CHEM1011 LECTURE 9

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THE ANATOMY OF ATOMS (QUANTUM NUMBERS)

CLASSICAL MECHANICS

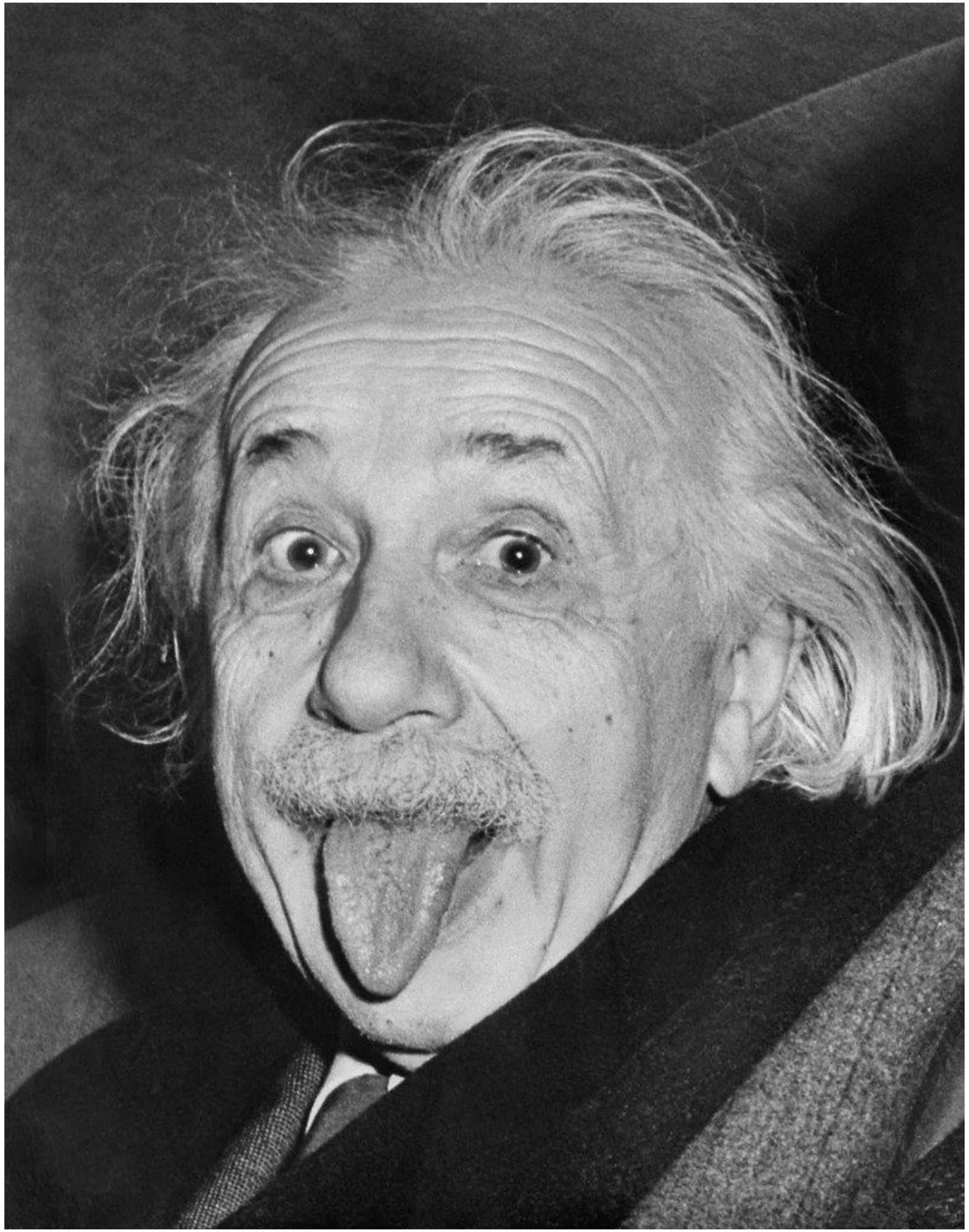
Classical mechanics (from Newton, who thought science was exclusively deterministic) **describes objects in terms of their position and velocity** and **works accurately for large objects** (those we can perceive directly).

But it does not work for objects the size of atoms or smaller. Classical mechanics cannot explain why atomic energies are quantised.

http://c2.thejournal.ie/media/2015/07/angry-birds-2-2.gif

Classical mechanics? Pfft.
Not here buddy!

We're talking QUANTUM mechanics and this s?*&'s weird!



QUANTUM MECHANICS

Werner Karl Heisenberg
(1901 –1976)
a German theoretical physicist and one of the key pioneers of quantum mechanics.

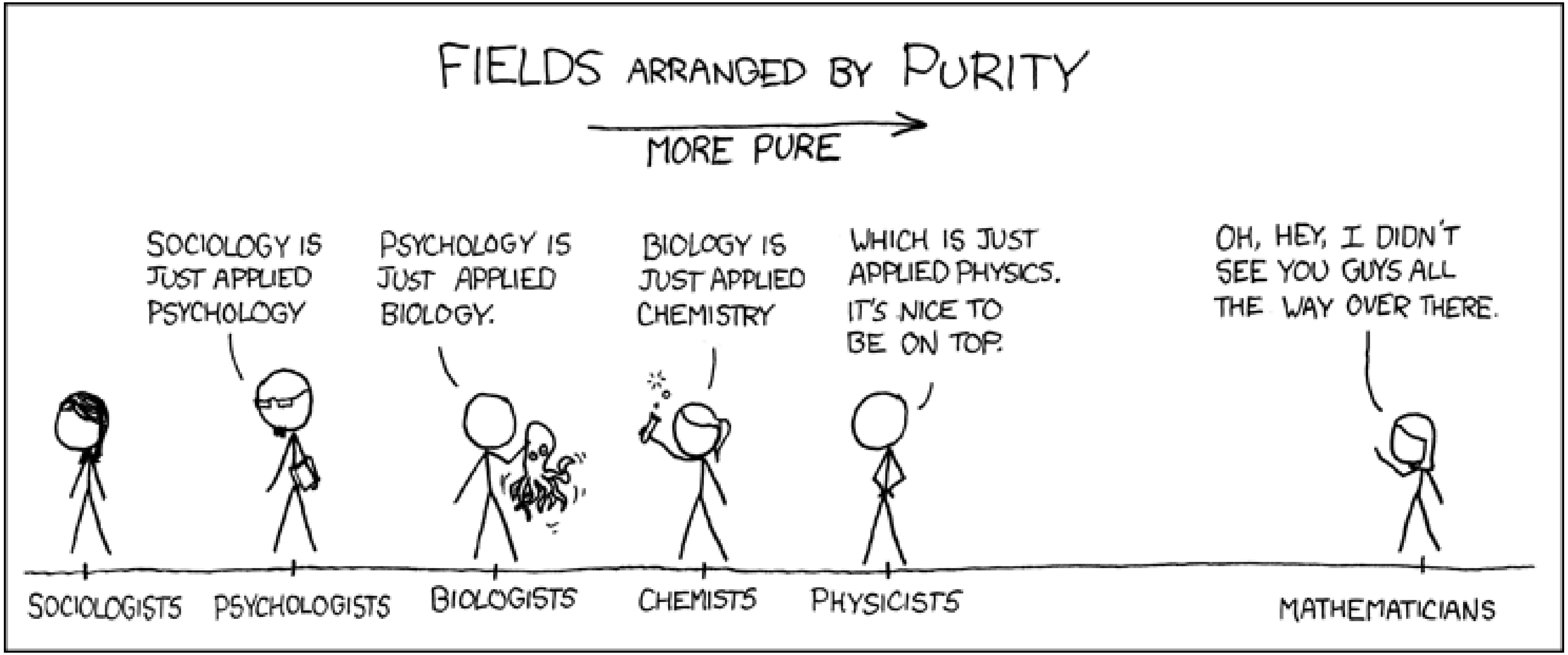
Nobel Prize in Physics for 1932

Quantum mechanics, based on a different set of concepts to classical mechanics, does **accurately describe objects at the atomic level (such as electrons).**

We cannot determine exactly where the electron is **located** at any time, we can only calculate the probability of it being in a particular volume of space. (This is related to the Heisenberg uncertainty principle which sets fundamental limits on the accuracy of experimental measurements.)

