## Limitations of the Bohr Model

The Bohr Model has several limitations:

- It cannot explain the spectra of atoms other than hydrogen.
- Electrons do not move about the nucleus in circular orbits.

However, the model introduces two important ideas:

- The energy of an electron is quantized; electrons exist only in certain energy levels described by quantum numbers.
- Energy gain or loss is involved in moving an electron from one energy level to another. **Spectra of stars to samples in the lab next week.**

**The Wave Behavior of Matter**

- Knowing that light has a particle nature, it seems reasonable to ask whether matter has a wave nature.
- Using Einstein's and Planck's equations, Louis deBroglie asked ……..

# Particles or Waves?

**De Broglie (1892–1987)**

- If electromagnetic radiation behaves as a particle, could a particle in motion, such as an electron, behave as a wave?

**De Broglie's equation:**

$\lambda$ = de Broglie wavelength

$$\lambda = \frac{hc}{E} = \frac{hc}{mc^2} = \frac{h}{mc} = \frac{h}{mu}$$

*m* = mass of electron (in kg)

*u* = velocity (in m/s)

*h* = Planck's constant

$\lambda$ = h/mv   Example Calculation

v electron = 6 x $10^6$ m/s,  m (mass) = 9.11 x $10^{-31}$ kg,  h = 6.626 x $10^{-34}$ J sec

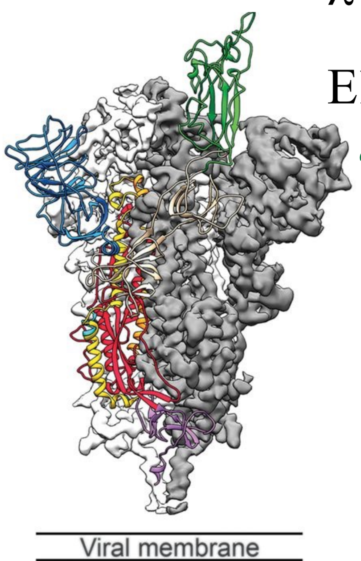
$\lambda$  = h/mv = 1.2 x $10^{-10}$ J*$s^2$/m kg          ( J = kg $m^2/s^2$)

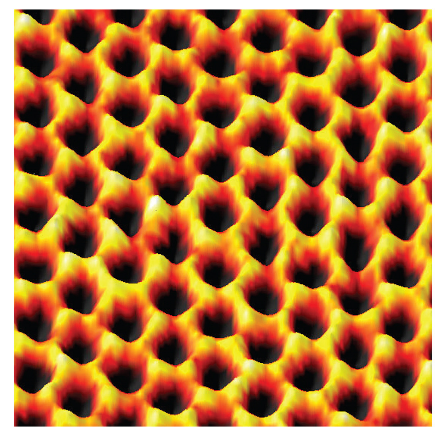
so …

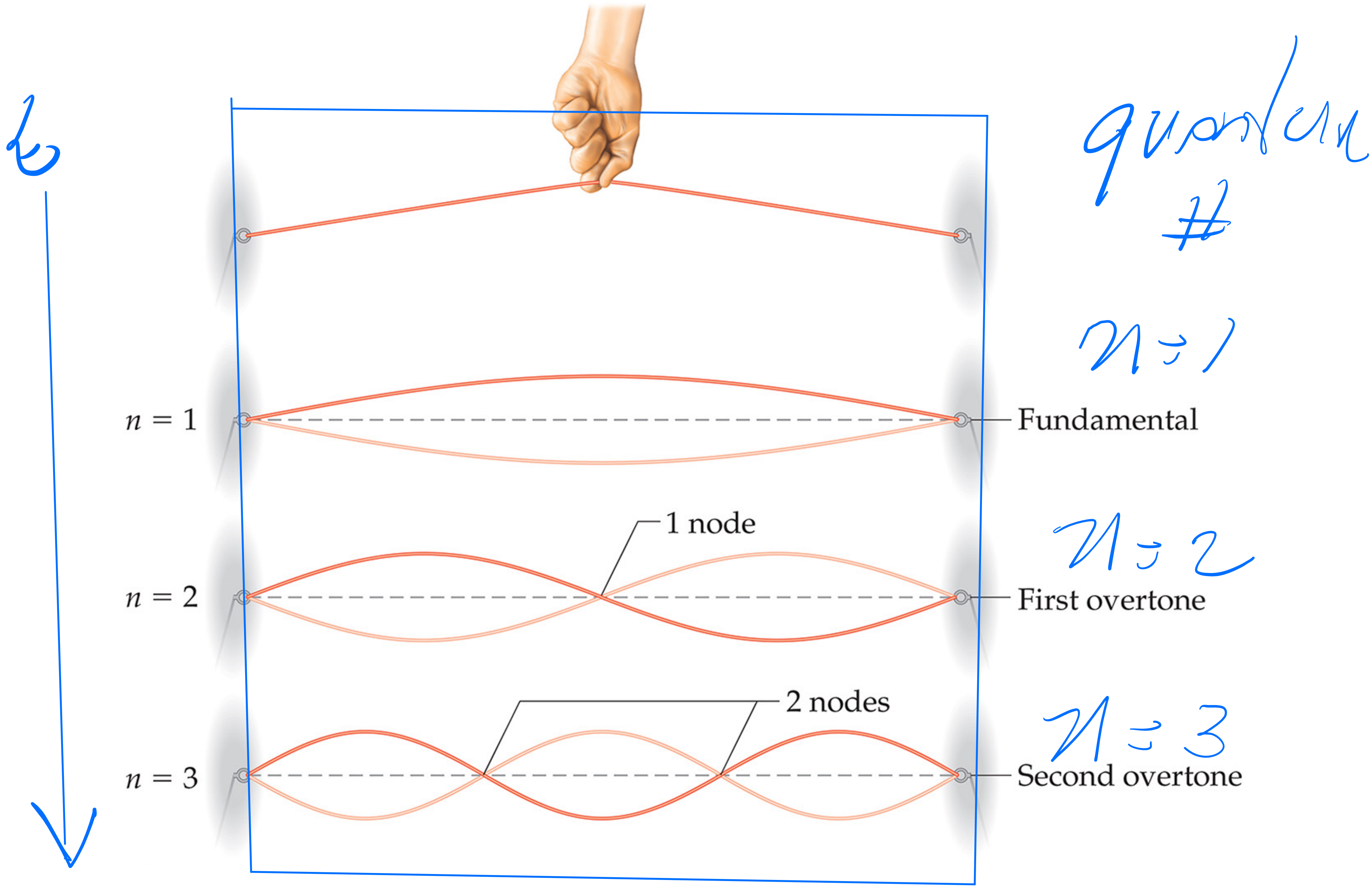
$$\frac{J\,s^2}{m\,kg} \quad \frac{kg\,m^2}{s^2} \Rightarrow m$$

$\lambda$ = h/mv = 0.12 nm  or 1.2 A

Electron wavelengths are of the same order as atom size!





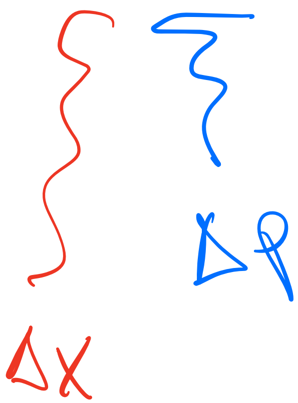
n = 1
Fundamental
1 node
n = 2
First overtone
2 nodes
n = 3
Second overtone

