Quantum Mechanics

Reading: Gray: (1–8) to (1–12)
OGN: (15.5)

A Timeline of the Atom

← **400 BC …… 0 ……. 1800 1850 1900 1950**

400	B.C. Democritus: idea of an atom
1808	John Dalton introduces his atomic theory.
1820	**Faraday: charge/mass ratio of protons**
1885	E. Goldstein: discovers a positively charged sub-atomic particle
1898	**J. J. Thompson finds a negatively charged particle called an electron.**
1909	**Robert Millikan experiments to find the charge and mass of the electron.**
1911	**Ernest Rutherford discovers the nucleus of an atom.**
1913	**Neils Bohr introduces his atomic theory.**
1919	The positively charged particle identified by Goldstein is found to be a proton.
1920s	**Heisenberg, de Broglie, and Schrödinger.**
1932	James Chadwick finds the neutron.
1964	The Up, Down, and Strange quark are discovered.
1974	The Charm quark is discovered.
1977	The Bottom quark is discovered.
1995	The Top (and final) quark is discovered.

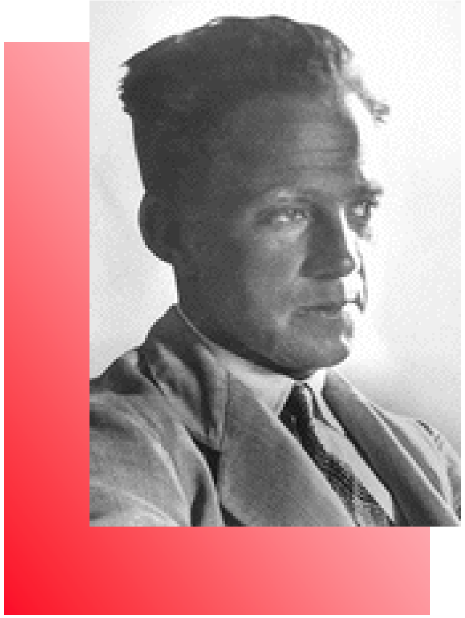
The Person Behind The Science

Werner Heisenberg

1901-1976

Highlights

- Studied under Max Born, James Franck, and Niels Bohr
- Received Nobel Prize in Physics (1932) for *"for the creation of quantum mechanics…"*

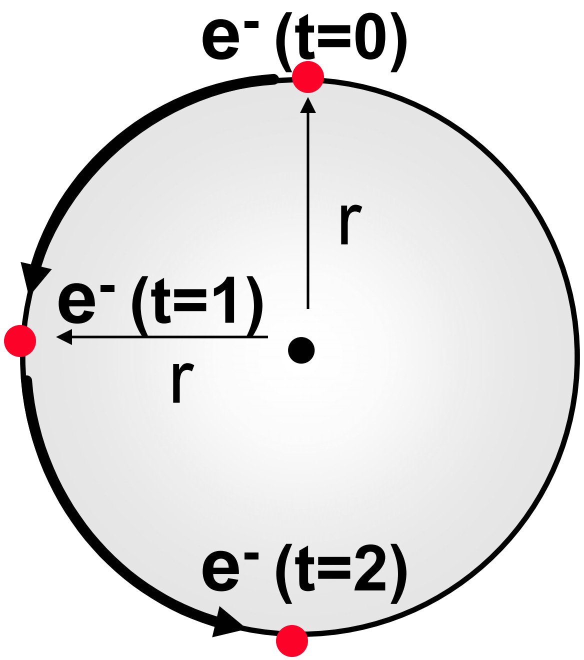


Moments in a Life

- With his help, the Max Planck Institute for Physics is founded (1948)
- Publishes his theory on quantum mechanics (1925, at the age of 23!)

The Modern Picture of the Hydrogen Atom

Bohr Model

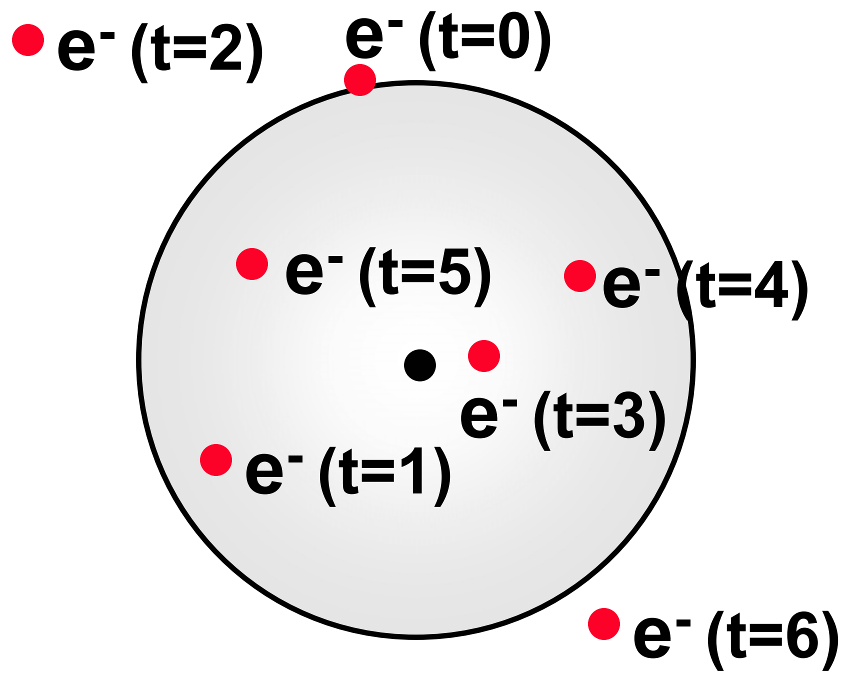


$\Delta x = 0; \Delta p = 0$

so $\Delta x \cdot \Delta p = 0 < \frac{h}{4\pi}$!

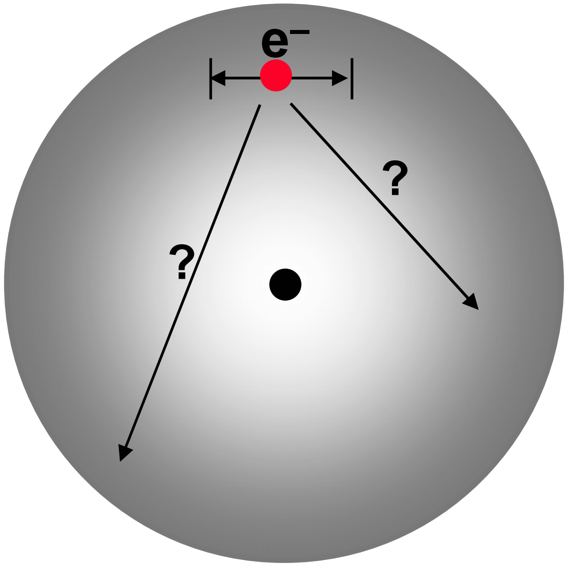
The Bohr model violates the uncertainty principle!

Current Model



The uncertainty in an electron's position is comparable to the diameter of the atom itself.

Uncertainty in Electron Momentum and Position



We want $\Delta x \approx 10^{-11}$ m (i.e., 0.1 Å)

$$\Delta p \bullet \Delta x \geq \frac{h}{4\pi} \quad \text{so} \quad \Delta p \geq \frac{h}{4\pi \bullet \Delta x}$$

$$\Delta p \geq \frac{6.6 \times 10^{-34}\, J \cdot s}{12.6 \times 10^{-11} m} = 5.3\text{x}10^{-24}\ kg \bullet m \bullet s^{-1}$$

How big is this uncertainty?

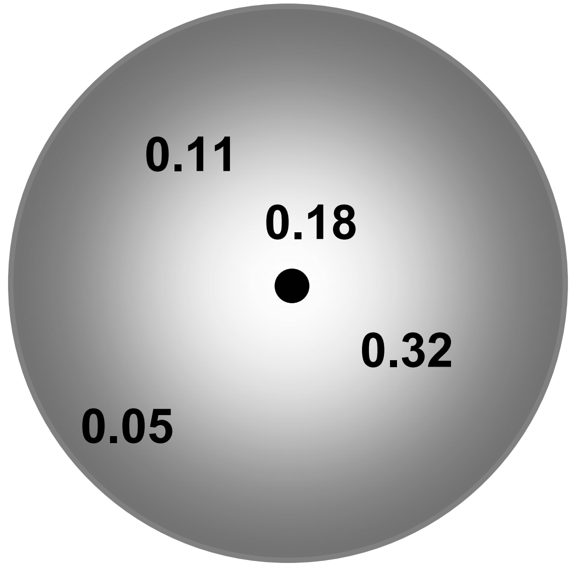
$$\Delta p = m_e \bullet \Delta v \quad \text{so} \quad \Delta v = \frac{\Delta p}{m_e}$$

$$\Delta v \approx \frac{10^{-23} kg \bullet m \bullet s^{-1}}{10^{-30} kg} = 10^{7} m \bullet s^{-1}$$

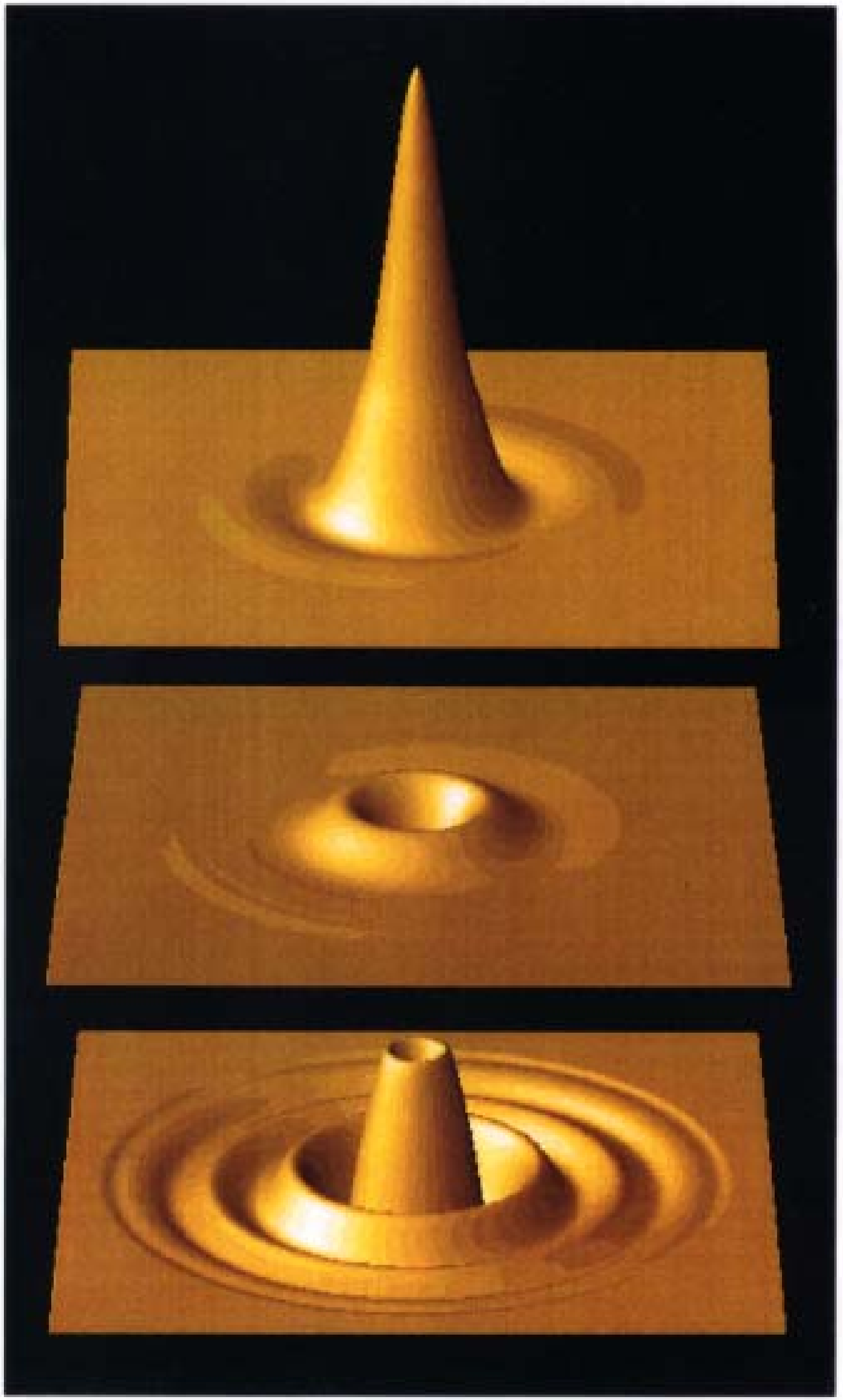
Suppose we look for the electron again after only $1\text{x}10^{-14}$ s:

