Quantum Mechanics 2:

- Schroedinger equation
- Atomic wave functions
- Atomic orbitals
- Quantum numbers

Wave Functions

In quantum mechanics a particle cannot be described using trajectory. Rather, it is best described as a wave distributed through the space

Therefore, we need a wave function that describes this wave behavior

Wave Functions

Wave functions are often complex functions (have both real and imaginary part) and have coordinates as dependent variable

Physical meaning of the wave function: The square of value of wave function at point x is proportional to the probability of finding an object it describes at this point

Wave Functions

We postulate that there exist a wave function that describes distribution of electron is space.
Because of uncertainty principle we cannot define the position of electron so we have to work with probabilities

Since probability of finding an electron somewhere is space is equal to 1,

$$\int \psi\psi^* \, dV = 1$$

Where ψ* is complex conjugate

Postulates of Quantum Mechanics

One of the postulates of quantum mechanics states that energy of the system is related to its wave function through Shroedinger equation (S.E.):

$$\underset{\substack{|\\ \text{Hamiltonian}\\ \text{Operator}\\ \text{(Energy operator)}}}{\hat{H}}\,\Psi = \underset{\substack{|\\ \text{Energy}\\ \text{eigenvalue}}}{E}\,\Psi$$

In mathematics, operator is a tool: a set of instructions to act upon a function.

For example: differentiate the function twice and then multiply by certain number

Operators in Mathematics

Operators look strange to you, this is normal.
Let's look at operator form for kinetic energy (KE) for a particle moving in the direction x (p_x is momentum):

$$KE = \frac{m_e v_x^2}{2} = \frac{p_x^2}{2m}$$

Obviously, if wave function has x as a dependent variable it needs to be differentiated twice to obtain KE.
Thus, you may expect operator for kinetic energy look like this:

$$\hat{E}_x = -\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2}$$

Hamiltonian Operator Extracts Energy from Wave Function

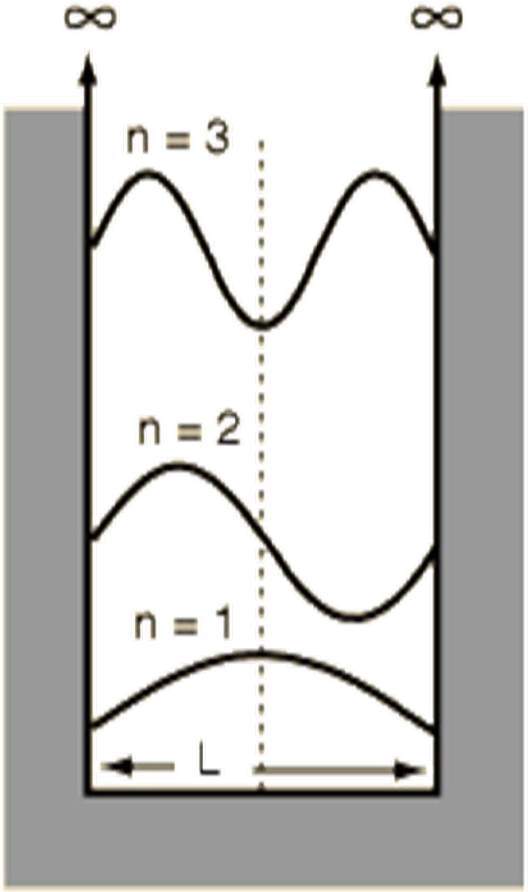
$$\underset{\substack{\text{Hamiltonian}\\ \text{Operator}\\ \text{(Energy operator)}}}{\hat{H}}\,\Psi = \underset{\substack{\text{Energy}\\ \text{eigenvalue}}}{E}\,\Psi$$

- **When Hamiltonian operator acts on a wave function it gives a wave function multiplied by a number.**
- **This number is a total energy of the system the wave function describes.**

$$\hat{H} = -\overbrace{\frac{\hbar}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)}^{\text{Kinetic energy operator}} + \overbrace{\tilde{V}(x)}^{\substack{\text{Potential energy}\\ \text{operator}}}$$

Hamiltonian Operator Extracts Energy from Wave Function

- Solution of Schroedinger equation for hydrogen atom is complex.
- We will consider a much simpler system called particle in the box

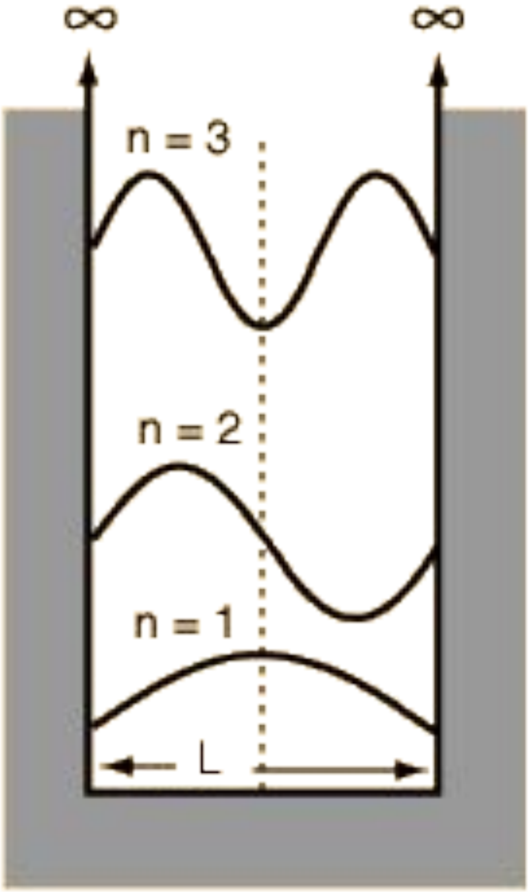


In this simple model potential energy, V, is set to zero inside the box

Boundary conditions:

- Outside the box potential energy is set to infinity (this is equivalent of saying that particle cannot escape the box)
- The length of the box is L

Particle in the Box



Solution of Schroedinger equation for particle in the box, application of boundary conditions and normalization gives a set of wave functions:

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

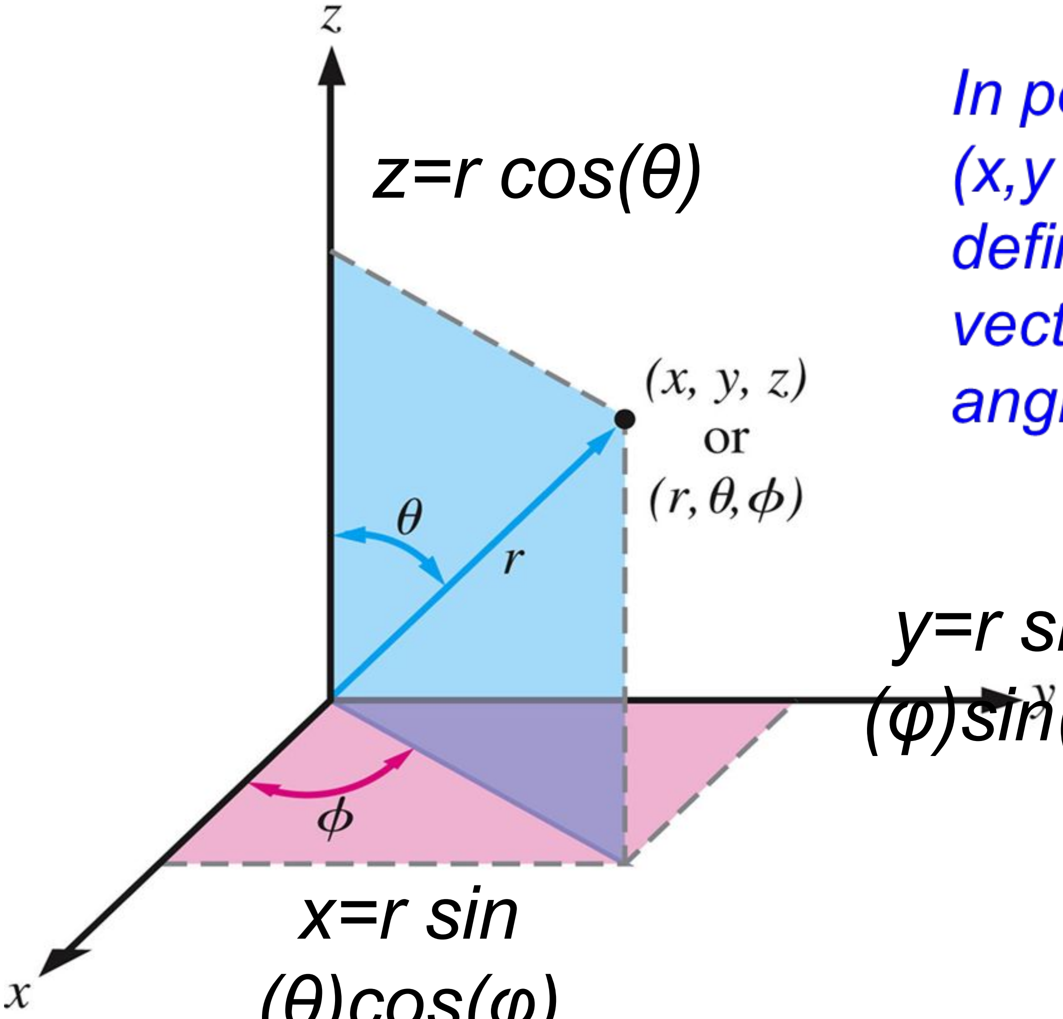
$$E_n = \frac{n^2 h_2}{8mL^2}$$

Conclusion: even in this simple system we see that energy levels are quantized.

We arrived at this conclusions only by assuming that Schroedinger equation is correct.

