Key Developments Leading to
Quantum Mechanical Model of the Atom

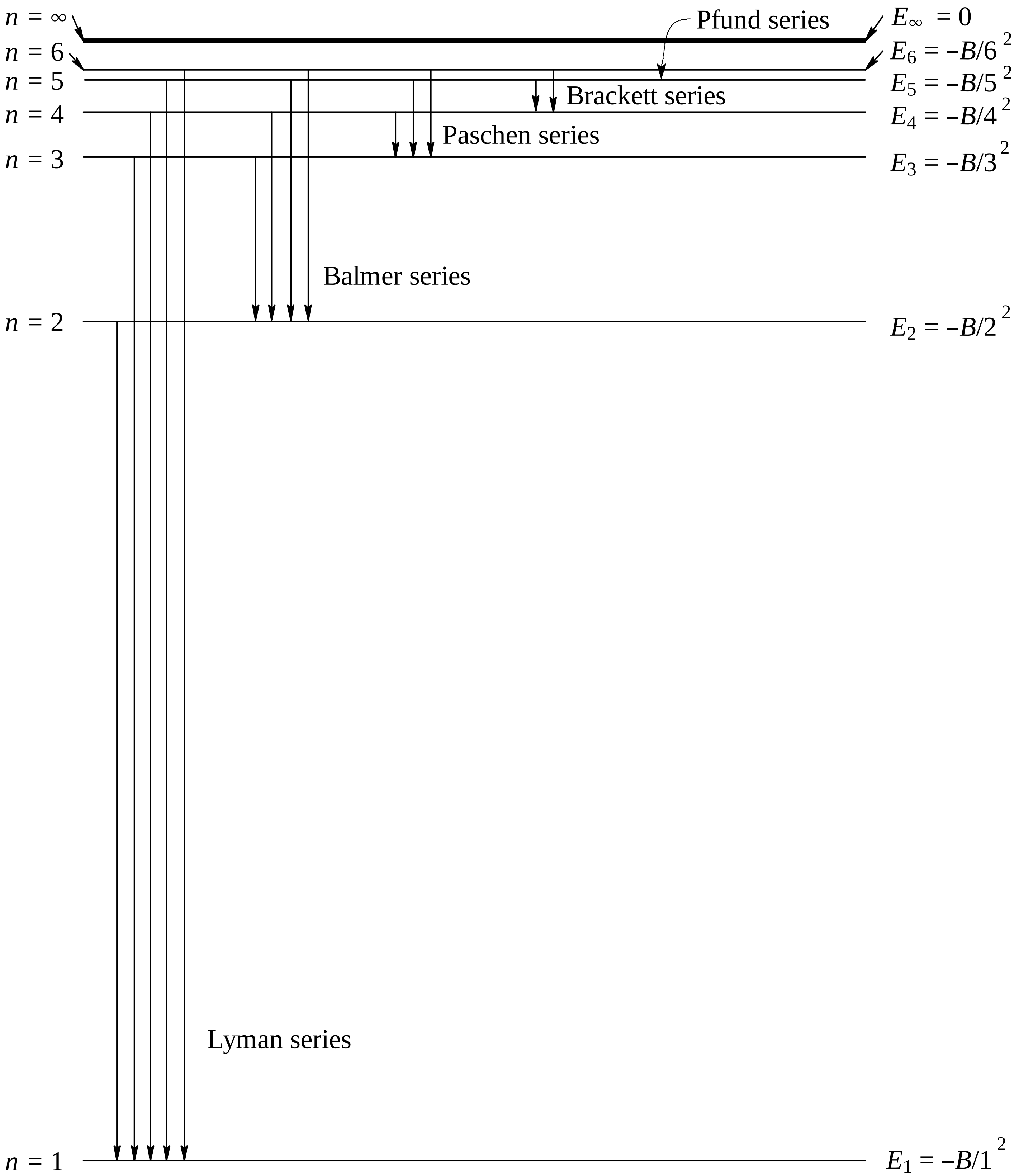
1900 Max Planck interprets black-body radiation on the basis of quantized oscillator model, leading to the fundamental equation for the energy of electromagnetic radiation, $E = h\nu$.

1905 Albert Einstein interprets photoelectric effect on the basis of quantized packets of light energy (photons).

1913 Niels Bohr applies quantum hypothesis to classical model of one-electron atoms and successfully interprets line spectra on the basis of quantized energy states given by

$$E = \frac{-2\pi^2 m Z^2 e^4}{n^2 h^2} = \frac{-BZ^2}{n^2} \qquad n = 1, 2, 3, \ldots$$

Energy Level Diagram for Hydrogen Atom



Key Developments Leading to Quantum Mechanical Model of the Atom

1923 Louis deBroglie develops equation for wave-particle duality of matter:

$$\lambda = h/p = h/mv$$

(Experimentally verified in 1927 from electron scattering experiments of Davisson and Germer, and by G. P. Thomson.)