$$\Delta x = (10^{7} m \bullet s^{-1}) \bullet (10^{-14} s) = 10^{-7} m = 1000\,Å!$$

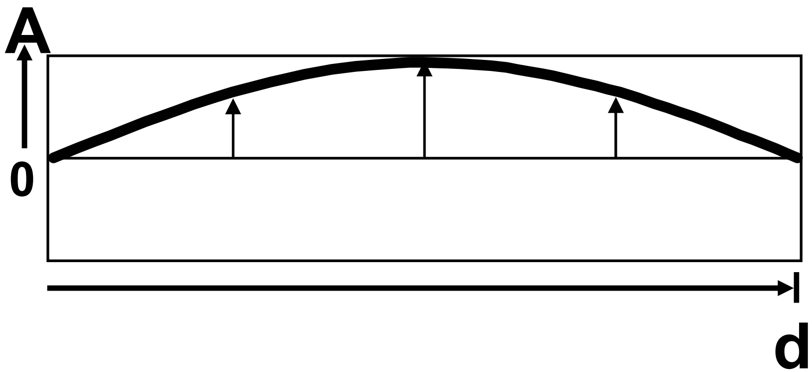
The Modern Picture of an Atom

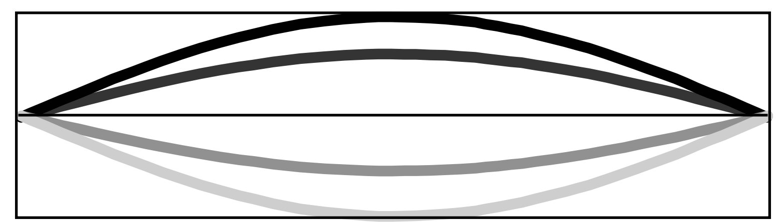


- The best we can do is say what the probability of finding an electron is at any given point for any individual observation
- Such information is described by a function with properties of a wave, hence the name **WAVEFUNCTION**



Waves in 1–D





For this example,

$$y = f(x) = A \sin\left(\frac{\pi x}{d}\right)$$

But f also varies with time

$$y = f(x,t) = A \sin\left(\frac{\pi x}{d}\right) \cos(\omega t)$$

The function is called the <u>Wavefunction</u>:
$\Psi(x,t)$

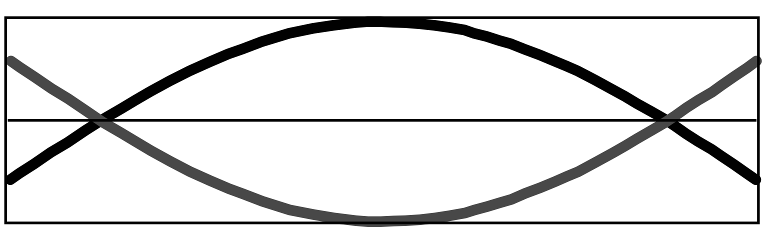
Boundary Conditions to Define Allowed Waves:

1) **Tie the Ends Down**
2) **Find a Standing Wave in the Box**

Allowed Standing Wave

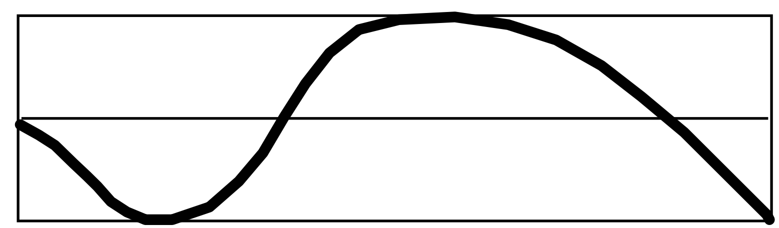
Ends are fixed at $\Psi = 0$ always

Not an Allowed Wave



Ends not Tied Down

Not Even a Standing Wave



A Traveling Wave

Nodes

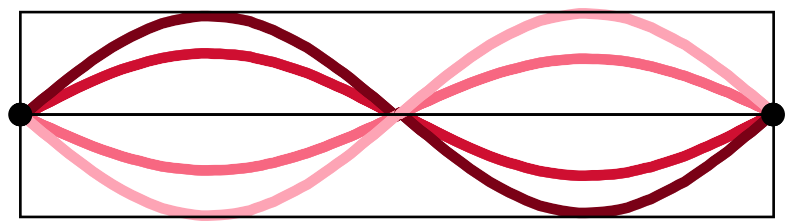
This Ψ has No Nodes

There are no points for which Ψ = 0 <u>at all times</u>

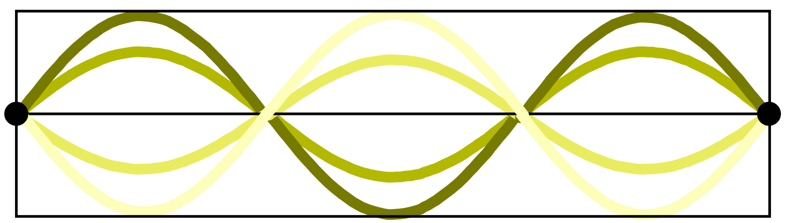
(The ends were fixed by the boundary conditions and therefore don't count as nodes)

Other Allowed Standing Waves

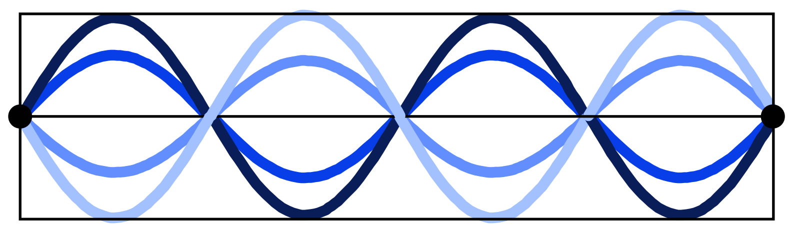
No nodes



One node (at $x=\frac{d}{2}$)

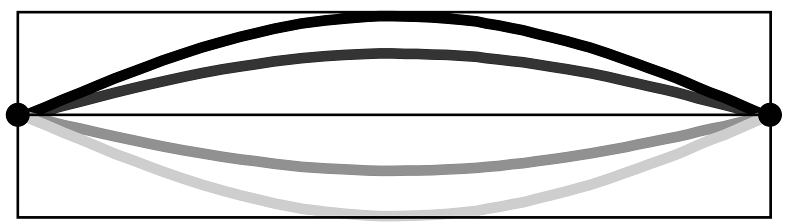


Two nodes ($x=\frac{d}{3}, \frac{2d}{3}$)



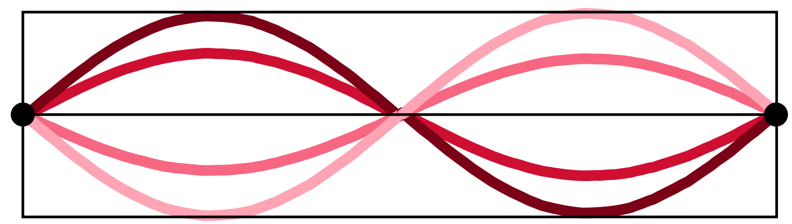
Three nodes ($x=\frac{d}{4}, \frac{d}{2}, \frac{3d}{4}$)

More Nodes = Higher Energy



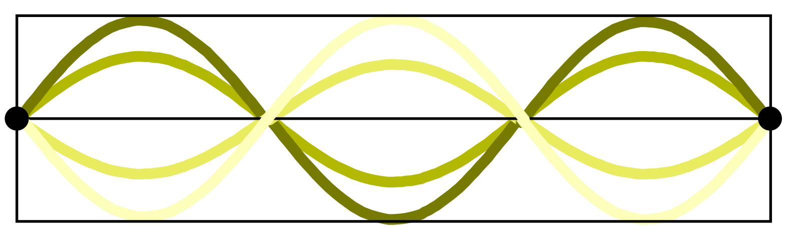
No nodes

Lowest Energy



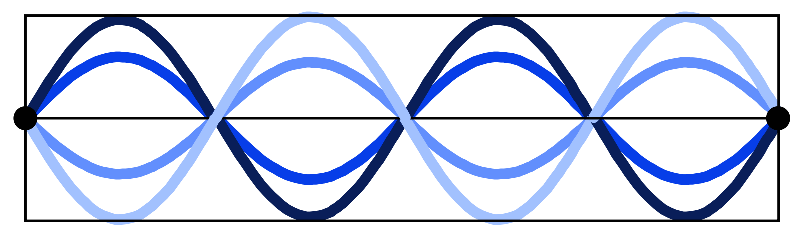
One node ($x=\frac{d}{2}$)

Next Lowest Energy



Two nodes ($x=\frac{d}{3}, \frac{2d}{3}$)

Higher Energy



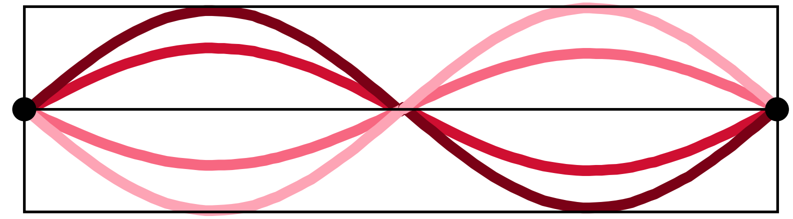
Three nodes ($x=\frac{d}{4}, \frac{d}{2}, \frac{3d}{4}$)