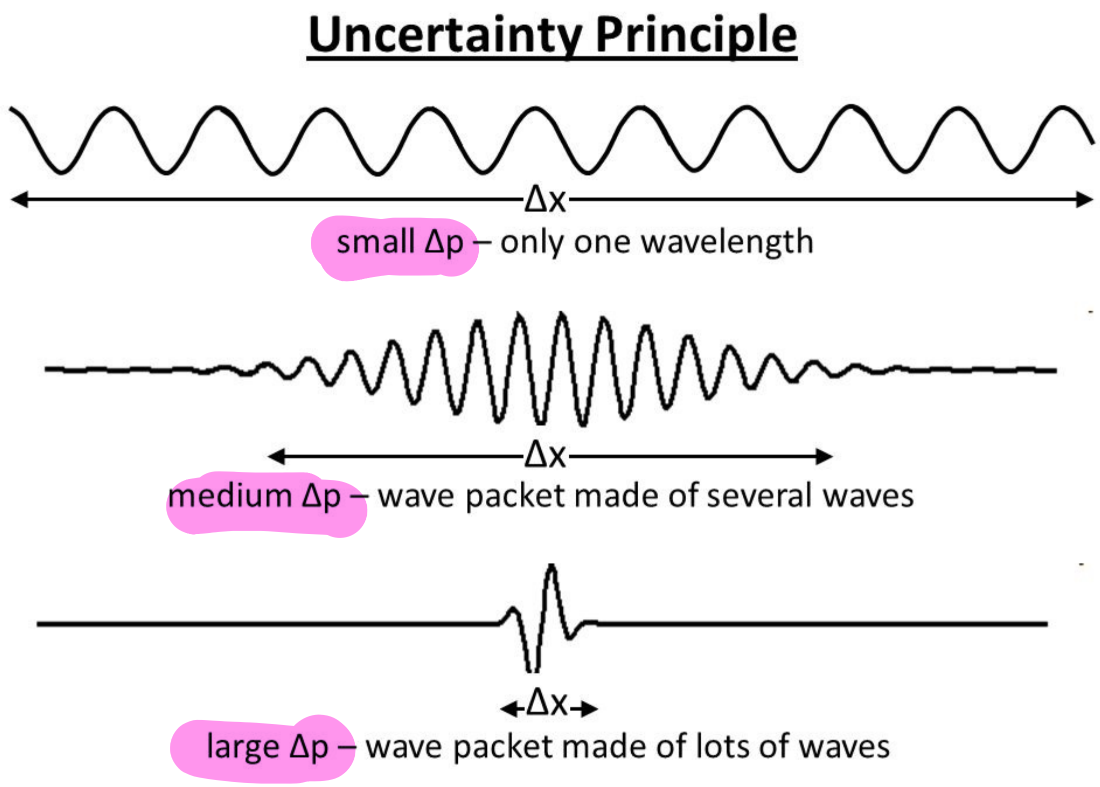
# The Uncertainty Principle

• **Heisenberg's uncertainty principle**: we cannot determine the *exact* position, direction of motion, and speed of subatomic particles simultaneously.

• For electrons: we cannot determine their momentum and position simultaneously.

$$\Delta X * \Delta(mV) \geq \frac{h}{4\pi}$$



**Do a calculation.**

$$\Delta X \geq \frac{h}{4\pi m \Delta V} = \frac{6.626 \times 10^{-34} \text{ j-s}}{4\pi\ (9.11 \times 10^{-31}\text{ kg})\ \Delta V} = 5.8 \times 10^{-5}/\Delta V \text{ meters}$$

$\Delta V$ = 1% error in velocity = $6 \times 10^{4}$ m/s

$\Delta X = 1 \times 10^{-9}$ m or 10 A  This is on the scale of an atom!

OUR BOX is 10 Å big

# Quantum Mechanics and Atomic Orbitals

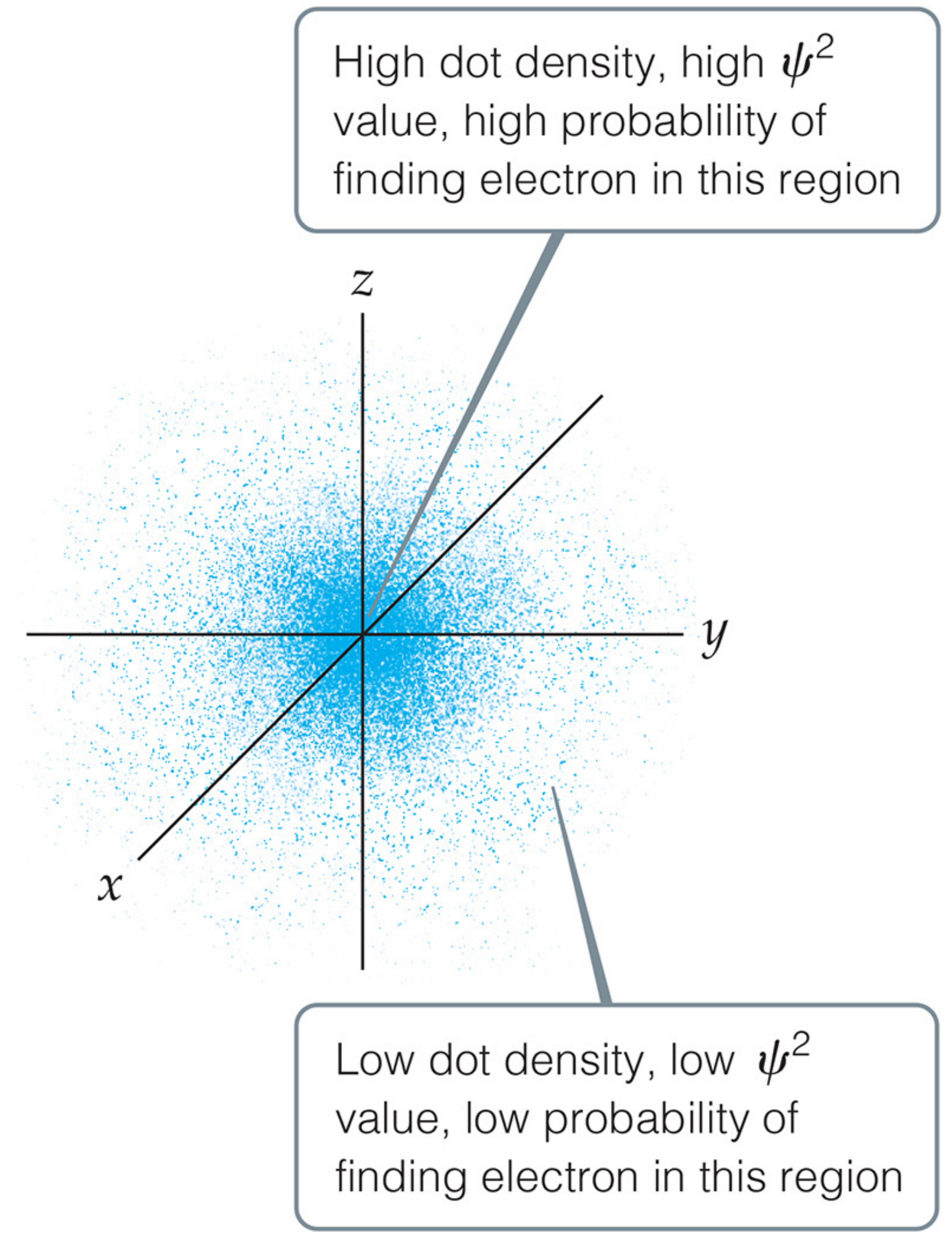
- Schrödinger proposed an equation containing both wave and particle terms.
- Solving the equation leads to **wave functions**, $\psi$.
- The wave function describes the **electron's matter wave**.

Show computer animation

- The square of the wave function, $\psi^2$, gives the probability of finding the electron.
- That is, $\psi^2$ gives the electron density for the atom.

- $\psi^2$ is called the **probability density**.
- **Electron density** is another way of expressing probability.
- A region of high electron density is one where there is a high probability of finding an electron.

Consider your probability function?


High dot density, high ψ2 value, high probablility of finding electron in this region
z
y
x
Low dot density, low ψ2 value, low probability of finding electron in this region

**Orbitals and Quantum Numbers**

- If we solve the Schrödinger equation we get wave functions and energies for the wave functions.
- We call $\psi$ **orbitals**.
- Schrödinger's equation requires three quantum numbers:
- ***Principal quantum number***, *n. This is the same as Bohr's n.*
- As *n* becomes larger, the atom becomes larger and the electron is further from the nucleus.
- ***Angular momentum quantum number, l.*** This quantum number depends on the value of *n*.
- The values of *l* begin at 0 and increase to $n - 1$.
- We usually use letters for *l* (*s*, *p*, *d* and *f* for $l = 0, 1, 2,$ and 3). Usually we refer to the *s*, *p*, *d* and *f* orbitals.
- This quantum number defines the shape of the orbital.

- ***Magnetic quantum number**, $m_l$.*
- This quantum number depends on *l*.
- The magnetic quantum number has integer values between –*l* and +*l*.
- There are $(2l+1)$ possible values of $m_l$.
- For example, for $l = \mathbf{1}$, there are $(2\times\mathbf{1}+1) = 3$ values of $m_l$: 0, +1, and -1.
- Consequently, for $l = 1$, there are 3 orbitals: $p_x$, $p_y$ and $p_z$.
- Magnetic quantum numbers give the three-dimensional orientation of each orbital.