1926 Irwin Schrödinger proposes wave equation for particles bound within a potential energy field, such as an atom:

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

(Application to one-electron atom case leads to same energy equation as Boh's model.)

1927 Werner Heisenberg proposes Uncertainty Principle, which sets limits on the ability to determine position and momentum simultaneously:

$$\Delta x \Delta p \geq h/4\pi$$

- ☞ These developments strongly indicated that a deterministic model, such as Bohr's, could not be correct.
- ☞ Model must be based on quantized energy, wave-particle duality, and statistical approach.

Schrödinger Equation in One Dimension (Particle on a Line)

In general

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

For a particle freely moving in one dimension, *x*

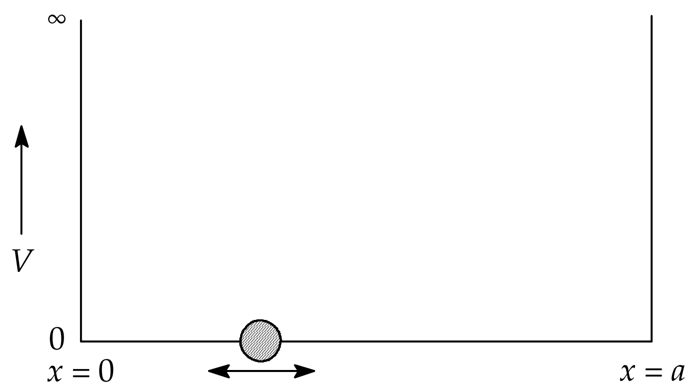
$$\left(\frac{-h^2}{8\pi^2 m} \frac{d^2}{dx^2} + V \right) \psi = E\psi$$

If no force acts on the particle, we may set $V = 0$.

$$\left(\frac{-h^2}{8\pi^2 m} \frac{d^2}{dx^2} \right) \psi = E\psi$$

Schrödinger Equation in One Dimension
(Particle in a Box)

Suppose the line segment has a length a, and $V = \infty$ at its ends.



- At the boundaries, where $V = \infty$, $x = 0$ and $x = a$, $\psi = 0$.

- Between $0 < x < a$,

$$\left(\frac{-h^2}{8\pi^2 m}\frac{d^2}{dx^2}\right)\psi = E\psi$$

- Solutions, ψ, must be continuous and single-valued.
- Therefore, at $x = 0$ and $x = a$ any solution must have $\psi = 0$ (boundary conditions).
- Solutions that meet the boundary conditions have the form

$$\psi = A\sin(n\pi x/a)$$

where $n = 1, 2, 3, \ldots$ and A is a proportionality constant.

☞ Note that $\sin(n\pi x/a) = 0$ when $x = 0$ and when $x = a$.

Proof of Solution

Substitute $\psi = A\sin(n\pi x/a)$ into $\left(\dfrac{-h^2}{8\pi^2 m}\dfrac{d^2}{dx^2}\right)\psi = E\psi$.

Left side:

$$\frac{-h^2}{8\pi^2 m}\left(\frac{-n^2\pi^2}{a^2}\right)A\sin\frac{n\pi x}{a} = \frac{n^2h^2}{8ma^2}A\sin\frac{n\pi x}{a}$$

Right side:

