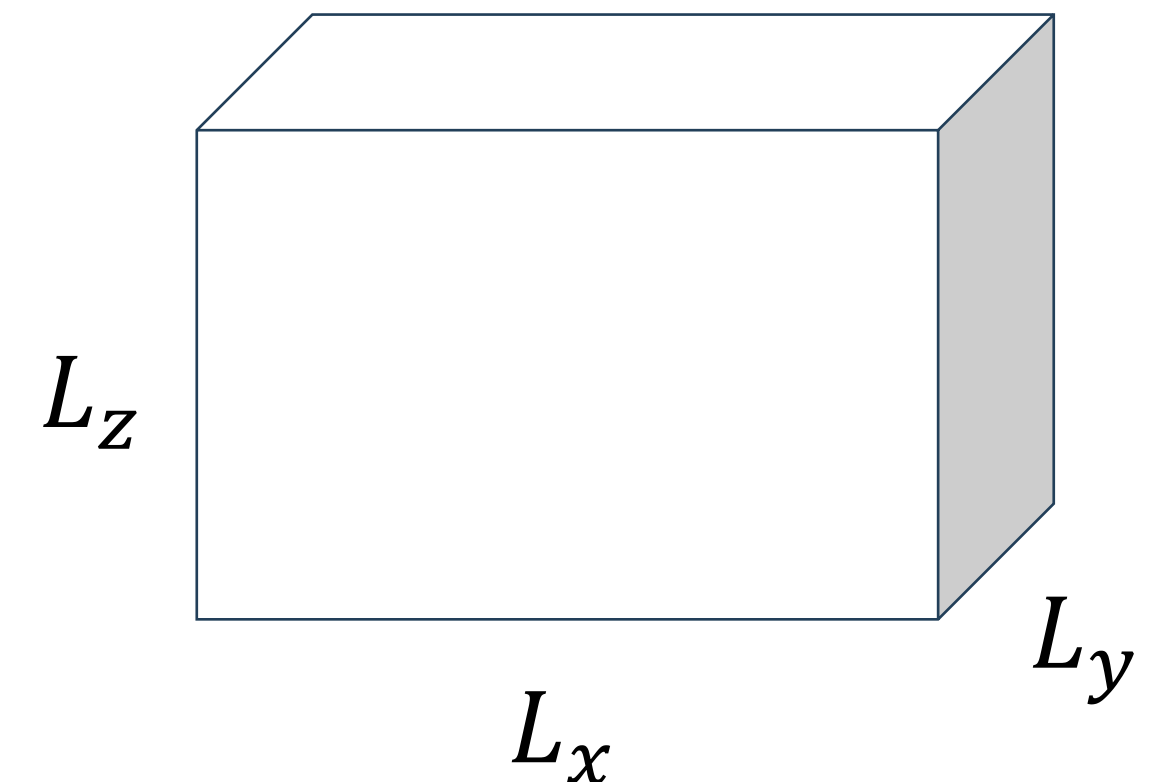
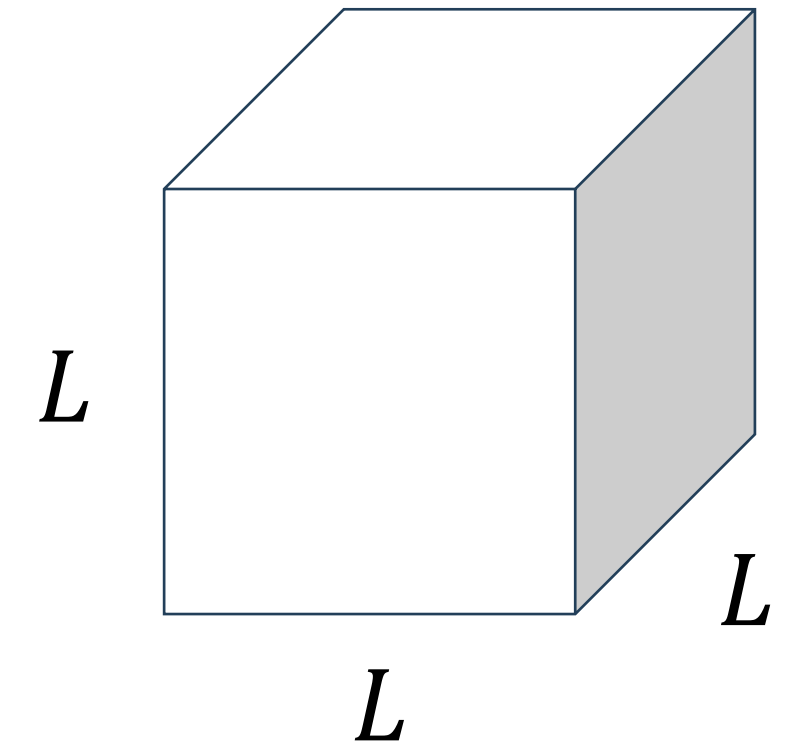
$$\psi(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

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Quantum model of the Hydrogen atom

QUANTUM MODEL OF THE HYDROGEN ATOM

- 3D time-independent Schrodinger equation:

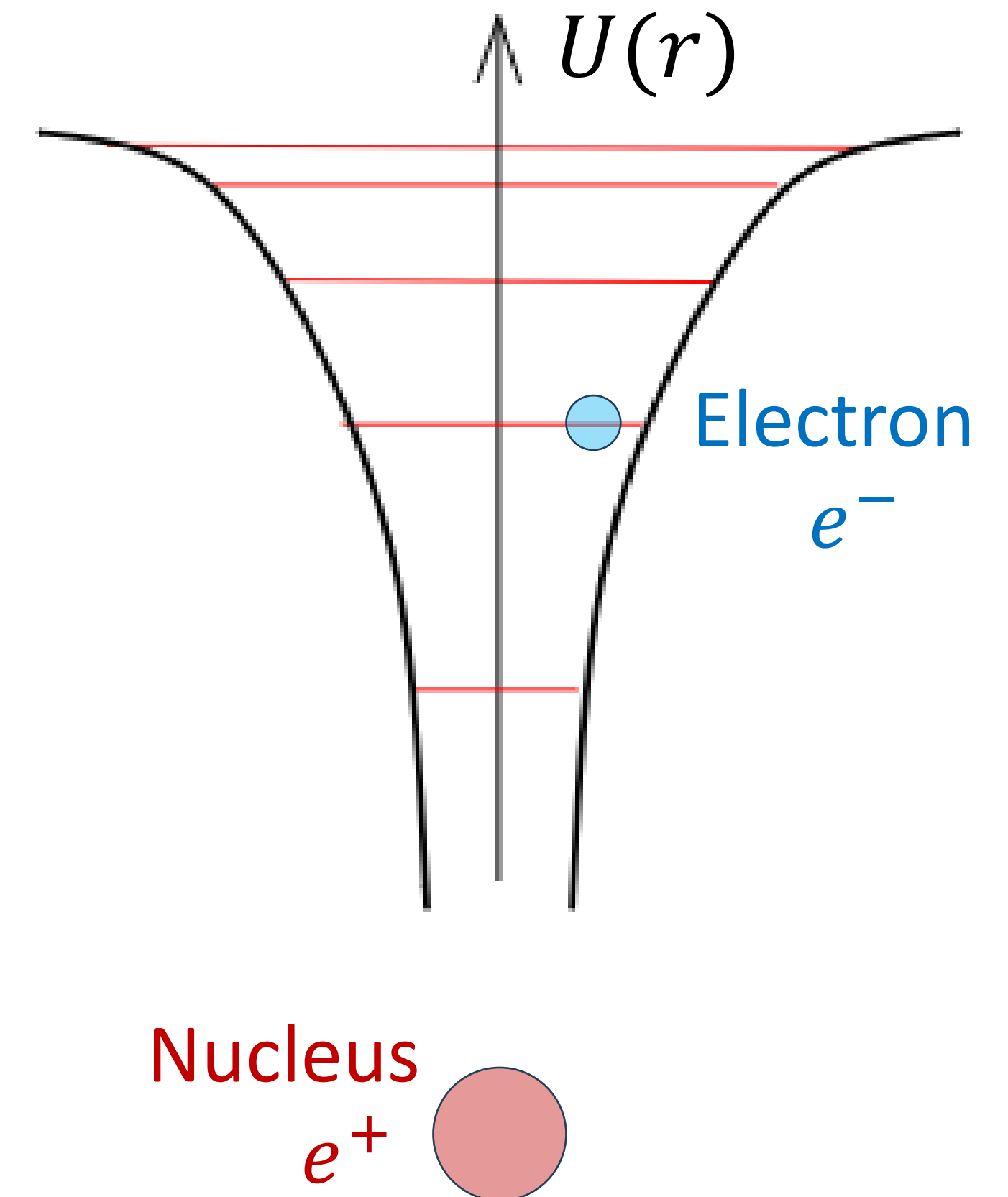
$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U \psi = E \psi$$

- Use the Coulomb interaction between proton and electron:

$$U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

- Spherical symmetry,
- convert to spherical coordinates:

$$\psi(x, y, z) \rightarrow \psi(r, \theta, \phi)$$



QUANTUM MODEL OF THE HYDROGEN ATOM

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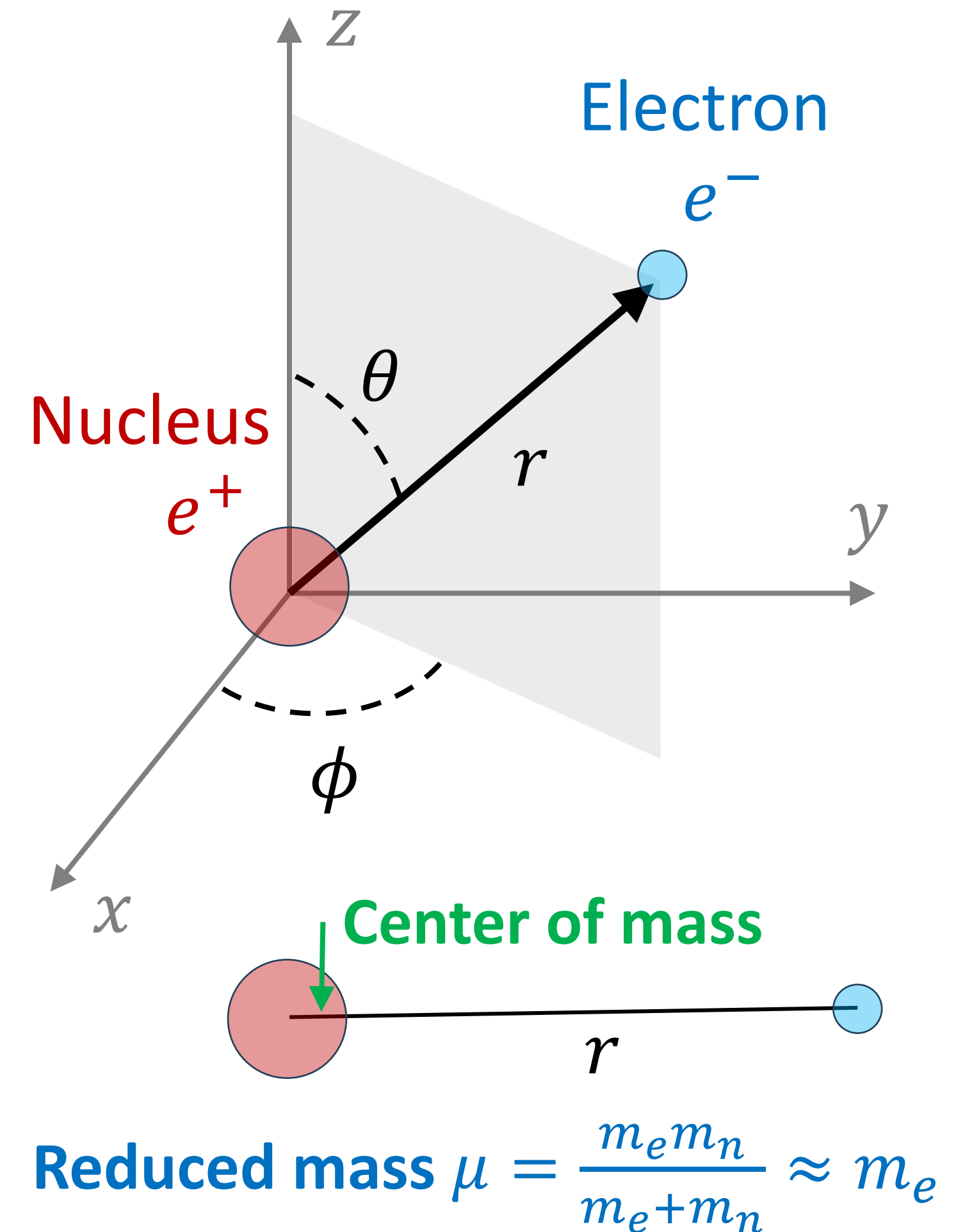
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HYDROGEN ATOM: SEPARATION OF VARIABLES

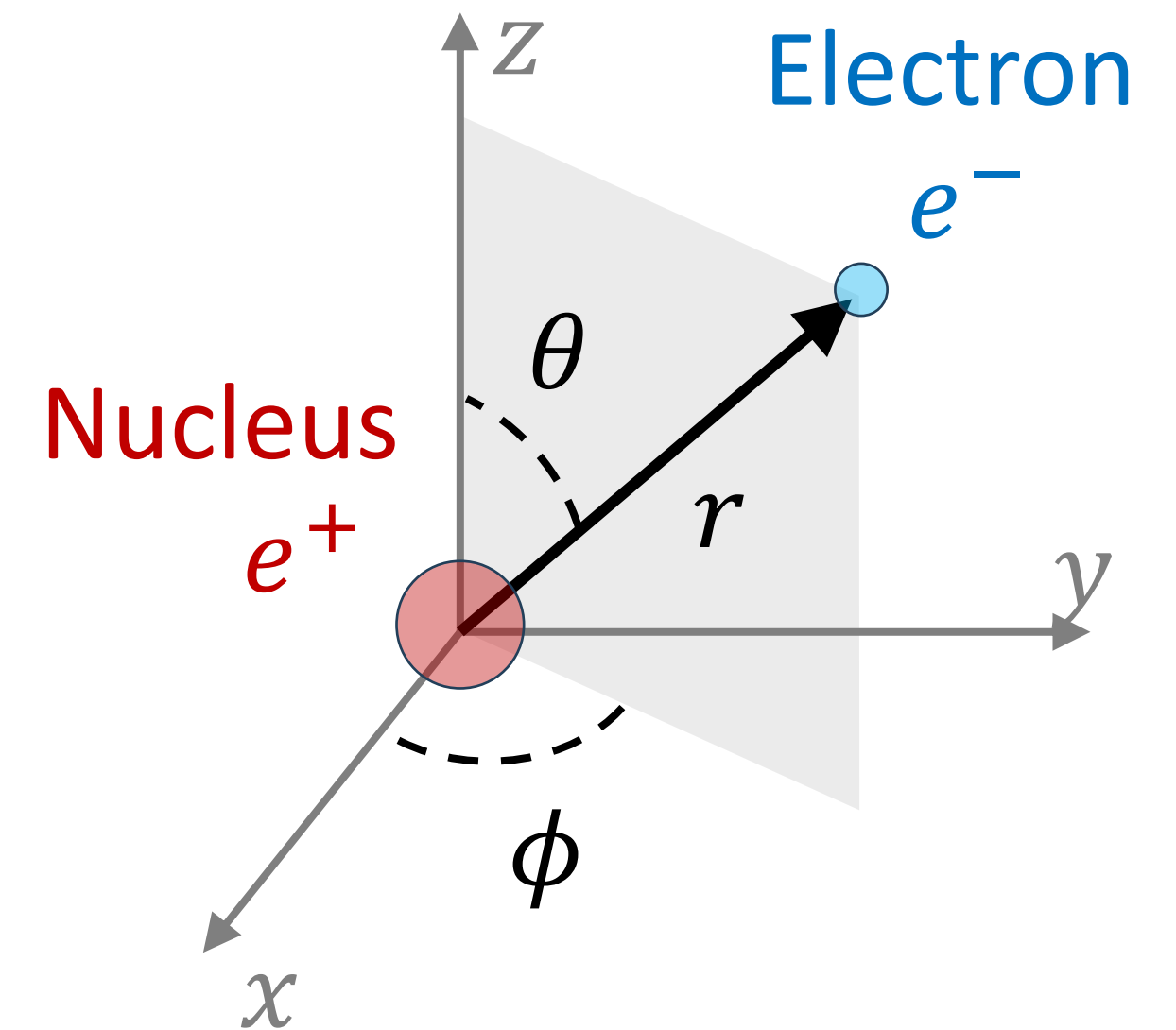
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- Separation of the variables (spherical coordinates):

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

$$\Rightarrow \left\{ \begin{array}{l} -\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left(\frac{\hbar^2 l(l+1)}{2\mu r^2} + U(r) \right) R(r) = E R(r) \\ -\frac{1}{\sin \theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left(l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right) \Theta(\theta) = 0 \\ \frac{d^2 \Phi(\phi)}{d\phi^2} + m_l^2 \Phi(\phi) = 0 \end{array} \right.$$

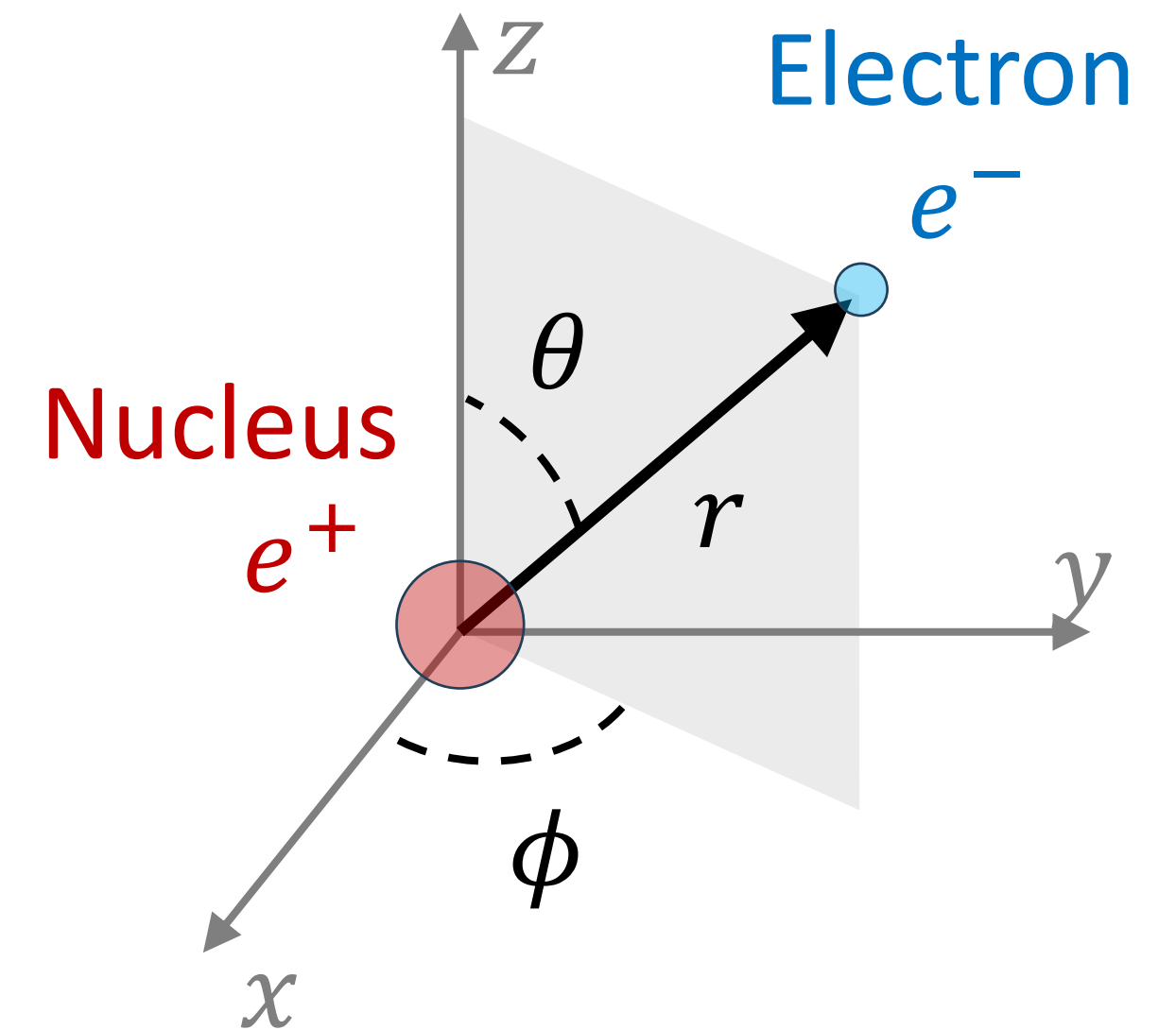


HYDROGEN ATOM: SEPARATION OF VARIABLES

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- Solutions?
- Let's first look at the conditions

$$\begin{array}{l} R(r \rightarrow \infty) \rightarrow 0 \\ \Phi(\phi) \text{ and } \Theta(\theta) \text{ finite everywhere} \\ \Phi(\phi + 2\pi) = \Phi(\phi) \end{array}$$