S.E. for H-like atoms Can be Solved in Polar Coordinates

To solve Schroedinger equation for hydrogen atom the use of spherical polar coordinates is necessary



$z = r\cos(\theta)$

$y = r\sin(\varphi)\sin(\theta)$

$x = r\sin(\theta)\cos(\varphi)$

In polar coordinates, instead of (x,y and z), coordinates are defined by the length of the vector (r) and value of two angles (θ and ϕ)

S.E. for H-atom Can be Solved in Polar Coordinates

Further, to solve Schroedinger equation for hydrogen atom a separation of variables in polar coordinates is necessary

Separation of variables allows expressing wave function as a product of:

- radial part (depends only on r)
- and angular part (depends on angles θ *and* ϕ)

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

Schroedinger Equation for H-like atoms

Even then, solution of Schroedinger equation is very complex.
Just to give you an idea about complexity:

$$\hat{H}\psi = E\psi, \quad \hat{H} = \hat{T} - \hat{V}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\hat{T} = -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\right)$$

$$\hat{T} = -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{2mr^2}\boxed{\hat{L}^2} \longrightarrow$$

angular momentum operator

radial part

Solution of S.E. for H-atom Produces a Set of Wave Functions

Just like in case of particle in the box, solutions of S.E. for H-atom provide us with a set of wave functions

Unlike in case of particle in the box, solutions of S.E. for H-atom include three numbers – n, l and m_l

Wave functions look like this:

$$\psi(\boldsymbol{r},\theta,\phi) = \underbrace{\boldsymbol{R}(\boldsymbol{r})}_{n}\overbrace{\Theta(\theta)}^{l}\underbrace{\Phi(\phi)}_{m_l}$$

Example of a Wave Function

Mathematically, the simplest solution of S.E. for H-atom is n=1, l=0 *and* $m_l=0$

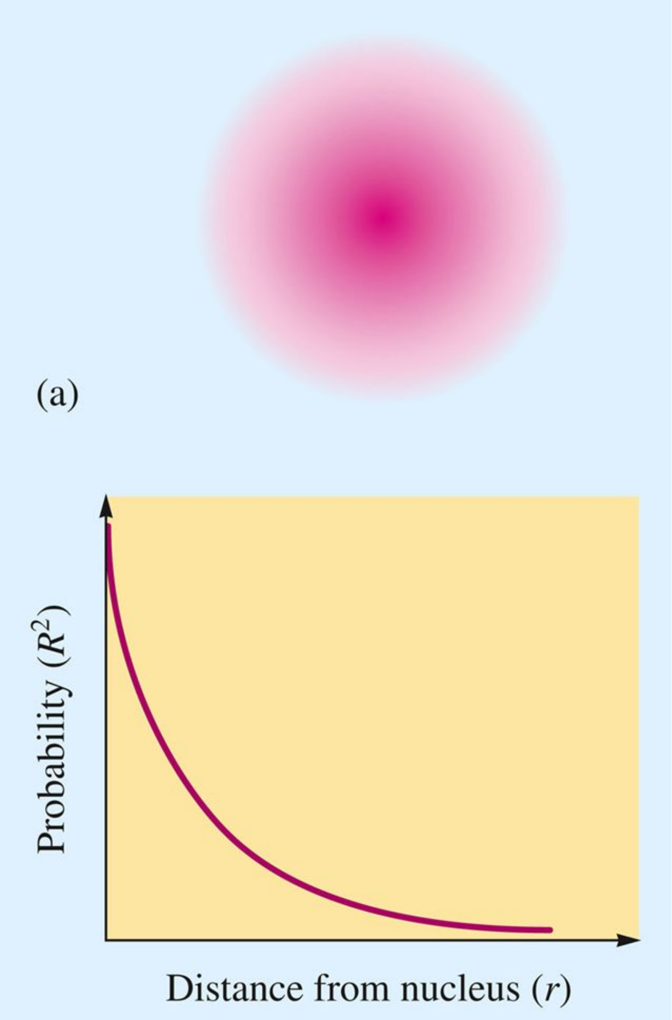
Corresponding wave function looks like this:

$$\Psi_{1,0,0} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \exp(-Zr/a_0)$$

This function describes mathematically something you know from school – a spherical 1s orbital

Physical Meaning of a Wave Function

$[\psi(r, \theta, \phi)]^2 dv$ = **probability of finding the electron in a small volume** dv

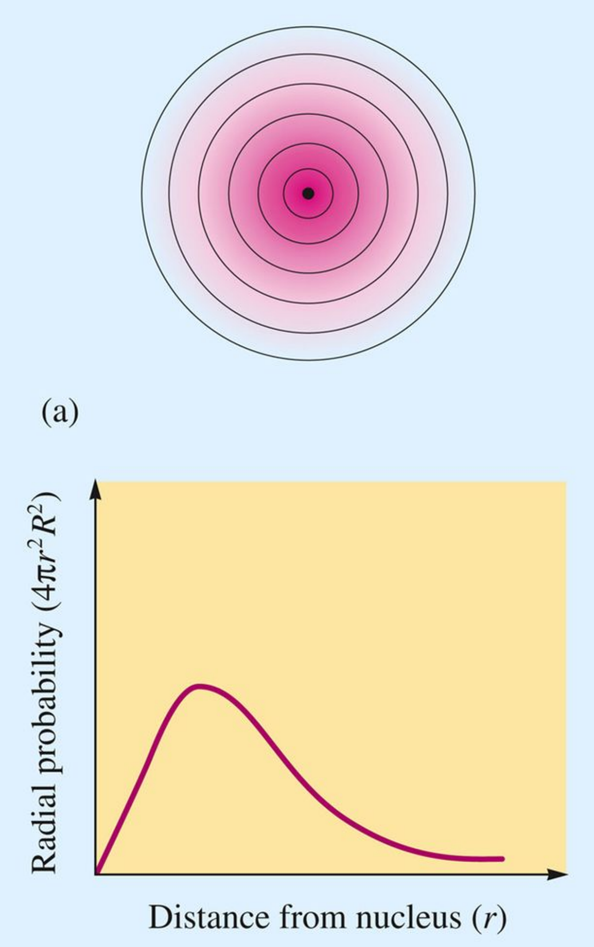


This plot represents electron density map – a probability of finding an electron at distance r from a nucleus

R^2 represents a square of a radial part of the wave function

Physical Meaning of a Wave Function

if we mutiply $[\psi(r, \theta, \phi)]^2 dv$ by $4\pi r^2$ we will obtain probability density

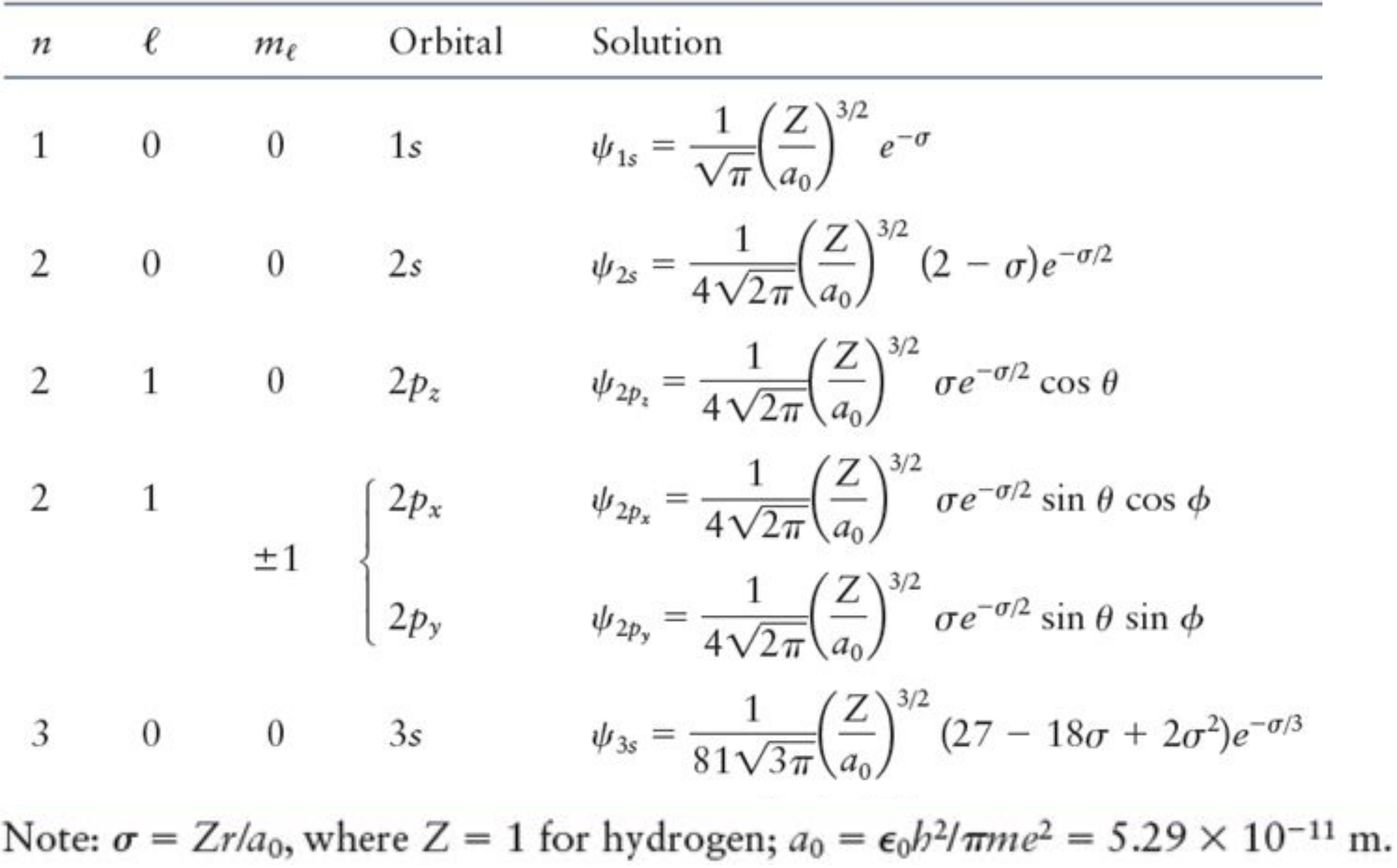


Probability density represents a probability to find an electron at a distance r in any direction from nucleus

Probability density can be viewed as a function that represents a shape of atomic orbital