How do we calculate the probability of an electron's location?

https://www.youtube.com/watch?v=YoQYnhHQ95U : double slit experiment



xkcd: Purity

https://xkcd.com/435/

SCHRÖDINGER EQUATION

Remember how electrons behave like waves?

A **wavefunction** Ψ (Greek *psi*) is a **mathematical function that contains all the information about a system** (e.g. H atom). Information like electrons' whereabouts!

Solving the Schrödinger equation will output many solutions…

SCHRÖDINGER EQUATION

Remember how electrons behave like waves?

Solving the Schrödinger equation will output **many solutions (atomic orbitals)** for the wavefunction. We use **quantum numbers** to label the variables identifying the solutions.

E = total energy associated with the wavefunction Ψ

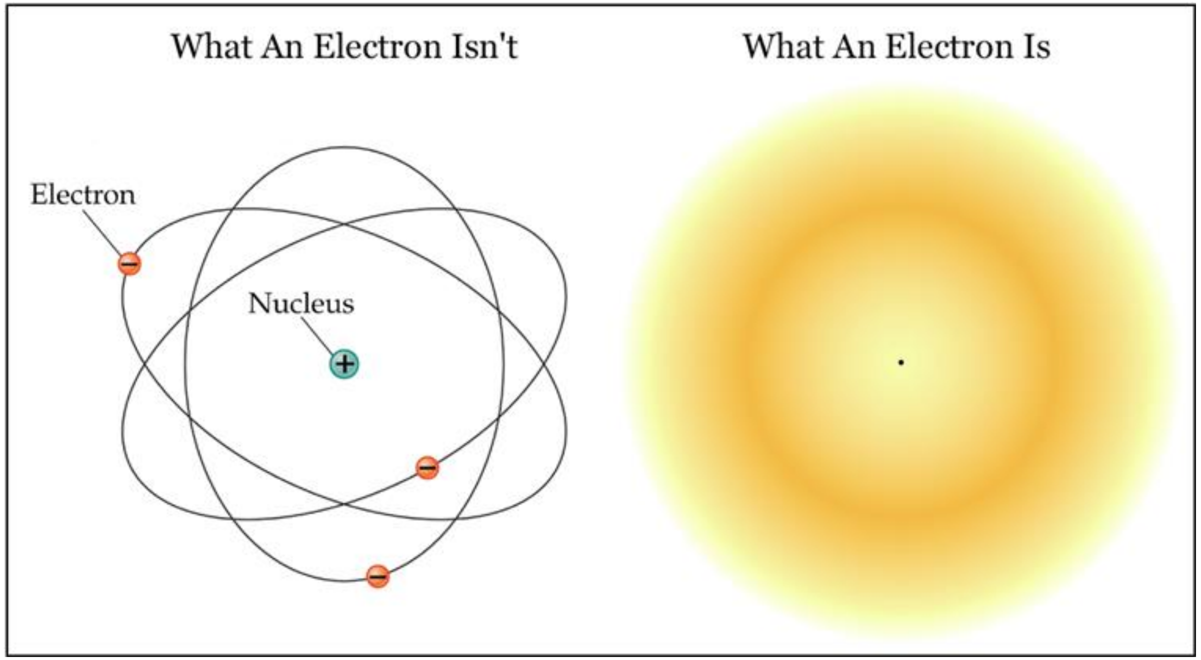
$$\hat{H}\Psi = E\Psi$$

Hamiltonian operator
which performs a mathematical operation on a mathematical function. Differentiation is another example of a mathematical operator.

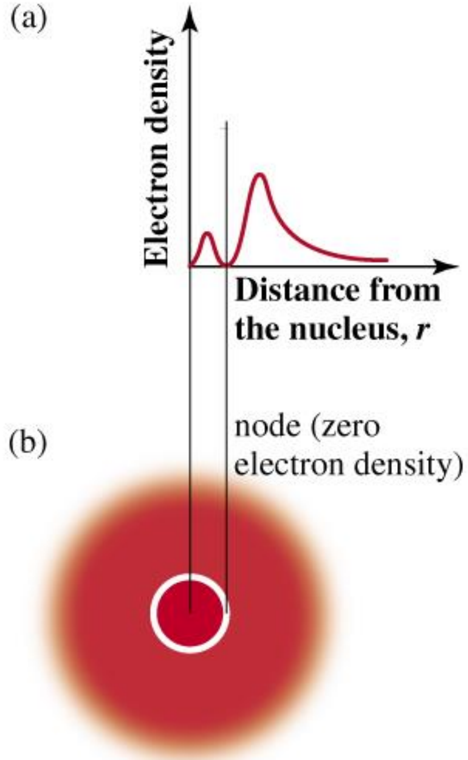
ELECTRON DENSITY

Squaring the wavefunction Ψ^2 will give us the **probability** of finding an electron around an atom.

Fuzzy electron cloud



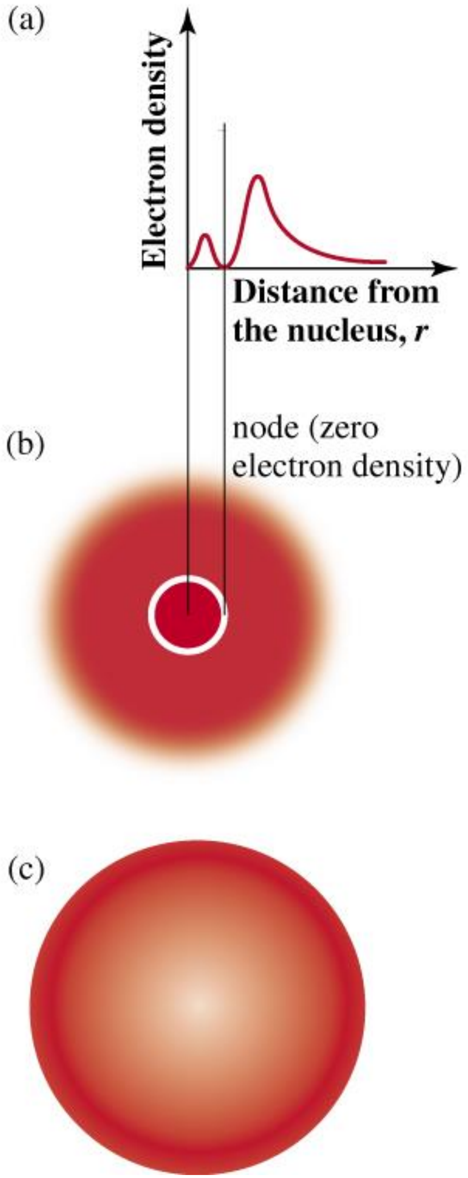
http://faculty.wcas.northwestern.edu/~infocom/The%20Website/graphics/e-clouds.png



ELECTRON DENSITY

Electron density: Squaring the wavefunction Ψ^2 will give us the **probability** of finding an electron around an atom.

The volume occupied by **90% of the electron density** provides a **boundary surface.** This gives us a clear point to describe the cutoff of where an electron can be found i.e. the spatial limit of an **atomic orbital**.