HYDROGEN ATOM: RADIAL EQUATION

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

Solution of the radial part:

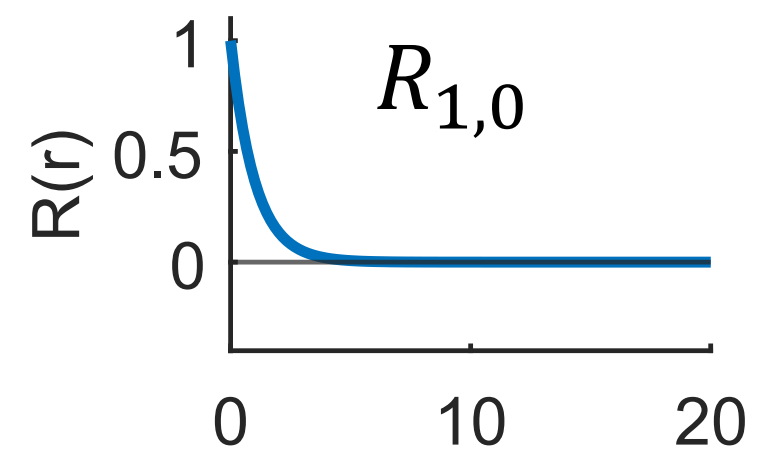
$$-\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left(\frac{\hbar^2 l(l+1)}{2\mu r^2} + U(r) \right) R(r) = E R(r)$$

- Condition: $R(r \rightarrow \infty) \rightarrow 0$
- Solutions

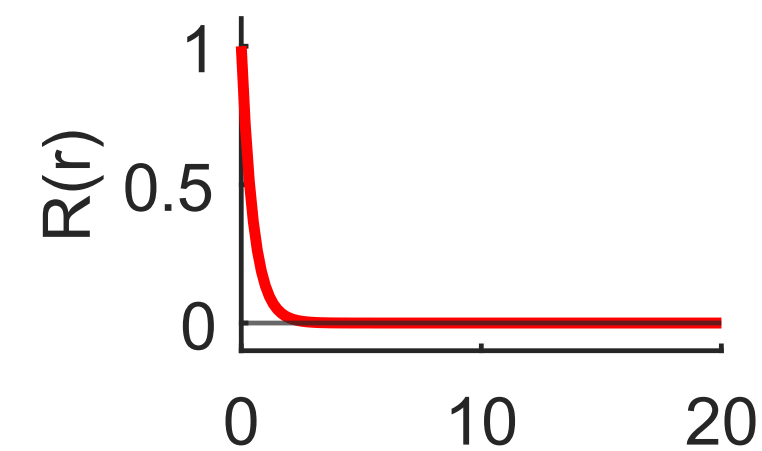
$$R_{n,l}(r) \propto \left(\frac{2r}{na_0} \right)^l L_{n-l-1}^{2l+1} \left(\frac{2r}{na_0} \right) \times e^{-\frac{r}{na_0}}$$

HYDROGEN ATOM: RADIAL EQUATION

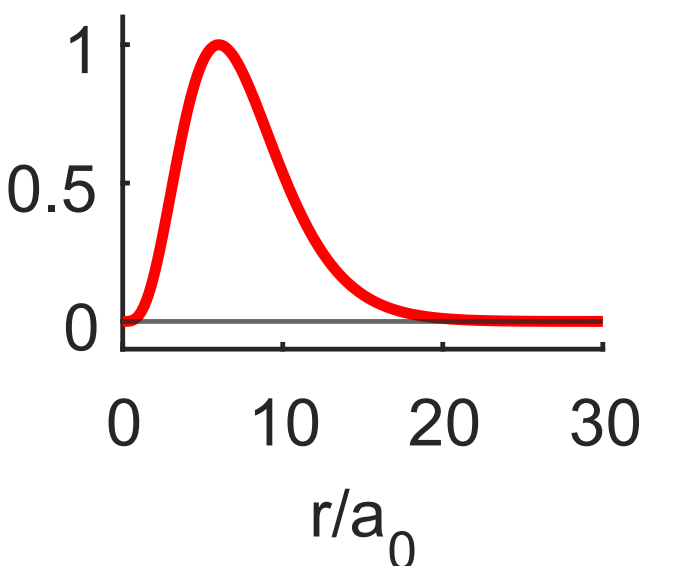
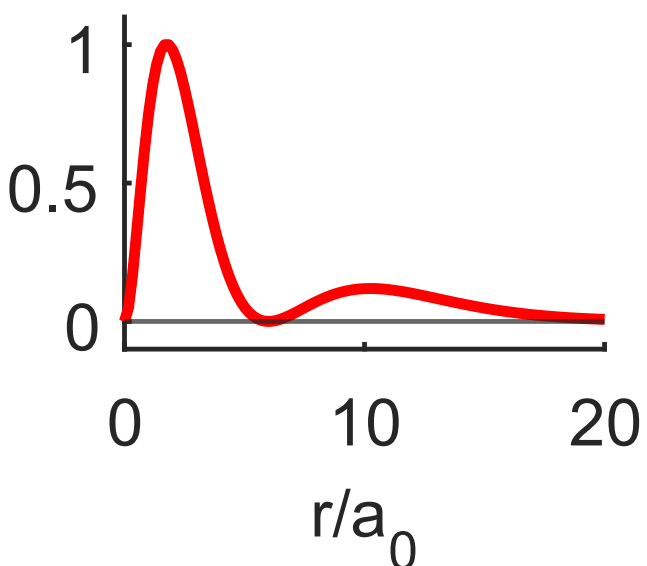
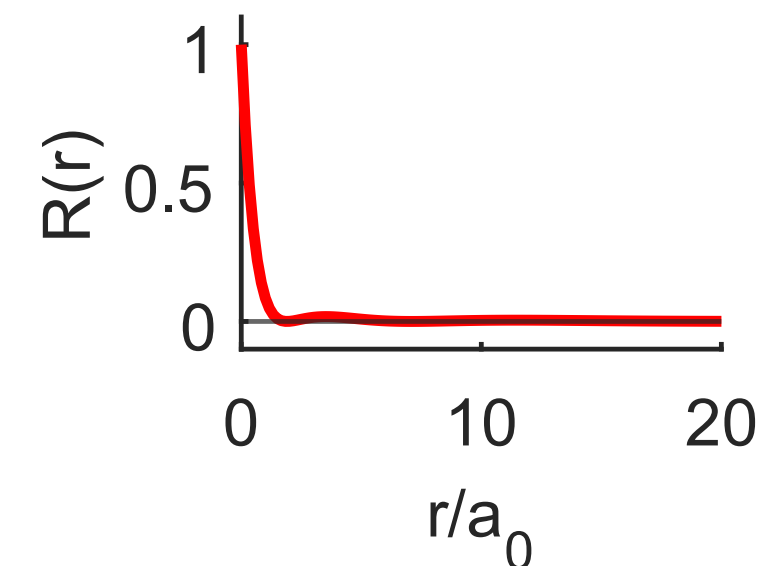
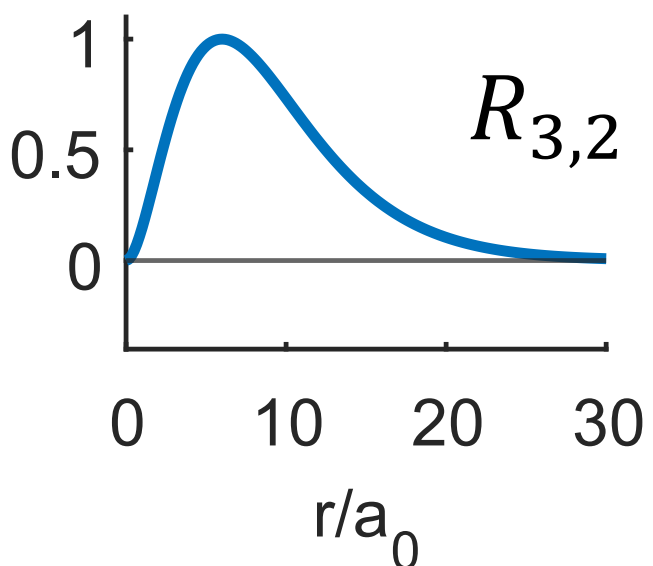
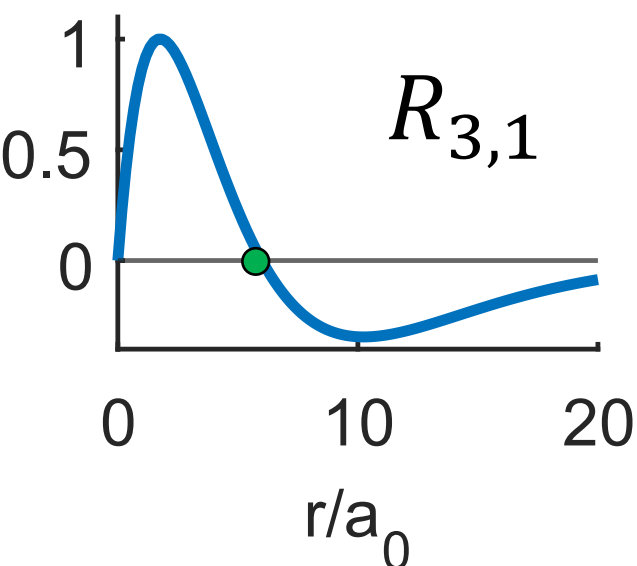
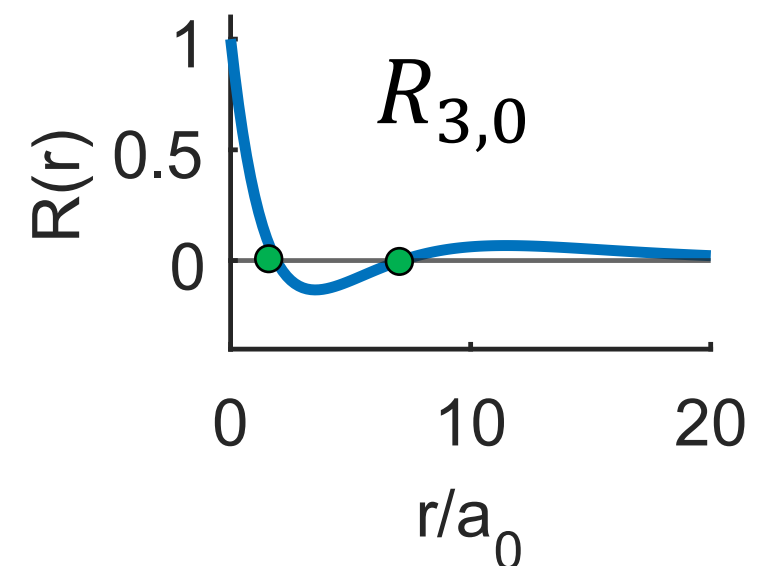
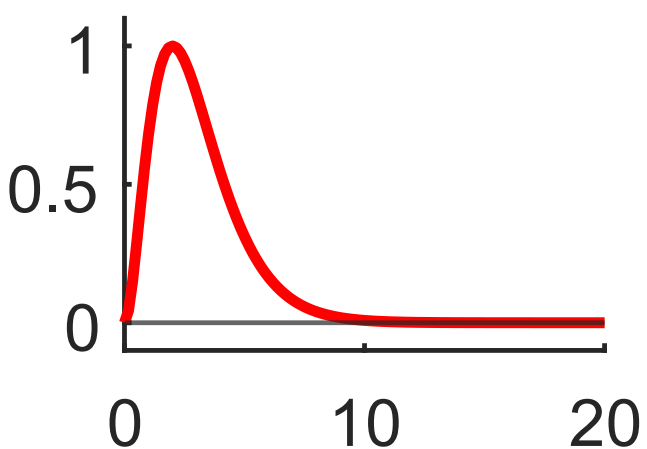
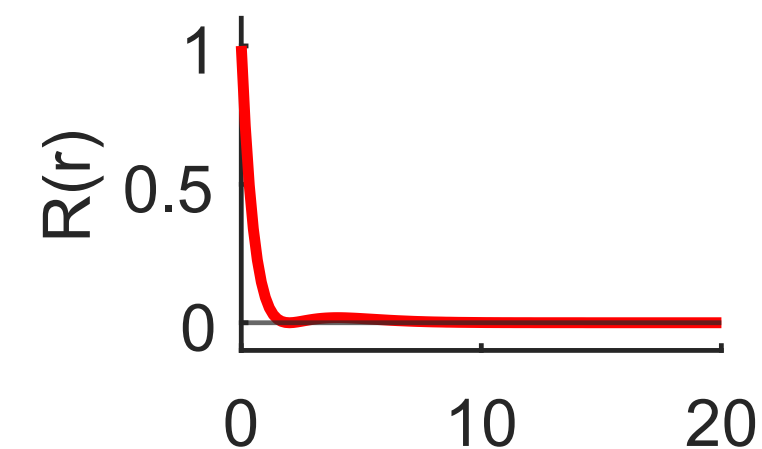
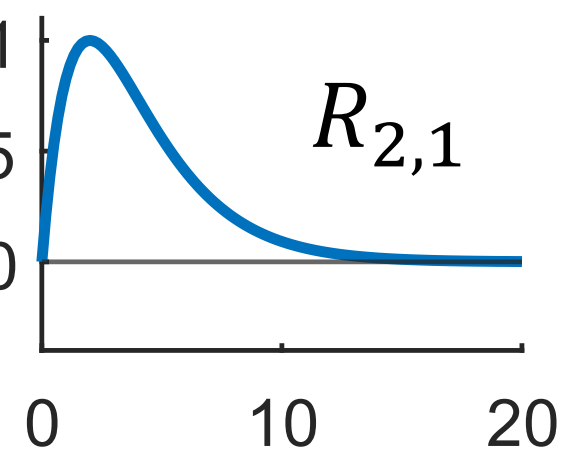
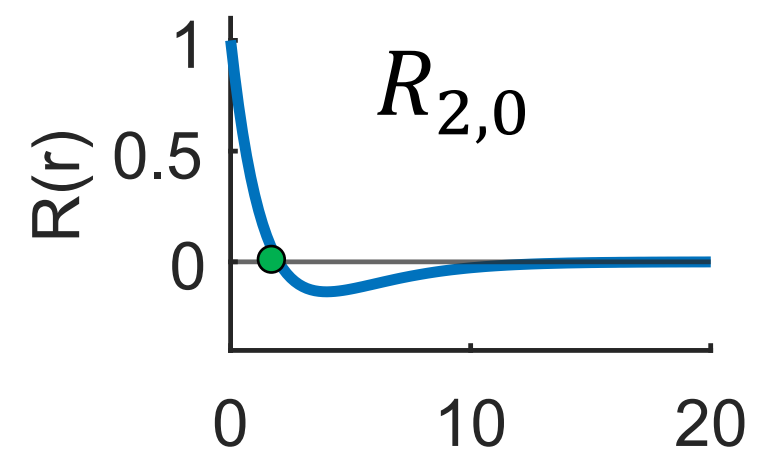
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$R_{n,l}(r)$
 $n - l - 1$ zeros