The rules for quantum numbers give us both SHAPE and ORIENTATION

**TABLE 6.2 Relationship among Values of $n$, $l$, and $m_l$ through $n = 4$**

| $n$ | Possible Values of $l$ | Subshell Designation | Possible Values of $m_l$ | Number of Orbitals in Subshell | Total Number of Orbitals in Shell |
|---|---|---|---|---|---|
| 1 | 0 | 1*s* | 0 | 1 | 1 |
| 2 | 0 | 2*s* | 0 | 1 | |
| | 1 | 2*p* | 1, 0, −1 | 3 | 4 |
| 3 | 0 | 3*s* | 0 | 1 | |
| | 1 | 3*p* | 1, 0, −1 | 3 | |
| | 2 | 3*d* | 2, 1, 0, −1, −2 | 5 | 9 |
| 4 | 0 | 4*s* | 0 | 1 | |
| | 1 | 4*p* | 1, 0, −1 | 3 | |
| | 2 | 4*d* | 2, 1, 0, −1, −2 | 5 | |
| | 3 | 4*f* | 3, 2, 1, 0, −1, −2, −3 | 7 | 16 |

## The *s* Orbitals

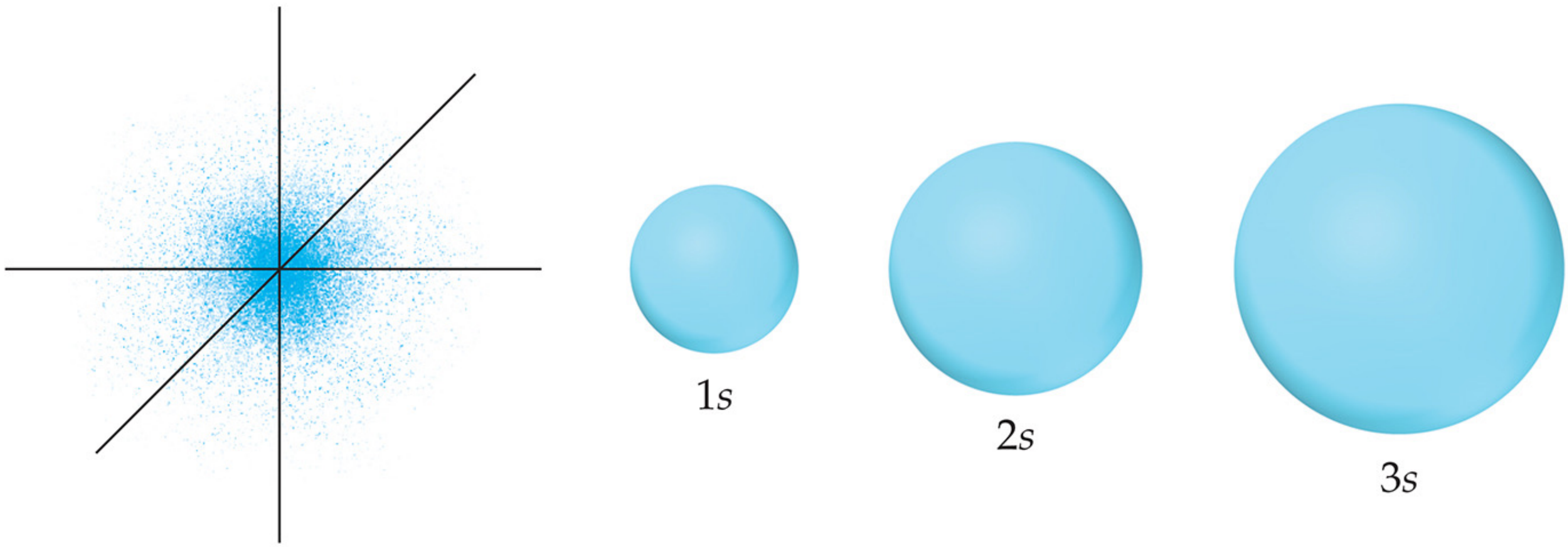
- All *s* orbitals are spherical.
- As *n* increases, the *s* orbitals get larger.
- As *n* increases, the number of **nodes** increases.
  - A node is a region in space where the probability of finding an electron is zero.

• $\psi_2 = 0$ at a node.

• For an *s* orbital the number of nodes is given by $n - 1$.

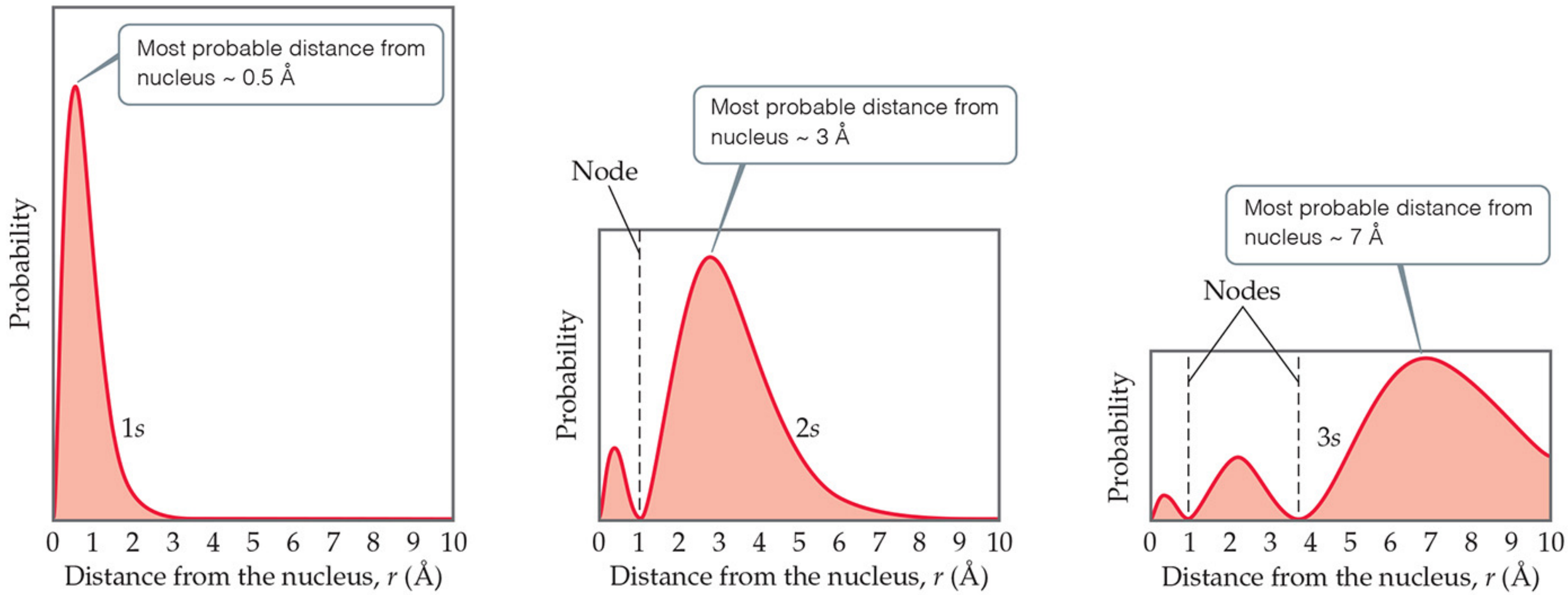
• We can plot a curve of *radial probability density* vs. distance (*r*) from the nucleus.

• This curve is the **radial probability function** for the orbital.