Solutions of Schroedinger Equation of Single-Electron Atom

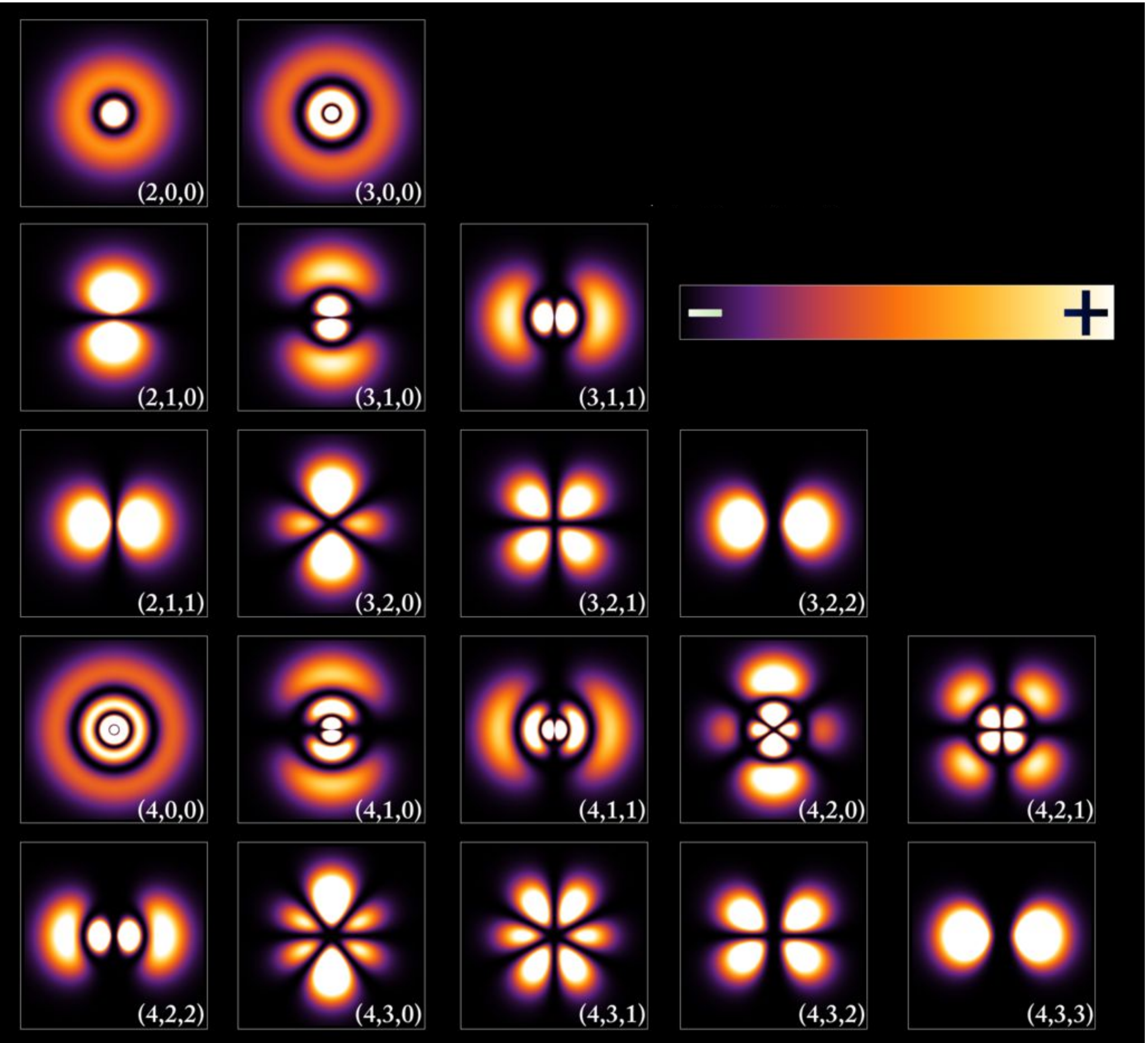
Only real parts of wave functions are shown



n	ℓ	m_ℓ	Orbital	Solution
1	0	0	1s	$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
2	0	0	2s	$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (2 - \sigma)e^{-\sigma/2}$
2	1	0	2p_z	$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \cos\theta$
2	1	±1	2p_x	$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta \cos\phi$
			2p_y	$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta \sin\phi$
3	0	0	3s	$\psi_{3s} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$

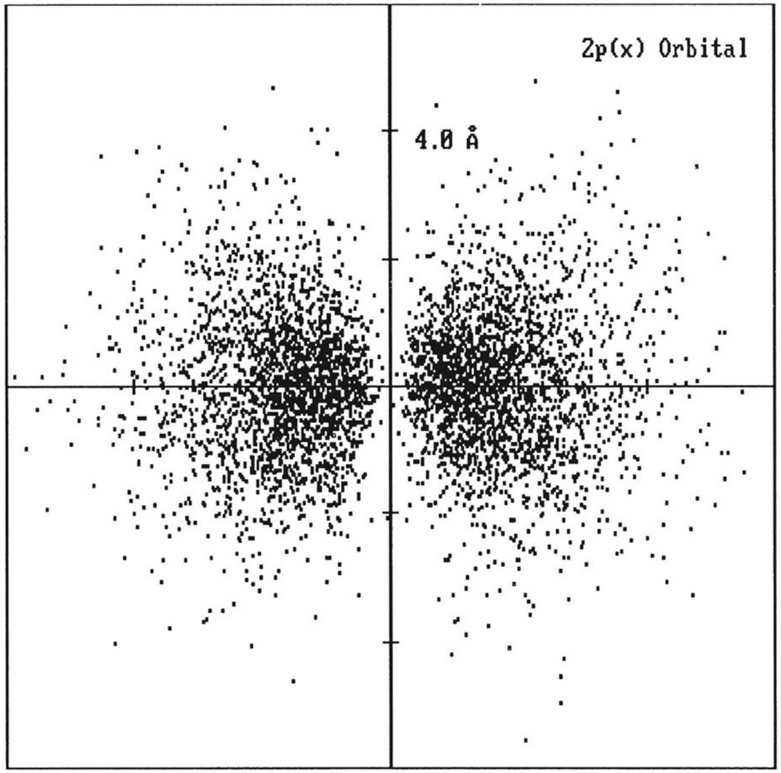
Note: $\sigma = Zr/a_0$, where Z = 1 for hydrogen; $a_0 = \epsilon_0 h^2/\pi m e^2 = 5.29 \times 10^{-11}$ m.

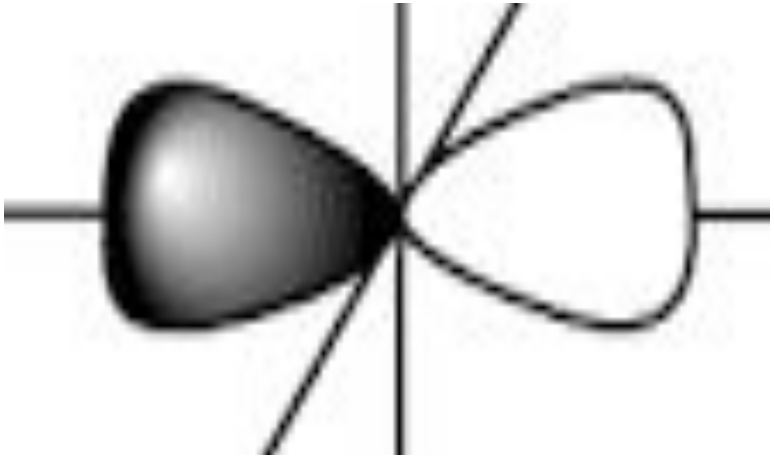
Probability Density Plots for Hydrogen Wave Functions



Orbitals are Depicted Schematically

Each orbital has a unique probability distribution which we can schematically depict as a shape of orbital





Quantum Numbers

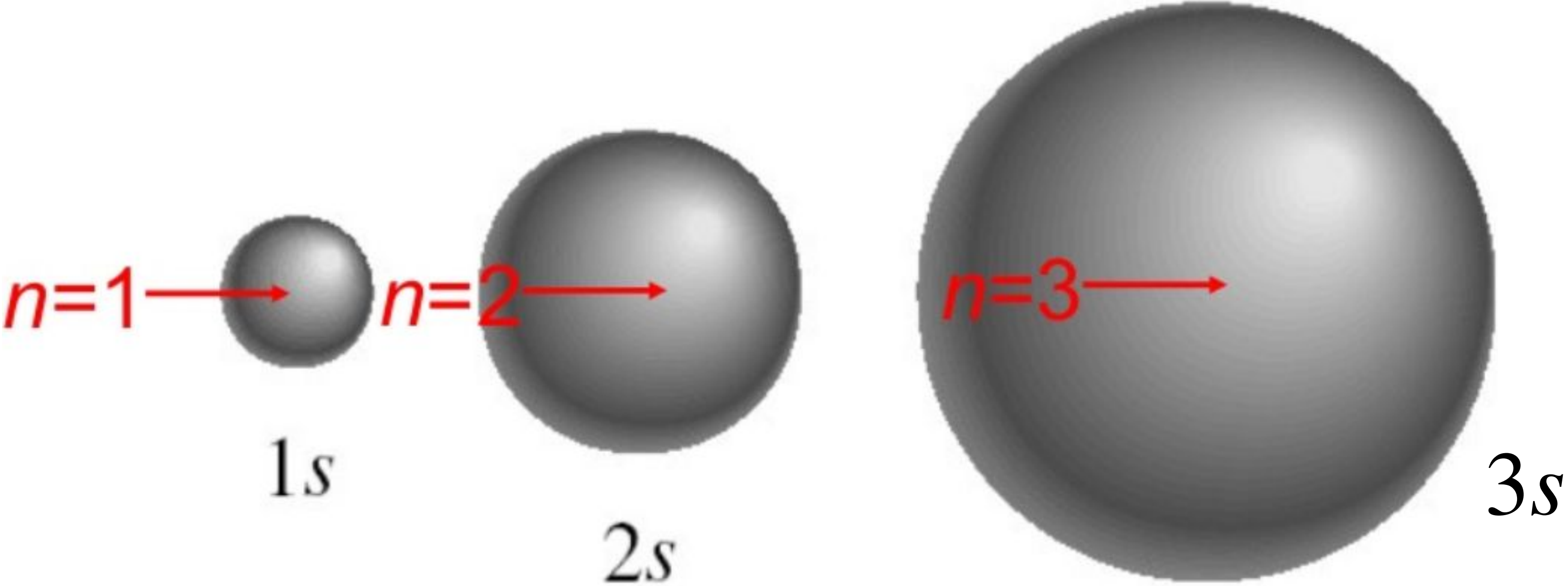
Quantum numbers are required to describe the *distribution of electron density* in an atom.

There are three quantum numbers necessary to describe an ***atomic orbital***.

- The ***principal quantum number (n)*** – designates size
- The ***angular moment quantum number (l)*** – describes shape
- The ***magnetic quantum number (m_l)*** – specifies orientation

Principal Quantum Number (n)

- **The *principal quantum number (n)* designates the energy level of the orbital.**
- **Larger values of *n* correspond to larger orbitals.**
- **The allowed values of *n* are integral numbers: 1, 2, 3 and so forth.**
- **A collection of orbitals with the same value of *n* is frequently called a *shell.***



Angular Momentum Quantum Number (l)

The ***angular moment quantum number (l)*** describes **the *shape* of the orbital**.

