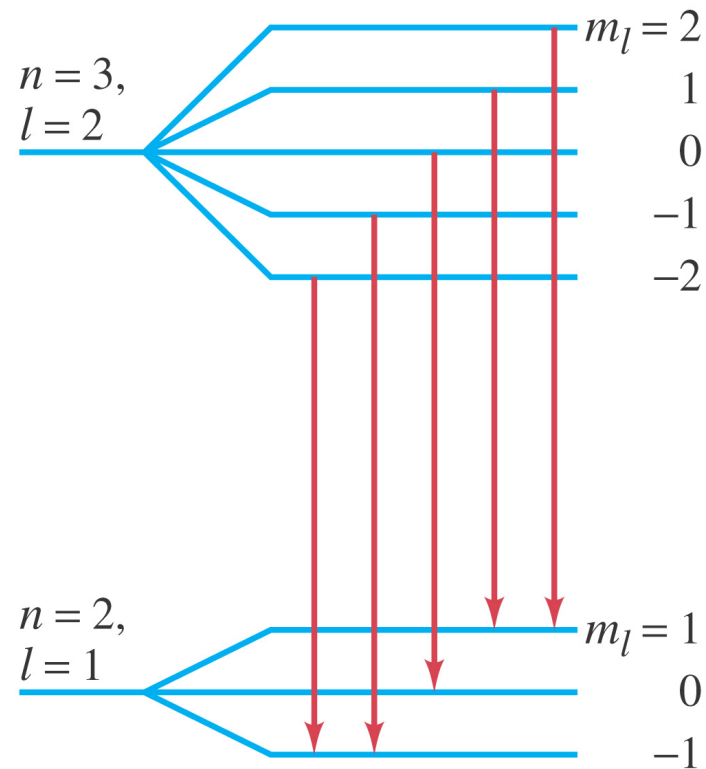# Chapter 28

Quantum Mechanics of Atoms

28.1 Quantum Mechanics – "The" Theory

Quantum mechanics incorporates wave-particle duality, and successfully explains energy states in complex atoms and molecules, the relative brightness of spectral lines, and many other phenomena.

It is widely accepted as being the fundamental theory underlying all physical processes.

On the flip side, quantum mechanics is famously strange and weird when its ideas are translated to the everyday world.