$$EA\sin(n\pi x/a)$$

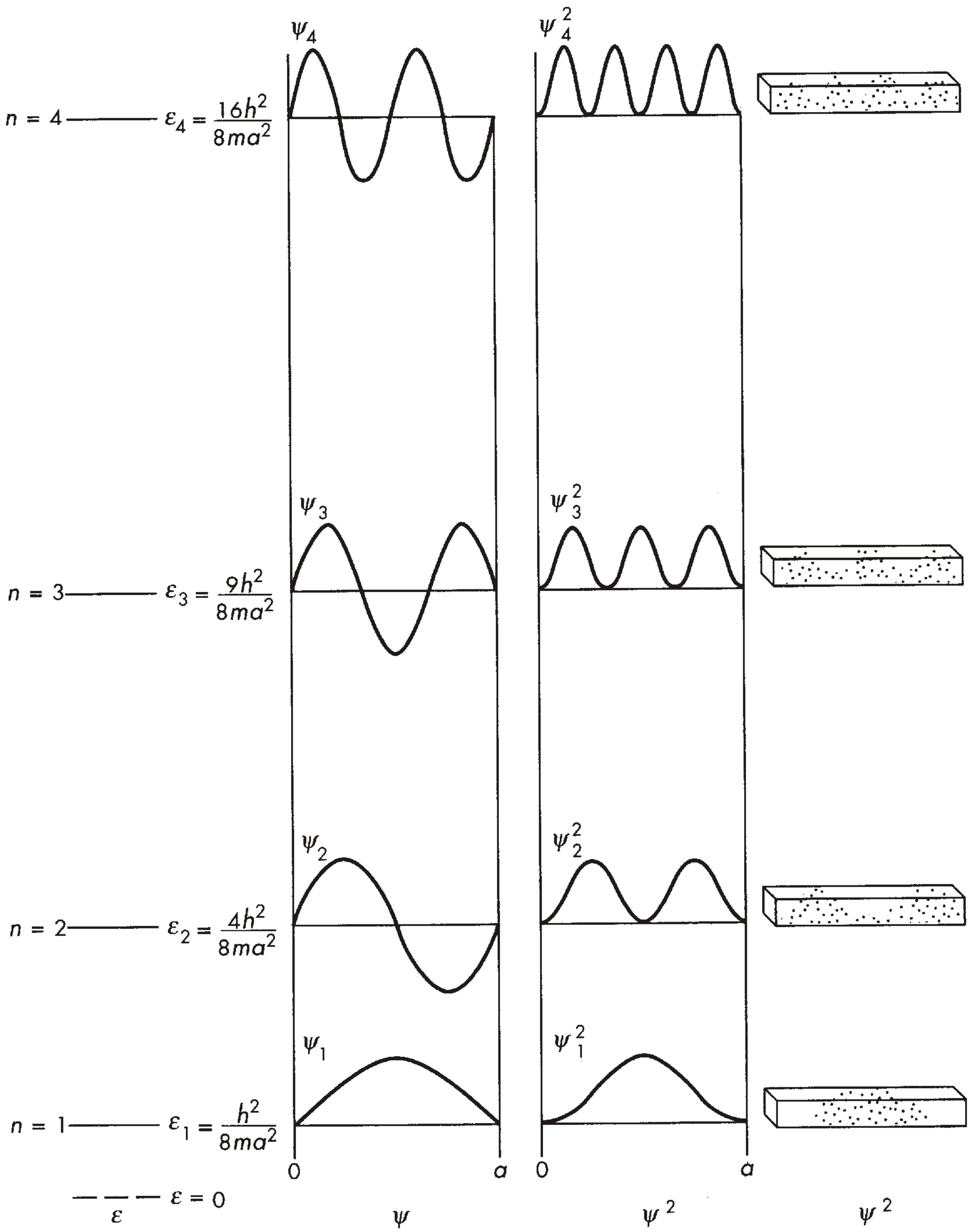
The left and right sides are equal, so $\psi = A\sin(n\pi x/a)$ is a solution if

$$E = n^2h^2/8ma^2 \qquad n = 1, 2, 3, \ldots$$

☞ Allowed energies for the system are quantized into discreet states such that

$$E \propto n^2$$

Energy Level Diagram for Particle in a Box



Schrödinger Wave Equation for One-Electron Atoms

$$\mathcal{H}\Psi = E\Psi$$

E	=	energy of the system (*eigen value*)
Ψ	=	wave function solution (*eigen function*)
$\mathcal{H}$	=	Hamiltonian operator, expressing potential and kinetic energy of the system

Explicit wave equation for hydrogen:

$$\left[-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{e^2}{r}\right]\Psi = E\Psi$$

Each Ψ solution is a mathematical expression that is a function of three *quantum numbers*: n, l, and m_l.

Probability of Finding the Electron Somewhere Around the Nucleus

For light, intensity is proportional to amplitude squared:

$$I \propto A^2$$

By analogy, the "intensity" of an electron at a point[1] in space (i.e., its *probability*) is proportional to the amplitude of its wave function squared, Ψ^2 (or if Ψ contains i, $\Psi\Psi^*$):

$$P \propto \Psi^2$$

This is the "Copenhagen Interpretation" of the wave function, due to Max Born and co-workers.

Einstein to Born:

> "Quantum mechanics is certainly imposing. But an inner voice tells me that it is not yet the real thing. The theory says a lot, but does not really bring us any closer to the secret of the 'old one'. I, at any rate, am convinced that He is not playing at dice." [2]

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[1]Strictly, a point has no volume and therefore $\psi = 0$ and $\psi^2 = 0$. The term "point" is used here to mean "a vanishingly small volume element".

[2]*The Born-Einstein Letters*, translated by Irene Born. New York: Walker and Company, 1971, pp. 90-91.

Restrictions on Ψ

1. Ψ *has a value for every point in space.* Otherwise the probability would be undefined somewhere.