The values of **l** are integers that depend on the value of the principal quantum number

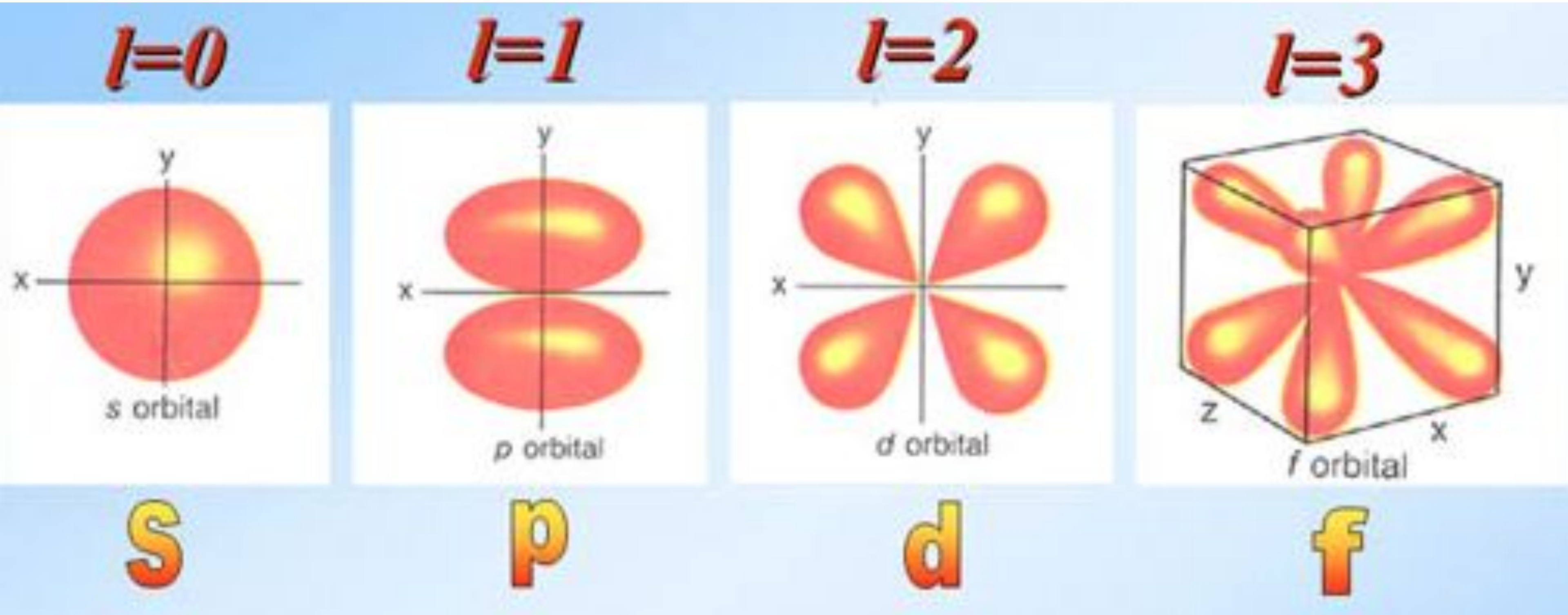
The allowed values of **l** range from 0 to **$n - 1$**.

- Example: If $n = 2$, **l** can be 0 or 1.

l	**0**	**1**	**2**	**3**
Orbital designation	*s*	*p*	*d*	*f*

A collection of orbitals with the same value of n and l is referred to as a *subshell.*

Angular Momentum Quantum Number (l)



With the increase in l the shape of orbital is becoming more and more complex, and the number of orbitals increases

For example, for any *n* there are three *p*-orbitals, 5 *d*-orbitals and seven *f*-orbitals

s- and p-Orbitals

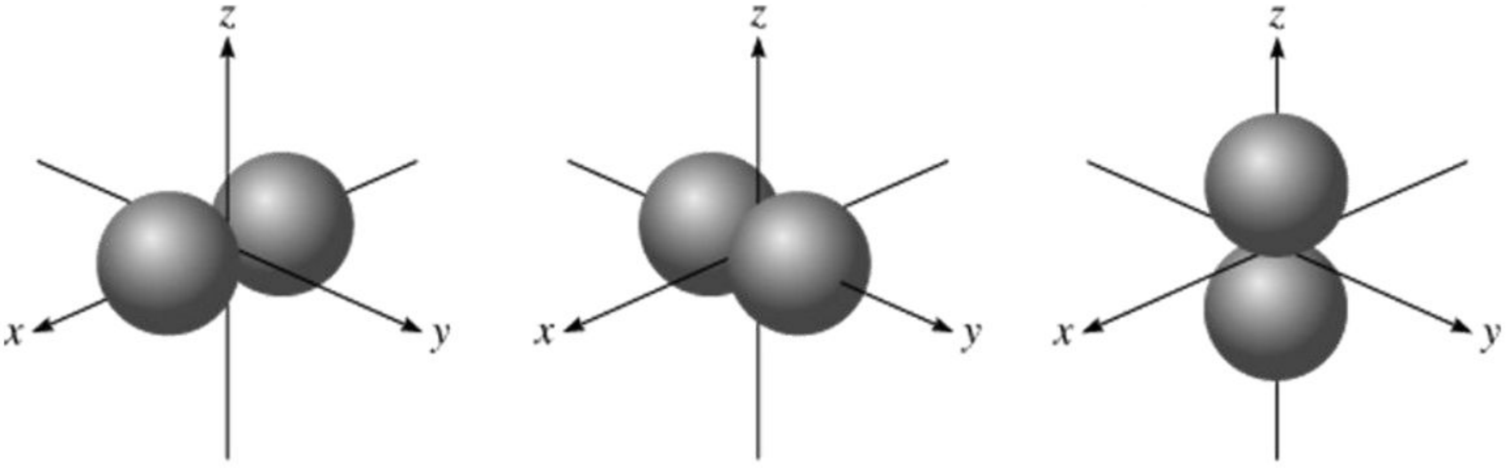
For any quantum number n, there is an orbital that corresponds to **l=0. It has a spherical shape and is called s-orbital**

$\ell = 0$ (s orbitals)

$1s$

Three p-orbitals corresponding to l=1 have a dumbbell shape and are perpendicular to each other

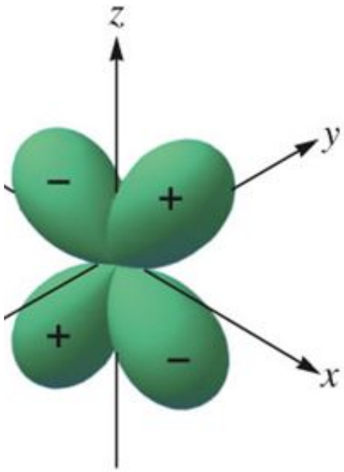
$\ell = 1$
(p orbitals)



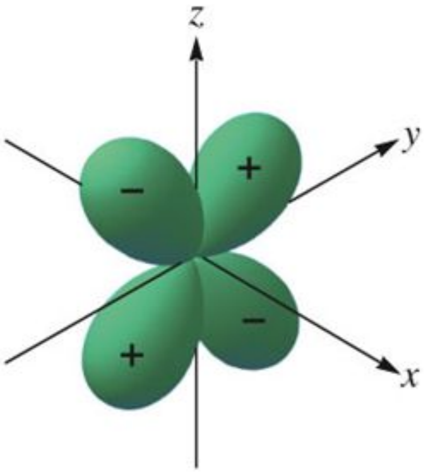
$2p_x$ $2p_y$ $2p_z$

d-Orbitals

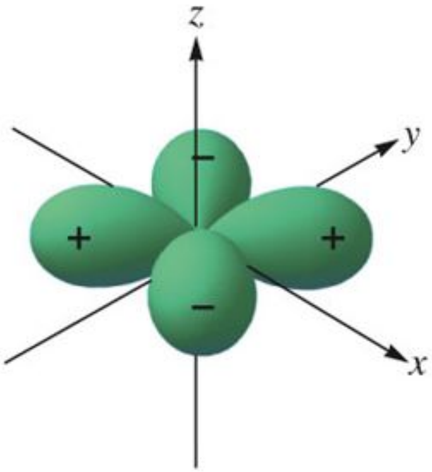
Shapes of five d-orbitals corresponding to l=2 is shown below