The Correspondence principle can resolve most of these paradoxes

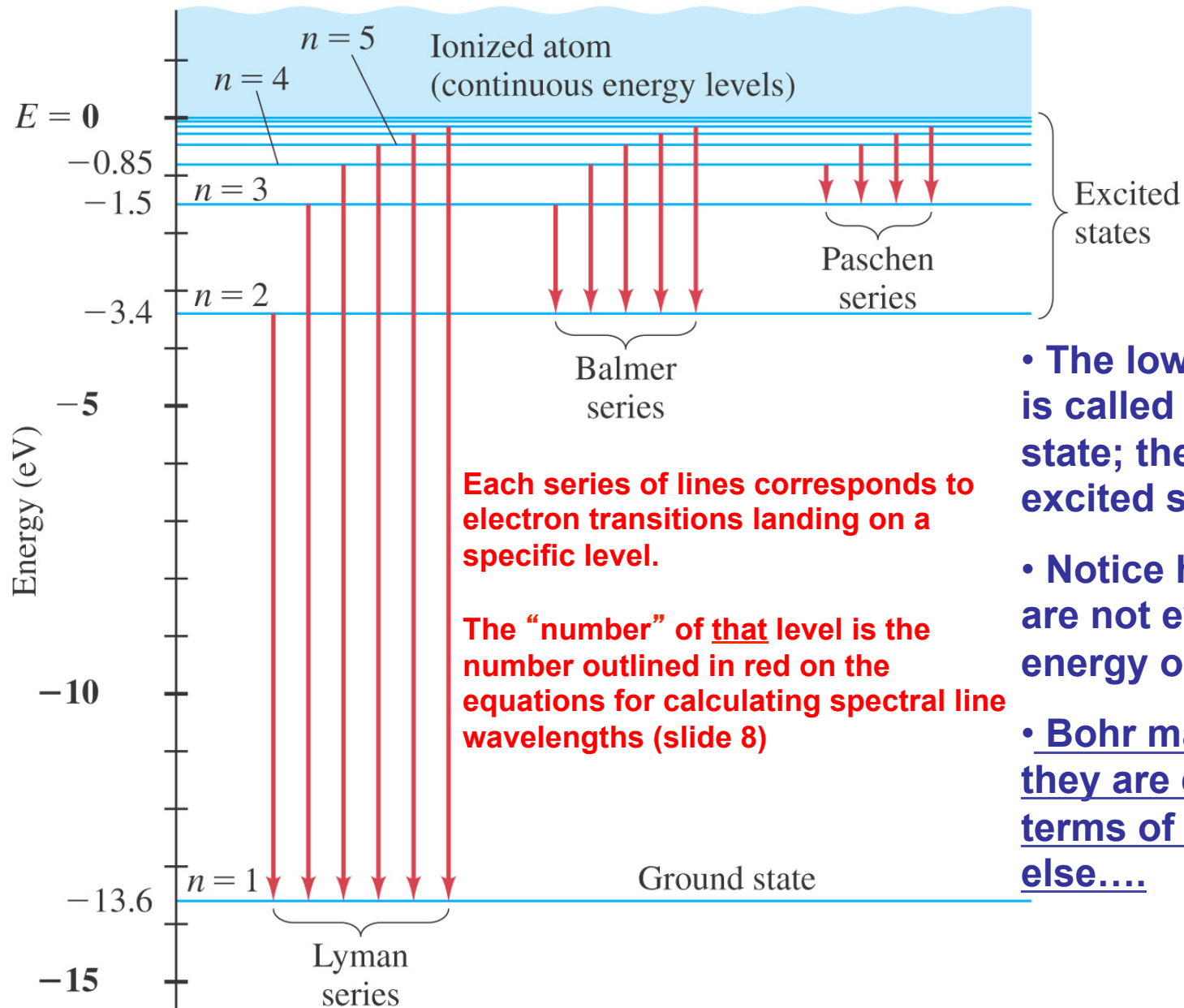# The Size of Atoms and the "hand of God".
More Quantum strangeness....
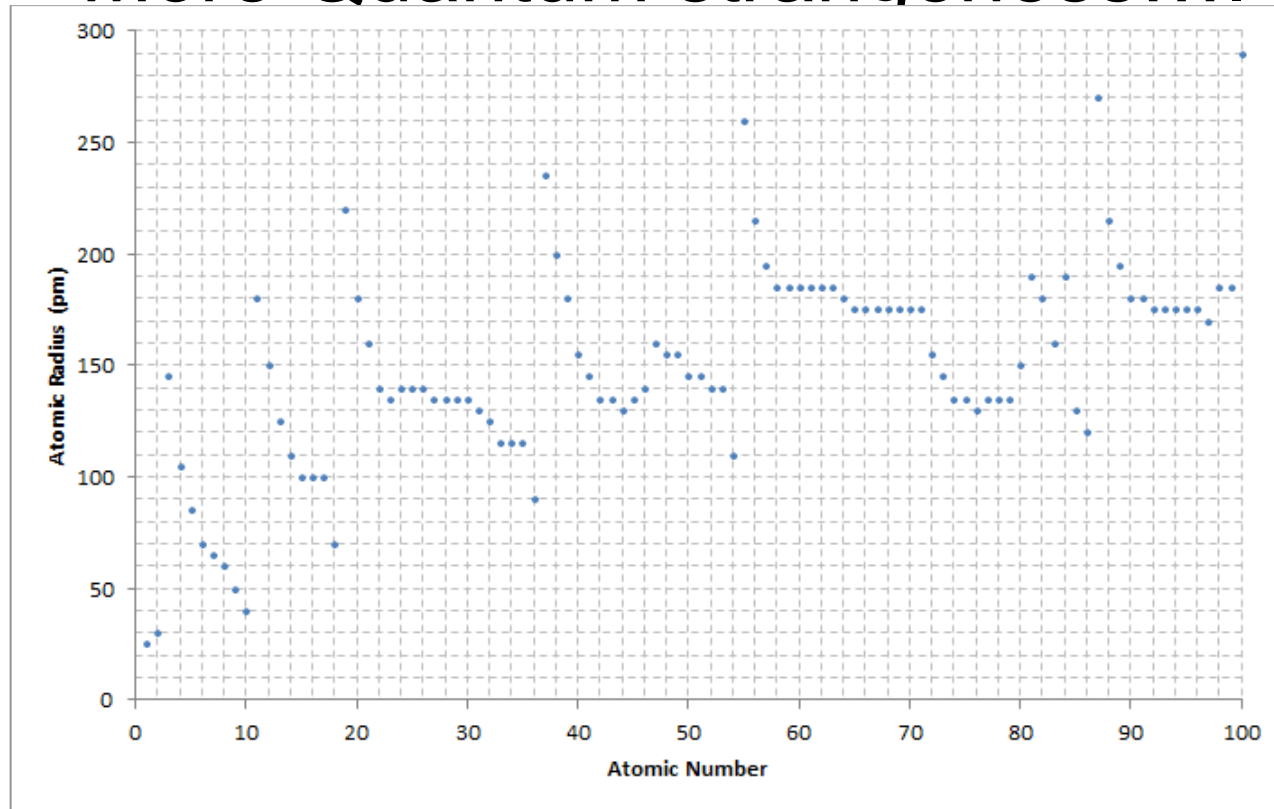
- Atomic radii increase with number of protons in the nucleus
- Interesting pattern of large jumps in size, each followed by a steady shrinkage
- Electrons appear to be arranging themselves into "shells"
- Note the even number of electrons per shell
- **What is the mysterious guiding hand, arranging the electrons in this way?**