**(a)** An electron density model

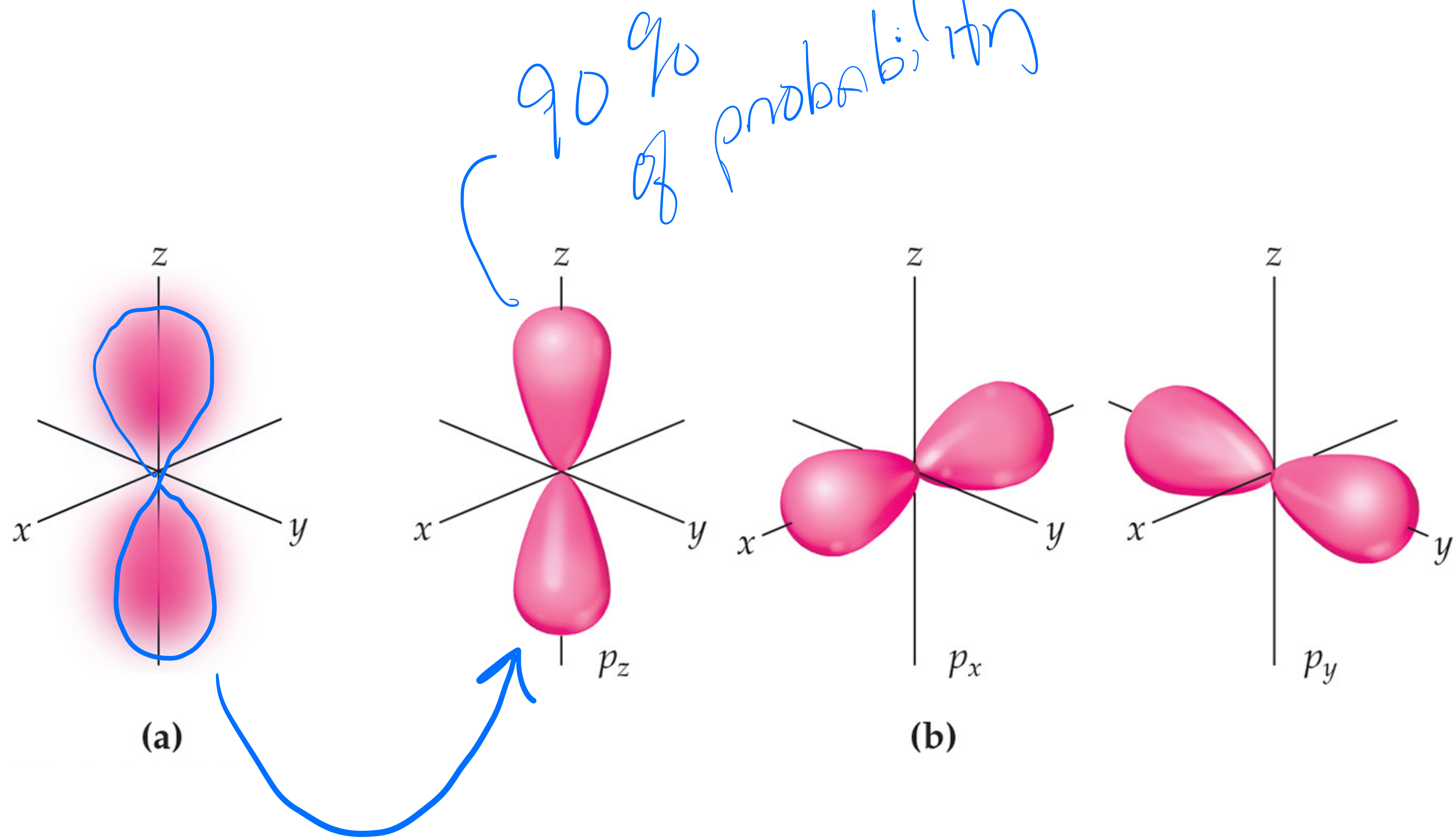
**(b)** Contour models




If we know the energy
then we don't know exact position!

## The *p* Orbitals

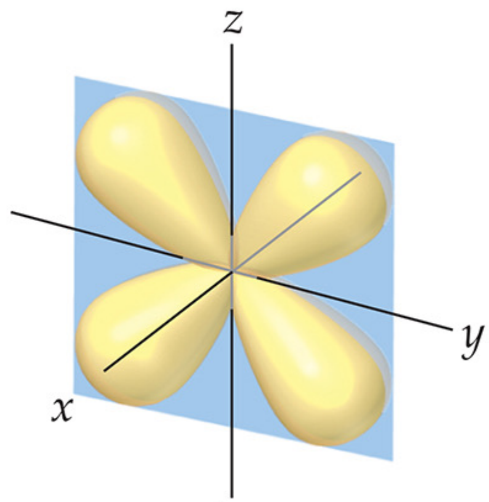
- There are three *p* orbitals: $p_x$, $p_y$ and $p_z$.
  - The three *p* orbitals lie along the *x*-, *y*-, and *z*-axes of a Cartesian system.
  - The letters correspond to allowed values of $m_l$ of –1, 0, and +1.
- The orbitals are dumbbell shaped; each has two *lobes*.
- As *n* increases, the *p* orbitals get larger.
- All *p* orbitals have a node at the nucleus.


90 %
of probability
z
x
y
$p_z$
$p_x$
$p_y$
(a)
(b)

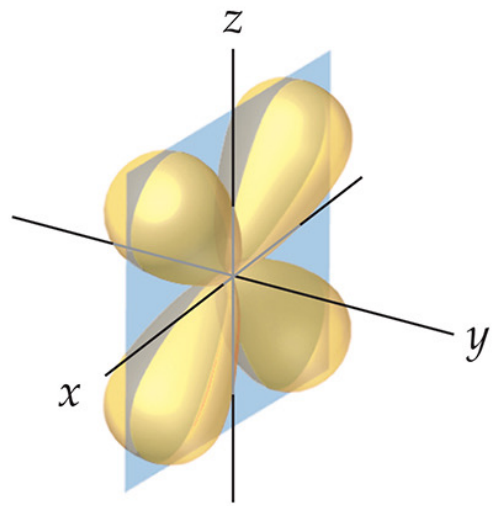
- **The *d* and *f* Orbitals**

• There are five *d* and seven f orbitals.

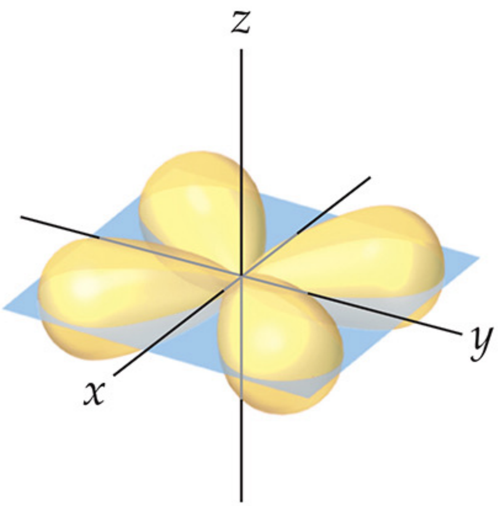
- Three of the *d* orbitals lie in a plane bisecting the *x*-, *y*-, and *z*-axes.
- Two of the *d* orbitals lie in a plane aligned along the *x*-, *y*-, and *z*-axes.
- Four of the *d* orbitals have four lobes each.
- One *d* orbital has two lobes and a collar.