$|R_{n,l}(r)|^2$

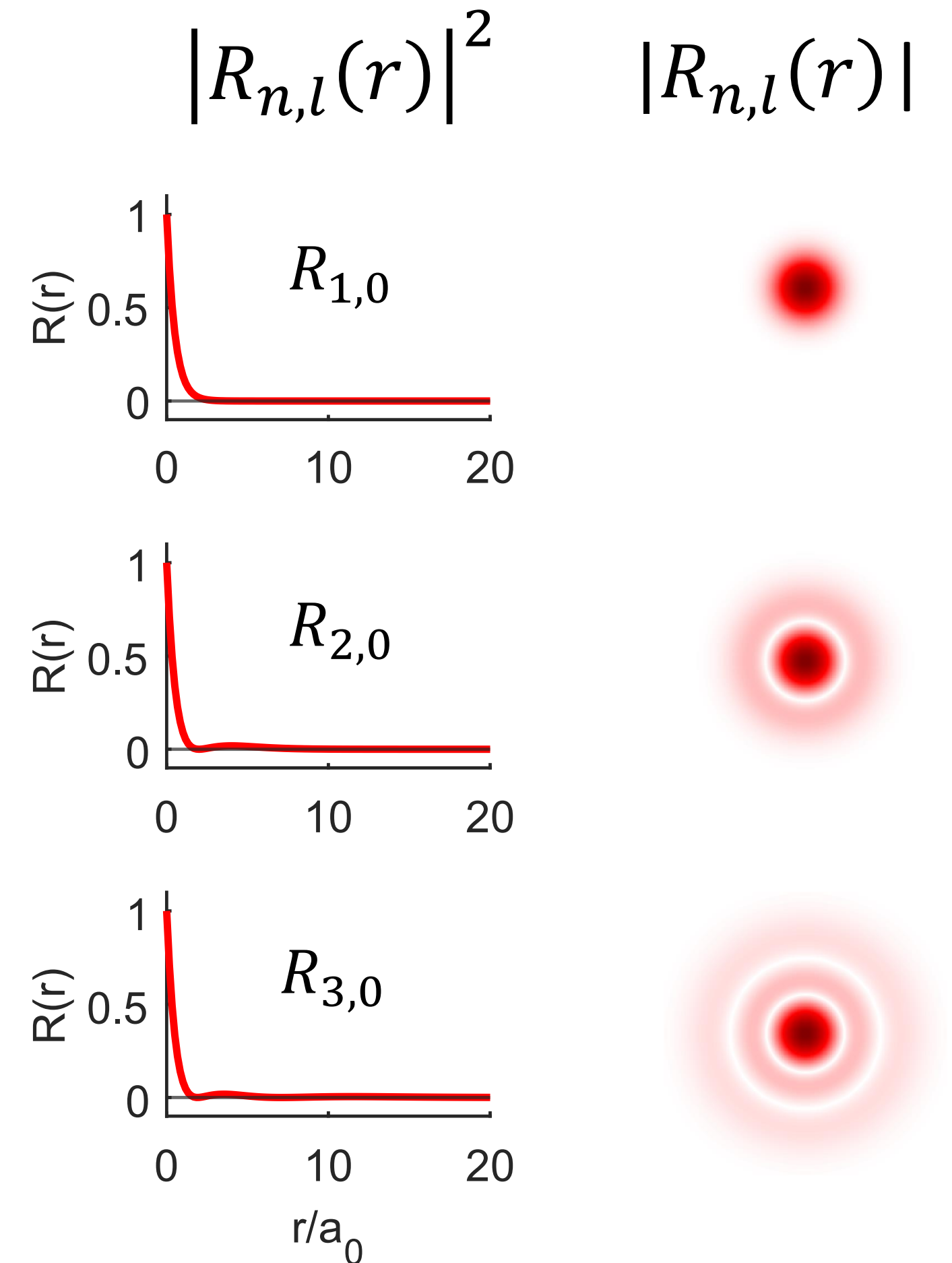


HYDROGEN ATOM: RADIAL EQUATION

$$R_{n,l}(r) \propto \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) \times e^{-\frac{r}{na_0}}$$

- **Principal quantum number:** $n = 1, 2, 3, \dots, \infty$
- **Orbital quantum number:** $l = 0, 1, 2, \dots, n-1$
- Radial part has $n - l - 1$ zeros in probability
- Energy is defined by the radial part:

$$E_n = -\frac{1}{(4\pi\epsilon_0)^2} \frac{\mu e^4}{2n^2 \hbar^2} = -\frac{13.6 \text{ eV}}{n^2}$$



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HYDROGEN ATOM: RADIUS OF S-ORBITAL