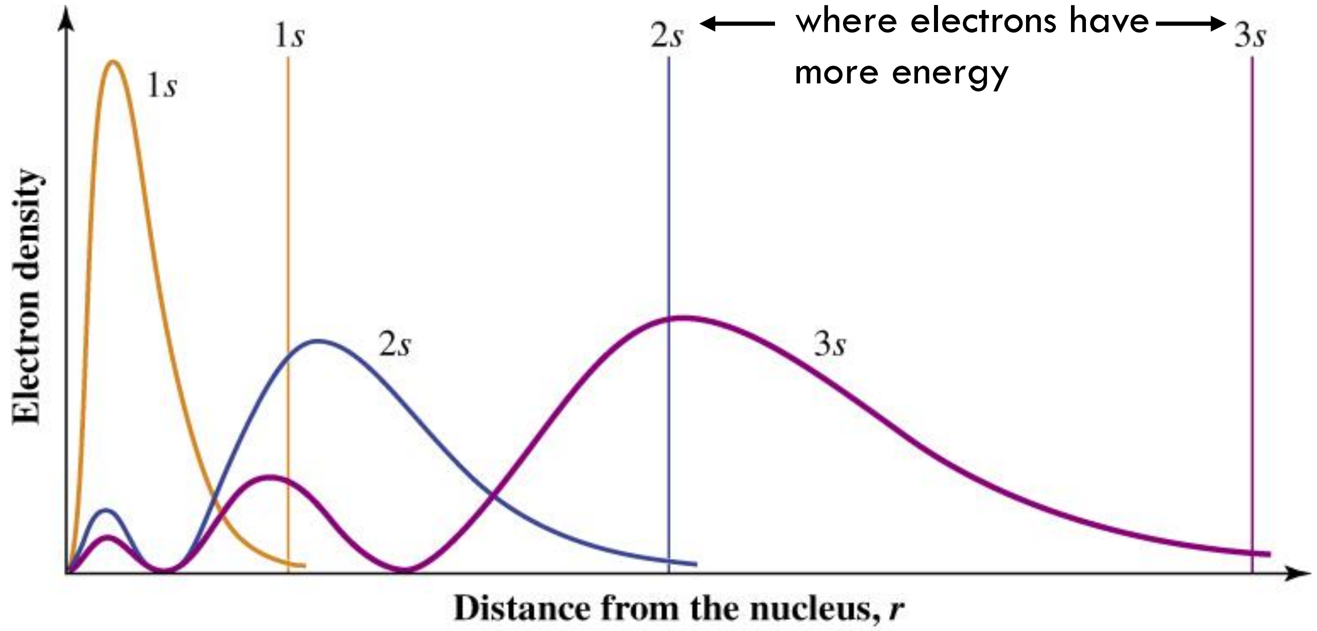


ATOMIC ORBITALS

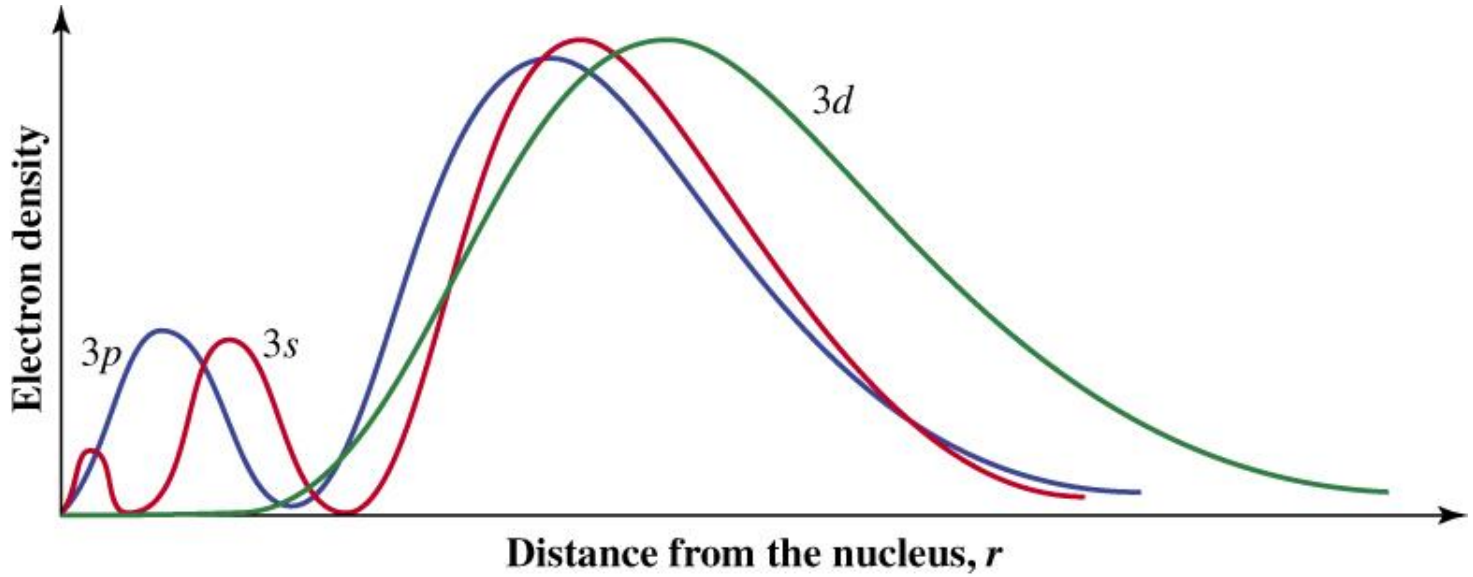
The region where the electron is calculated to be present is called an **orbital**. Each orbital is one solution to the Schrödinger equation.

Limit of 1*s* orbital – 90% density inside sphere with this radius

These are orbitals where electrons have more energy



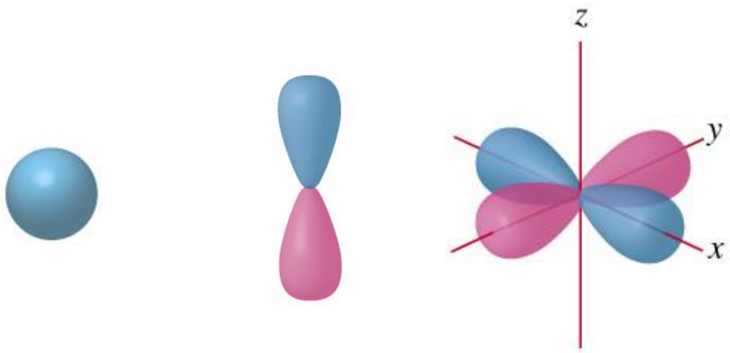
MORE ATOMIC ORBITALS



QUANTUM NUMBERS AND ATOMIC ORBITALS

Each orbital in an atom is characterised by a **unique set of variables** (called quantum numbers) n, ℓ, and m_ℓ, which respectively correspond to the **orbital's energy, angular momentum,** and the **magnetic quantum number.**

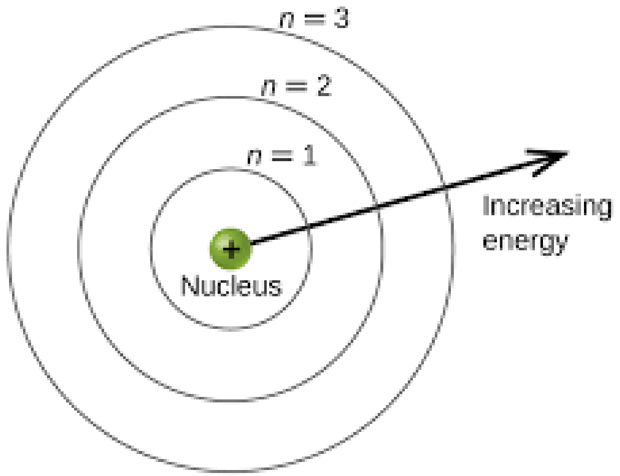
Each orbital can house a maximum of 2 electrons (the fourth quantum number m_s distinguishes between the two). So quantum numbers help us to predict where each electron in an atom most likely is (and where they are not)