Even Higher Energy

Quantization

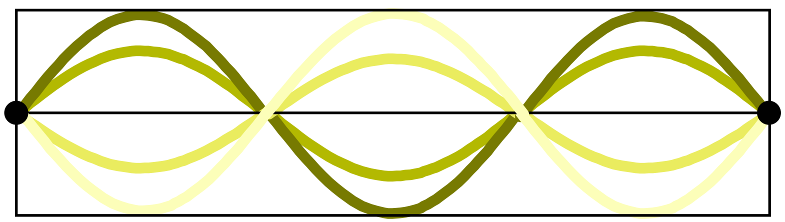
No nodes

Lowest Energy

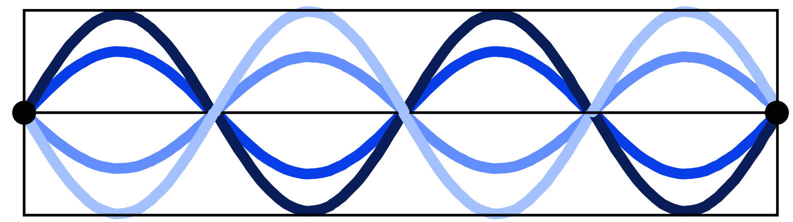


One node ($x=\frac{d}{2}$)

Next Lowest Energy



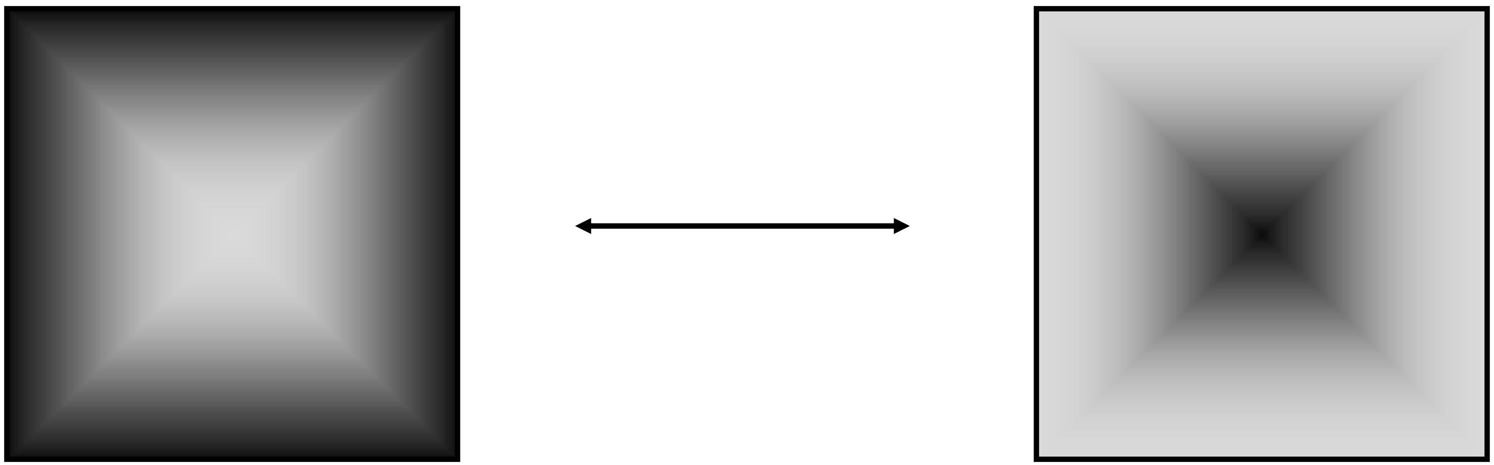
Two nodes ($x=\frac{d}{3}, \frac{2d}{3}$)



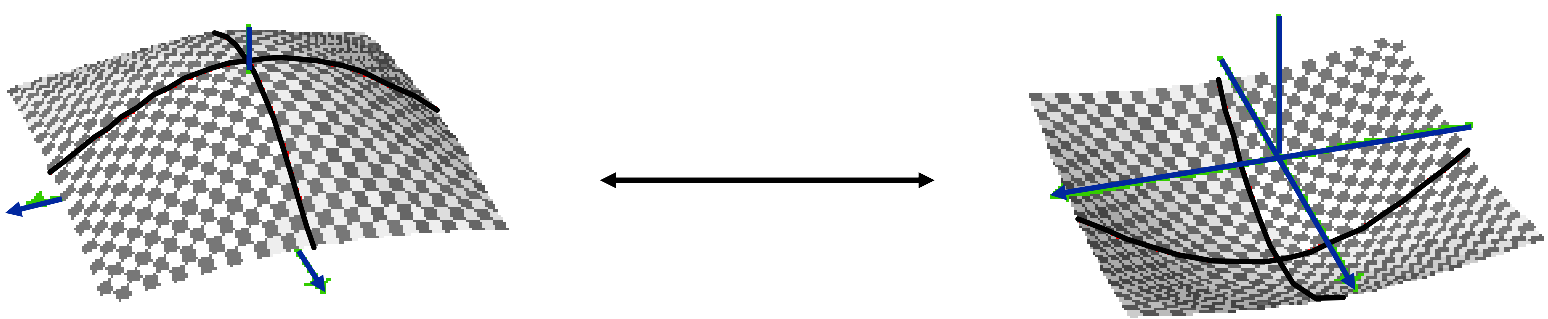
Three nodes ($x=\frac{d}{4}, \frac{d}{2}, \frac{3d}{4}$)

- Only certain wavefunctions are allowed solutions
- The "Quantum Number" defines each wavefunction and its energy