2. Ψ *can have only one value at any point.* Otherwise the probability would be ambiguous at some points.

3. Ψ *cannot be infinite at any point in space.* Otherwise its position would be fixed, in violation of the Heisenberg Uncertainty Principle.

4. Ψ *can be zero at some points in space (node).*
   This means the electron is not there.

5. *Probability of the electron at a point (zero volume) is vanishingly small.*
   Therefore, we calculate Ψ^2 for small volume segment $dx\, dy\, dz$.
   $$P(x, y, z)\, dx\, dy\, dz = P\, d\tau$$

6. *The sum of* Ψ^2 *over all space is unity*.
   $$\int \Psi^2\, d\tau = \int P\, d\tau = 1$$
   The electron must be somewhere.

Depicting the Wave Function and Orbitals

- Ψ is usually cast in polar coordinates r, θ, φ :
$$\Psi = R(r)\Theta(\theta)\Phi(\varphi)$$

- Customarily, $R(r)$ vs. r is plotted, and separate plots of $\Theta(\theta)\Phi(\varphi)$ are generated, often in three dimensions.

- $R(r)$ is called the radial function, and $\Theta(\theta)\Phi(\varphi)$ is called the angular function.

- $R(r)$ depends on n and l; $\Theta(\theta)\Phi(\varphi)$ depends on l and m_l.

- To depict probability, the squares of the functions are rendered.

- Modern graphical depictions can convincingly show the overall three-dimensionality of all three functions simultaneously.

Representations of Orbitals

1. *Radial Plot*:
   Two-dimensional plot of R vs. r or R^2 vs. r without trying to show the three dimensional aspects of the distribution. Sometimes a particular direction in space is chosen (x, y, z) instead of any direction r.

2. *Radial Distribution Function*:
   Plot of $4\pi r^2 R^2$ vs. r. Probability of finding the electron within a vanishingly thin spherical shell with a radius of r from the nucleus. Going out from the nucleus, this shows the variation in probability on the surface of increasingly larger spherical shells.

3. *Electron Charge Cloud (Electron Density) Diagram*
   Three-dimensional picture of Ψ^2 in which higher probability is rendered by darker shading or stippling. Most of such diagrams are meant to show approximately 90-99% of the total probability.

Representations of Orbitals

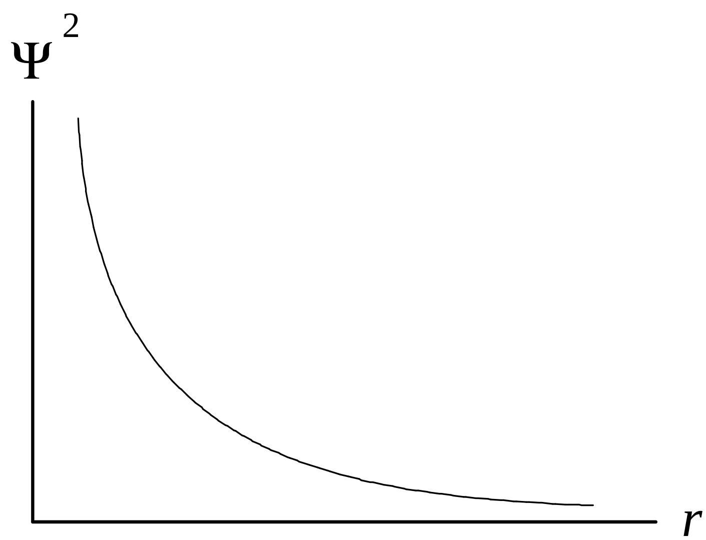
4. *Contour Diagram*

   Two-dimensional cross section (slice) through the probability distribution, Ψ^2. Lines on the drawing connect regions of equal probability, much like isobars on a weather map connect regions of equal pressure.