$1s$ $2p_z$ $3d_{x^2-y^2}$

PRINCIPAL QUANTUM NUMBER

The principal quantum number must be a positive integer (*n* = 1,2,3…)



These are the energy levels in the atom

- *n* is correlated with orbital size
- As *n* increases, the energy of the electron increases, its orbital gets bigger and it is less tightly bound to the atom

AZIMUTHAL QUANTUM NUMBER

- Indexes the angular momentum of the orbital
- The value correlates with the number of preferred axes in a particular orbital
- It thereby identifies the shape of the electron distribution within the orbital
- ℓ can be zero or any positive integer smaller than *n*

Value of ℓ	***0***	***1***	***2***	***3***	***4***
Orbital designation	***s***	***p***	***d***	***f***	***g***

AZIMUTHAL QUANTUM NUMBER

ℓ = 0,1,2… (n-1) can be zero or any positive integer smaller than *n*

n = 3

ℓ = 0,1,2
(n-1)

ℓ = 0

s orbital

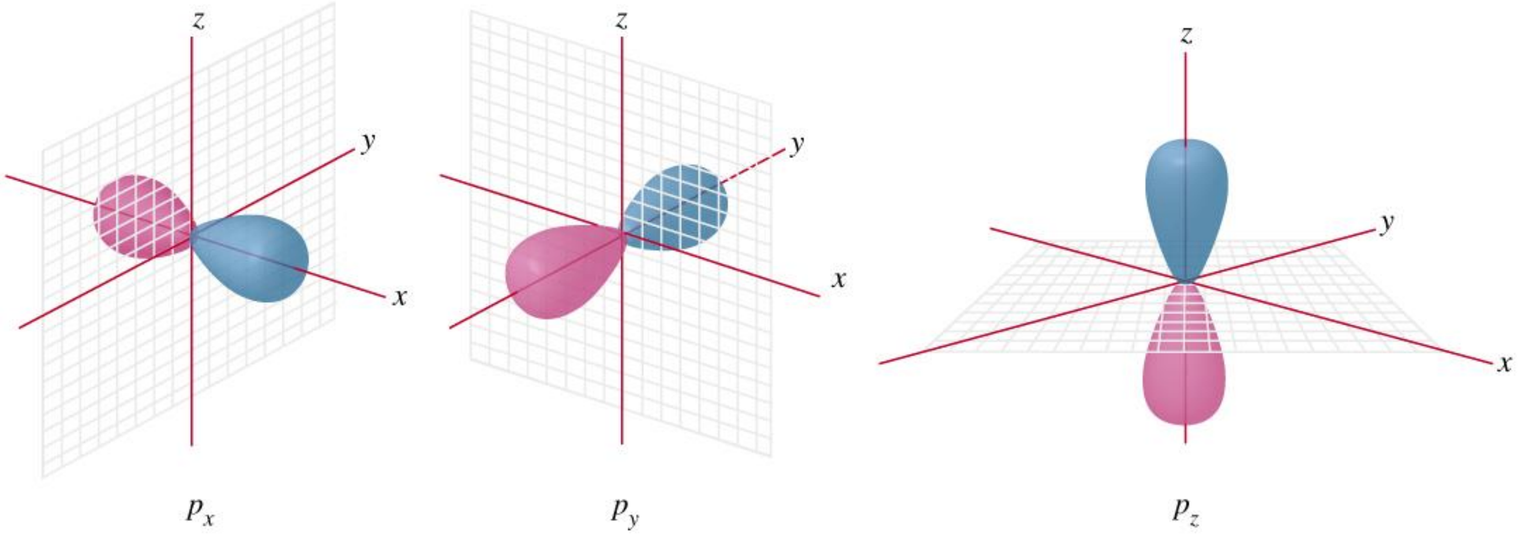
AZIMUTHAL QUANTUM NUMBER

ℓ = 0,1,2… (n-1) can be zero or any positive integer smaller than *n*

n = 3

***ℓ* = 0,1,2**
(n-1)

***ℓ* = 1**



p orbitals

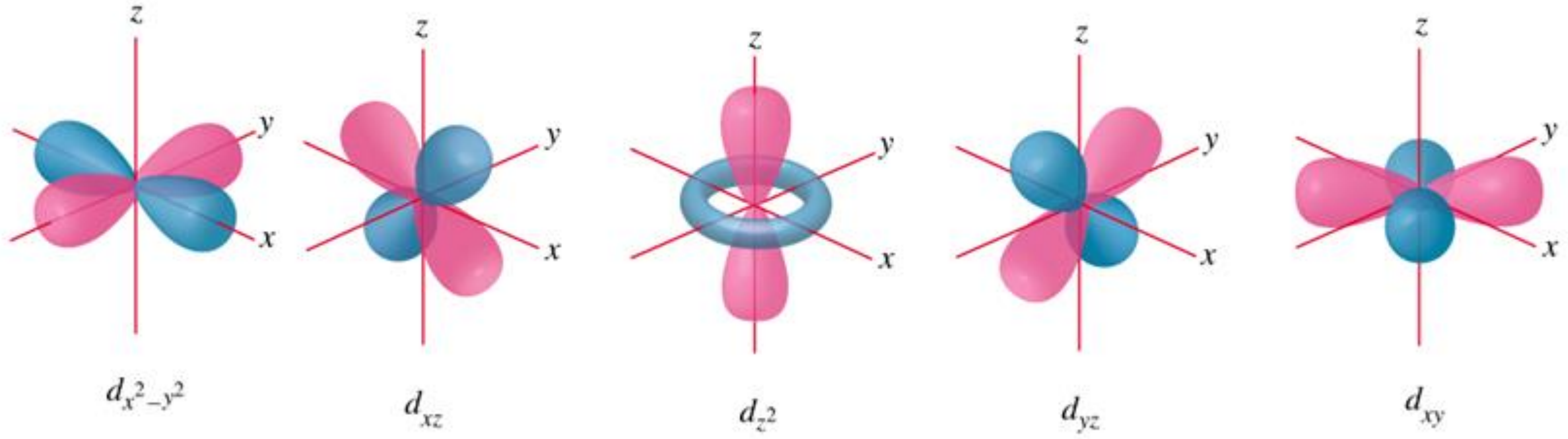
AZIMUTHAL QUANTUM NUMBER

***ℓ* = 0,1,2… (n-1)** can be zero or any positive integer smaller than *n*

n = 3

***ℓ* = 0,1,2**
(n-1)

***ℓ* = 2**

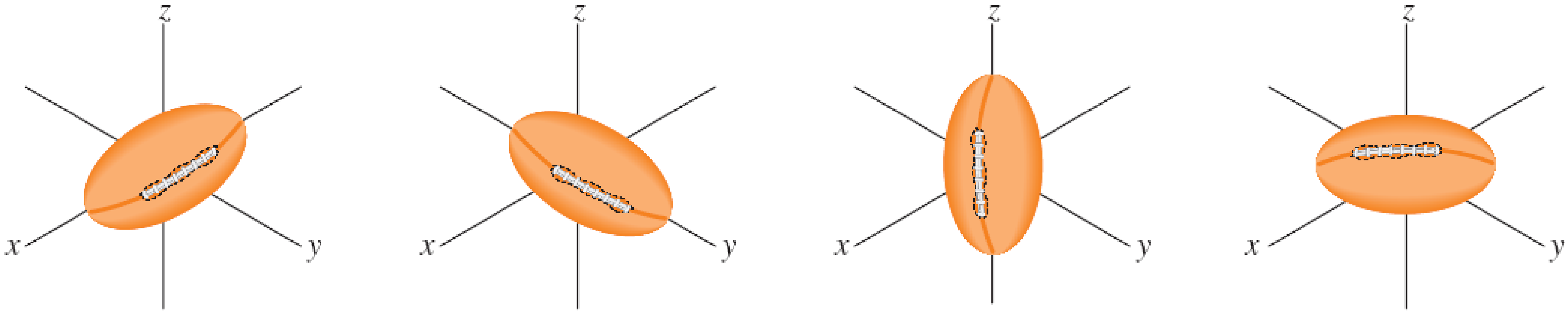


d orbitals

MAGNETIC QUANTUM NUMBER

Magnetic quantum number *m_ℓ* The magnetic quantum number indexes the restricted numbers of possible orientations of each orbital