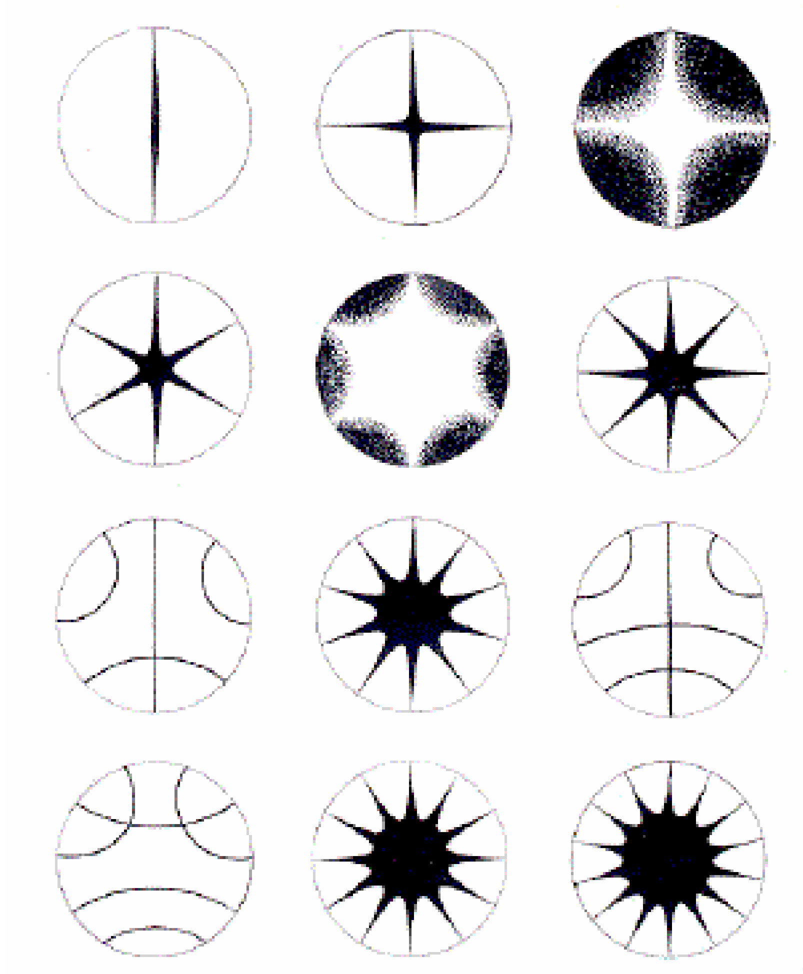
Waves in 2-D



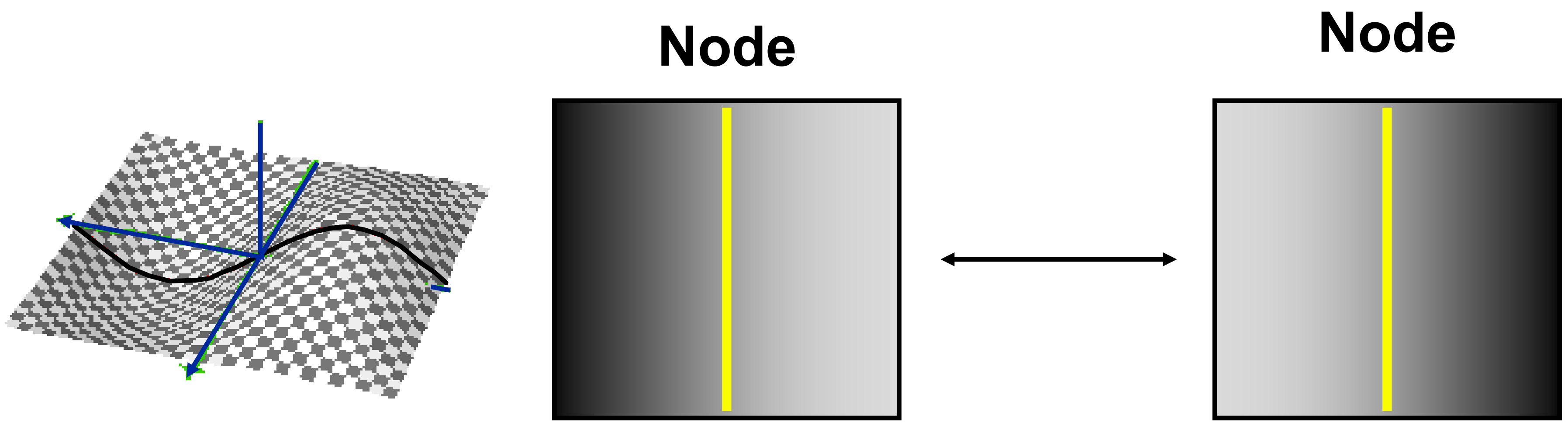
No Nodes--Lowest Energy

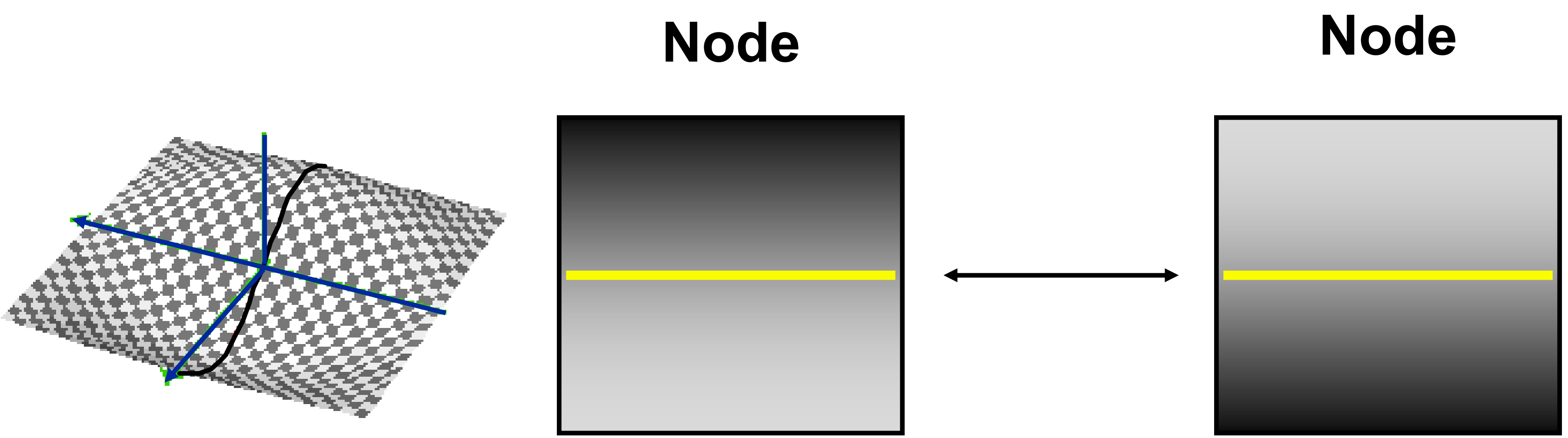


Chladni Patterns

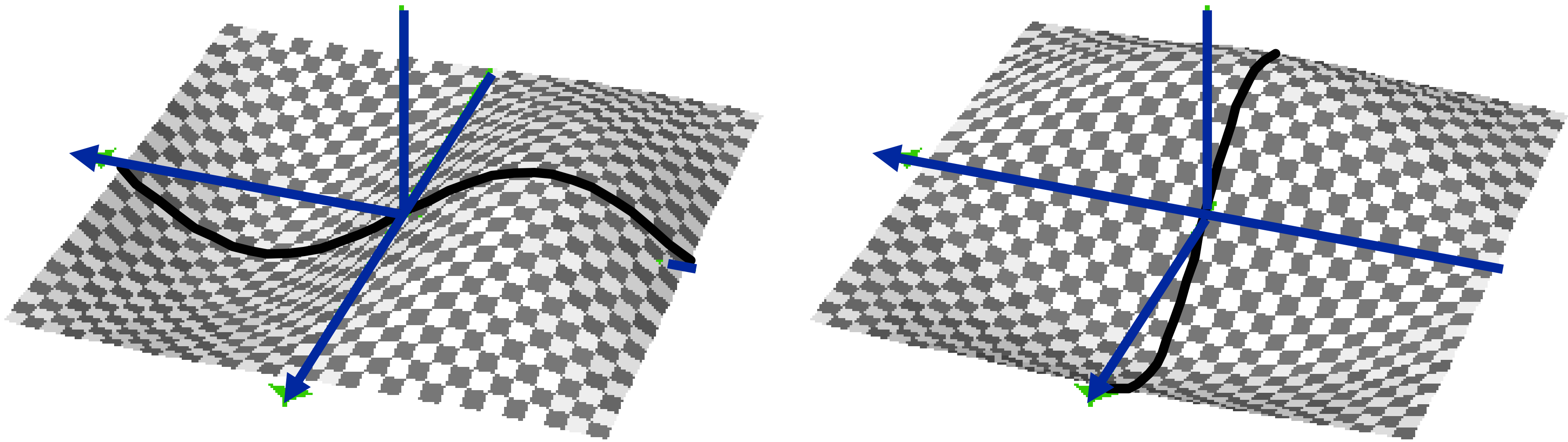


Waves in 2-D





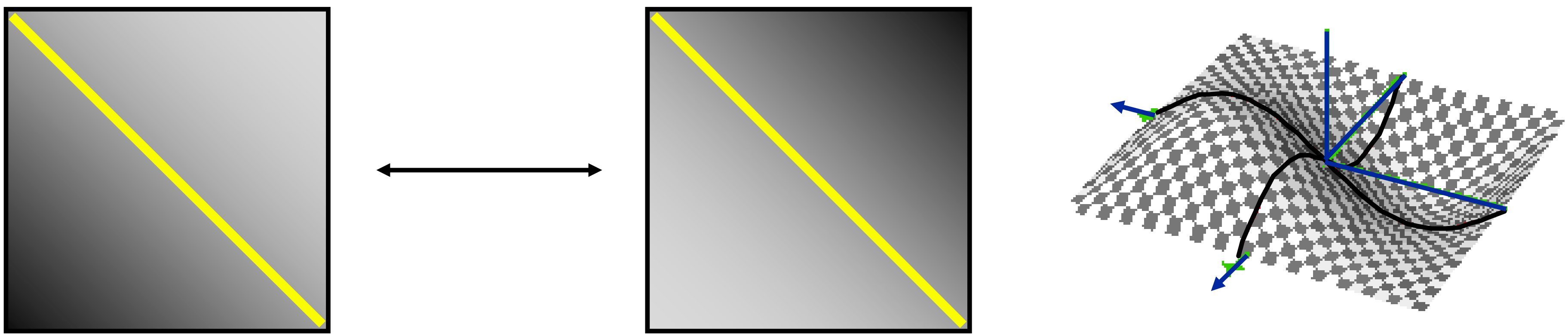
Waves in 2-D: A Degenerate Set

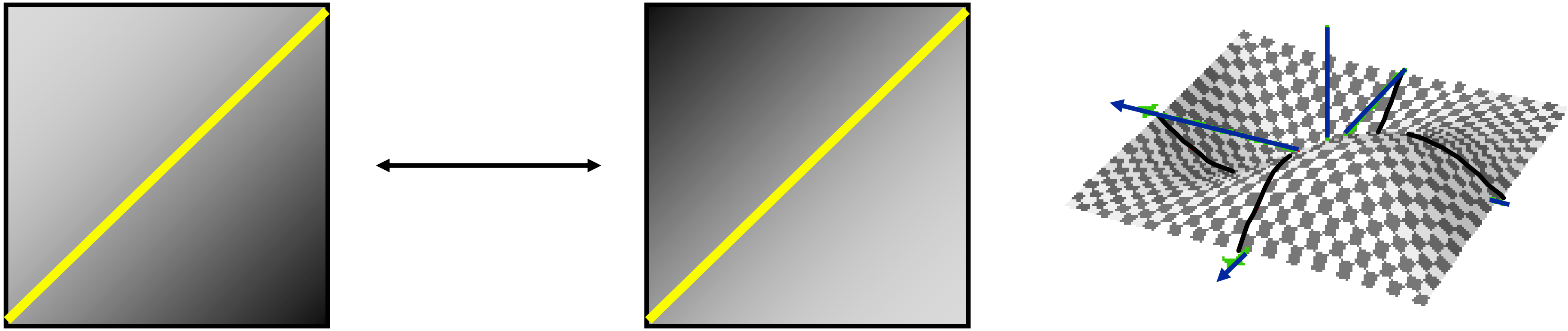


Each has one node:
These are higher in energy than the Ψ with no nodes.

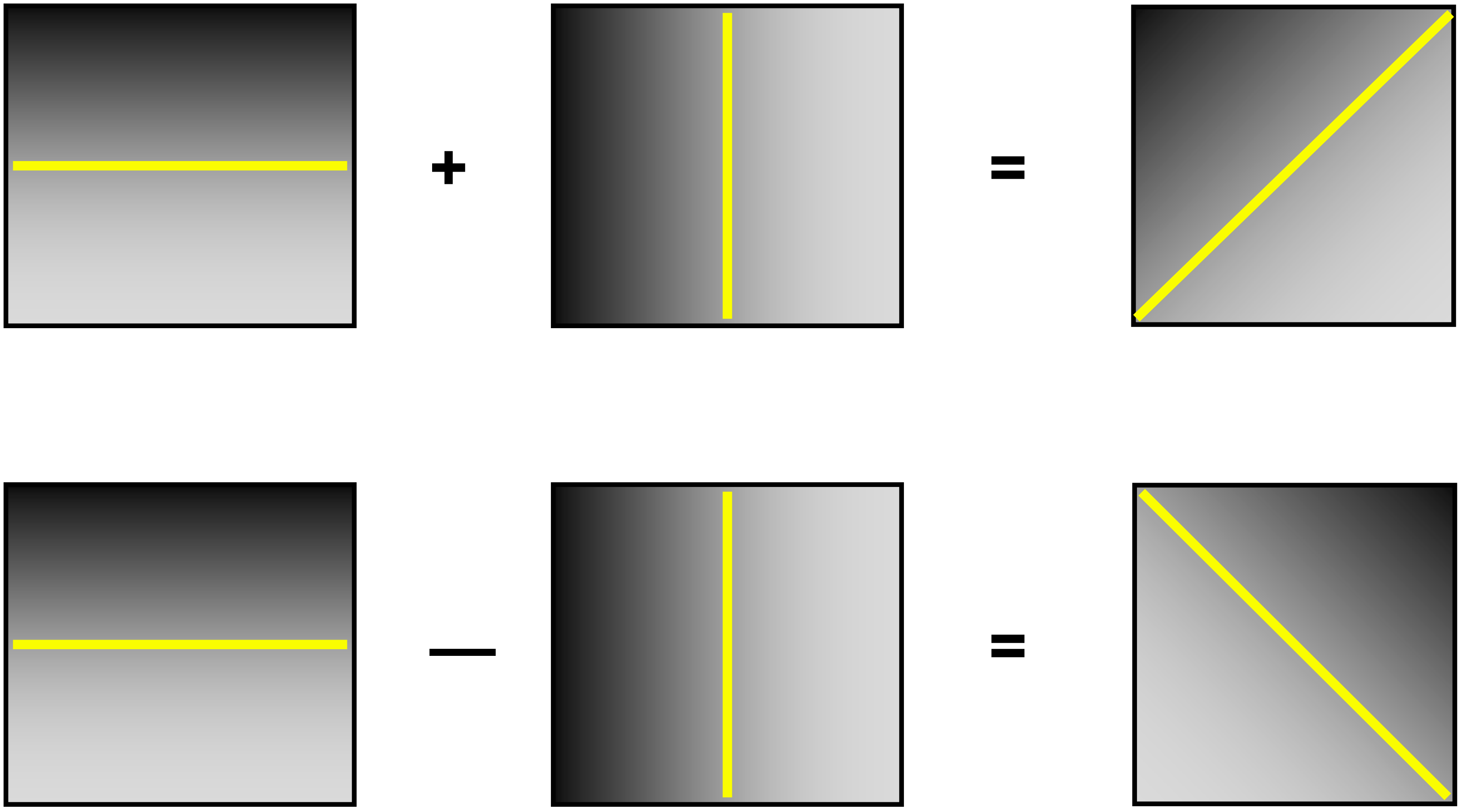
Both are equal in energy and are related by symmetry.
Both are needed to complete the solution set.