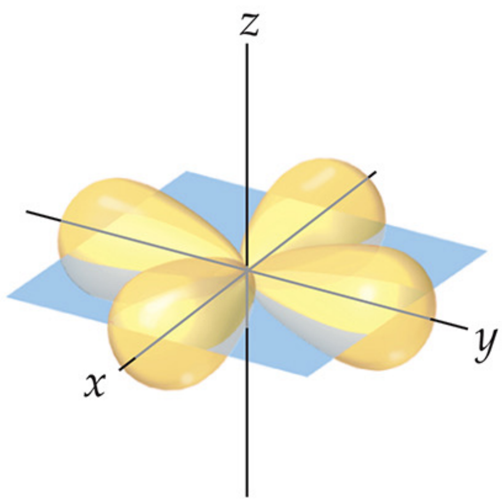

$d_{yz}$



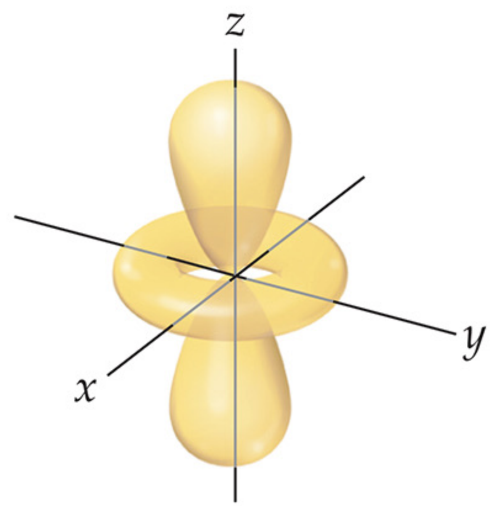

$d_{xz}$




$d_{xy}$

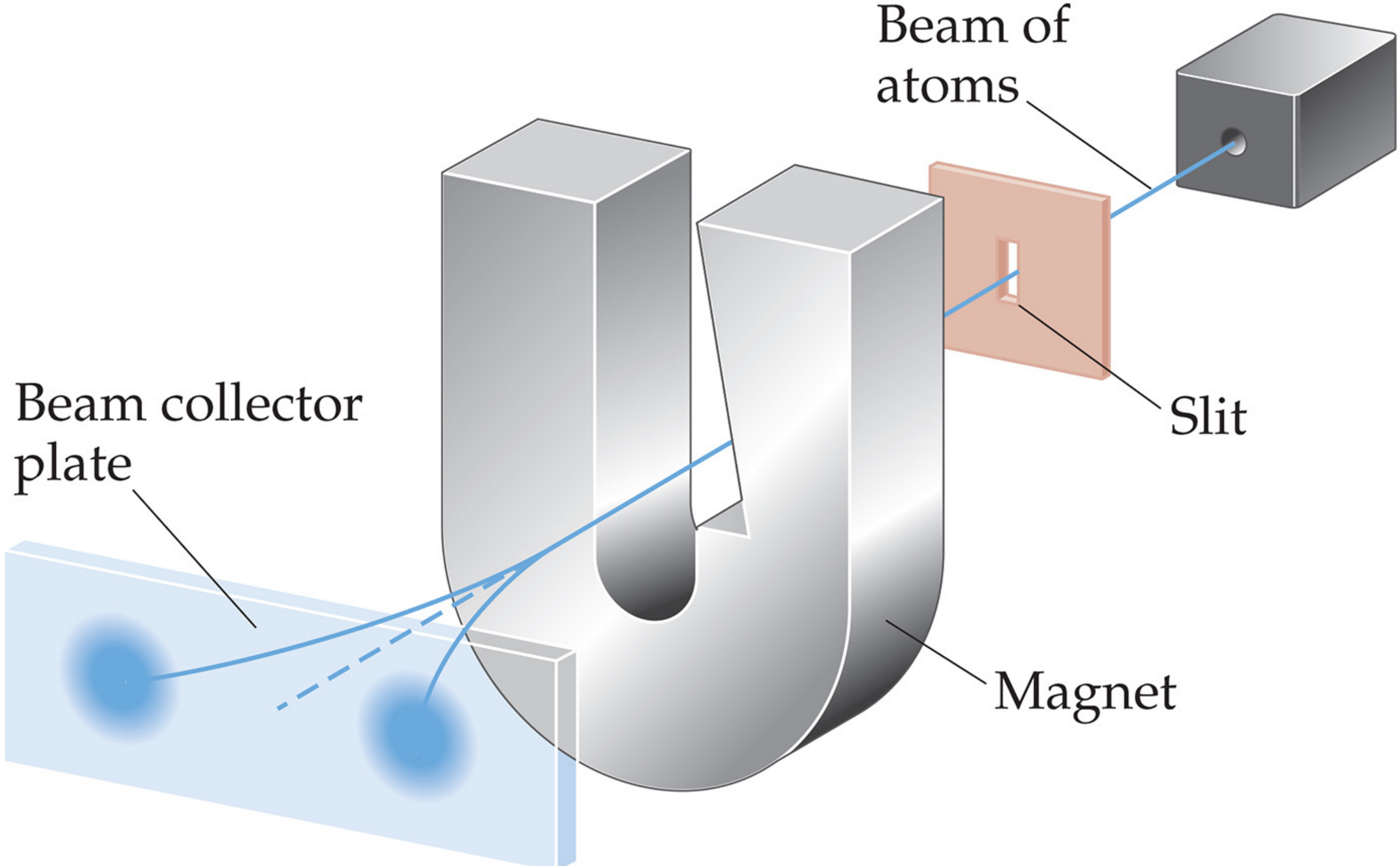



$d_{x^2-y^2}$

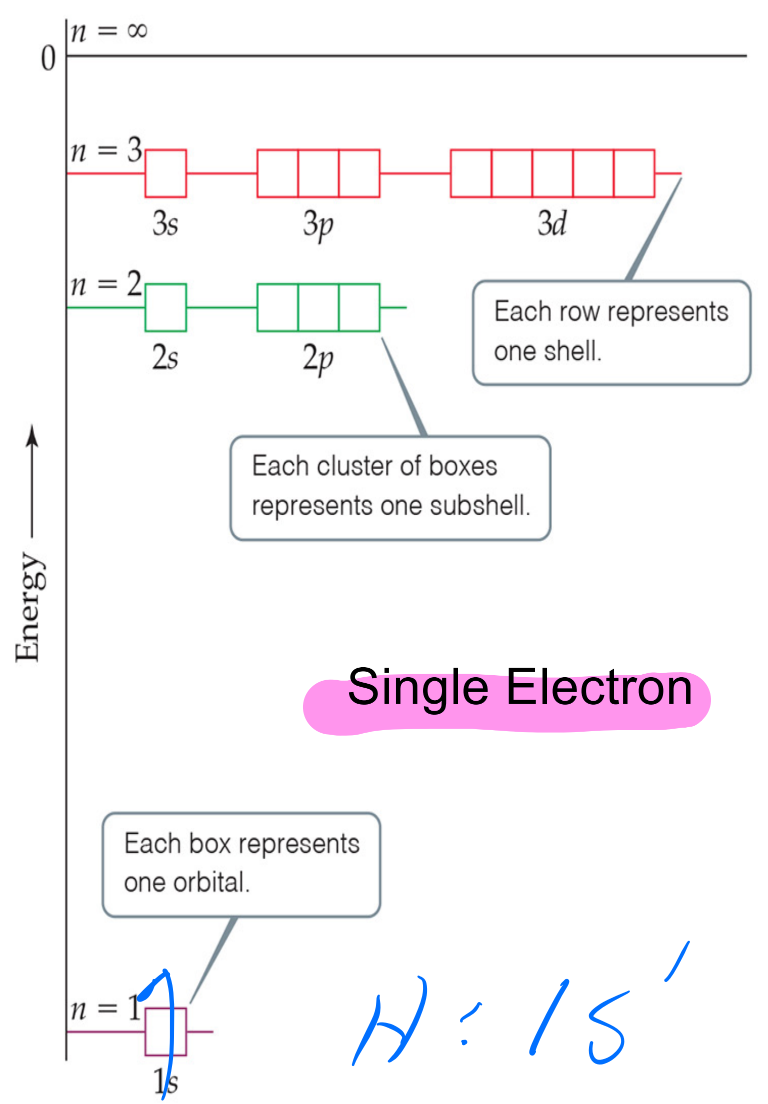



$d_{z^2}$

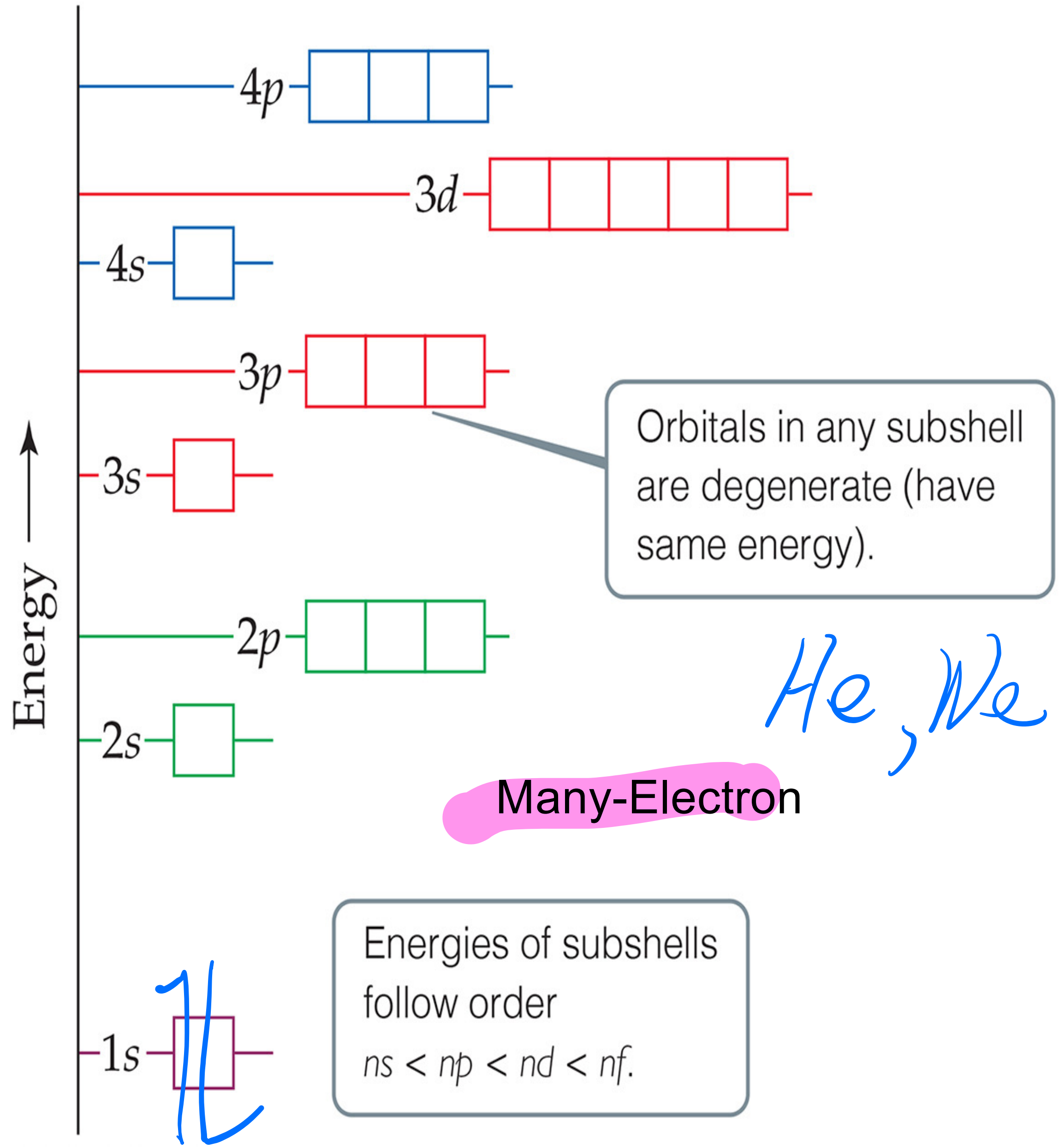
hot box



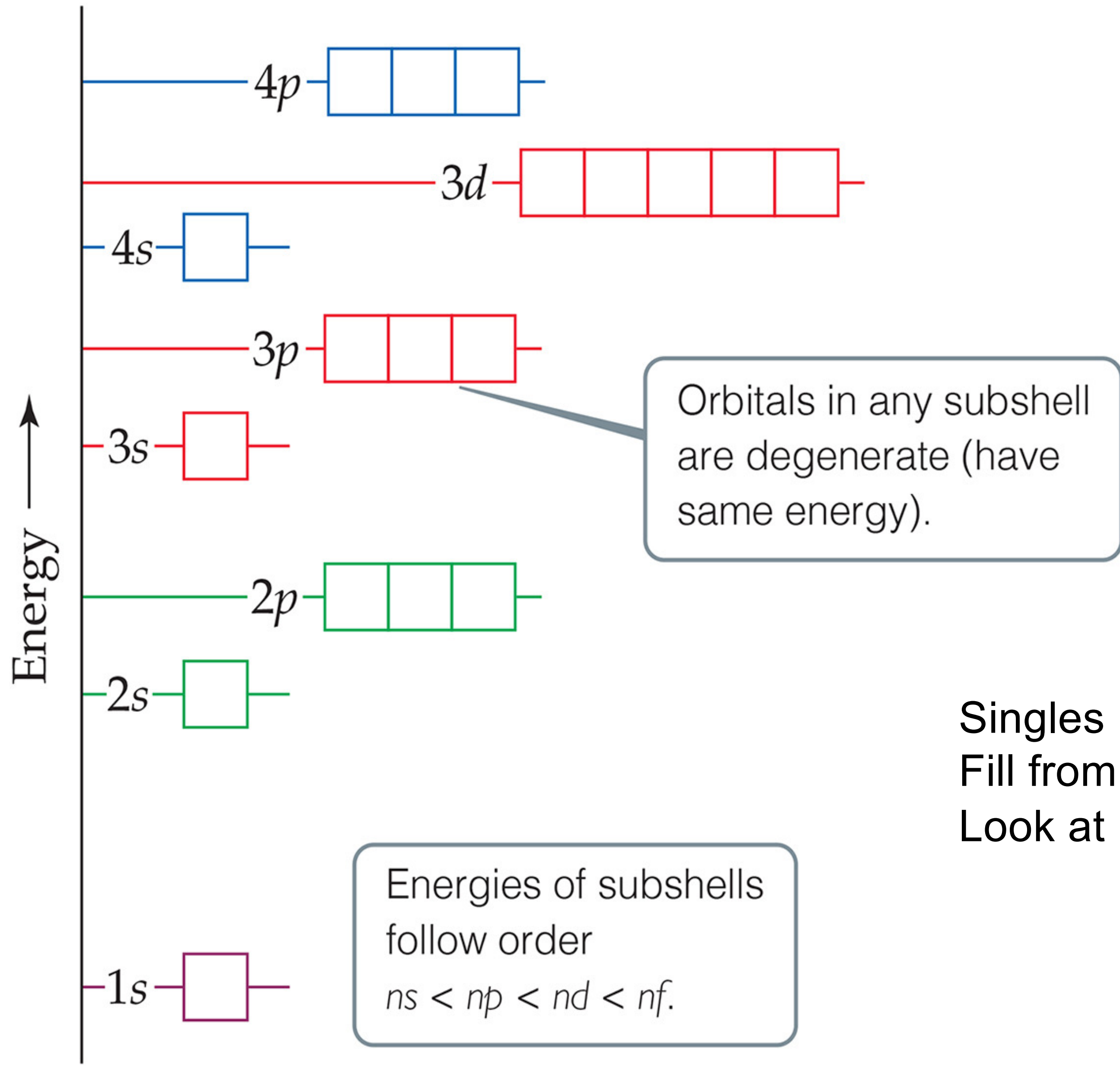

Electrons have spin.




$n = 1$ shell has one orbital
$n = 2$ shell has two subshells composed of four orbitals
$n = 3$ shell has three subshells composed of nine orbitals



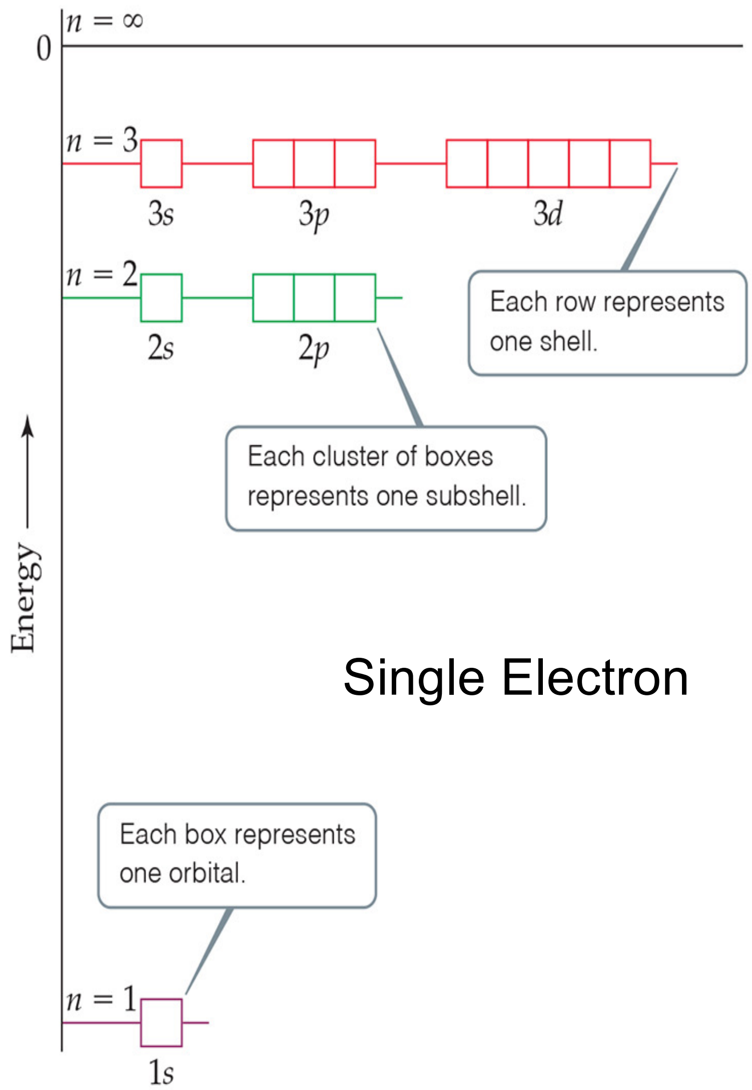
- A collection of orbitals with the same value of $n$ is called an **electron shell**.
- There are $n^2$ orbitals in a shell described by a the $n$ value.
- For example, for $n = \mathbf{3}$, there are $\mathbf{3}^2 = 9$ orbitals.
- A set of orbitals with the same $n$ and $l$ is called a **subshell**.
- Each subshell is designated by a number and a letter.
- For example, 3*p* orbitals have $n = 3$ and $l = 1$.
- There are $n$ types of subshells in a shell described by a the $n$ value.
- For example, for $n = \mathbf{3}$, there are **3** subshells: 3*s*, 3*p* and 3*d*.
- **Orbitals can be ranked in terms of energy to yield an Aufbau diagram.**
- As $n$ increases, note that the spacing between energy levels becomes smaller.




Singles before pairs
Fill from the bottom
Look at pTable.