Units of Chapter 28

- The Wave Function and Its Interpretation; the Double-Slit Experiment

- The Heisenberg Uncertainty Principle

- Philosophic Implications; Probability versus Determinism Schrödinger's Cat

- Quantum-Mechanical View of Atoms

- Quantum Numbers

- Complex Atoms; the Exclusion Principle

- The Periodic Table of Elements

- Fluorescence and Phosphorescence

- Lasers

27.12 The Bohr Atom

$n = 5$ Ionized atom (continuous energy levels)

$n = 4$

$E = 0$

-0.85

-1.5 $n = 3$

-3.4 $n = 2$

-5

Energy (eV)

-10

-13.6 $n = 1$ Ground state

-15

Paschen series

Excited states
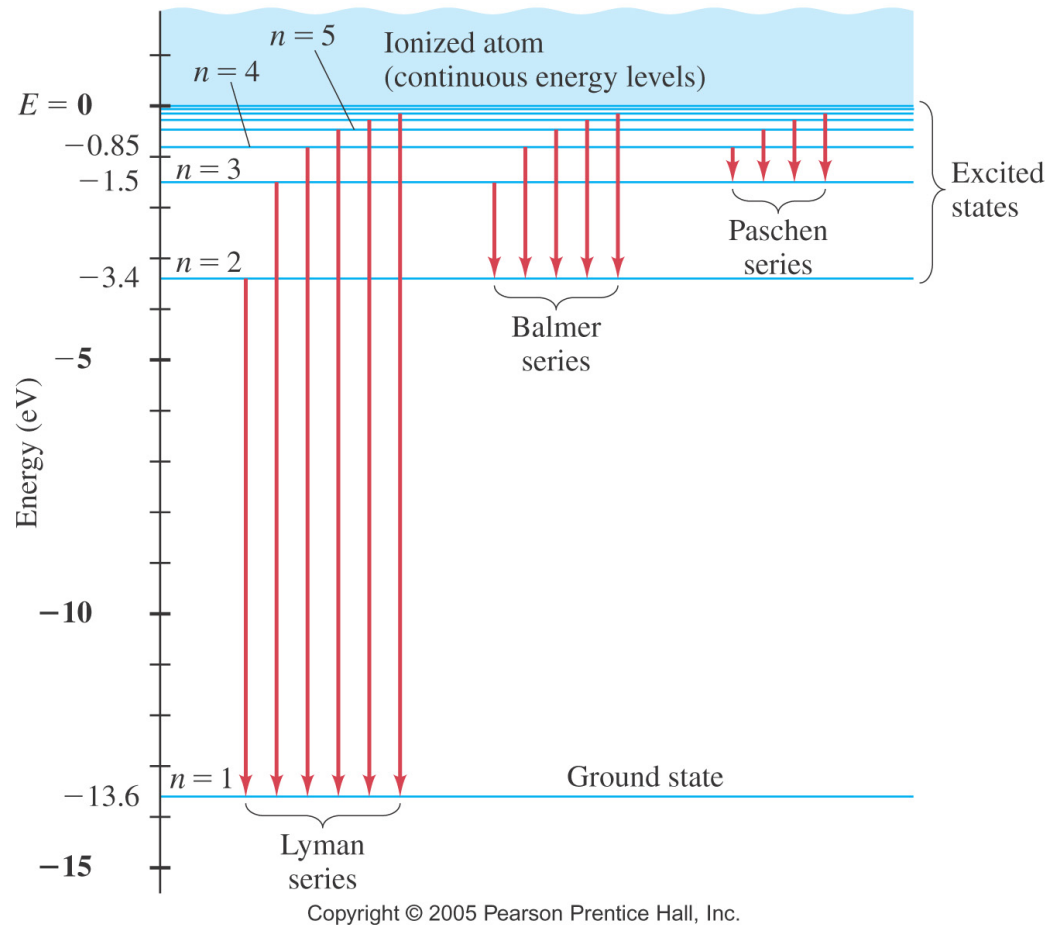
Balmer series

Lyman series

Each series of lines corresponds to electron transitions landing on a specific level.

The "number" of that level is the number outlined in red on the equations for calculating spectral line wavelengths (slide 8)

• **The lowest energy level is called the ground state; the others are excited states.**

• **Notice how the levels are not evenly spaced in energy or in radius.**

• **Bohr managed to show they are evenly spaced in terms of something else….**

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All transitions ending in the ground state, produce photons in what part of the spectrum ?

$n = 5$ Ionized atom (continuous energy levels)

$n = 4$

$E = 0$

-0.85

-1.5 $n = 3$

-3.4 $n = 2$

-5

Energy (eV)

-10

-13.6 $n = 1$ Ground state

-15

Paschen series

Excited states

Balmer series

Lyman series

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A. Visible

B. Infrared

C. Ultraviolet

D. Some in the visible, some in the UV

ConcepTest 27.4   Ionization

How much energy does it
take to ionize a hydrogen
atom in its ground state?

1) 0 eV

2) 13.6 eV

3) 41.2 eV

4) 54.4 eV

5) 108.8 eV

ConcepTest 27.4   Ionization

How much energy does it take to ionize a hydrogen atom in its ground state?

1) 0 eV
2) 13.6 eV
3) 41.2 eV
4) 54.4 eV
5) 108.8 eV

The energy of the ground state is the energy that binds the electron to the nucleus. Thus, an amount equal to this binding energy must be supplied in order to kick the electron out of the atom.

$$E_n = E_1 \frac{Z^2}{n^2}$$

Follow-up: How much energy does it take to change a He$^+$ ion into a He^{++} ion? Keep in mind that $Z = 2$ for helium.