Other Solutions with 1 Node

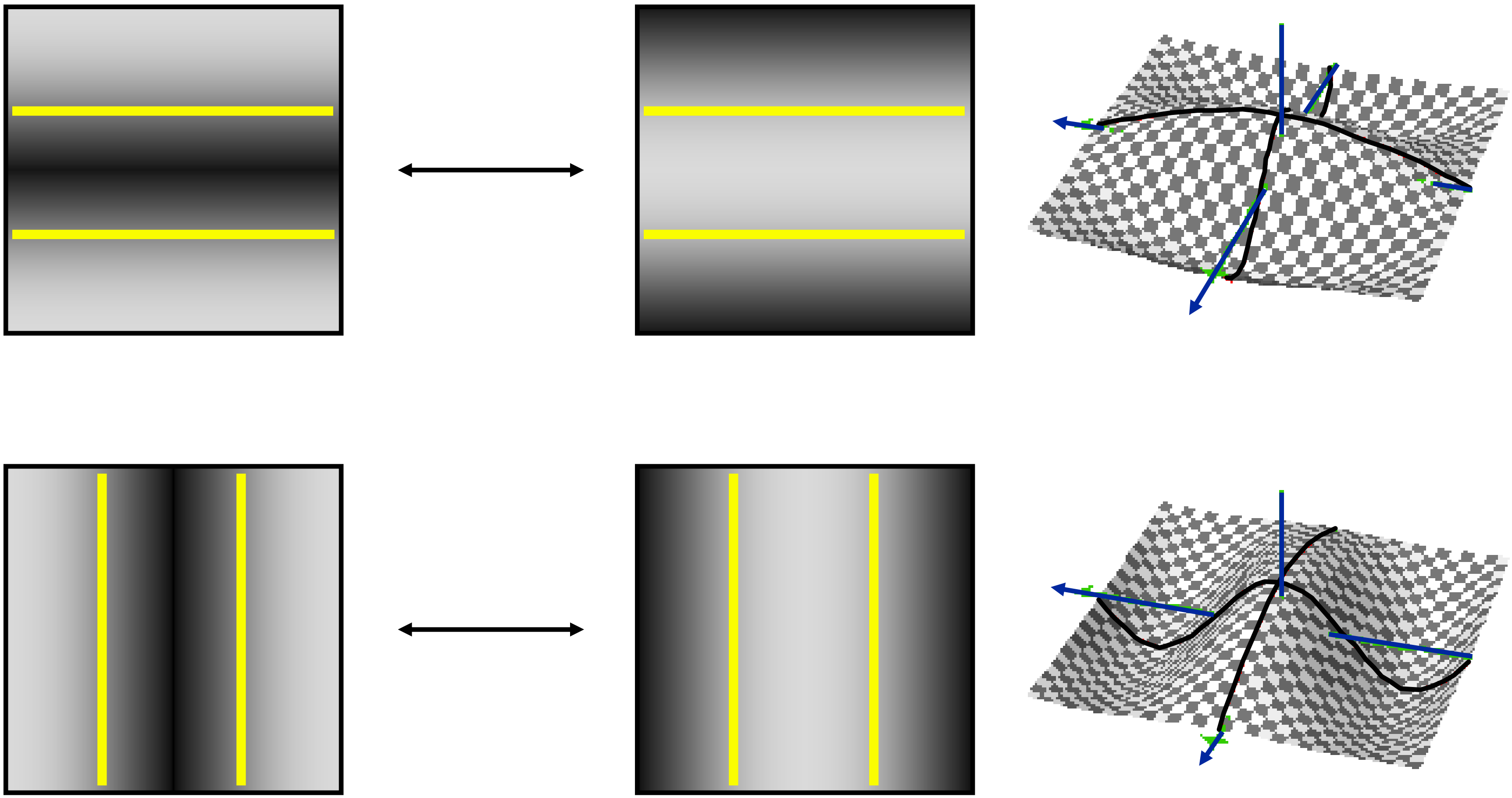




The Last Pair is “Redundant”



Solutions with 2 Nodes



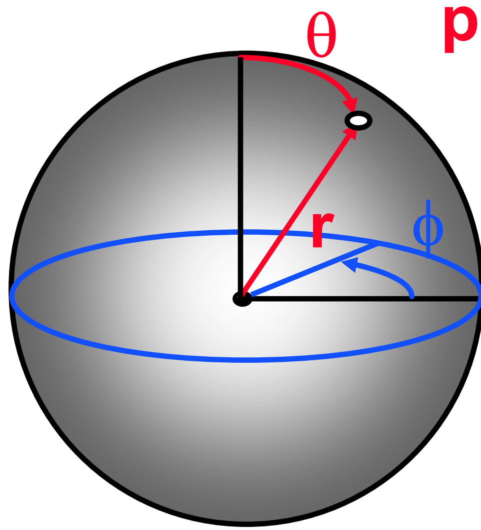
Another Degenerate Set

This set has a higher energy than the set with one node.

Review

- **Allowed Waves are Limited by Physical Boundary Conditions: Tie Down Ends, Stay inside Box, etc.**
- **Higher Number of Nodes means Higher Energy**
- **In 2-D (and 3-D), Degenerate Sets are Found**

Waves in 3-D



polar angle $0 \le \theta \le \pi$
(latitude)

Azimuthal angle $0 \le \phi \le 2\pi$
(longitude)

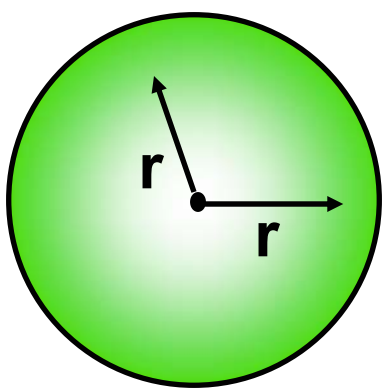
Ψ (x,y,z,t) is represented as Ψ (r,θ,ϕ,t)

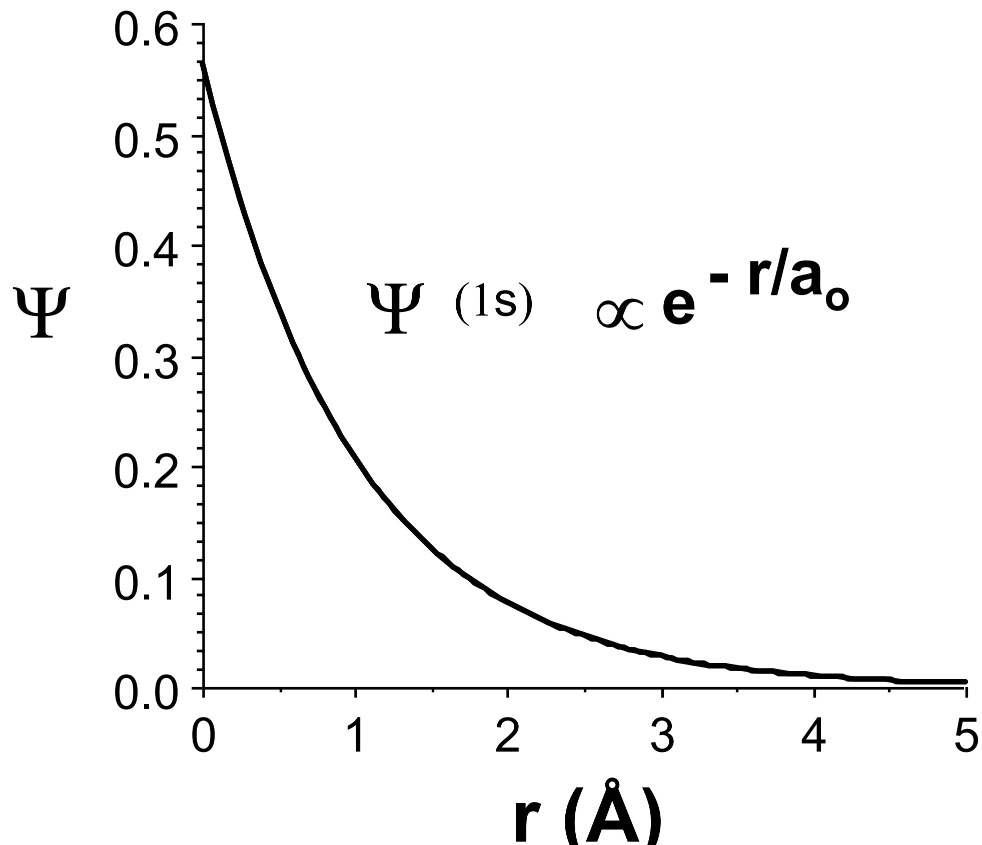
- **Boundary Conditions:**

  $\Psi \rightarrow 0$ as $r \rightarrow \infty$ (the electron is on the atom!)
- **Solutions Must be Standing Waves**