- The magnetic quantum number (m_ℓ) can be any positive or negative integer between 0 and *l* : m_ℓ = 0,± 1,± 2…
- there are 2ℓ+1 possible values for m_ℓ



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MAGNETIC QUANTUM NUMBER

The magnetic quantum number (m_ℓ) can be any positive or negative integer between 0 and ℓ

$m_\ell = 0, \pm 1, \pm 2 \ldots$

$\boldsymbol{\ell = 0}$

$m_\ell = 0$

$m_\ell = 0$

There is 1 s orbital in each energy level of an atom

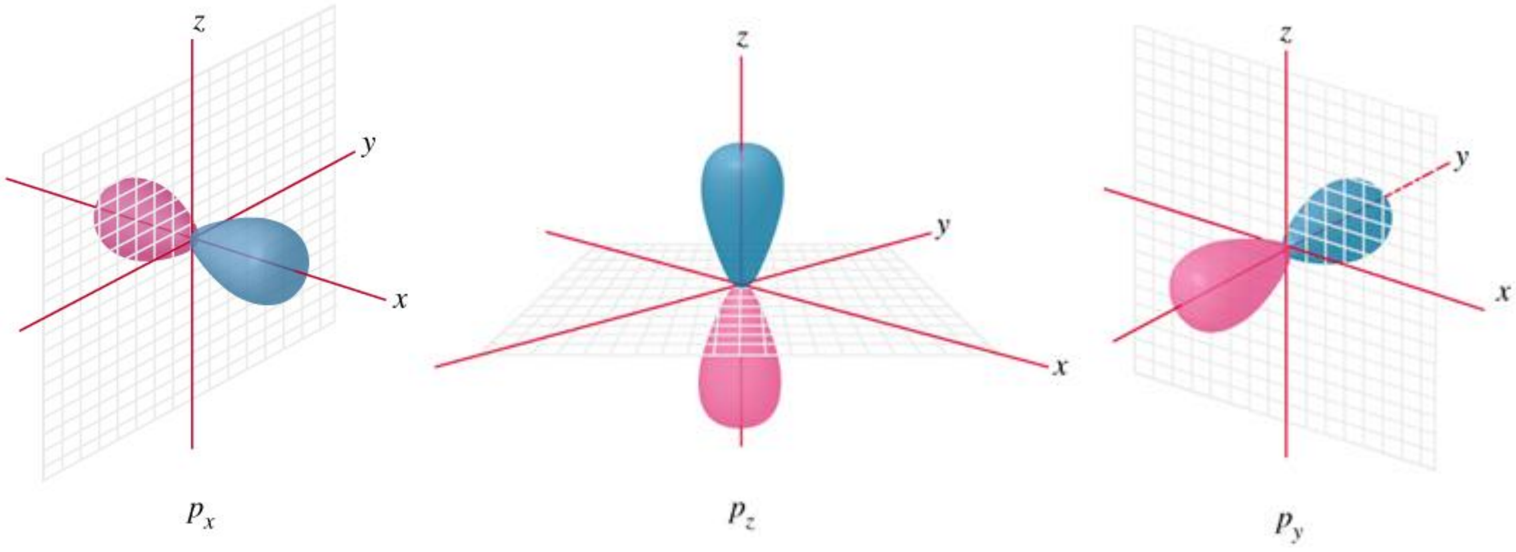
MAGNETIC QUANTUM NUMBER

The magnetic quantum number (m_ℓ) can be any positive or negative integer between 0 and ℓ

$$m_\ell = 0, \pm 1, \pm 2\ldots$$

ℓ = 1

m_ℓ = -1, 0, 1



m_ℓ=-1 m_ℓ =0 m_ℓ =1

There are 3 p orbitals in each energy level from n=2 onwards

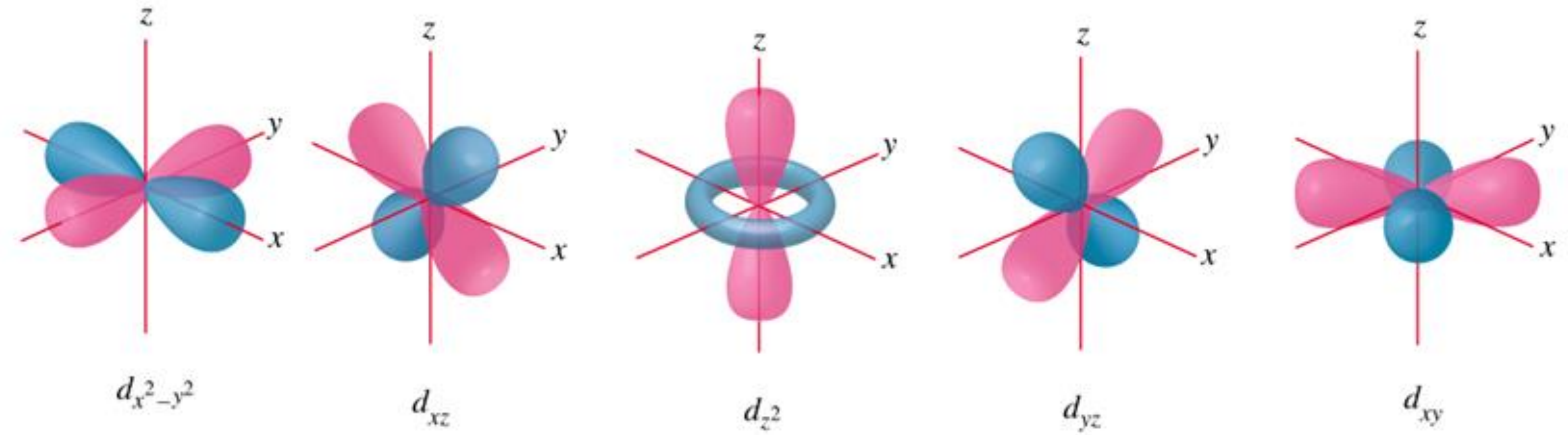
MAGNETIC QUANTUM NUMBER

The magnetic quantum number (m_ℓ) can be any positive or negative integer between 0 and ℓ