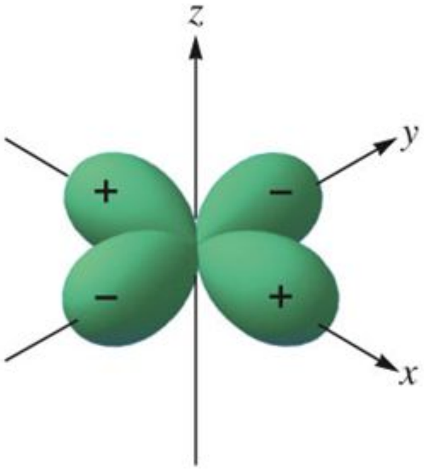
d_{xz}



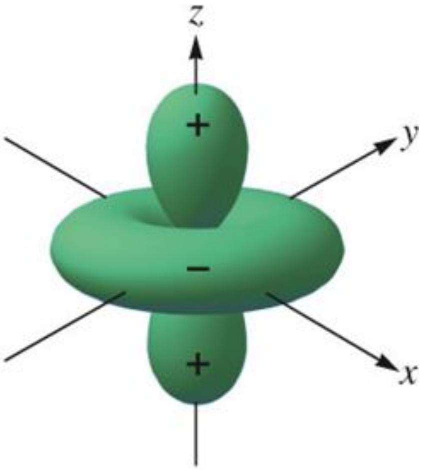
d_{yz}



d_{xy}



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

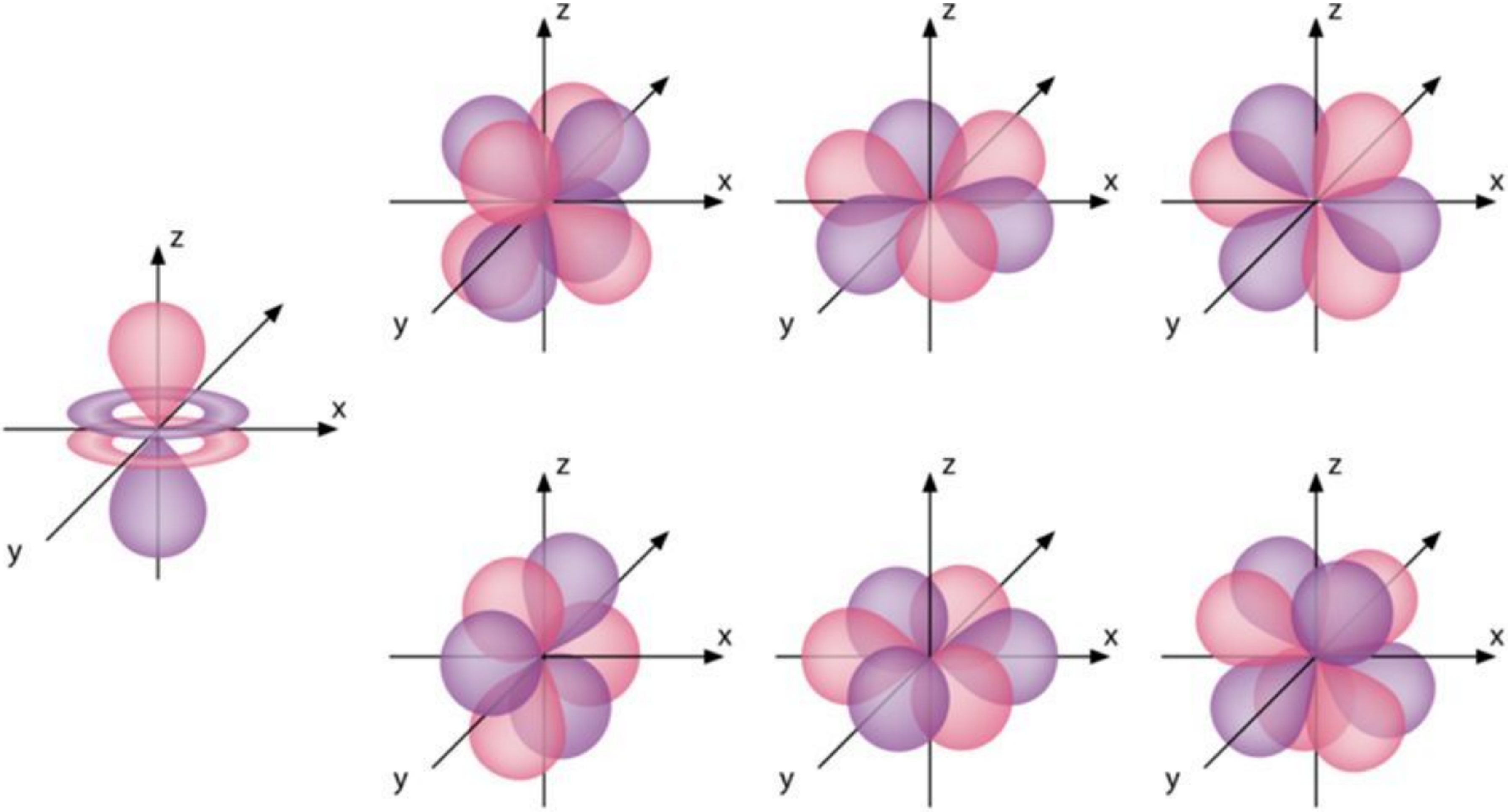


d_{z^2}

+ and – denote a sign of wave function

f-Orbitals

Shapes of seven f-orbitals corresponding to l=3 is shown below



Magnetic Quantum Number (m_l)

The ***magnetic quantum number (m_l)*** describes the ***orientation*** of the orbital in space.

The values of m_l are integers that depend on the value of the angular moment quantum number:

$$-l, \ldots 0, \ldots + l$$

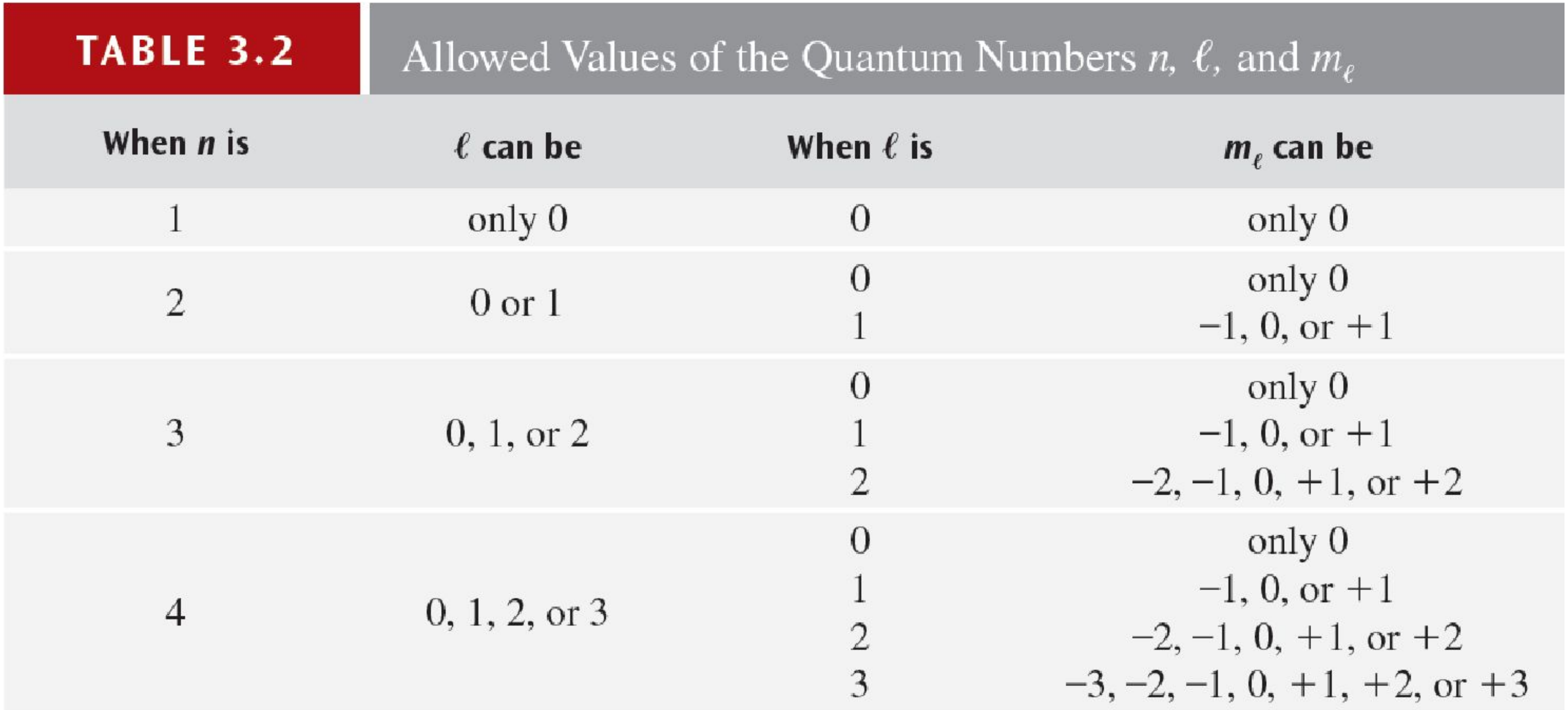


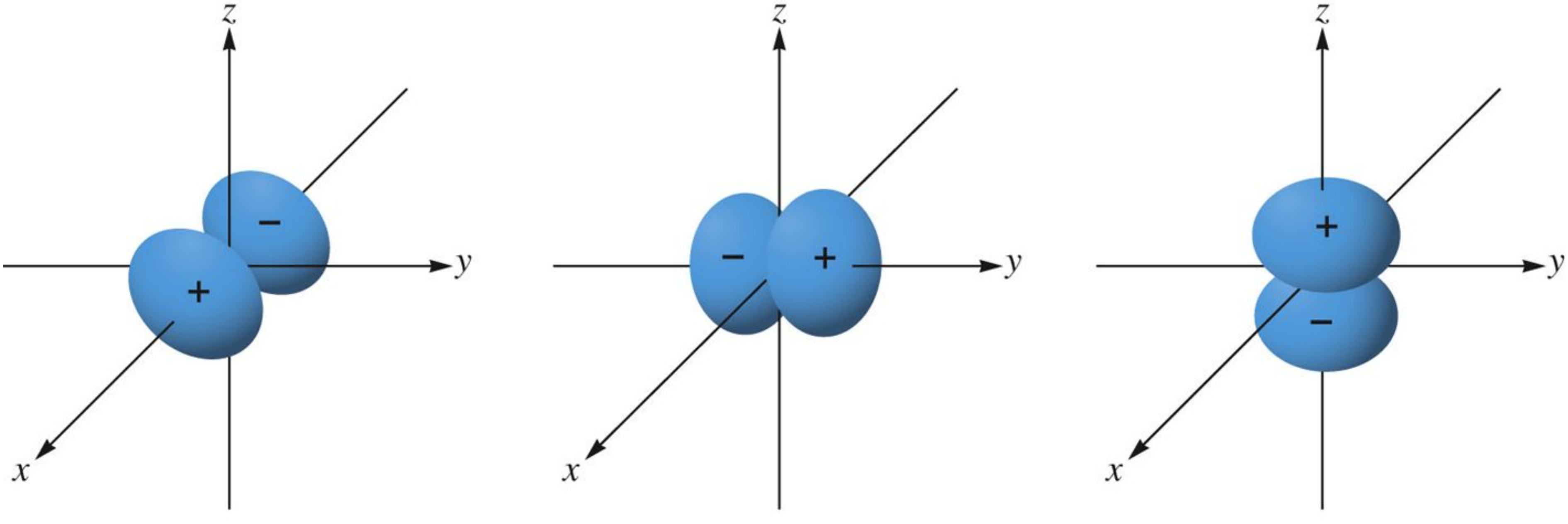
TABLE 3.2 Allowed Values of the Quantum Numbers n, ℓ, and m_ℓ

When n is	ℓ can be	When ℓ is	m_ℓ can be
1	only 0	0	only 0
2	0 or 1	0	only 0
		1	−1, 0, or +1
3	0, 1, or 2	0	only 0
		1	−1, 0, or +1
		2	−2, −1, 0, +1, or +2
4	0, 1, 2, or 3	0	only 0
		1	−1, 0, or +1
		2	−2, −1, 0, +1, or +2
		3	−3, −2, −1, 0, +1, +2, or +3

Magnetic Quantum Number (m_l)