- Is the electron likely to be at the nucleus?
- Expected radius of the electron?
- Consider the ground state:

$$\psi_{1,0,0}(r) \propto \sqrt{\frac{1}{\pi a_0^3}} e^{-\frac{r}{a_0}}$$

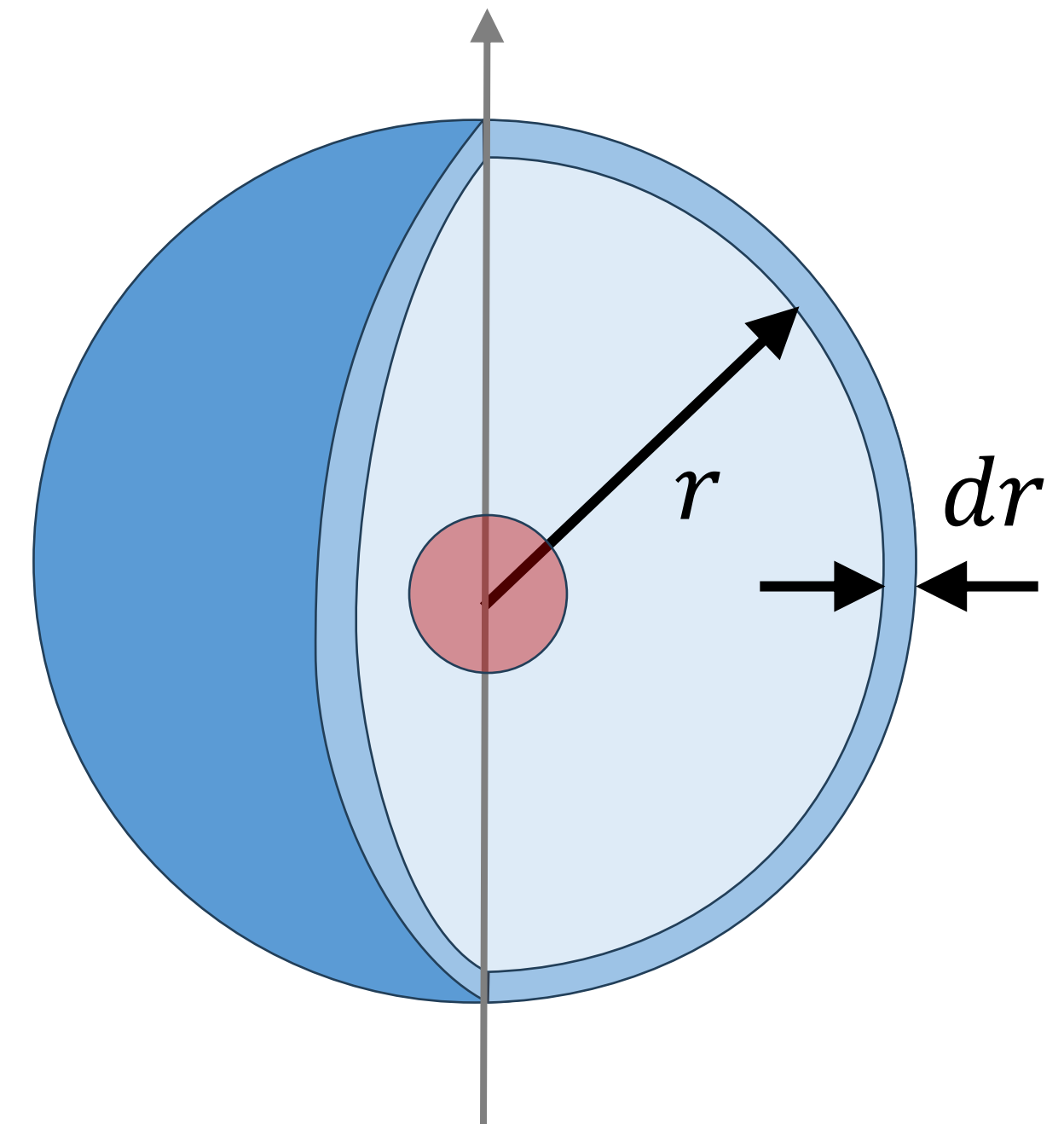
- Probability to have radius r :

$$P(r) dV = |\psi_{1,0,0}(r)|^2 dV$$

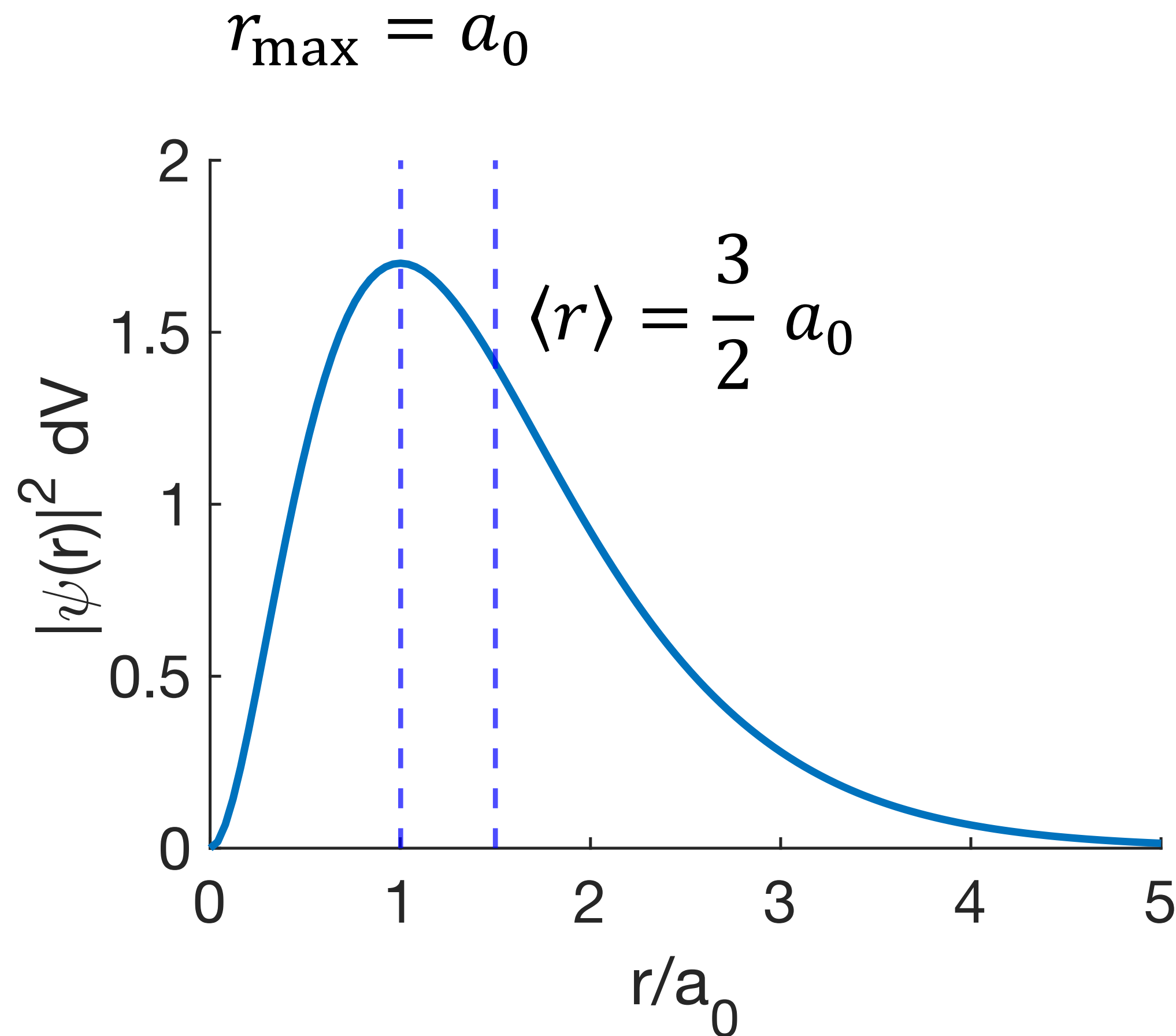
- Volume infinitesimal thin shell radius r :