$$m_\ell = 0, \pm 1, \pm 2 \ldots$$

$\boldsymbol{\ell = 2}$

m_ℓ = -2,-1,0,1,2



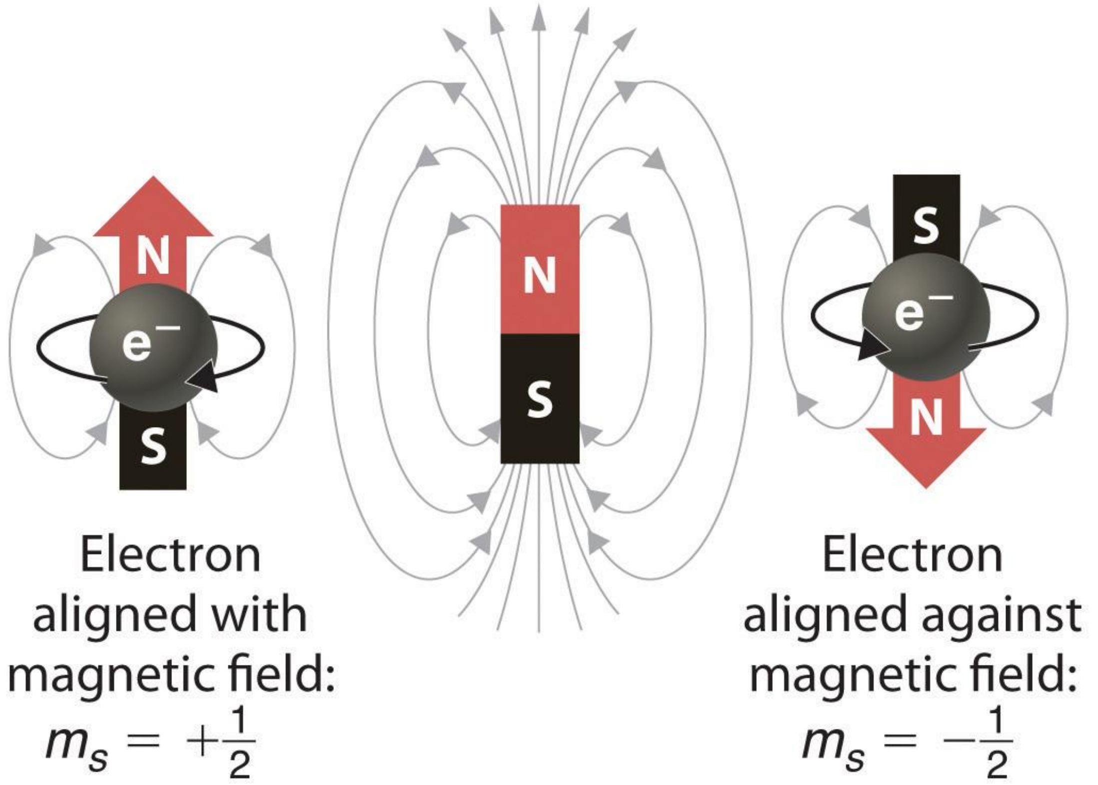
m_ℓ =-2 | m_ℓ =-1 | m_ℓ =0 | m_ℓ =1 | m_ℓ =2

There are 5 d orbitals in each energy level from n =3 onwards

SPIN QUANTUM NUMBER, M_S

Each orbital can hold up to 2 electrons

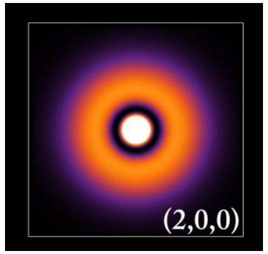
Each electron occupying an orbital can have a spin of either up ($+\frac{1}{2}$) or down ($-\frac{1}{2}$) :



http://images.flatworldknowledge.com/averillfwk/averillfwk-fig06_031.jpg

QUANTUM NUMBERS

2s orbital:



n, **principal quantum number**

(size of orbital, energy level or **shell**)

Eg. **2**s

ℓ, **angular momentum**

(orbital shape)

Eg. 2***s***

m_ℓ, **magnetic quantum number**

(orbital direction)

	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$	...
$n = 1$	$m_\ell = 0$					
$n = 2$	0	−1, 0, 1				
$n = 3$	0	−1, 0, 1	−2, −1, 0, 1, 2			
$n = 4$	0	−1, 0, 1	−2, −1, 0, 1, 2	−3, −2, −1, 0, 1, 2, 3		
$n = 5$	0	−1, 0, 1	−2, −1, 0, 1, 2	−3, −2, −1, 0, 1, 2, 3	−4, −3, −2, −1, 0, 1, 2, 3, 4	
...	...	...	...	...	...	...

Table from https://en.wikipedia.org/wiki/Atomic_orbital

QUANTUM NUMBERS

The *s*, *p*, *d* and *f* orbitals correspond to:

A $n = 1, 2, 3$ & 4

B $l = 0, 1, 2$ & 3 ✓

	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$	...
$n = 1$	$m_\ell = 0$					
$n = 2$	0	−1, 0, 1				
$n = 3$	0	−1, 0, 1	−2, −1, 0, 1, 2			
$n = 4$	0	−1, 0, 1	−2, −1, 0, 1, 2	−3, −2, −1, 0, 1, 2, 3		
$n = 5$	0	−1, 0, 1	−2, −1, 0, 1, 2	−3, −2, −1, 0, 1, 2, 3	−4, −3, −2, −1, 0, 1, 2, 3, 4	
...	...	...	...	...	...	...

C $n = 2$, $l = 1$ and $m_l = -1$ or 1

https://en.wikipedia.org/wiki/Atomic_orbital

D Don't know

0

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QUANTUM NUMBERS EXAMPLE

Number	Symbol	Possible Values
Principal Quantum Number	n	$1, 2, 3, 4, \ldots$
Angular Momentum Quantum Number	ℓ	$0, 1, 2, 3, \ldots, (n-1)$
Magnetic Quantum Number	m_l	$-\ell, \ldots, -1, 0, 1, \ldots, \ell$
Spin Quantum Number	m_s	$+1/2, -1/2$

For an orbital with $n = 2$, what values of l and m_l are allowed?

l can only have values up to $n - 1$:

If $n = 2$, then l can go up to 2 – 1 = 1. So $l = 0$ and 1

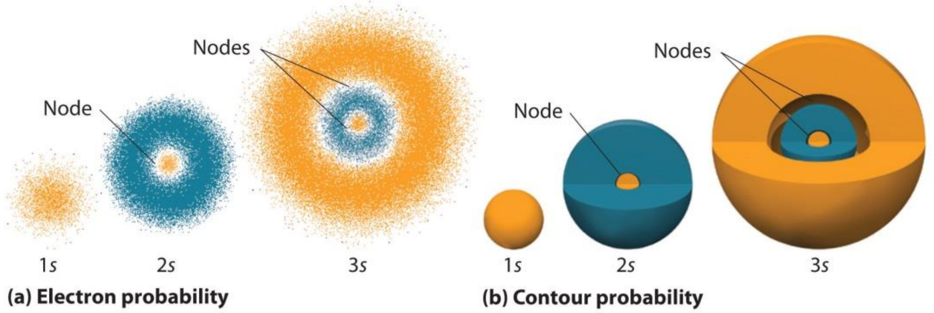
m_l can have values from $-l$ to $+l$:

If $l = 0$, then m_l must be 0

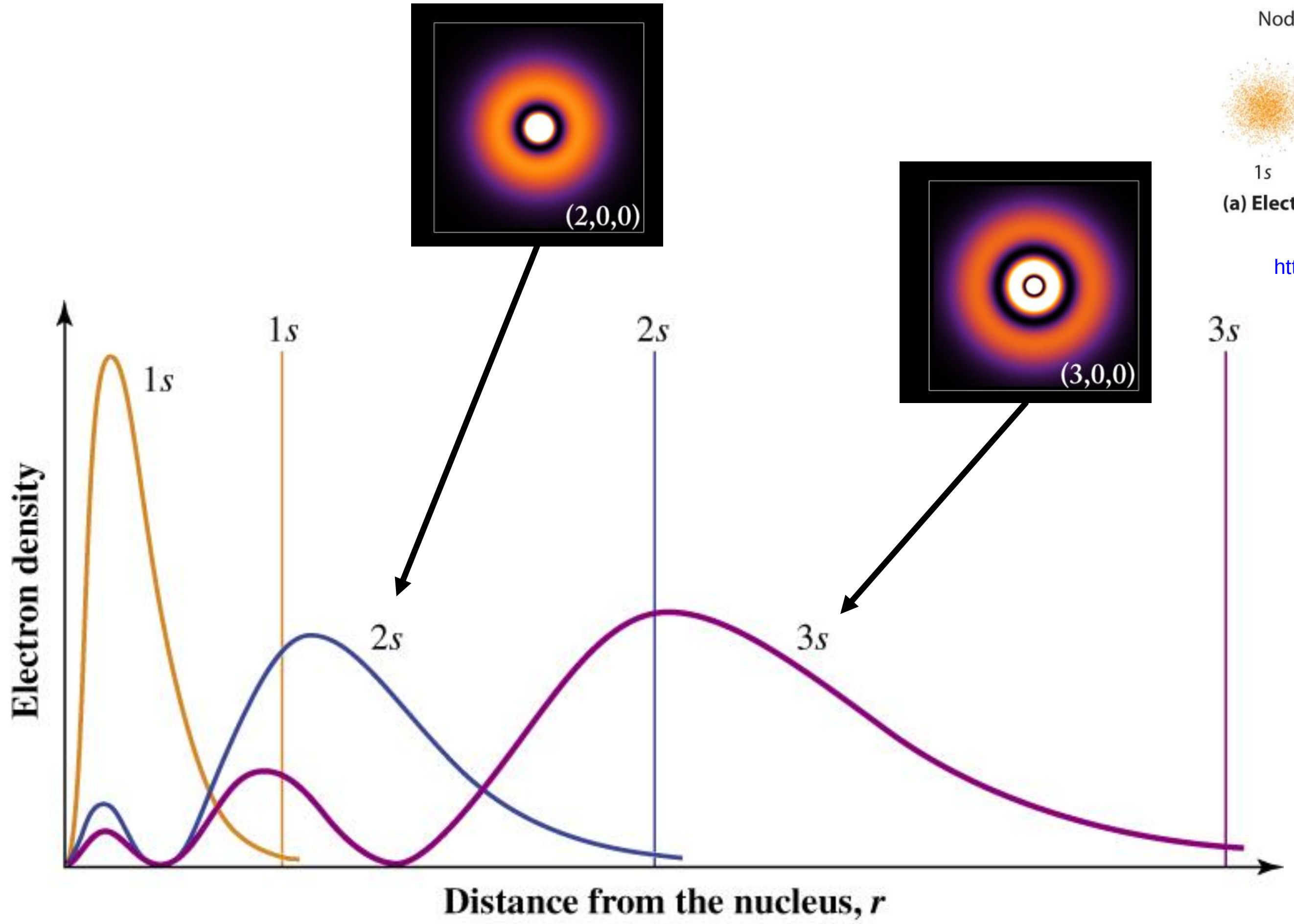
If $l = 1$, then m_l can be -1, 0 and +1

Conclusion: 2nd energy level of an atom has 1 s orbital and 3 p orbitals and can hold 8 electrons

HYDROGEN'S ATOMIC ORBITALS



http://images.flatworldknowledge.com/averillfwk/averillfwk-fig06_023-26.jpg



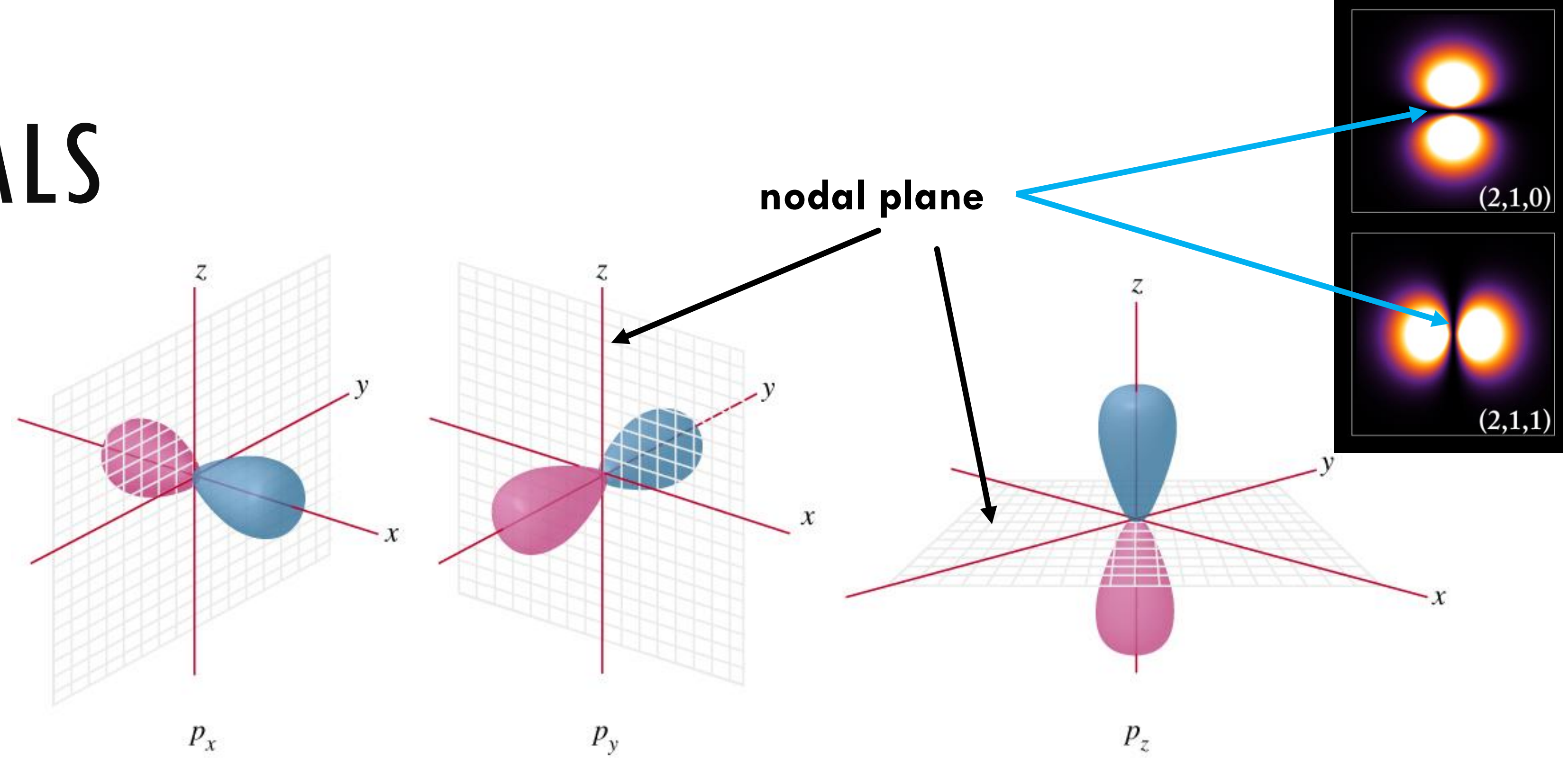
s orbitals

(sharp)

Hydrogen orbitals By PoorLeno, 2008, Public Domain, https://commons.wikimedia.org/w/index.php?curid=5854697

P ORBITALS

(PRINCIPAL)



For each *p* orbital the electron density is concentrated in two regions on either side of the nucleus, forming two lobes. The orbital can have three orientations, one in each of the x, y and z planes.

The pink and blue coloration denotes different phases of the orbital (essentially the same but opposite side of nucleus here). Together they make 1 orbital (i.e. there is a **nodal plane** intersecting the two halves of the orbital).