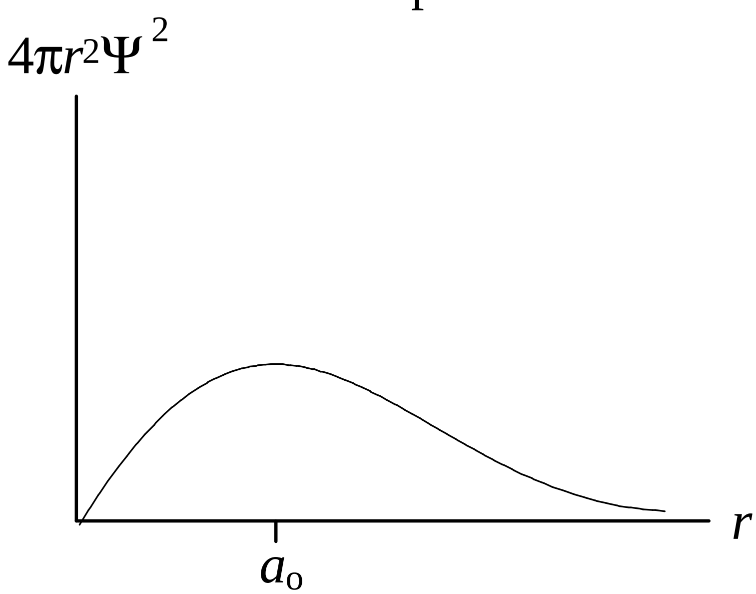
5. *Boundary Surface Diagram*

   Three-dimensional solid model (or a picture of such a model) constructed so as to represent a surface that encloses approximately 90-99% of the total probability. These are sometimes called "balloon models". Sketches of orbitals used in routine work are generally two-dimensional representations of "balloon models".

Probability vs. Distance from Nucleus
1*s* Wave Function
$n = 1, l = 0, m_l = 0$

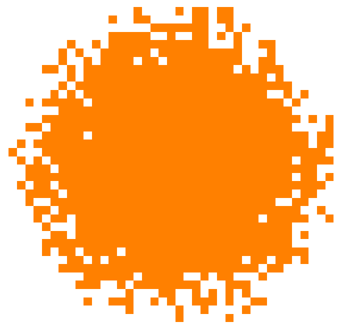


Radial plot

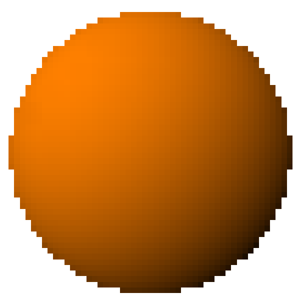


Radial distribution plot

Three-Dimensional Representation of a 1*s* Orbital

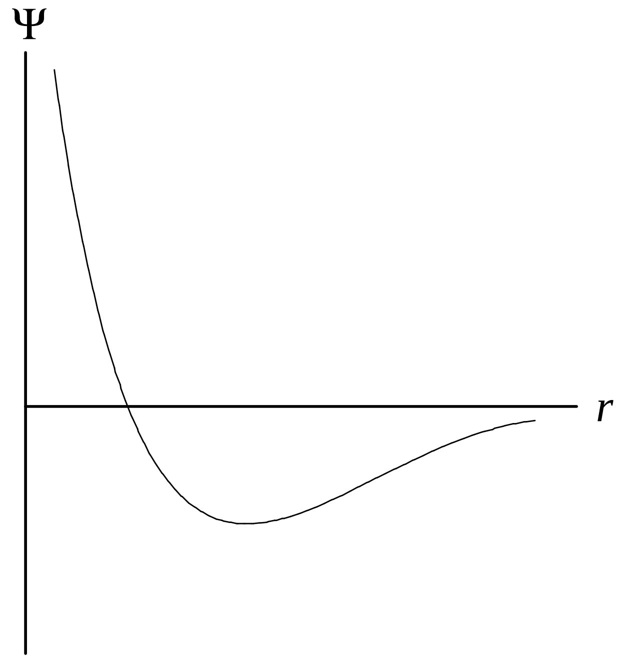


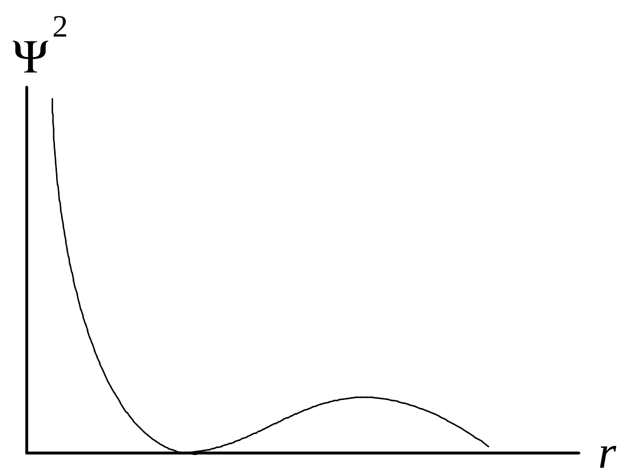
Electron Cloud Representation



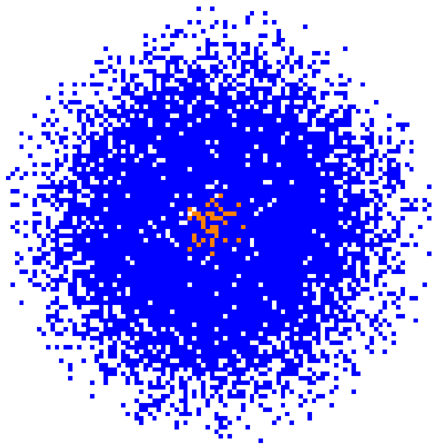
Boundary Surface Model

Ψ and Ψ^2 vs. Distance from the Nucleus
2*s* Wave Function
$n = 2, l = 0, m_l = 0$