$$V_{\text{shell}} = 4\pi r^2 dr$$

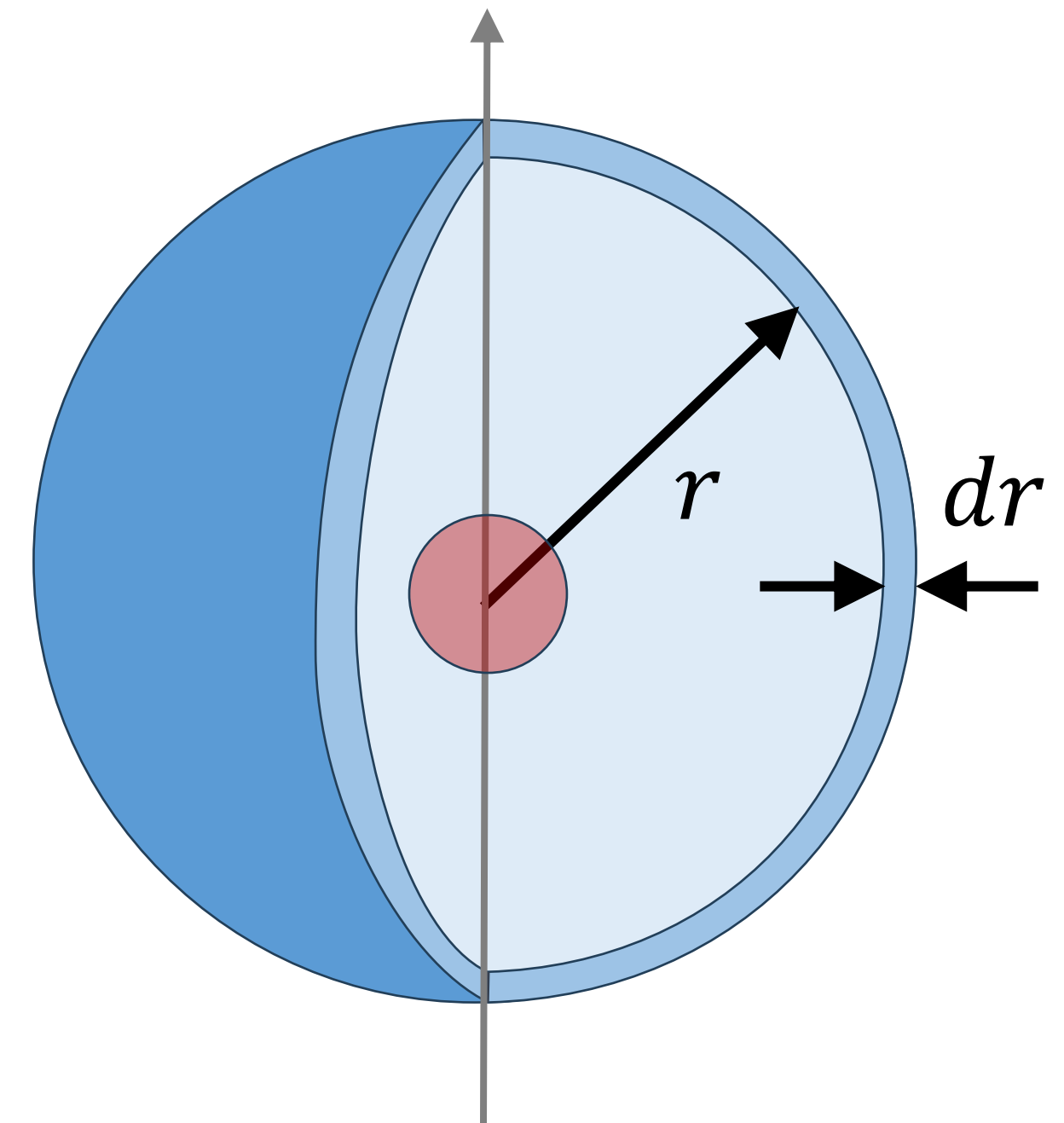
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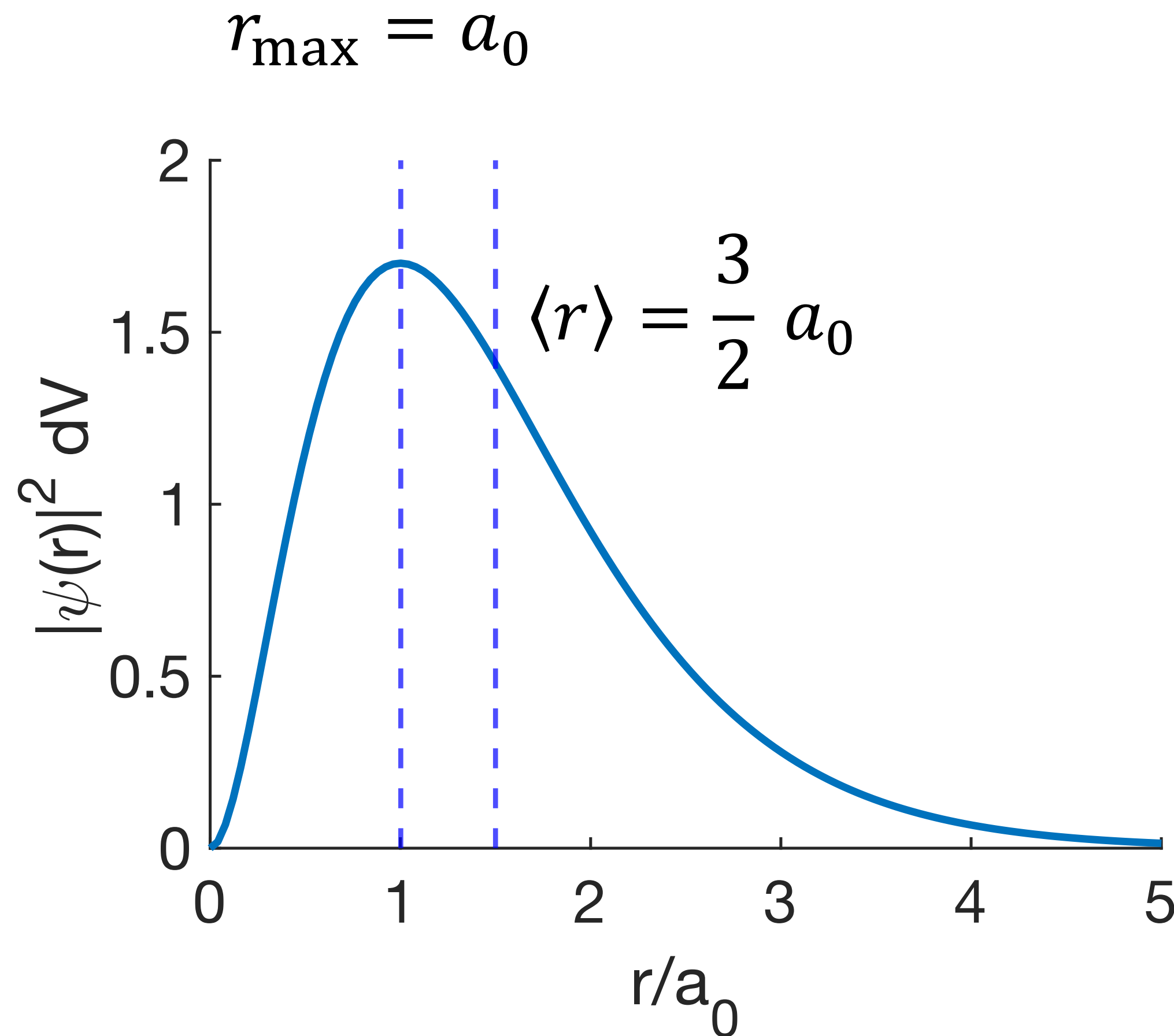
HYDROGEN ATOM: RADIUS OF S-ORBITAL



$$P(r) dV = |\psi_{1,0,0}(r)|^2 4\pi r^2 dr$$



HYDROGEN ATOM: RADIUS OF S-ORBITAL



- Expectation value for radius r

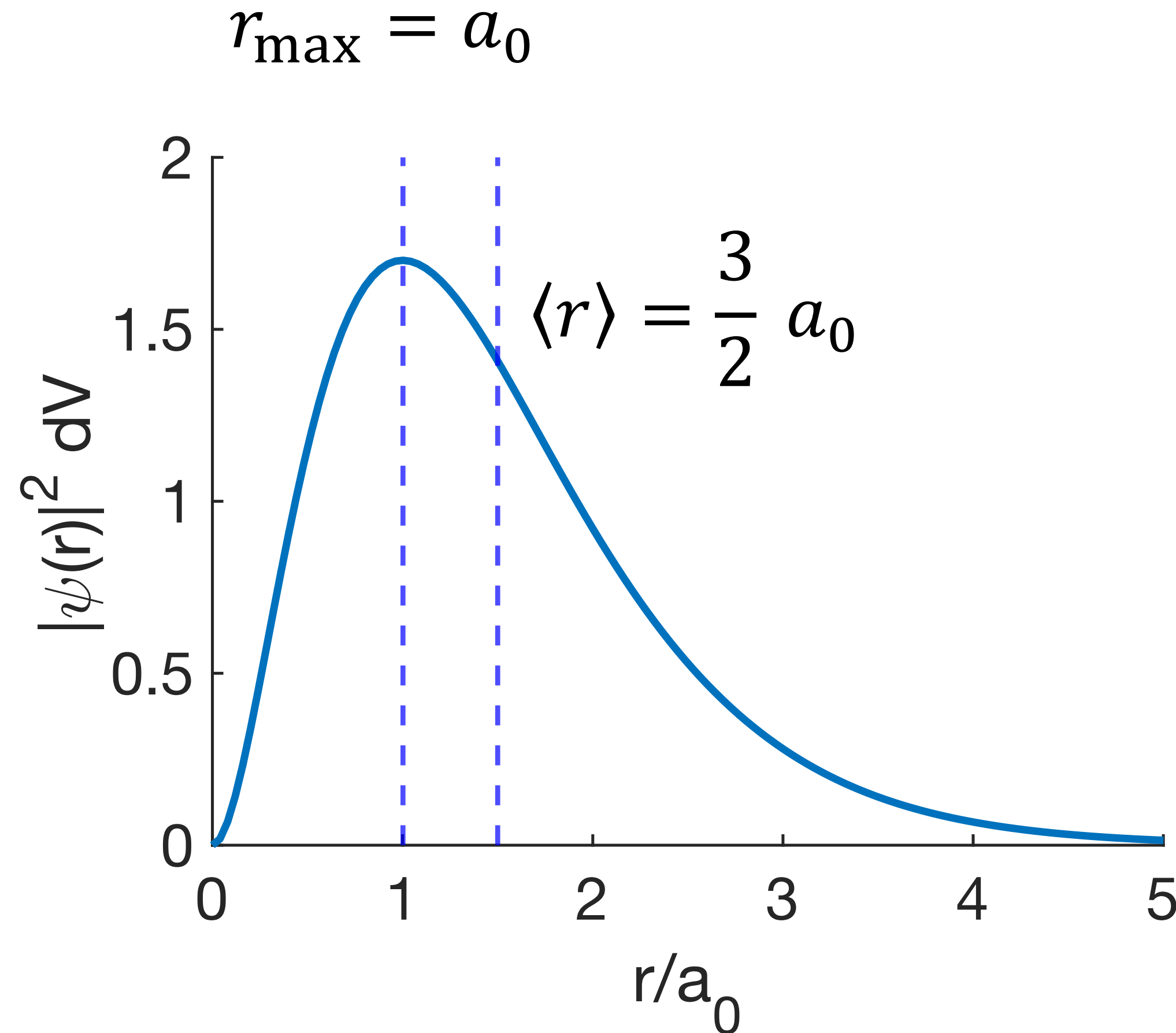
$$\langle r \rangle = \int_0^\infty r |\psi_{1,0,0}(r)|^2 4\pi r^2 dr$$