ConcepTest 27.5b   Atomic Transitions II

The Balmer series for hydrogen can be observed in the visible part of the spectrum. Which transition leads to the reddest line in the spectrum?
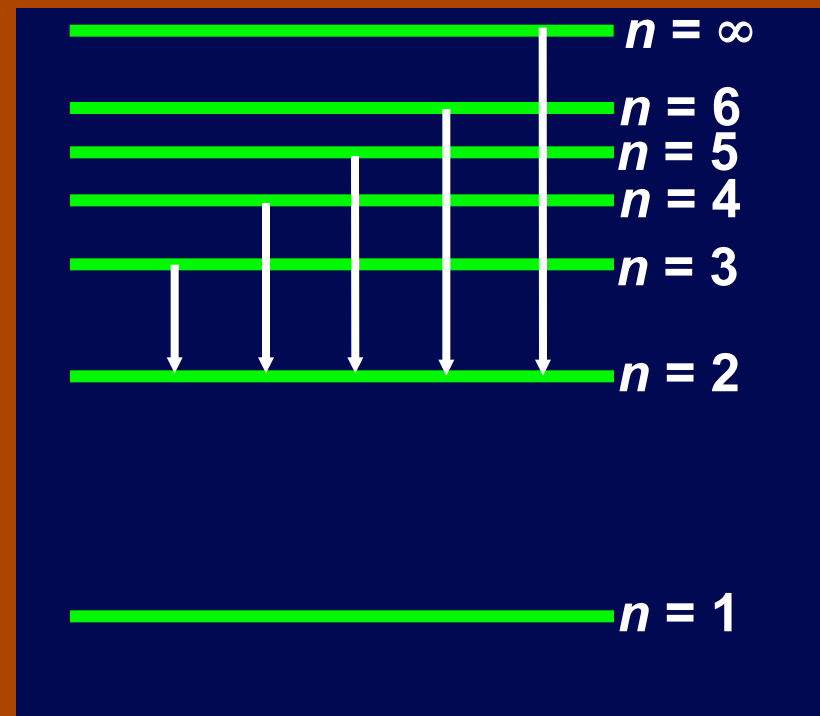
1) 3 → 2

2) 4 → 2

3) 5 → 2

4) 6 → 2

5) ∞ → 2

$n = \infty$

$n = 6$
$n = 5$
$n = 4$

$n = 3$

$n = 2$

$n = 1$

ConcepTest 27.5b   Atomic Transitions II

The Balmer series for hydrogen can be observed in the visible part of the spectrum. Which transition leads to the reddest line in the spectrum?
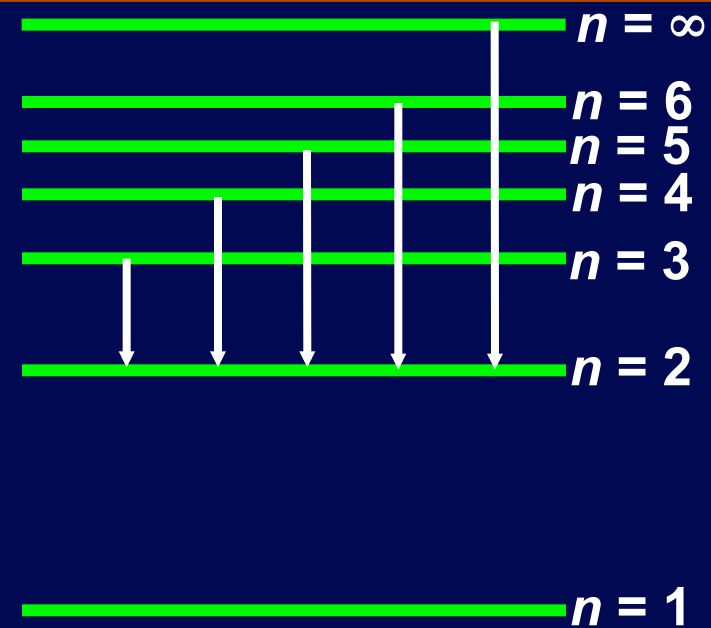
1) 3 → 2
2) 4 → 2
3) 5 → 2
4) 6 → 2
5) ∞ → 2

The transition **3 → 2** has the **lowest energy** and thus the **lowest frequency** photon, which corresponds to the **longest wavelength** (and therefore the "**reddest**") line in the spectrum.

n = ∞
n = 6
n = 5
n = 4
n = 3
n = 2
n = 1

Follow-up: Which transition leads to the shortest wavelength photon?