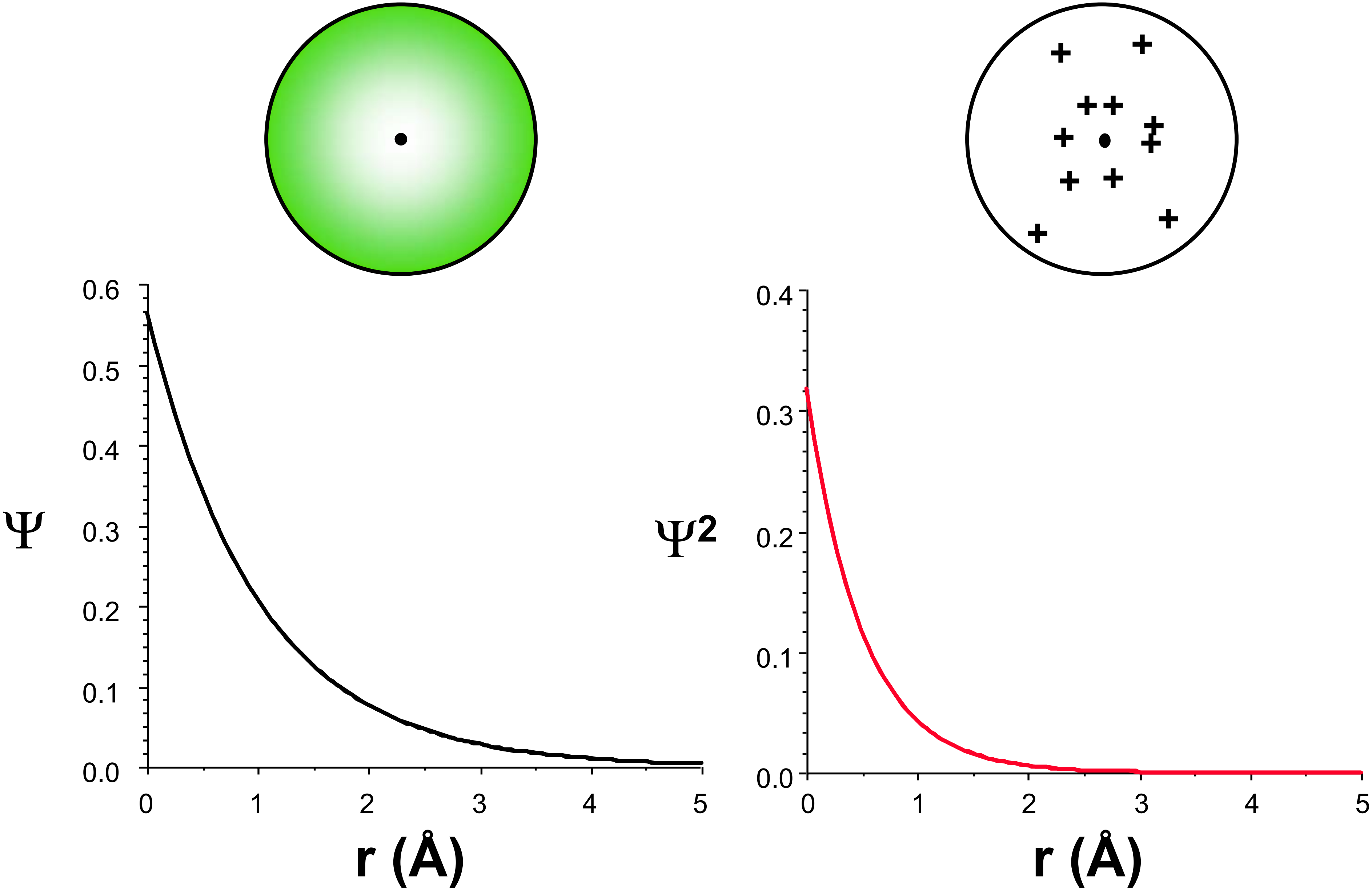
Radially Symmetric Solutions

Ψ is Independent of Angle





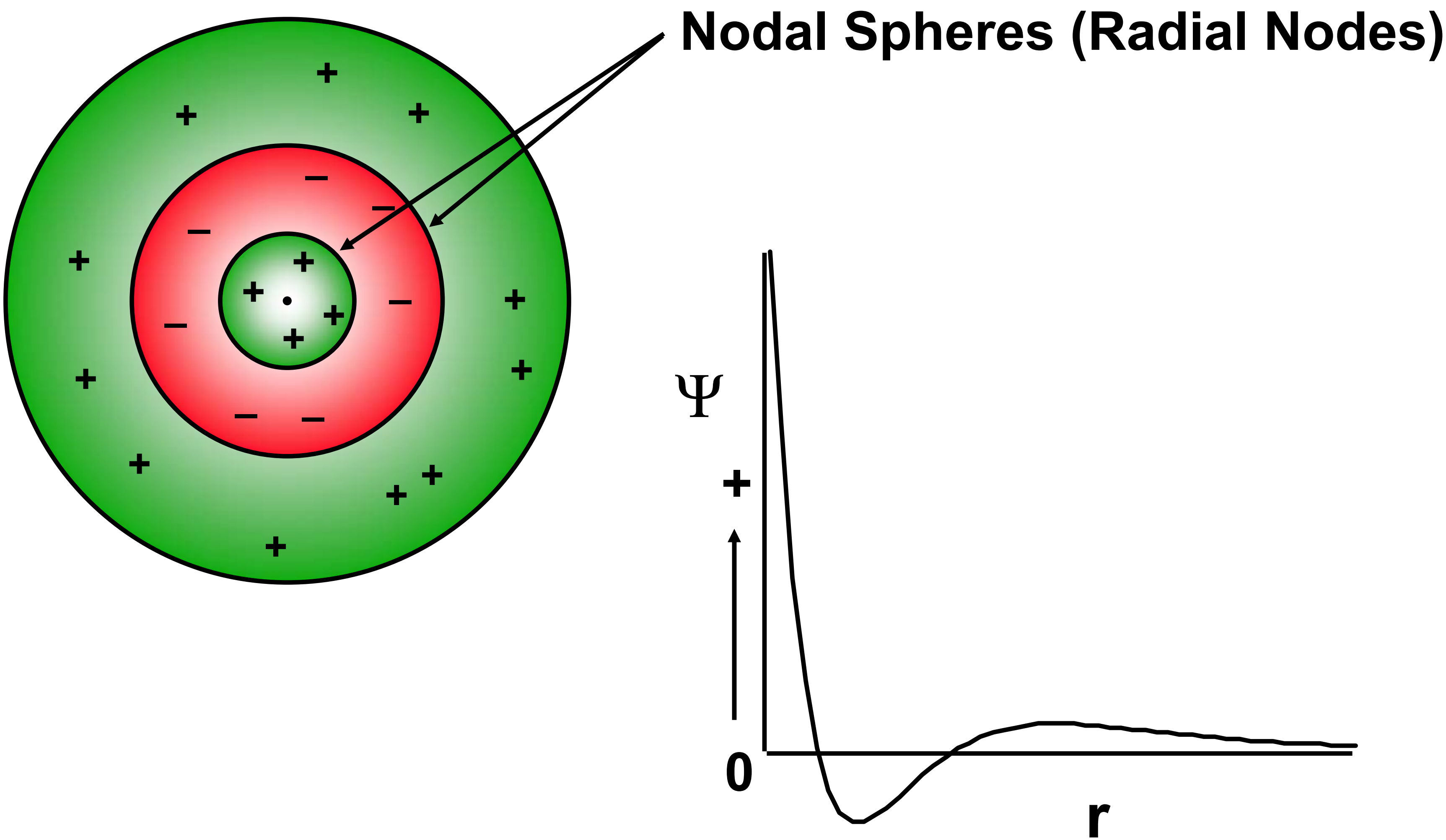
The 1s Orbital



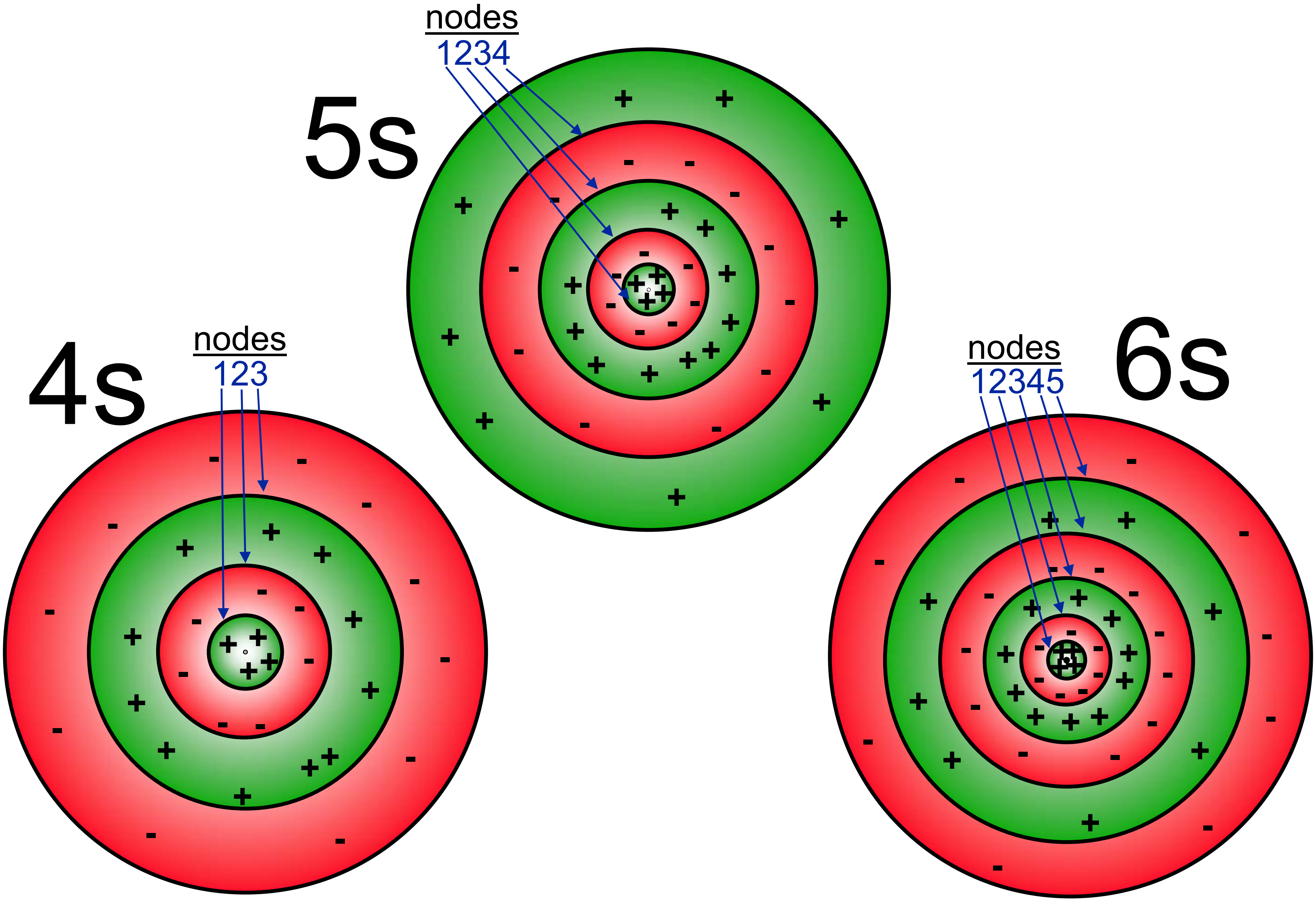
The 2s Orbital

The 2s Orbital has One Radial Node (Nodal Sphere)
E(2s) > E(1s)