$$= \frac{1}{\pi a_0^3} 4\pi \int_0^\infty r^3 e^{-\frac{2r}{a_0}} dr$$

$$= \frac{4}{a_0^3} \frac{3!}{\left(\frac{2}{a_0}\right)^4} = \frac{3}{2} a_0$$

HYDROGEN ATOM: RADIUS OF S-ORBITAL

- Most likely radius r



$$0 = \frac{d}{dr} \left(|\psi_{1,0,0}(r)|^2 4\pi r^2 \right)$$

$$= \frac{d}{dr} \left(\frac{4}{a_0^3} r^2 e^{-\frac{2r}{a_0}} \right)$$

$$= \frac{4}{a_0^3} \left(2 - \frac{2r}{a_0} \right) r e^{-\frac{2r}{a_0}}$$

$$\Rightarrow 2 = \frac{2r}{a_0} \Rightarrow r_{\max} = a_0$$

HYDROGEN ATOM: ANGULAR MOMENTUM

- Quantization of angular momentum

$$L = \sqrt{l(l+1)} \hbar \quad \text{with } l = 0, 1, \dots, n-1$$

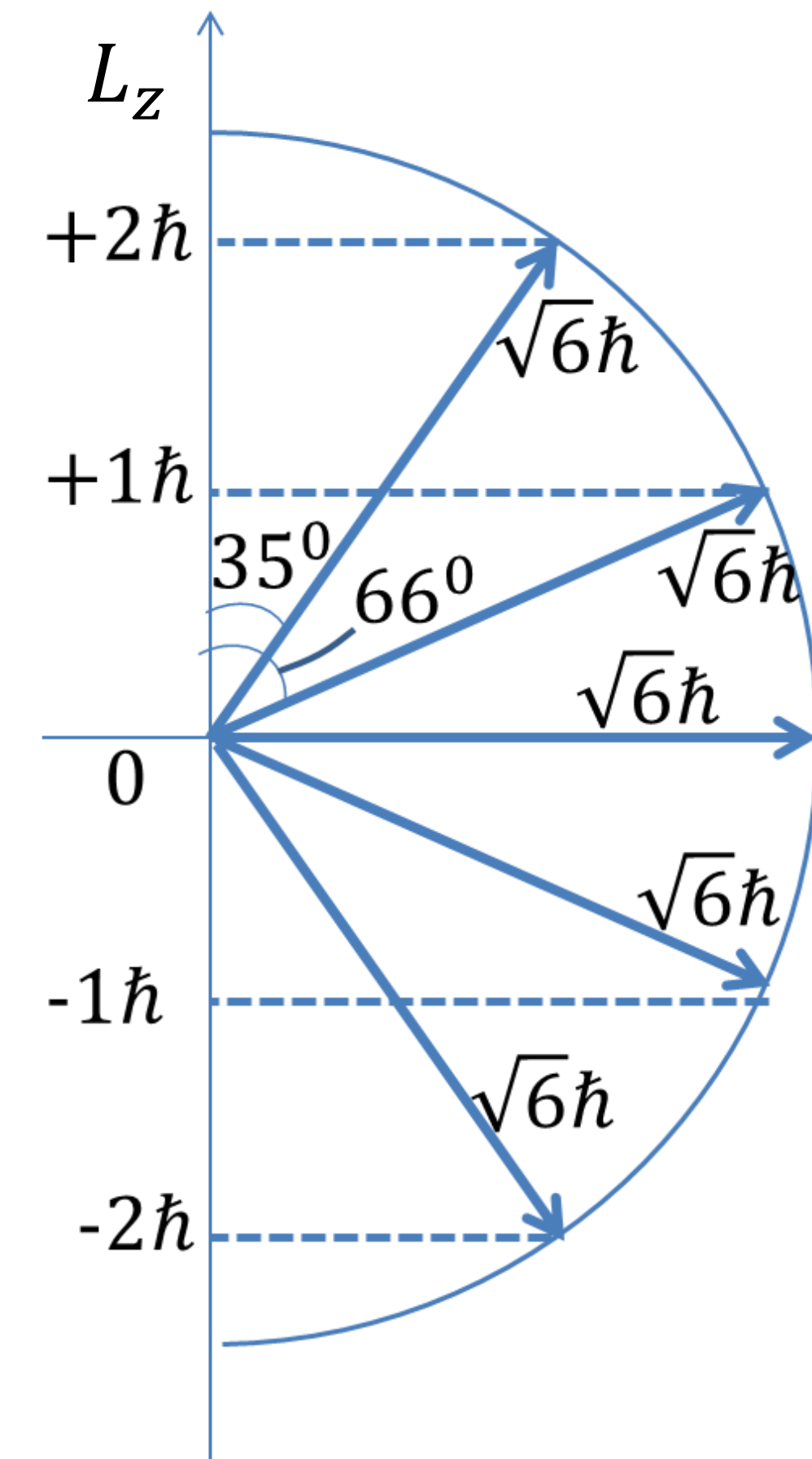
- Different from Bohr's: $l = 0 \Rightarrow L = 0$
- Condition $\Phi(\phi) = \Phi(\phi + 2\pi)$ gives:

$$L_z = m_l \hbar \quad \text{with } m_l = 0, \pm 1, \dots, \pm l$$

Quantum numbers so far:

n : principal quantum number
 l : orbital quantum number
 m_l : magnetic quantum number

Graphical representation
relation L_z and L



HYDROGEN ATOM: ANGULAR SOLUTIONS

- Quantization of angular momentum

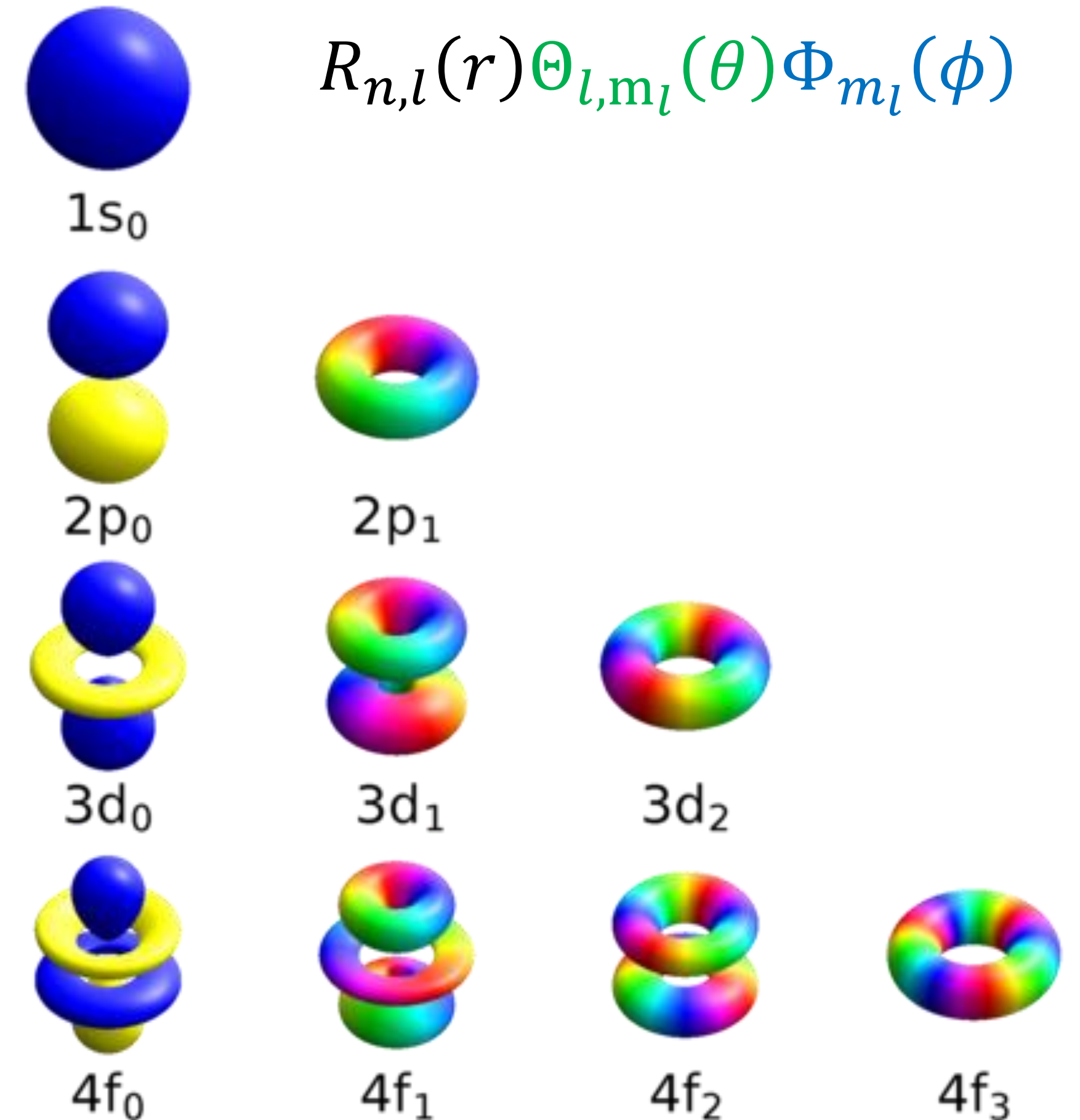
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HYDROGEN ATOM: ANGULAR EQUATIONS

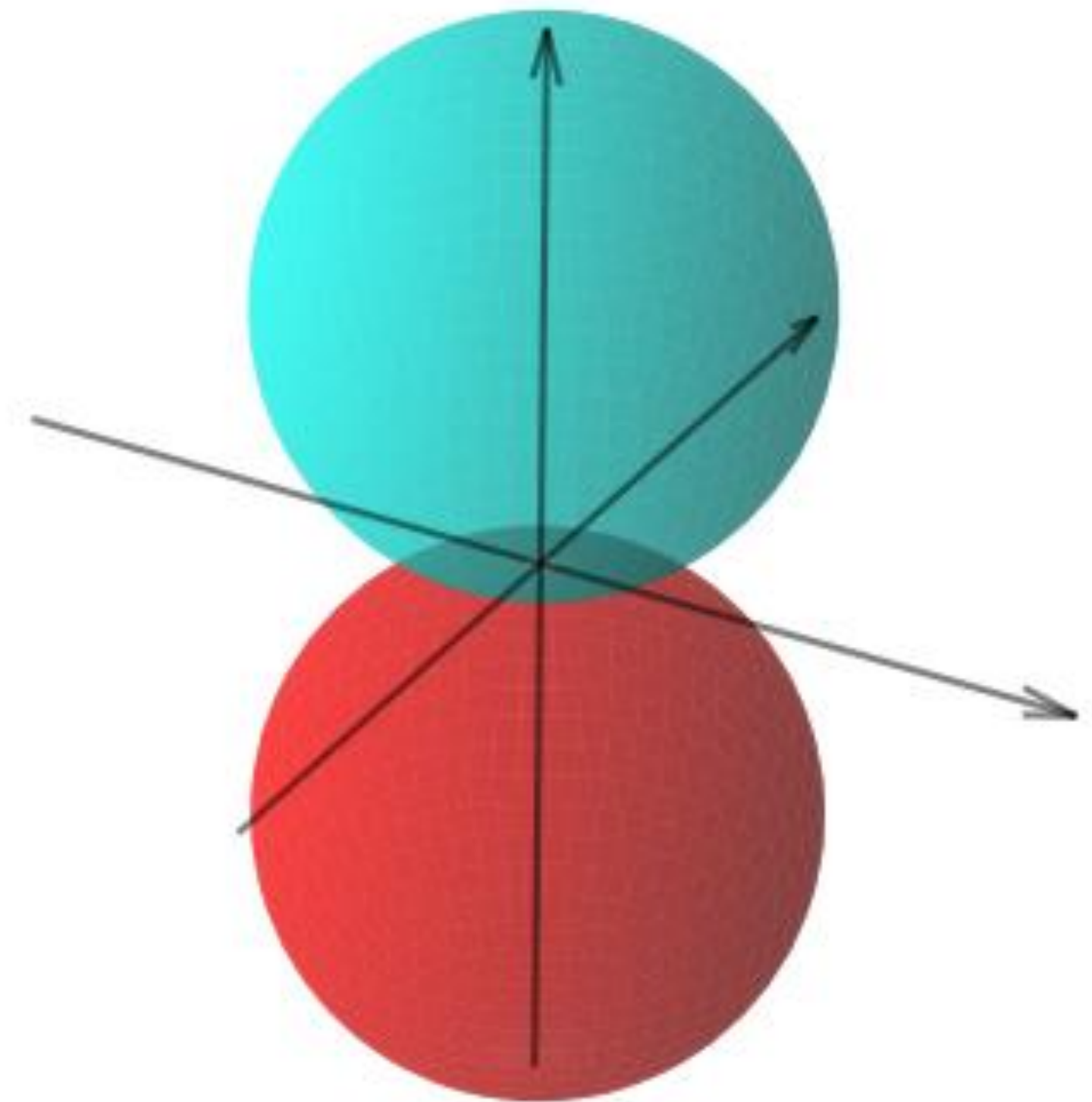
$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