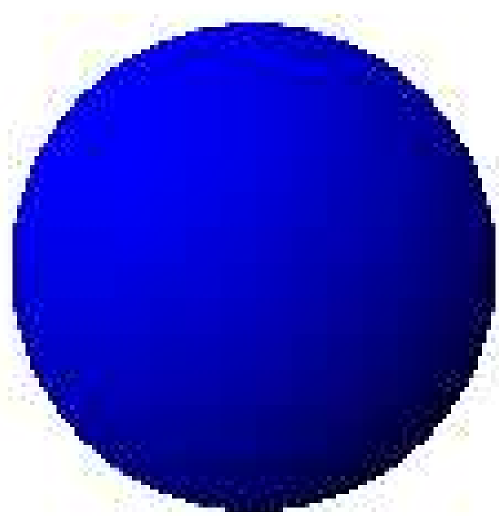




Three-Dimensional Representation of a 2*s* Orbital

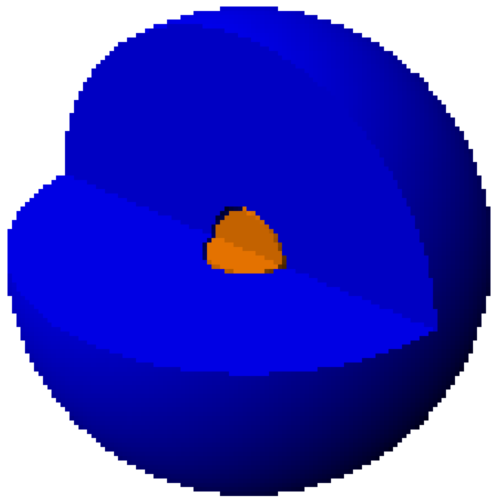


Electron Cloud Representation



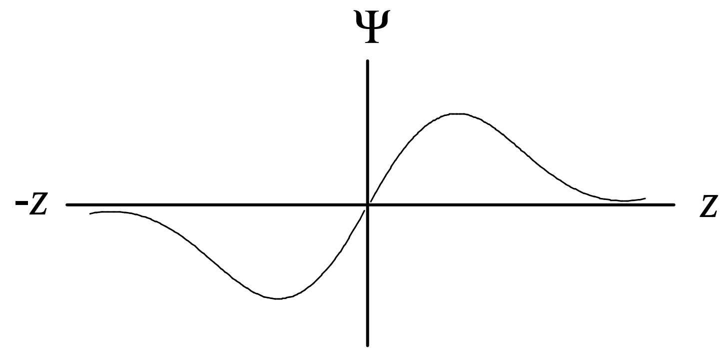
Boundary Surface Model

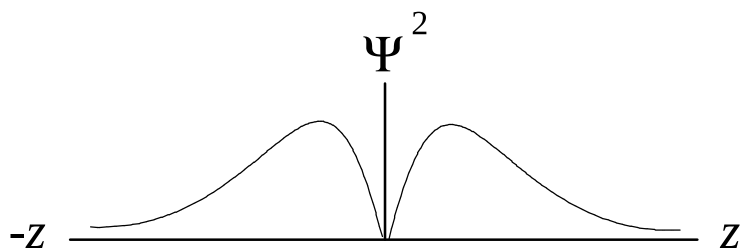
Cutaway Model of 2*s* Orbital



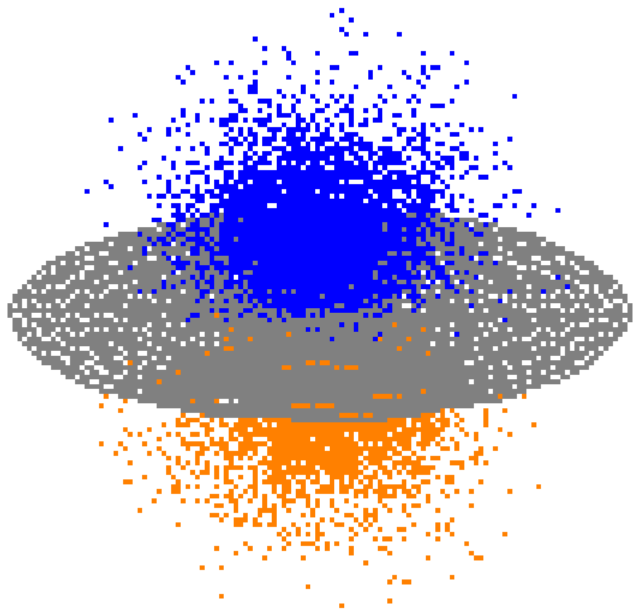
The 2*s* orbital has one spherical node.