The 3s Orbital



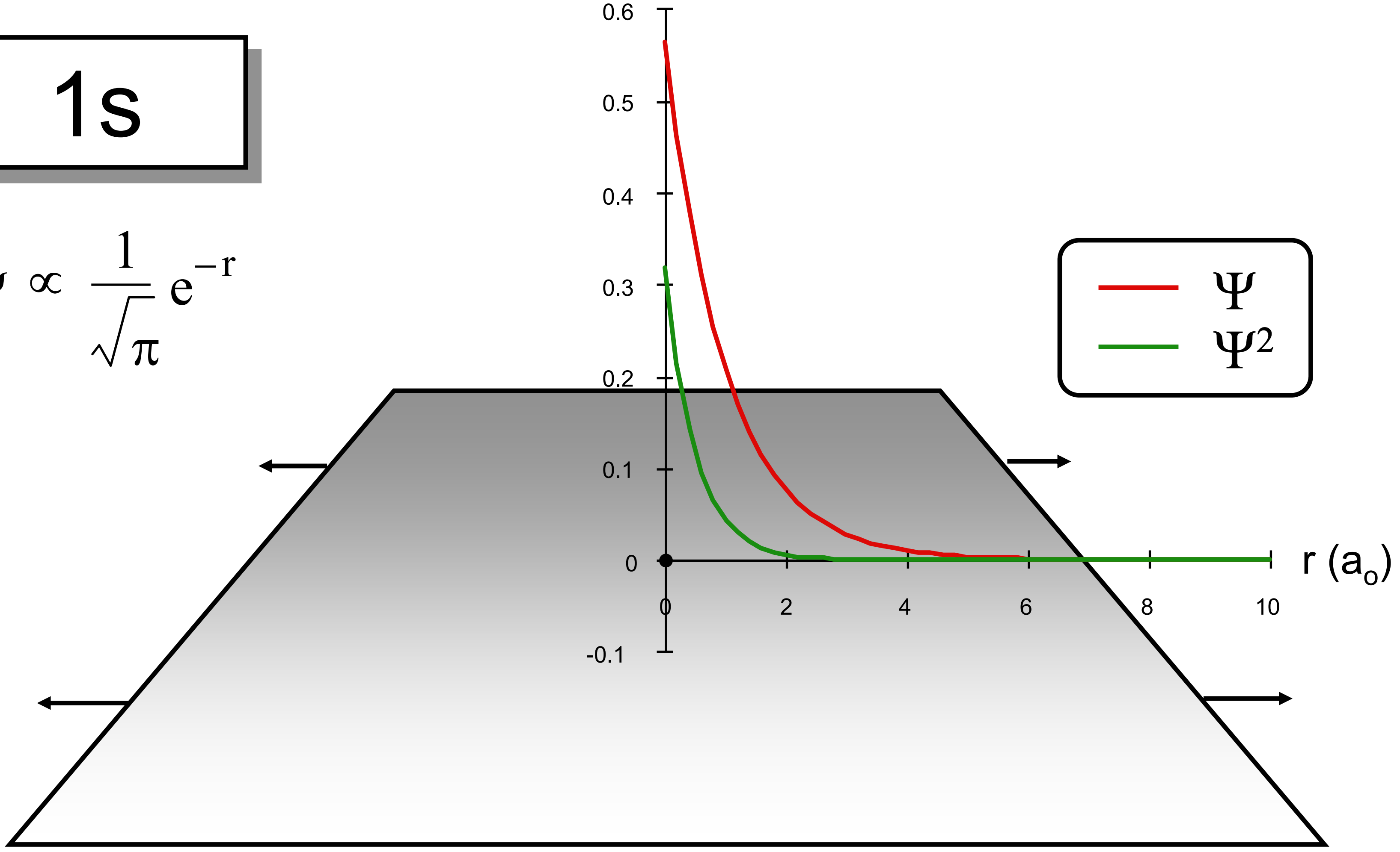
Other s Orbitals



Ψ^2, Not Ψ, is Related to the Probability of Finding an Electron

1s

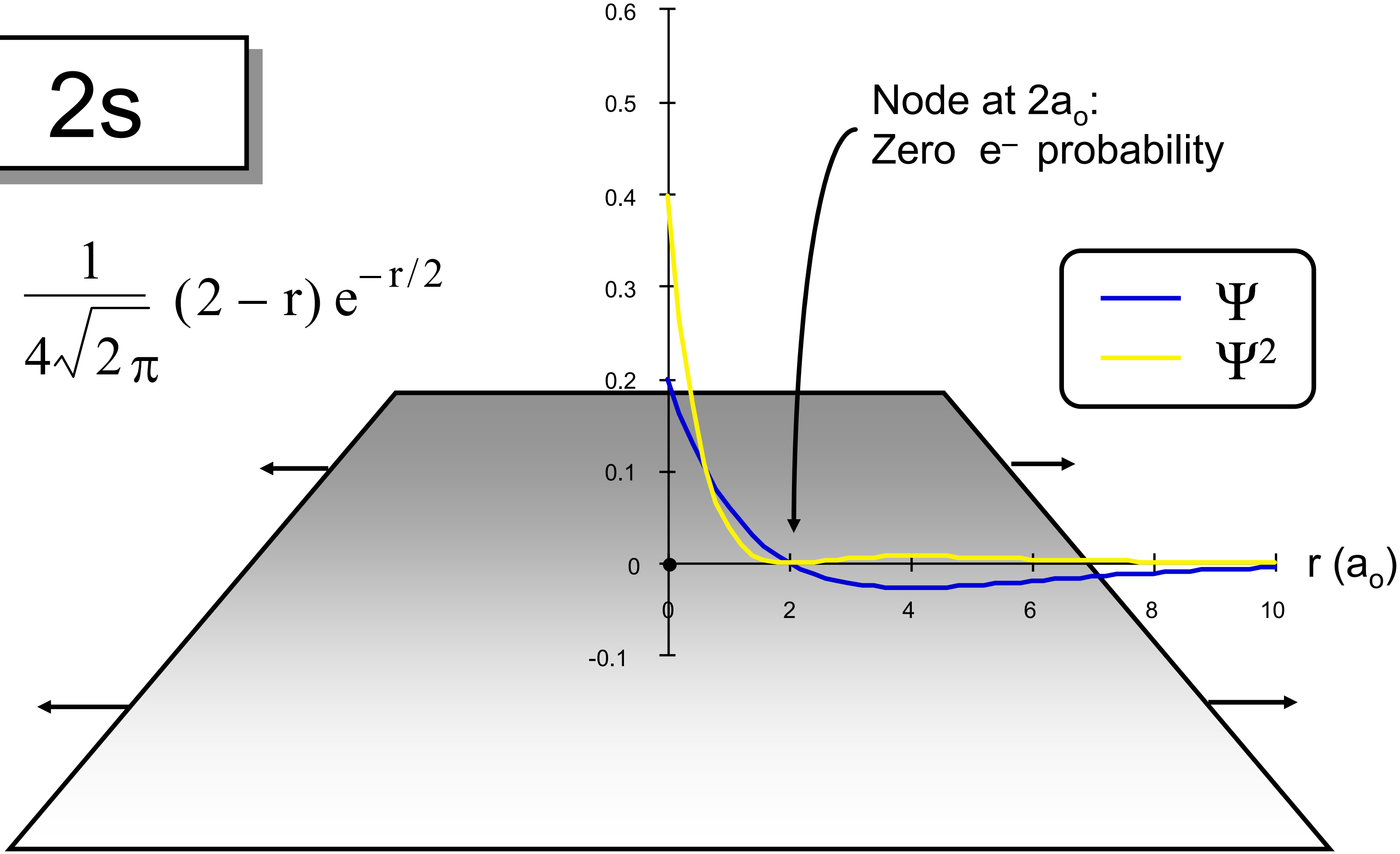
$$\Psi \propto \frac{1}{\sqrt{\pi}} e^{-r}$$



Ψ^2, Not Ψ, is Related to the Probability of Finding an Electron

2s

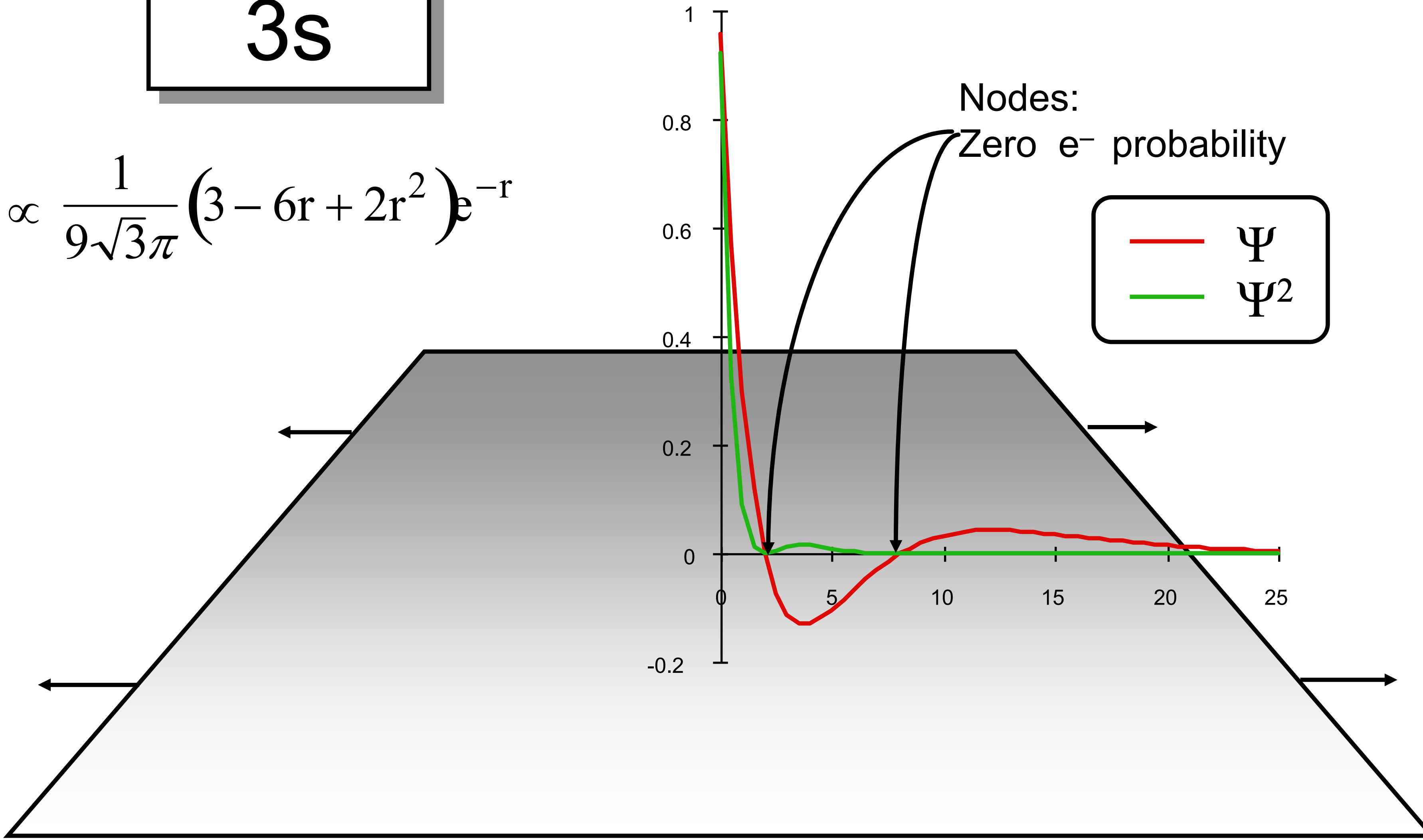
$$\Psi \propto \frac{1}{4\sqrt{2\pi}}(2-r)\,e^{-r/2}$$