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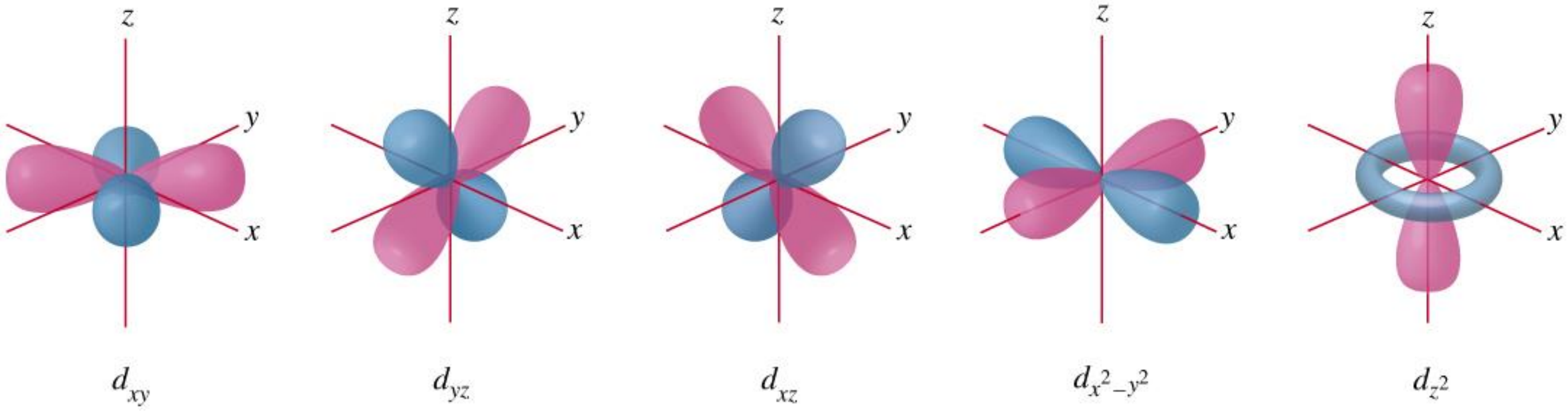
D ORBITALS

(DIFFUSE)

The *d* orbitals have 2 nodal planes.

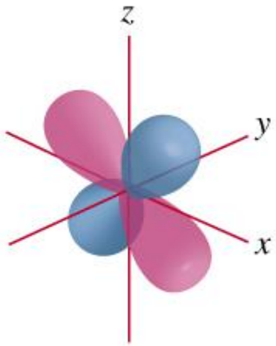


These 3 d orbitals lie *between* the axes.

These 2 d orbitals lie *on* the axes.

THE SHAPE OF …

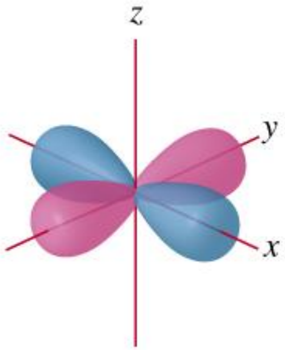
Which orbital corresponds to 1*s*?



A

B

C



D

E Don't know

49

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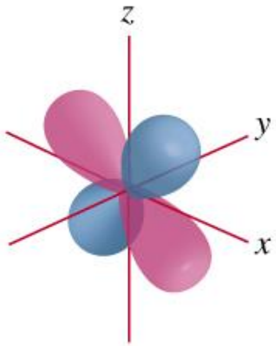
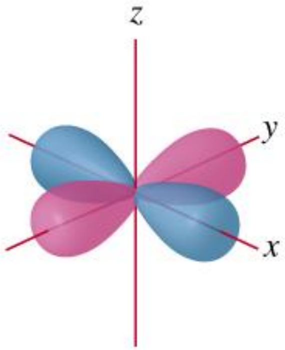
THE SHAPE OF …

Which orbital corresponds to $2p_z$?





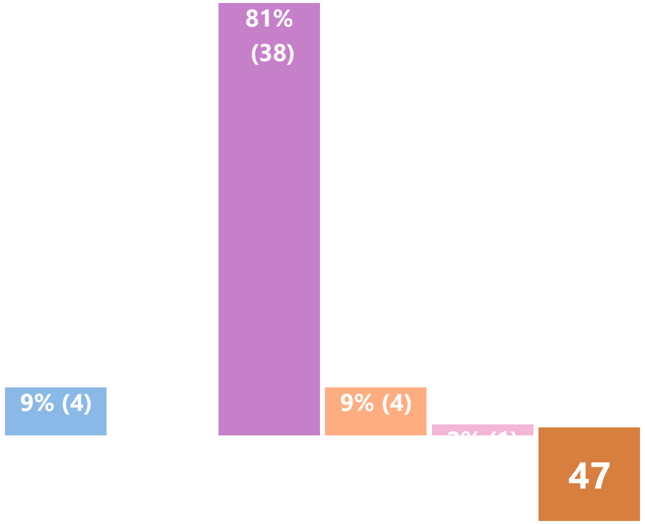
A

B

C

D

E Don't know



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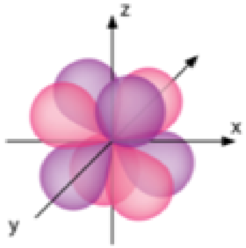
THE SHAPE OF ...

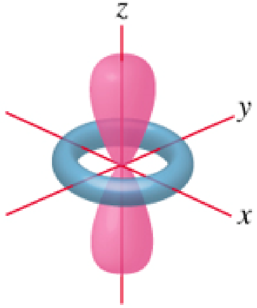
Which orbital corresponds to $3d_{z^2}$?



A

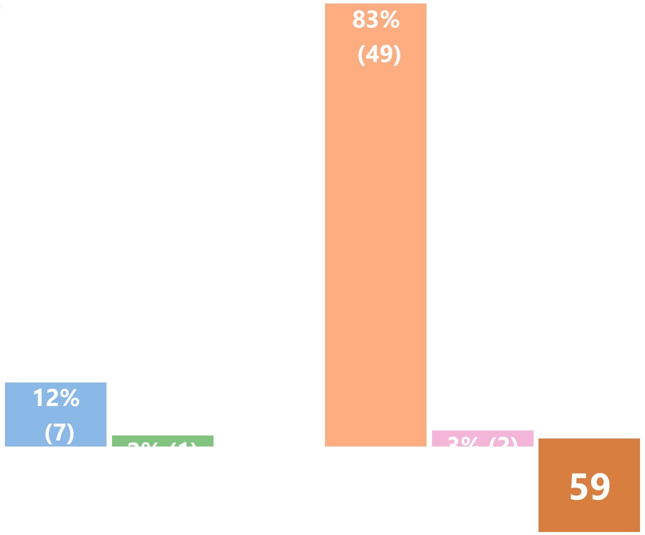
B

C



D

E None of them



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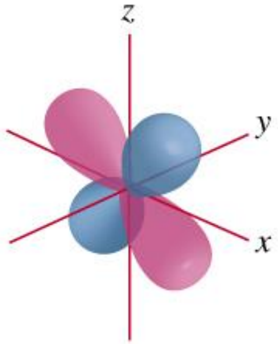
THE SHAPE OF …

https://youtu.be/f8FAJXPBdOg

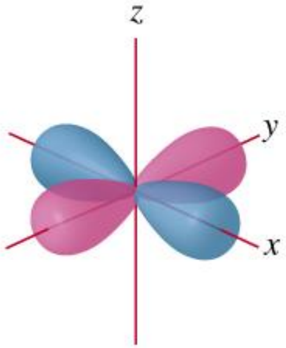
Check this out when you need a break from studying for exams – it ties together many different topics from the semester, and give a peek at future chemistry!



$3d_{xz}$

$1s$

$2p_z$



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

QUANTUM NUMBERS RECAP

- **Electrons** behave like particles but also like **waves.**
- Electrons in atoms behave in a wave-like manner that **cannot be described using classical mechanics.**
- **Quantum mechanics can describe the energy and probability of locating an electron** in an atom by finding solutions to the Schrödinger equation (these **solutions are atomic orbitals**, regions where electron density is high).
- There are four variables (**quantum numbers**) used to describe the electron in an orbital: n, ℓ, m_ℓ ,and m_s

Useful resource:
https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Quantum_Mechanics/09._The_Hydrogen_Atom/Atomic_Theory/Electrons_in_Atoms/Atomic_Spectra