# Electron Configurations

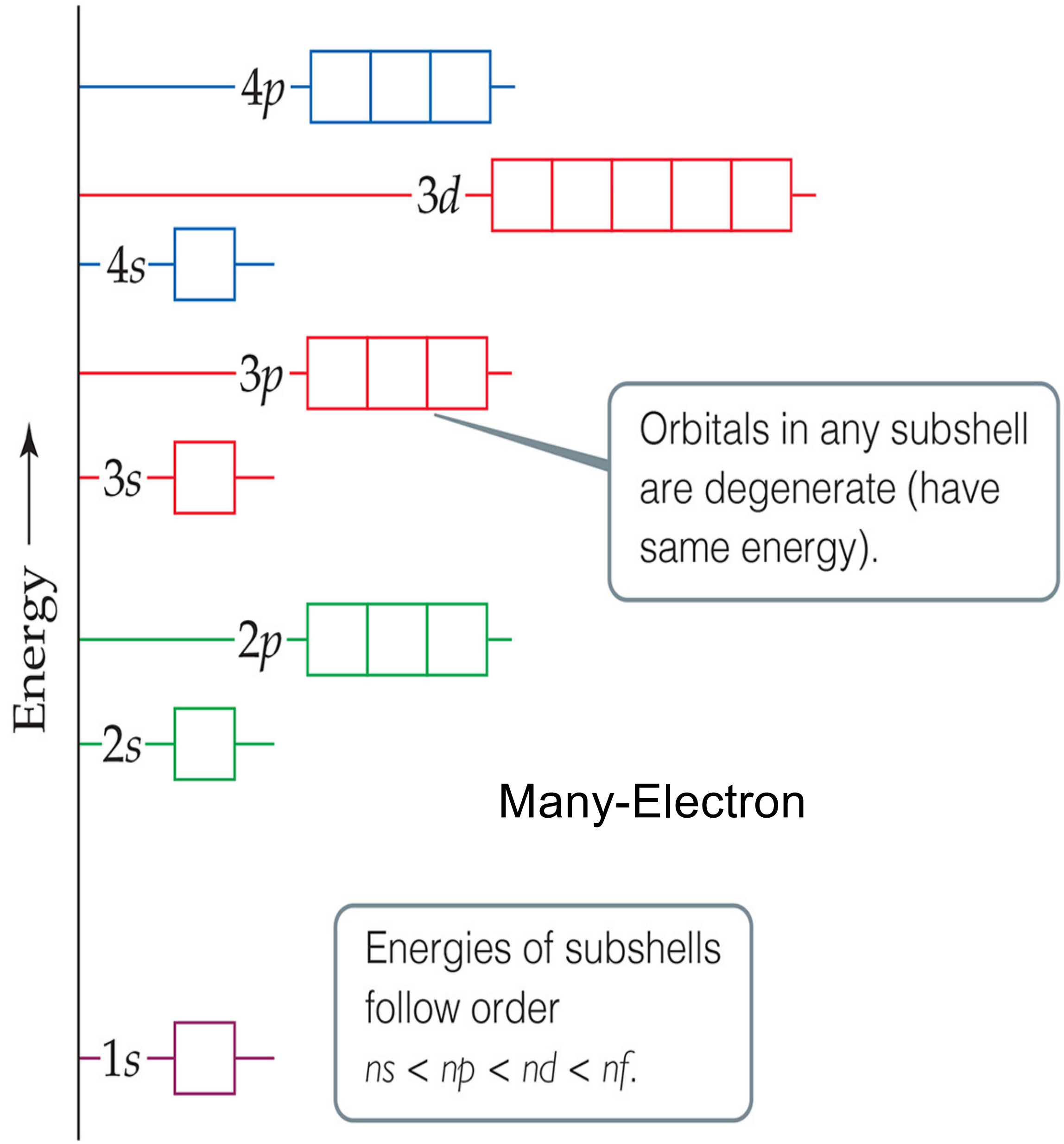
- **Electron configurations** tell us how the electrons are distributed among the various orbitals of an atom.
- The most stable configuration, or ground state, is that in which the electrons are in the lowest possible energy state.
- We represent the configuration with an **orbital diagram.**
  - Each orbital is denoted with a box and each electron with a half arrow.
  - Electrons fill orbitals in order of increasing energy with no more than two electrons per orbital.
  - No two electrons can fill one orbital with the same spin (Pauli).
  - For degenerate orbitals, electrons fill each orbital singly before any orbital gets a second electron.