Three orientations: **l**= 1 (as required for a *p* orbital)

m_l = –1, 0, +1

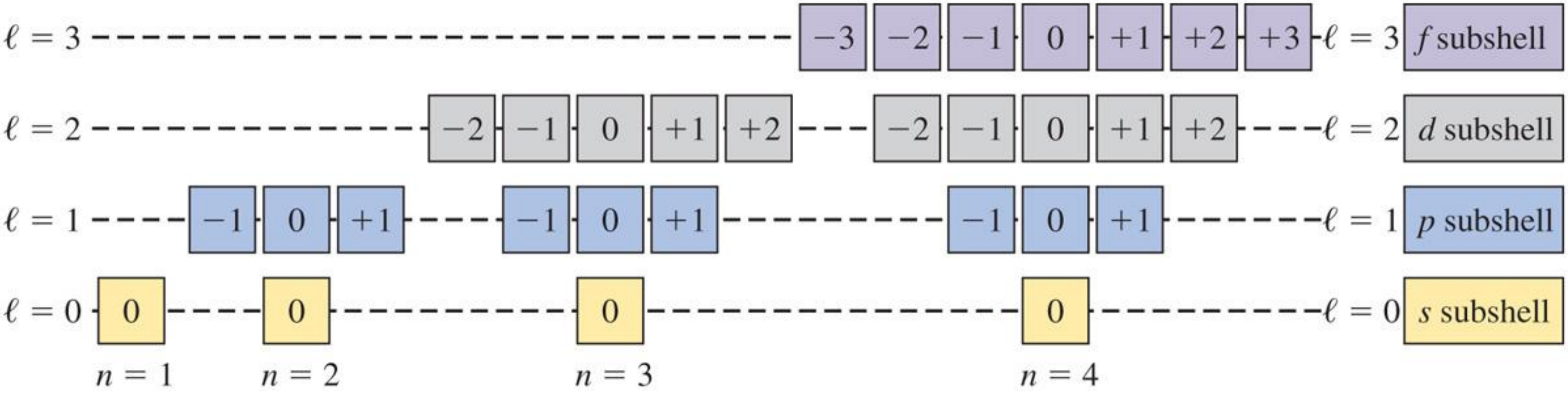


$2p_x$ $2p_y$ $2p_z$

+ and – denote a sign of wave function

Quantum Numbers

Quantum numbers designate shells, subshells, and orbitals.



Example of a problem

What are the possible values for the magnetic quantum number (m_l) when the principal quantum number (*n*) is 3 and the angular quantum number (l) is 1?

Recall that the possible values of m_l depend on the value of l, not on the value of *n*.

The possible values of m_l are –l,…0,…+ l.

Therefore, the possible values of m_l are –1, 0, and +1

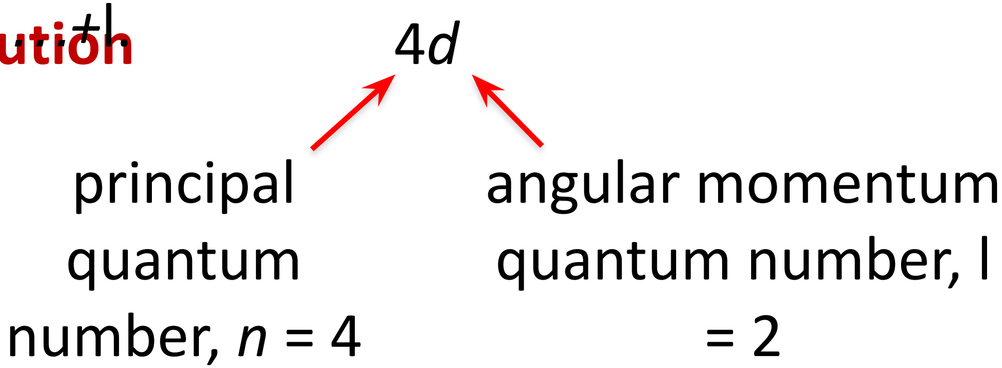
Example of a problem

List the values of *n*, l, and m_l for each of the orbitals in a 4*d* subshell.

Strategy Consider the significance of the number and the letter in the 4*d* designation and determine the values of *n* and l. There are multiple values for m_l, which will have to be deduced from the value of l.

Setup The integer at the beginning of the orbital designation is the principal quantum number (*n*). The letter in an orbital designation gives the value of the angular momentum quantum number (l). The magnetic quantum number (m_l) can have integral values of –l,...0,...+l.

Solution



4*d*

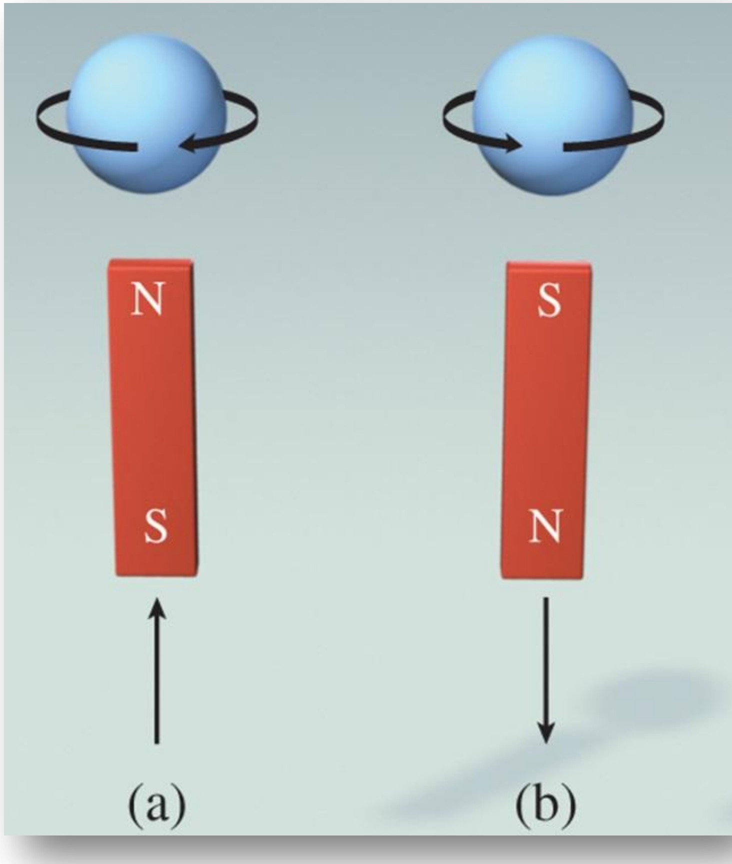
principal quantum number, *n* = 4

angular momentum quantum number, l = 2

Possible m_l are -2, -1, 0, +1, +2.

Electron Spin Quantum Number (m_s)

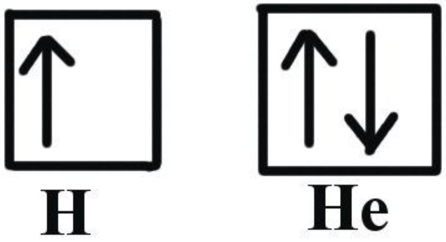
The ***electron spin quantum number (m_s)*** is used to specify an electron's spin.



There are two possible directions of spin.

Allowed values of m_s are $+½$ and $–½$.

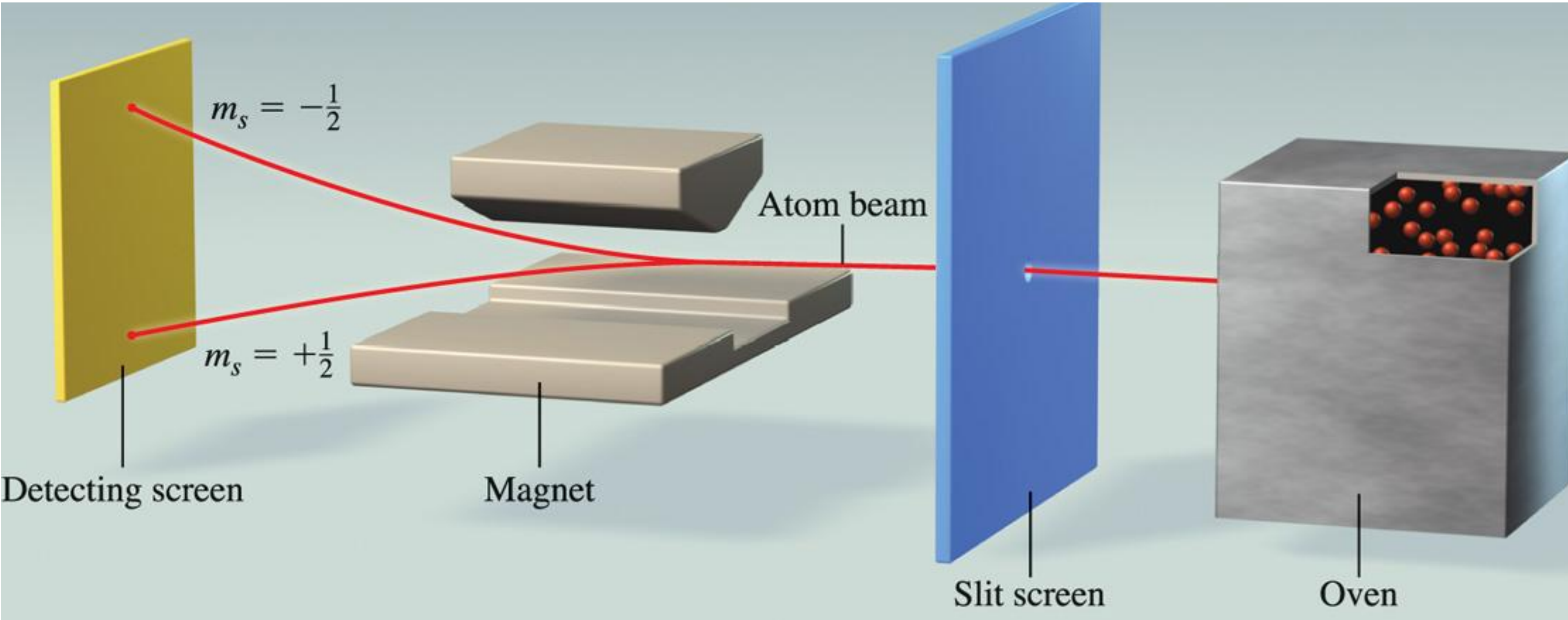
Directions are often depicted schematically as up and down arrows:



Electrons Can be Separated According to Their Spin

A beam of atoms is split by a magnetic field.

Statistically, half of the electrons spin clockwise, the other half spin counterclockwise.