Ψ and $Ψ^2$ vs. Distance from the Nucleus
$2p_z$ Wave Function





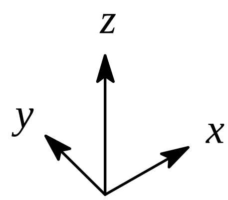
Electron Cloud Representation of a 2p_z Orbital



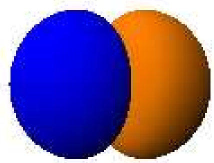
The plane perpendicular to z (xy plane) passing through the nucleus is a node.

The Three Degenerate 2*p* Orbitals

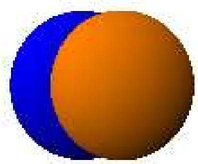
$n = 2, l = 1, m_l = +1, 0, -1$



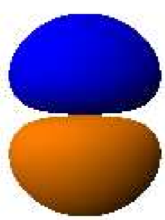
$2p_x$



$2p_y$

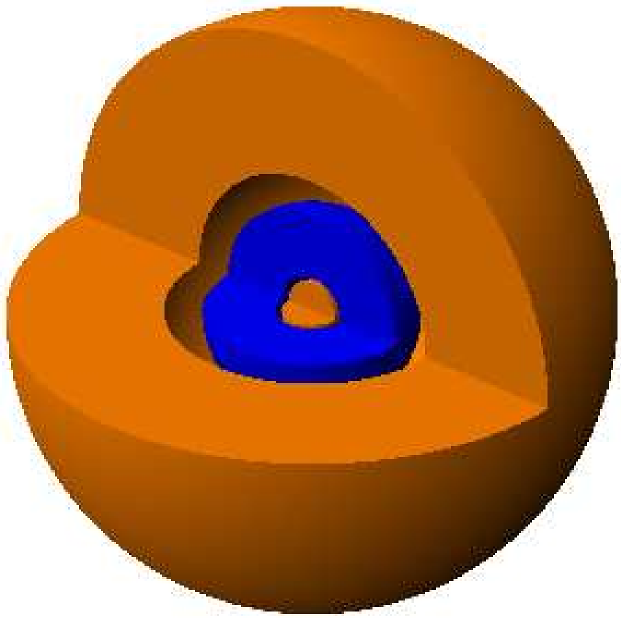


$2p_z$



Cutaway Model of 3*s* Orbital

$n = 3$, $l = 0$, $m_l = 0$



The 3*s* orbital has two spherical nodes.

3*p* Orbitals

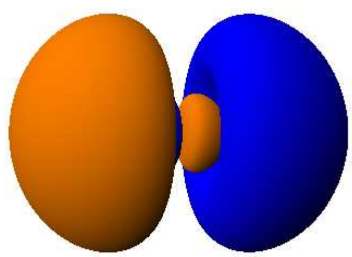
$n = 3$, $l = 1$, $m_l = +1, 0, -1$

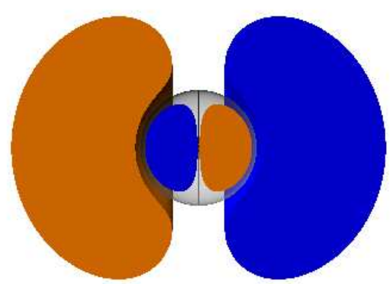
Three degenerate 3*p* orbitals, oriented along the axes of the coordinate system ($3p_x$, $3p_y$, $3p_z$).

More extensive (bigger) than 2*p* with additional lobes.

In addition to the nodal plane, inner lobes are separated from outer lobes by a spherical node.