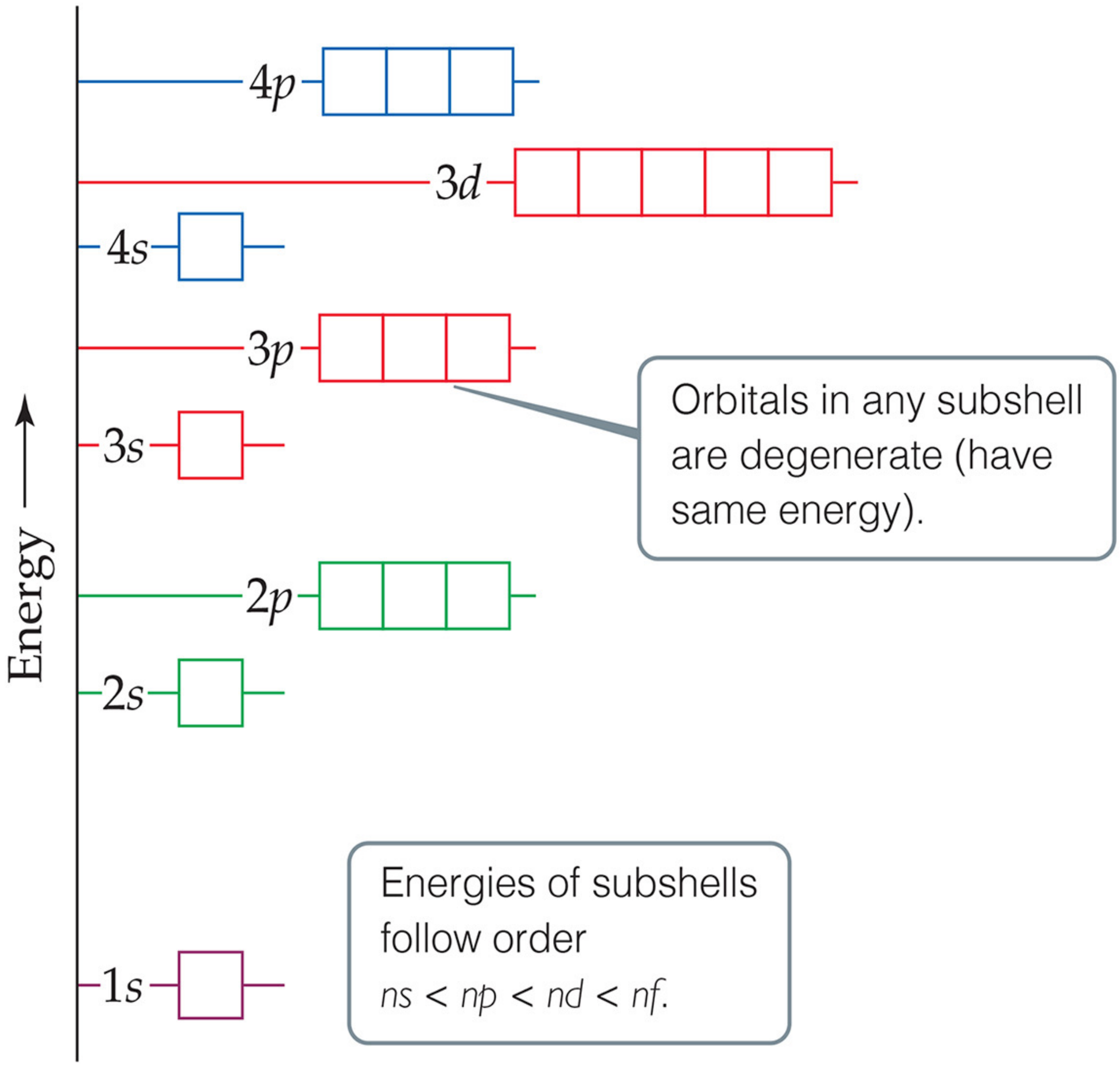

$n = 1$ shell has one orbital

$n = 2$ shell has two subshells composed of four orbitals

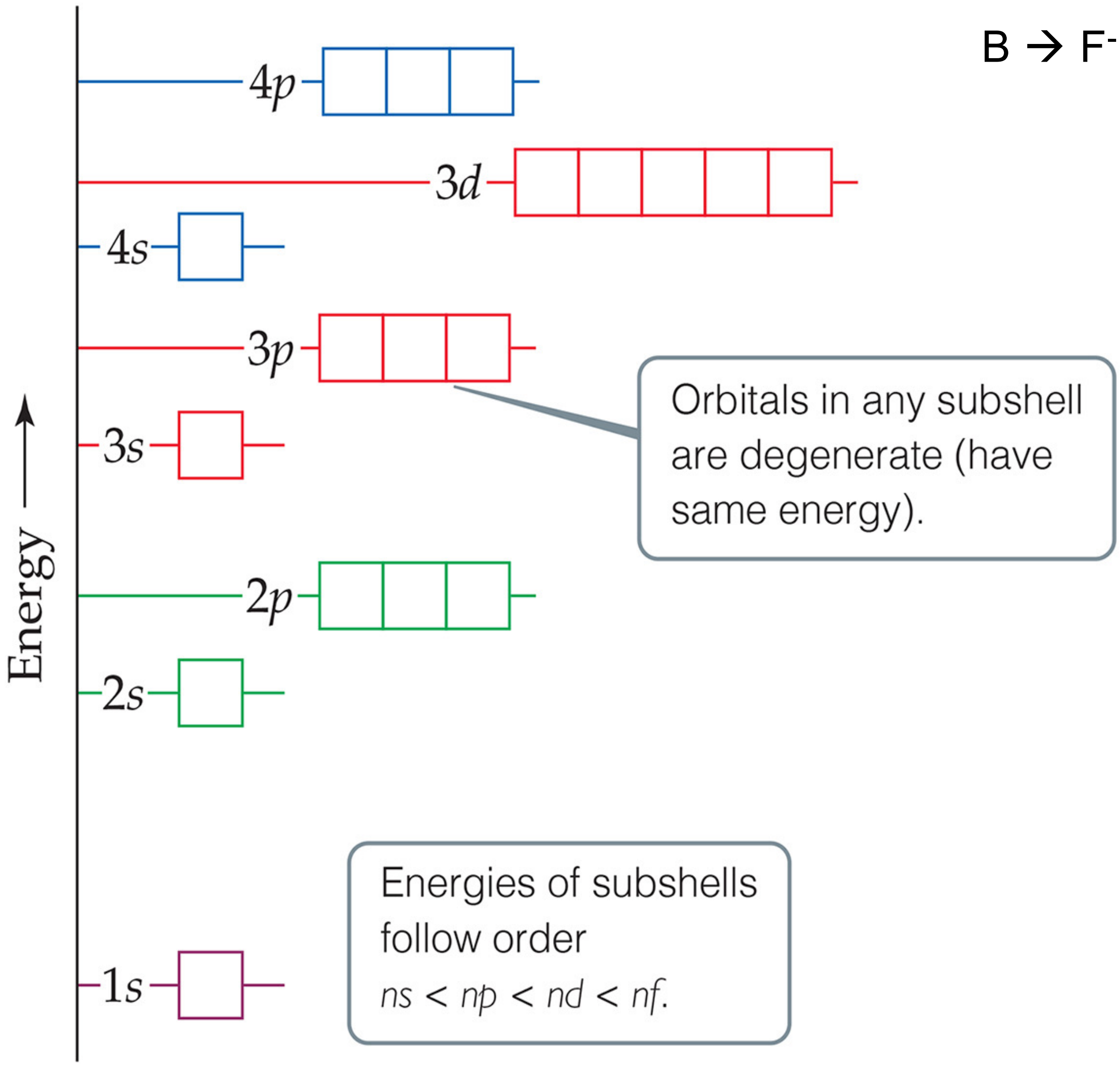
$n = 3$ shell has three subshells composed of nine orbitals



H, He
Look at pTable



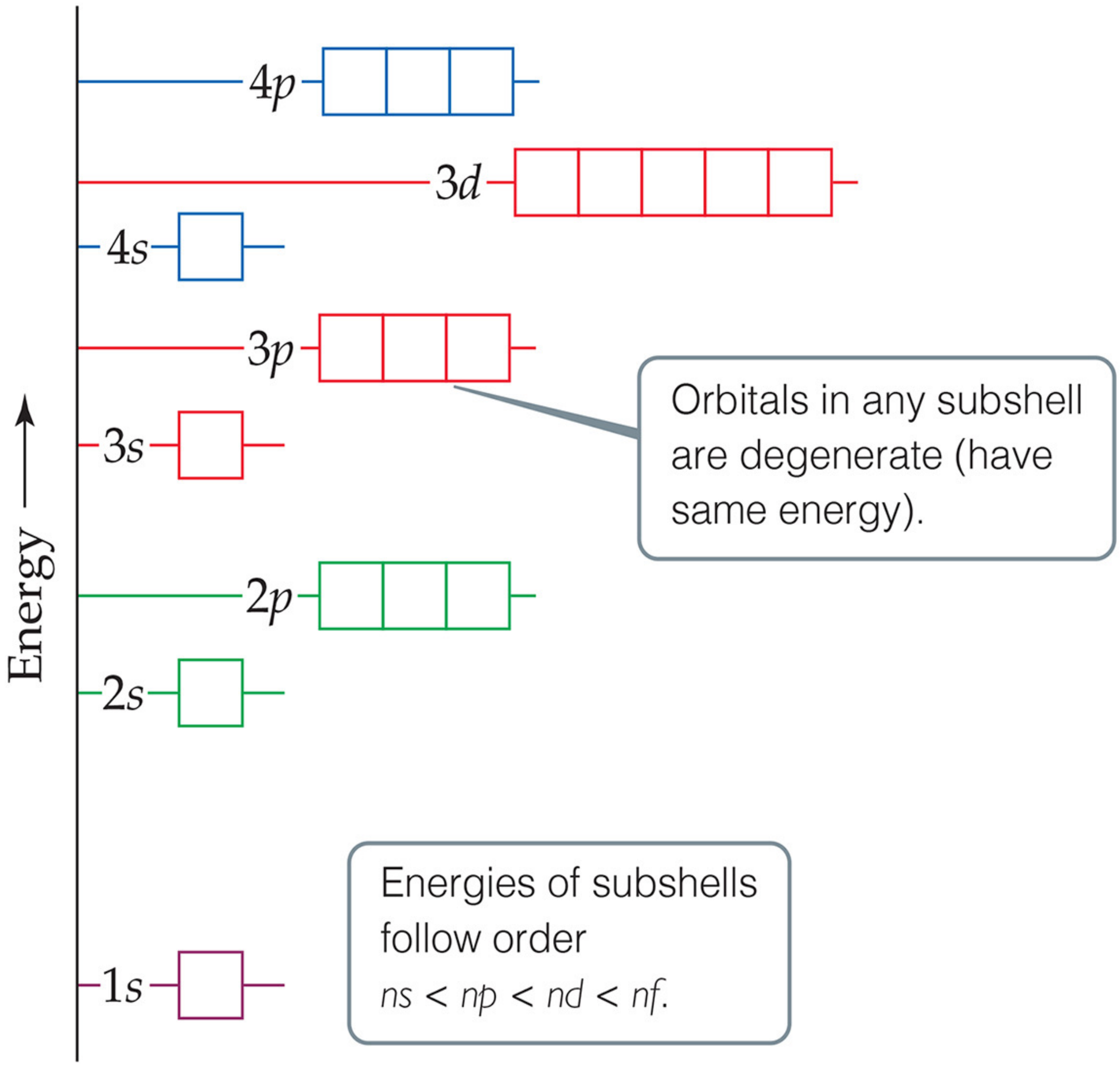
$B \rightarrow F^-$



## TABLE 6.3 Electron Configurations of Several Lighter Elements

| Element | Total Electrons | Orbital Diagram 1*s* | 2*s* | 2*p* | | | 3*s* | Electron Configuration |
|---|---|---|---|---|---|---|---|---|
| Li | 3 | ↑↓ | ↑ | | | | | $1s^2 2s^1$ |
| Be | 4 | ↑↓ | ↑↓ | | | | | $1s^2 2s^2$ |
| B | 5 | ↑↓ | ↑↓ | ↑ | | | | $1s^2 2s^2 2p^1$ |
| C | 6 | ↑↓ | ↑↓ | ↑ | ↑ | | | $1s^2 2s^2 2p^2$ |
| N | 7 | ↑↓ | ↑↓ | ↑ | ↑ | ↑ | | $1s^2 2s^2 2p^3$ |
| Ne | 10 | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | | $1s^2 2s^2 2p^6$ |
| Na | 11 | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ | $1s^2 2s^2 2p^6 3s^1$ |

Fe



Energy
4p
3d
4s
3p
3s
2p
2s
1s
Orbitals in any subshell are degenerate (have same energy).
Energies of subshells follow order
ns < np < nd < nf.

There are many elements that appear to violate the electron configuration guidelines.

- Examples:
  - Chromium is $[Ar]3d^5 4s^1$ instead of $[Ar]3d^4 4s^2$.
  - Copper is $[Ar]3d^{10} 4s^1$ instead of $[Ar]3d^9 4s^2$.
- Half-full ($d^5$) and full ($d^{10}$) *d* subshells are particularly stable.

Use pTable to see exceptions.