Quantum Numbers: Summary

principal (n) – size

angular (**l**) – shape

magnetic (m_l) – orientation

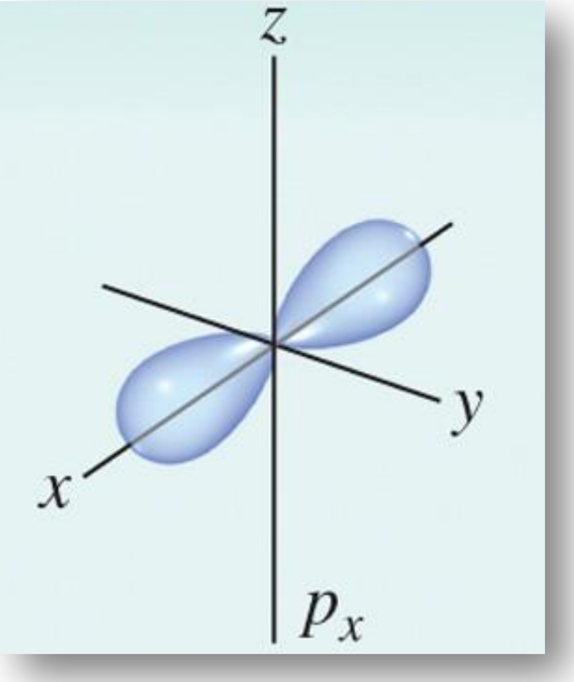
Describes an atomic orbital

principal (n = 2)

$2p_x$

related to the magnetic quantum number (m_l)

angular momentum (**l** = 1)



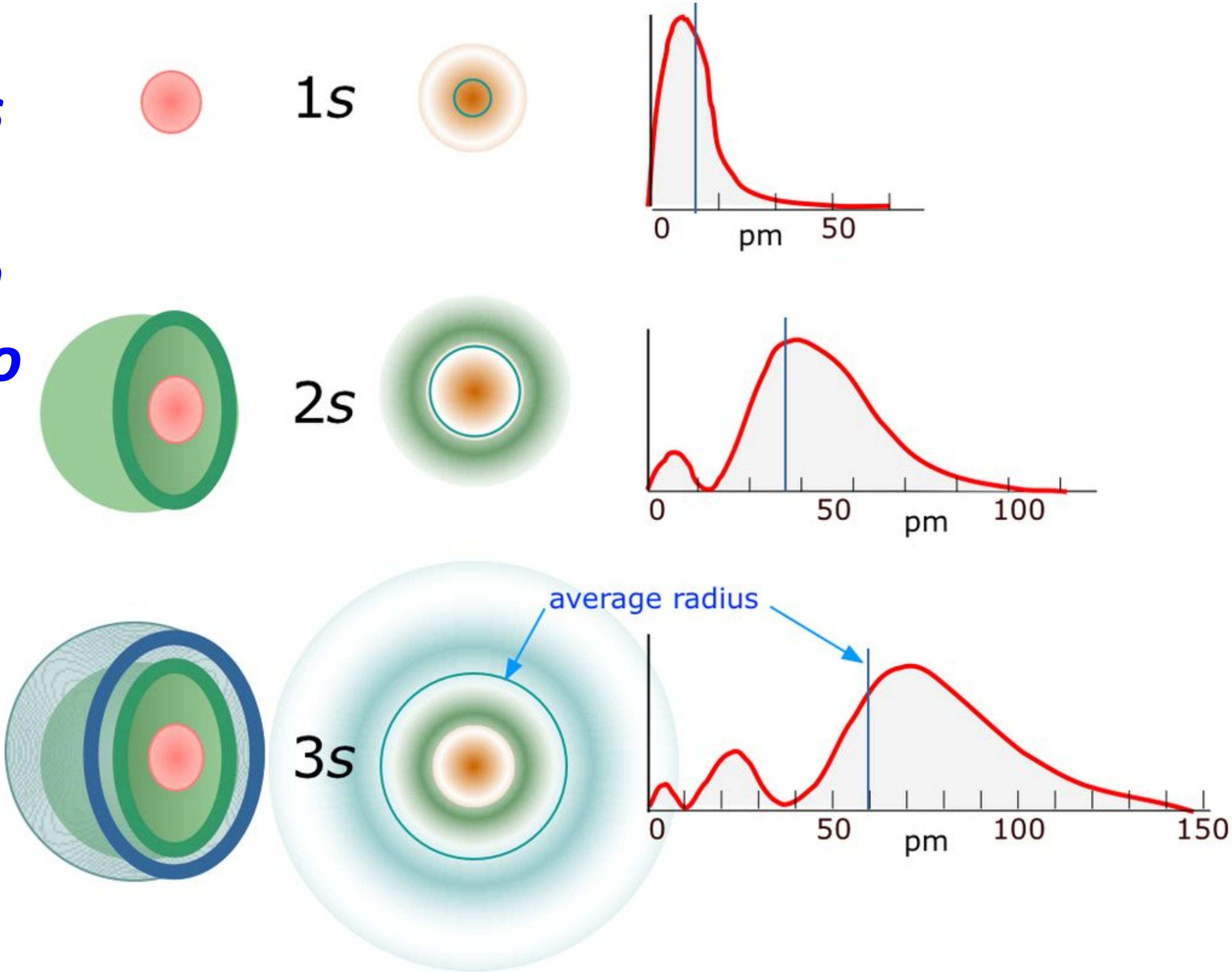
Describes an electron in an atomic orbital

electron spin (m_s) direction of spin

s-Orbitals and Radial Nodes

All *s orbitals* are spherical in shape but differ in size: 1*s* < 2*s* < 3*s*

Nodes are regions in orbitals where the wave function has a value of zero



Total number of nodes = n-1

This means that every orbital with n>1 has at least one node

Example of a Problem

(Zumdahl, Ch.12, problem 64)

The wave function of 3s orbital in the hydrogen atom is:

$$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}(27 - 18\sigma + 2\sigma^2)exp\left(-\frac{\sigma}{3}\right)$$

$$where \quad \sigma = \frac{r}{a_0} \qquad a_0 = 5.29\text{x}10^{-11}\text{ m}$$

Calculate the position of the nodes for this wave function

p d and f Orbitals Have Angular Nodes

There may be 2 types of nodes in an orbital:

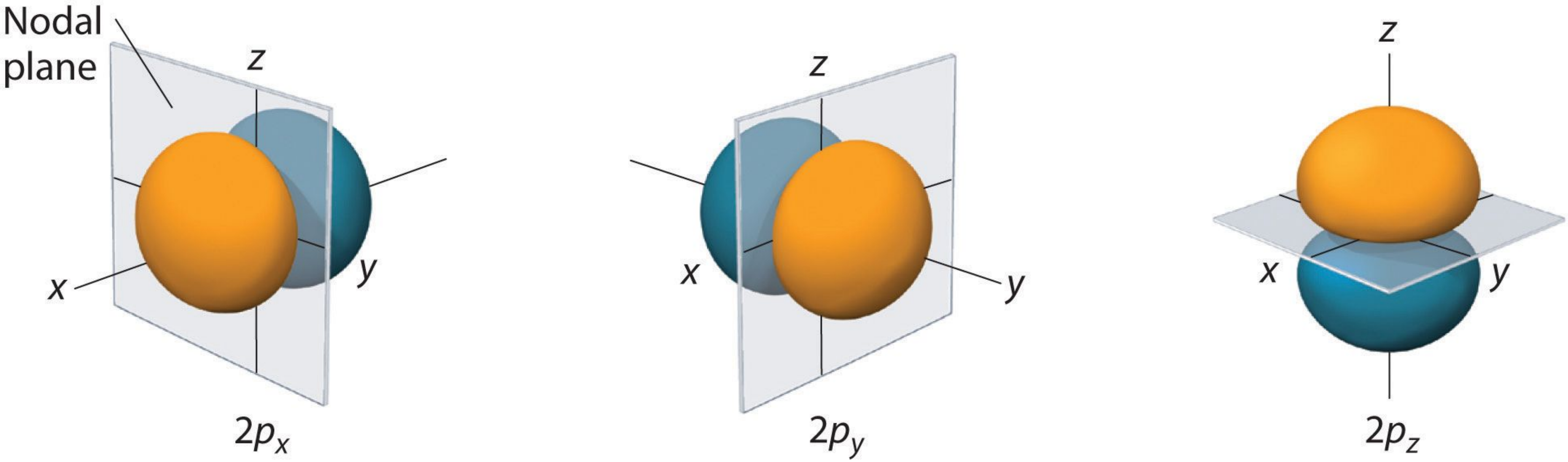
- Radial (spherical surface)
- Angular (plane or cone)

The number of angular nodes is equal to quantum number ℓ

Since total number of nodes is n-1, you can determine the number of angular and radial nodes for any orbital