Solving the $\Phi(\phi)$ part:

$$\frac{d^2\Phi(\phi)}{d\phi^2} + m_l^2\Phi(\phi) = 0$$

- Conditions:
 $\Phi(\phi)$ finite everywhere, and
 $\Phi(\phi + 2\pi) = \Phi(\phi)$
- Solution: a **complex phase factor**

$$\Phi_{m_l}(\phi) \propto e^{im_l\phi}$$



HYDROGEN ATOM: ANGULAR EQUATIONS

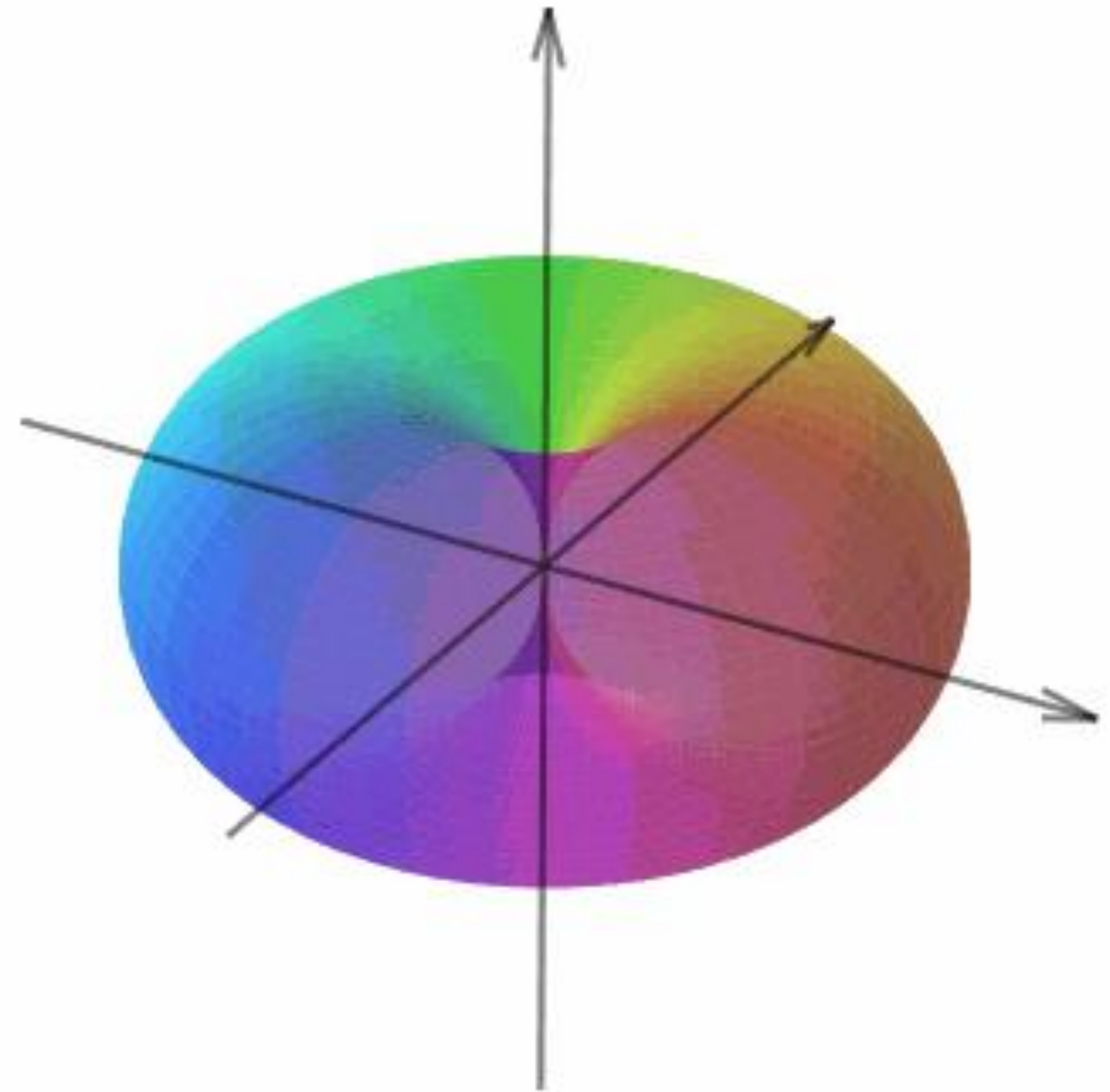
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HYDROGEN ATOM: SYMMETRY & SUPERPOSITION

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

2P_x – orbital

$$R(r)\Theta(\theta) \times (e^{im_l\phi} + e^{-im_l\phi})$$

- Solution: a **complex phase factor**

$$\Phi_{m_l}(\phi) \propto e^{im_l\phi}$$

$$0.99|2p1\rangle + 0.11|2p-1\rangle$$

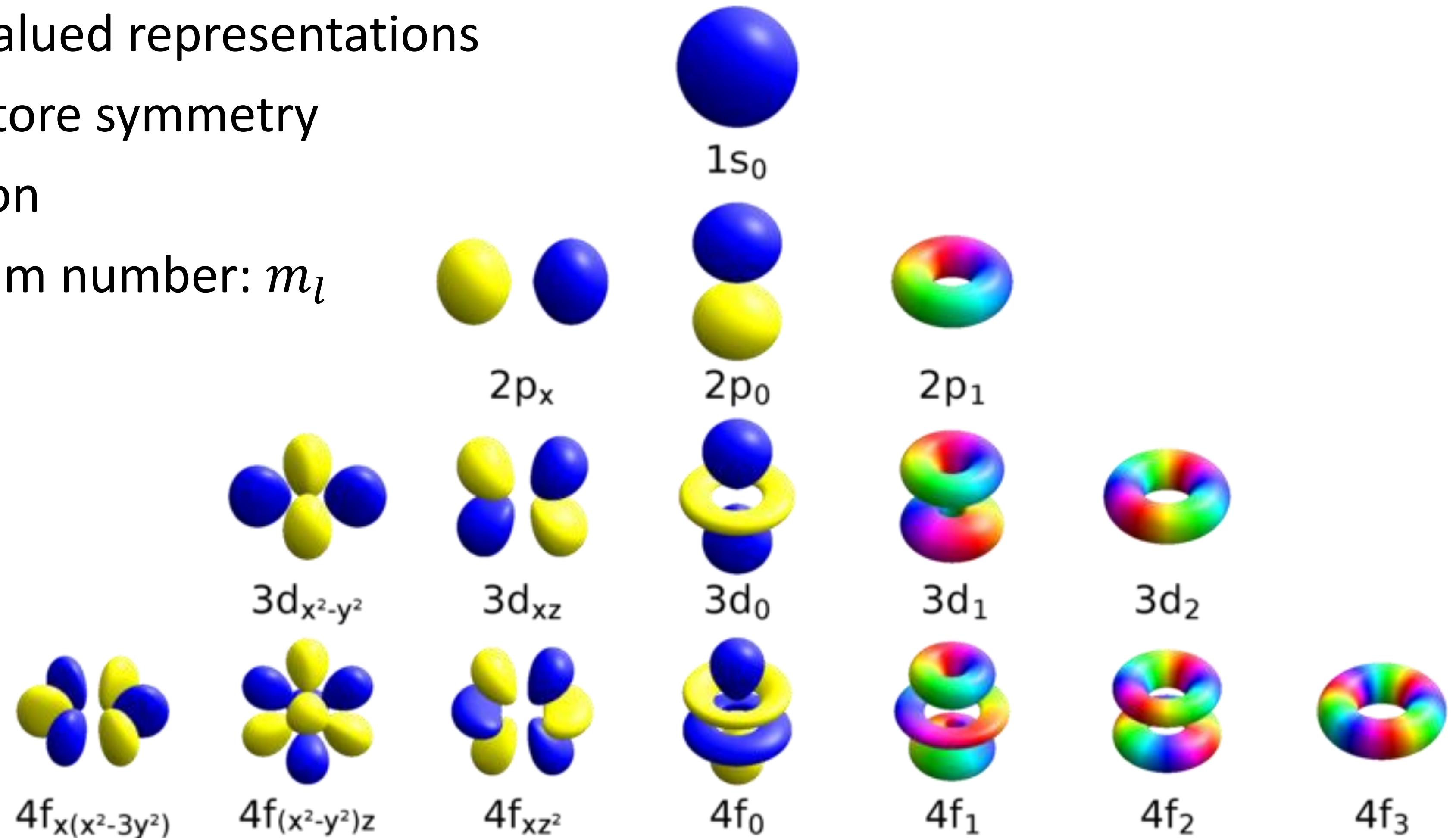
- Solution with P₀



$$0.78|2p_x\rangle + 0.63i|2p_y\rangle$$

HYDROGEN ATOM: SUMMARY

- More real-valued representations
- Partially restore symmetry
- Superposition
- Lose quantum number: m_l



HYDROGEN ATOM: QUANTIZATION AND NAMING

- Quantization of energy, linear momentum and radius
- Quantization of orbital/azimuthal momentum
- Energy E_n is degenerate: l and m_l do not influence it
- Expected radius/energy close to Bohr's model
- Labeling and naming conventions:

Principal quantum number	Shell name
$n = 1$	K shell
$n = 2$	L shell
$n = 3$	M shell
$n = 4$	N shell

Azimuthal quantum number	Subshell name
$l = 0$	S states
$l = 1$	P states
$l = 2$	D states
$l = 3$	F states