$3p_x$

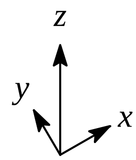


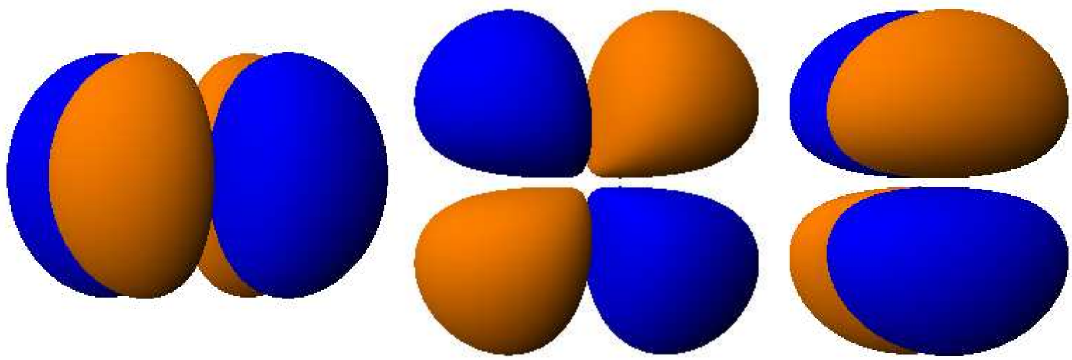


Cutaway model showing nodes

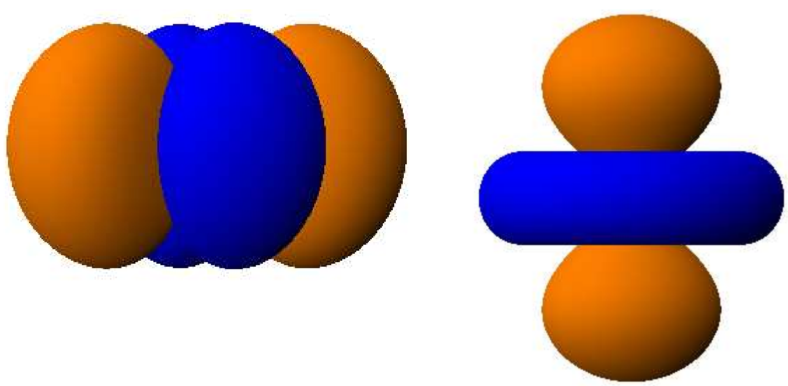
3*d* Orbitals

$n = 3$, $l = 2$, $m_l = +2, +1, 0, -1, -2$





$3d_{xy}$ $3d_{xz}$ $3d_{yz}$



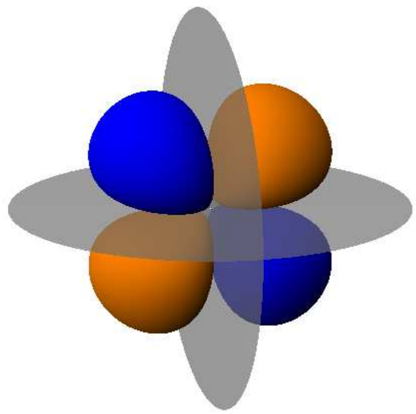
$3d_{x^2-y^2}$ $3d_{z^2}$

☞ The $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals' lobes are *between* the axes in their names.

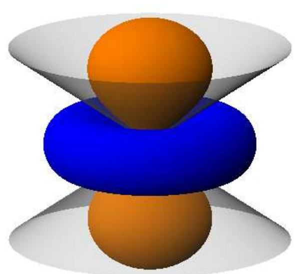
☞ The $3d_{x^2-y^2}$ orbital's lobes are *on* the *x* and *y* axes.

Nodes of 3*d* Orbitals

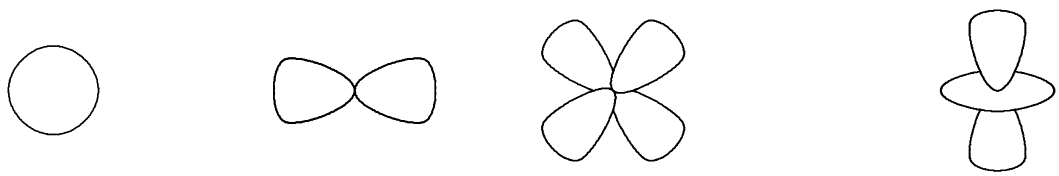
☞ "Cloverleaf" shaped 3*d* orbitals have two nodal planes intersecting at the nucleus, which separate the four lobes.



☞ The $3d_{z^2}$ orbital has two nodal cones whose tips meet at the nucleus, which separate the "dumbbell" lobes from the "doughnut" ring.



"Balloon" Models of Atomic Orbitals for Routine Sketching



s *p* “cloverleaf” *d* d_{z^2}

Summary
Orbitals in One-electron Atoms (H, He^+, Li^{2+}, ...)

1. All orbitals with the same value of the principal quantum number *n* have the same energy; e.g., 4*s* = 4*p* = 4*d* = 4*f*. (This is *not* true for multielectron atoms.)

2. The number of equivalent (degenerate) orbitals in each subshell is equal to 2*l* + 1.

3. For orbitals with the same *l* value, size and energy increase with *n*; e.g., 1*s* < 2*s* < 3*s*.

4. For orbitals of the same *l* value, the number of nodes increases with *n*.

Orbital	1*s*	2*s*	3*s*	4*s*
Nodes	0	1	2	3
Orbital		2*p*	3*p*	4*p*
Nodes		1	2	3