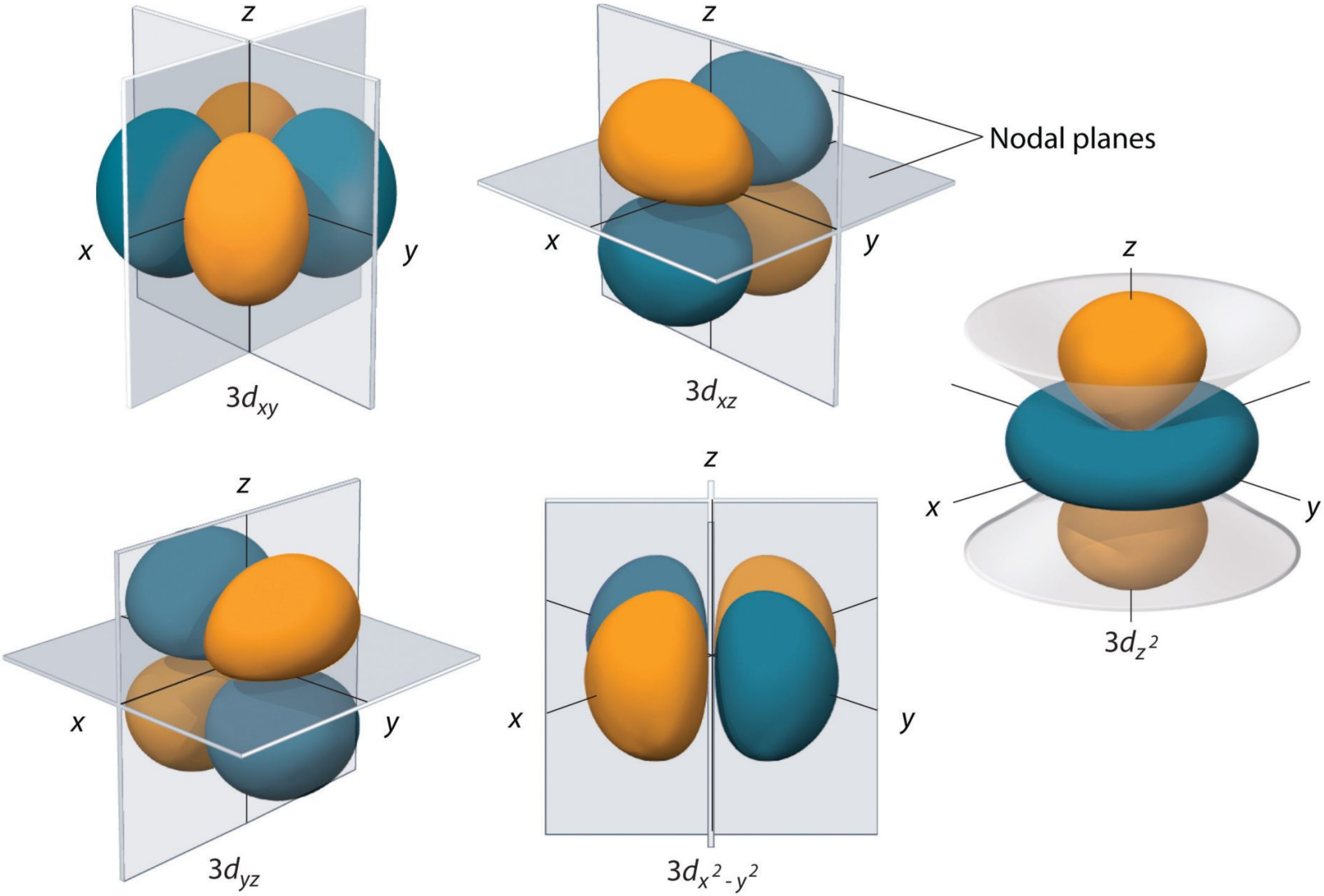
p-Orbitals Have One Angular Node

***p orbitals** have one angular node – a plane in every point of which there is zero probability of finding an electron*

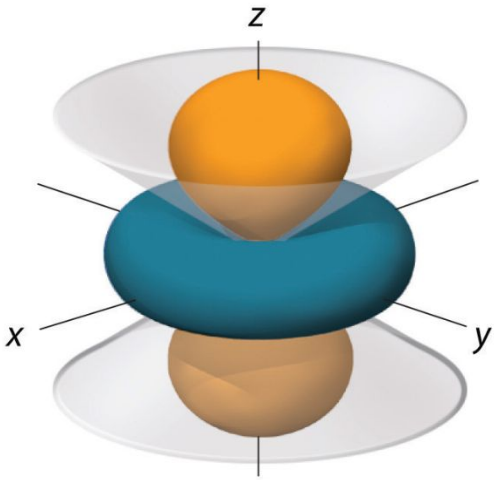


Wave function on opposing sides of the node have different sign (depicted by a color of the orbital)

d-Orbitals Have Two Angular Nodes



d-Orbitals Have Two Angular Nodes



$3d_{z^2}$

Note that you can see how nodes may look like directly from the equation for wave function. For example the wave function for $3dz^2$ orbital is:

$$3\mathrm{d}_{z^2} = \underbrace{\left[\frac{4}{81\sqrt{30}}a_0^{-3/2}\left(\frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{3a_0}\right)\right]}_{\text{radial: } R_{32}} \underbrace{\left[\sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)\right]}_{\text{angular: } Y_{20}}$$

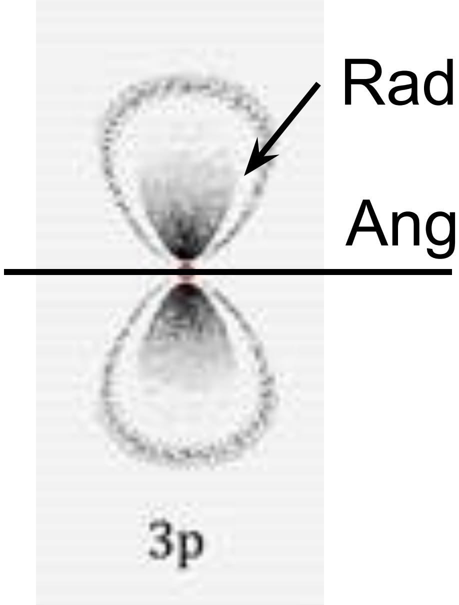
You can see that there are no radial nodes but two angular nodes: Equation $3\cos^2\theta=1$ has two solutions $\theta=54.7°$ and $125.3°$ corresponding to two cone surfaces you can see on the picture

Example of a problem

Sketch 3p orbital

- Total number of nodes n-1 = 2
- Number of angular nodes = $\ell = 1$
- This means the number of radial nodes =1 (You can also note that total number of radial nodes = n-1-ℓ)

So, you should draw something like this



Radial node

Angular node

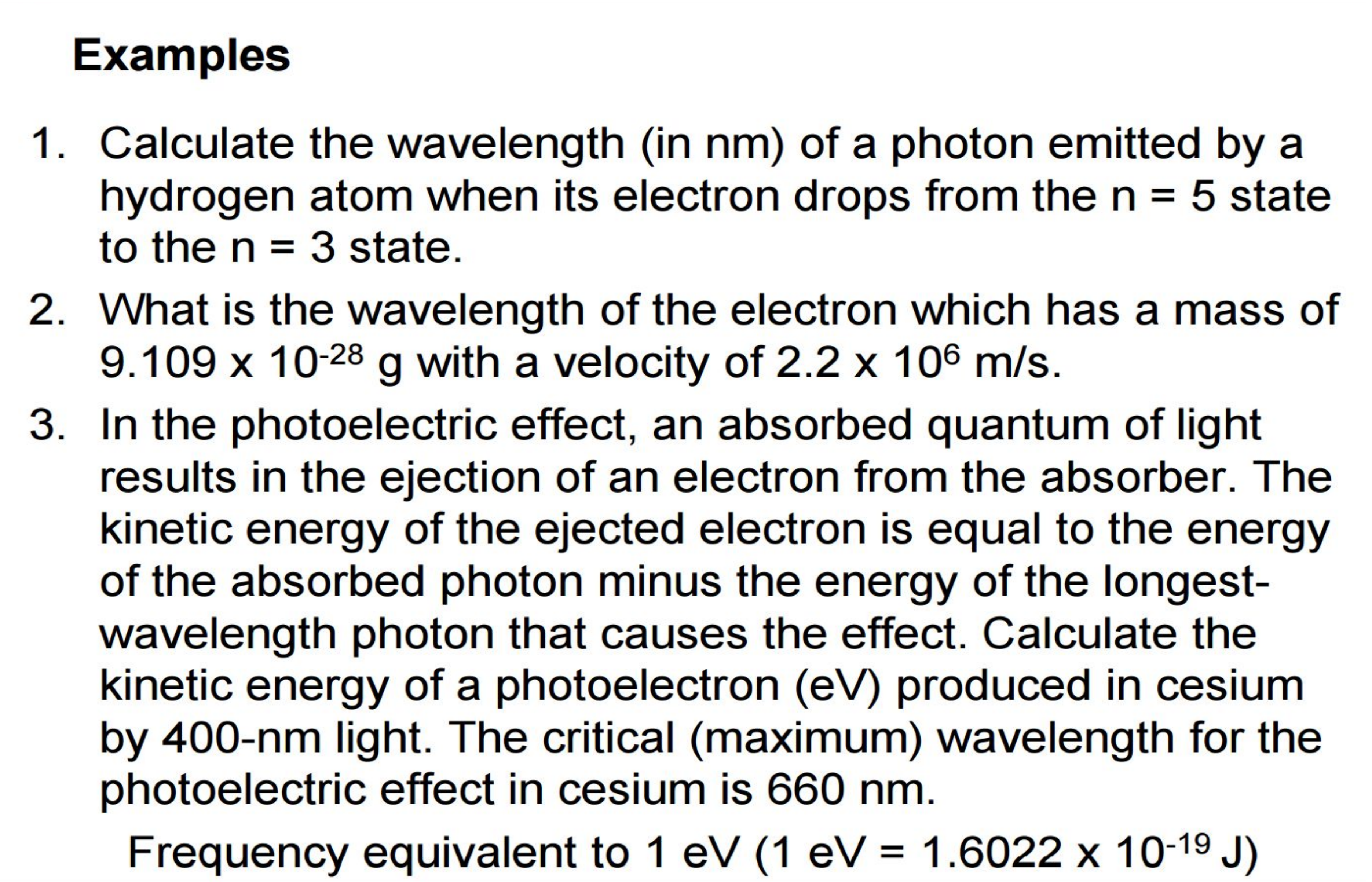
S.E. for Polyelectronic Atoms Cannot be Solved in Analytical Form

In polyelectronic atoms electrons influence each other (their motion is correlated) and this influence cannot be described in exact terms

S.E. nowadays is solved by <u>numerical methods</u>. The program minimizes energy of the system trying to find optimum electron density in polyelectronic atoms

These calculations allow predicting a large number of parameters from NMR and optical absorbance spectra, to bond length, angles, stability of conformational isomers etc

Are you ready for Monday?



Examples

1. Calculate the wavelength (in nm) of a photon emitted by a hydrogen atom when its electron drops from the n = 5 state to the n = 3 state.
2. What is the wavelength of the electron which has a mass of 9.109×10^{-28} g with a velocity of 2.2×10^{6} m/s.
3. In the photoelectric effect, an absorbed quantum of light results in the ejection of an electron from the absorber. The kinetic energy of the ejected electron is equal to the energy of the absorbed photon minus the energy of the longest-wavelength photon that causes the effect. Calculate the kinetic energy of a photoelectron (eV) produced in cesium by 400-nm light. The critical (maximum) wavelength for the photoelectric effect in cesium is 660 nm.

Frequency equivalent to 1 eV (1 eV = 1.6022×10^{-19} J)

Example

4. A certain microwave oven delivers 750. watts (J/s) of power to a coffee cup containing 50.0 g water at 25.0°C. If the wavelength of microwaves in the oven is 9.75 cm, how long does it take, and how many photons must be absorbed, to make the water boil? The specific heat capacity of water is 4.18 J $^{o}C^{-1}$ g^{-1}. Assume that only the water absorbs the energy of the microwaves.

Example

5. Assume that four electrons are confined to a 1-D box 5.64×10^{-10} m in length. If two electrons can occupy each allowed energy level, calculate the wavelength of electromagnetic radiation necessary to promote the highest-energy electron into the first excited state.