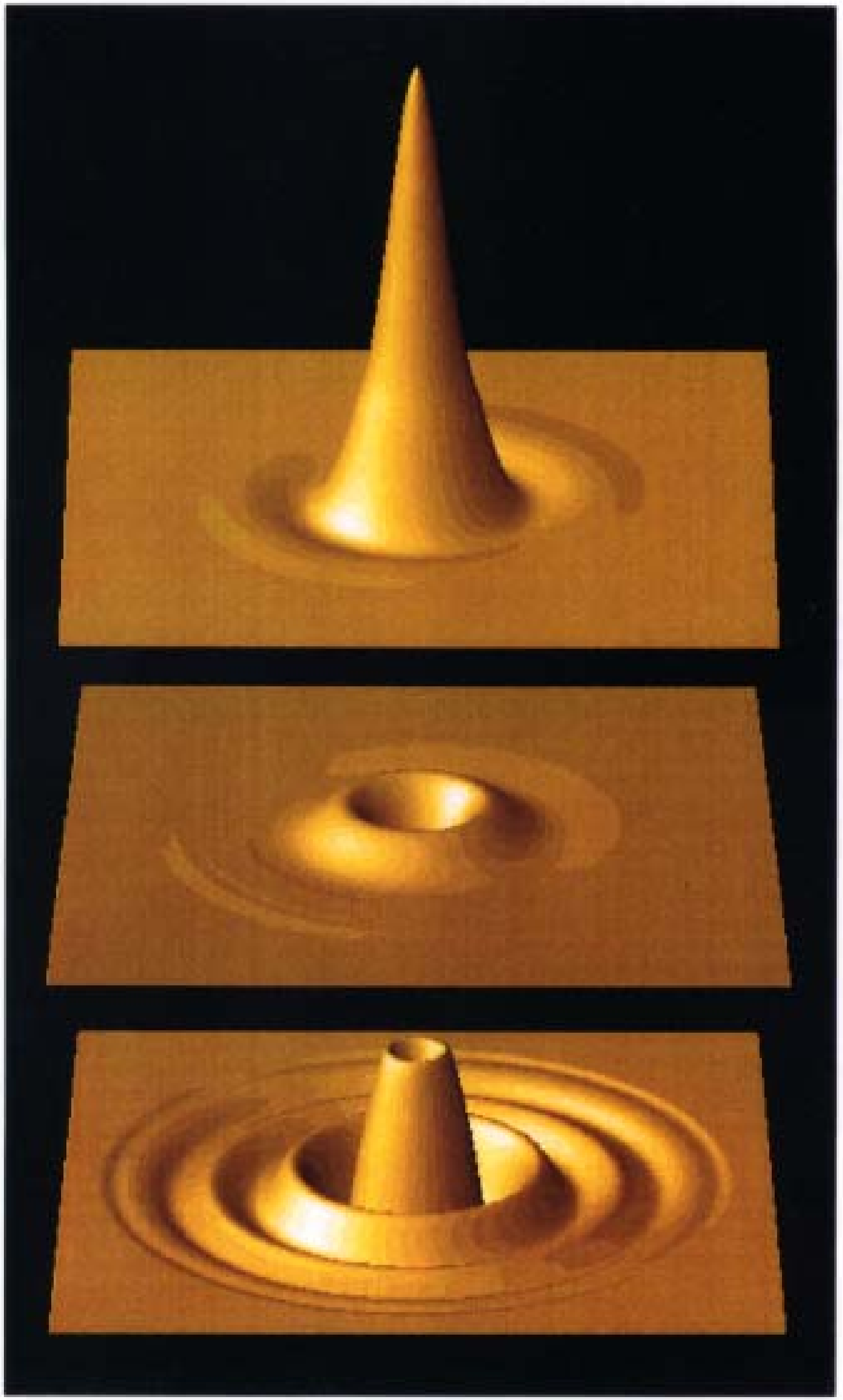


The 3s Orbital

3s

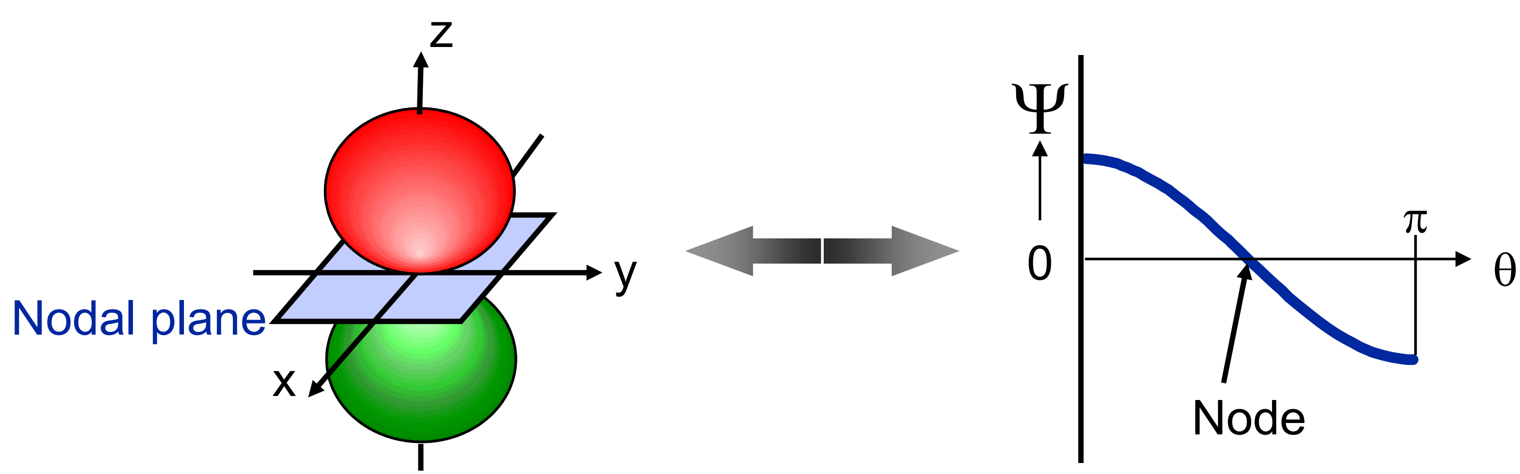
$$\Psi \propto \frac{1}{9\sqrt{3}\pi}\left(3 - 6r + 2r^2\right)e^{-r}$$





Allowed Wavefunctions that are Not Radially Symmetric

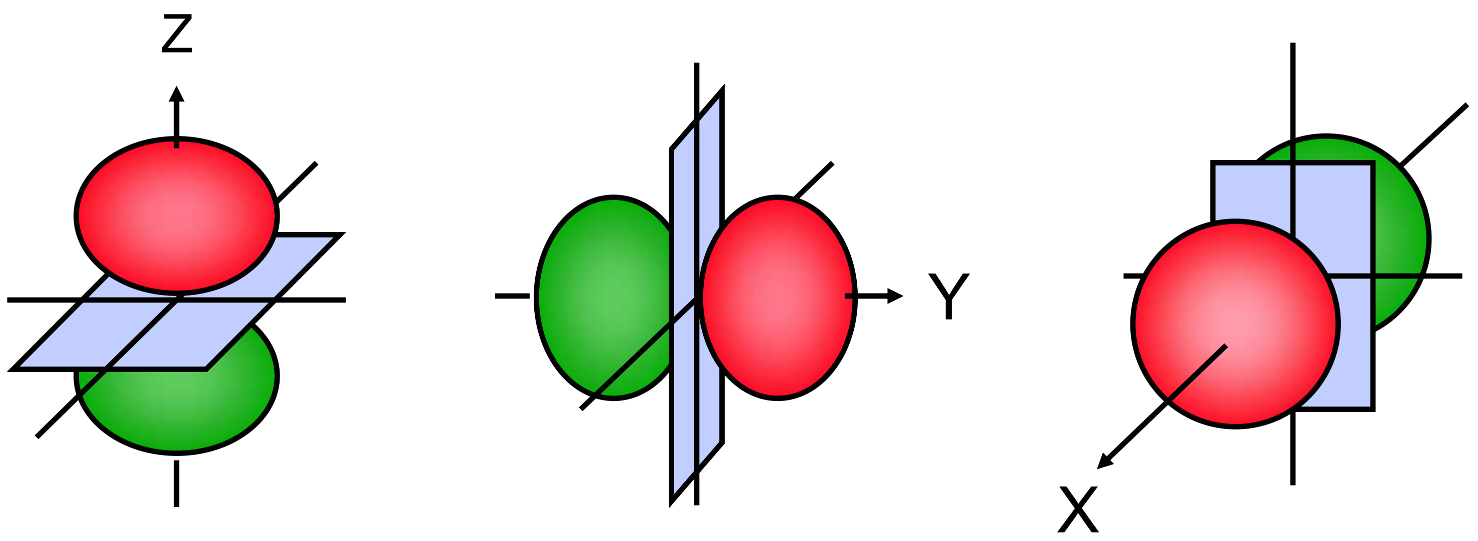
Functions with 1 Angular Node



2p$_z$ orbital

The angular dependence of **2p$_z$** at a fixed radius

Other Ψ's with 1 Angular Node



The 2p orbitals have 1 Nodal Surface, like the 2s Orbitals.
So for H atoms, E(2p) ≈ E(2s) > E(1s)

Naming Orbitals

n = principal quantum number

n = (total # of nodes) + 1

ℓ = number of angular nodes
ℓ = 0 (no angular nodes) implies an "s" orbital
ℓ = 1 (1 angular node) implies a "p" orbital
ℓ = 2 $\Rightarrow$ a "d" orbital
ℓ = 3 $\Rightarrow$ an "f" orbital
ℓ = 4 $\Rightarrow$ "g"
ℓ = 5 $\Rightarrow$ "h"
and so on as needed...

Naming Orbitals Cont'd

***Q: Name an orbital with no angular nodes, but two total nodes*:**

ℓ = (# of angular nodes) = 0 = s,

n = (total # of nodes) + 1 = 2 + 1 = 3

Answer: The 3s orbital

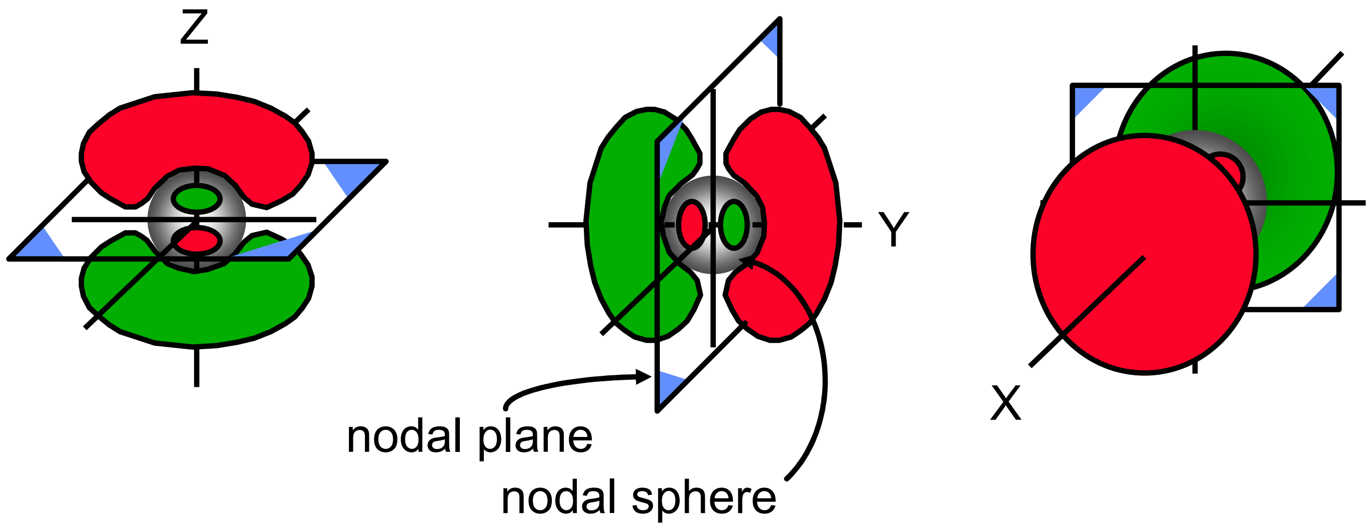
Q: Name an orbital with one angular node and no radial nodes:

ℓ = (# of angular nodes) = 1 = p

n = (total # of nodes) + 1 = 1 + 1 = 2

Answer: A 2p orbital

The 3p Orbitals



The **3p** orbitals have both radial nodes (nodal spheres) and angular nodes (nodal planes).

Naming Orbitals (Cont'd Again)

n = principal quantum number

n = (total # of nodes) + 1

ℓ = # of angular nodes

m = an integer "index" running from -ℓ to +ℓ

m cannot be associated directly with our "real space" orbitals, but it tells us how many orbitals with a given value of ℓ are needed to complete a degenerate set

END

Quantum Mechanics

Reading: Gray: (1–8) to (1–12)
OGN: (15.5)