Energy, Mass, and Momentum of a Photon

- A photon must travel at the speed of light.

- Quantum theory (photoelectric effect) says
$$E_{photon} = hf \qquad (1)$$

- Look at the relativistic equation for the energy of a particle : $E^2 = p^2c^2 + m^2c^4$

- The photon has no mass, so this reduces to
$$E_{photon} = pc. \qquad (2)$$

- We combine equations 1 & 2 and find that a photon <u>must</u> carry momentum!

$$p = \frac{E}{c} = \frac{hf}{c} = \frac{h}{\lambda} \qquad \text{(27-6)}$$

Consequence of Photons having momentum: - they can exert a force!
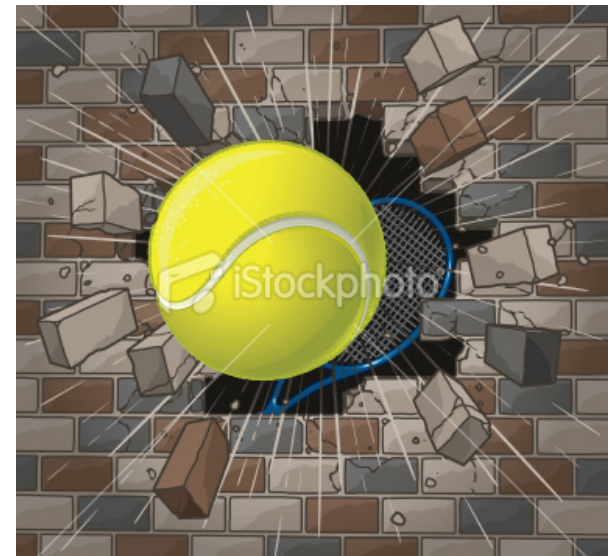
If photons carry momentum, than they should exert
A force when they strike something

Imagine a tennis ball striking a wall - it imparts an impulse, and
exerts a force on the wall.

Remember Newton's 2nd law:
        F=ma or F = "rate of change of momentum"

This effect is called RADIATION PRESSURE
and is another unique prediction of
Quantum Theory and Relativity!

Radiation Pressure

How much radiation pressure is exerted by sunlight?

Could the pressure of Sunlight be harnessed to "sail" across the solar system?

If we know for example the amount of energy emitted by the Sun (1300 W/m^2 at Earth), and the "average wavelength" of sunlight (500 nm)….

Then we can calculate the number of photons per second:
E_{phot} = hf   (c=fλ)

$\quad$ = hc/λ = $6.67 \times 10^{-34} \cdot 3 \times 10^8$ / 500×10^{-9} = 4×10^{-19} J

N_{phot} = 1300/ 4×10^{-19}
$\quad\quad$ = 3.24×10^{21} photons per second per square meter

P_{phot} = h/ λ = 6.67×10^{-34} / 500×10^{-9} = 1.3×10^{-37}

So Momentum per second = N_{phot} p_{phot} = 3.24×10^{21} x 1.3×10^{-37}

$\quad\quad\quad\quad$ which is a Pressure of $\quad$ 4.2×10^{-16} N/m^2

de Broglie and the Wave Nature of Matter

•Louis de Broglie, arguing from the idea of symmetry in nature, proposed:

• Just as light sometimes behaves as a particle, matter sometimes behaves like a wave.

• The wavelength of a particle of matter is:

$$\lambda = \frac{h}{p} \qquad \text{(27-8)}$$

De Broglie wavelength depends on the particle's momentum.

The de Broglie wavelength of a very fast moving electron is _____ that of a slow moving electron.

A. Shorter than

B. Longer than

C. The same as

28.2 The Wave Function.

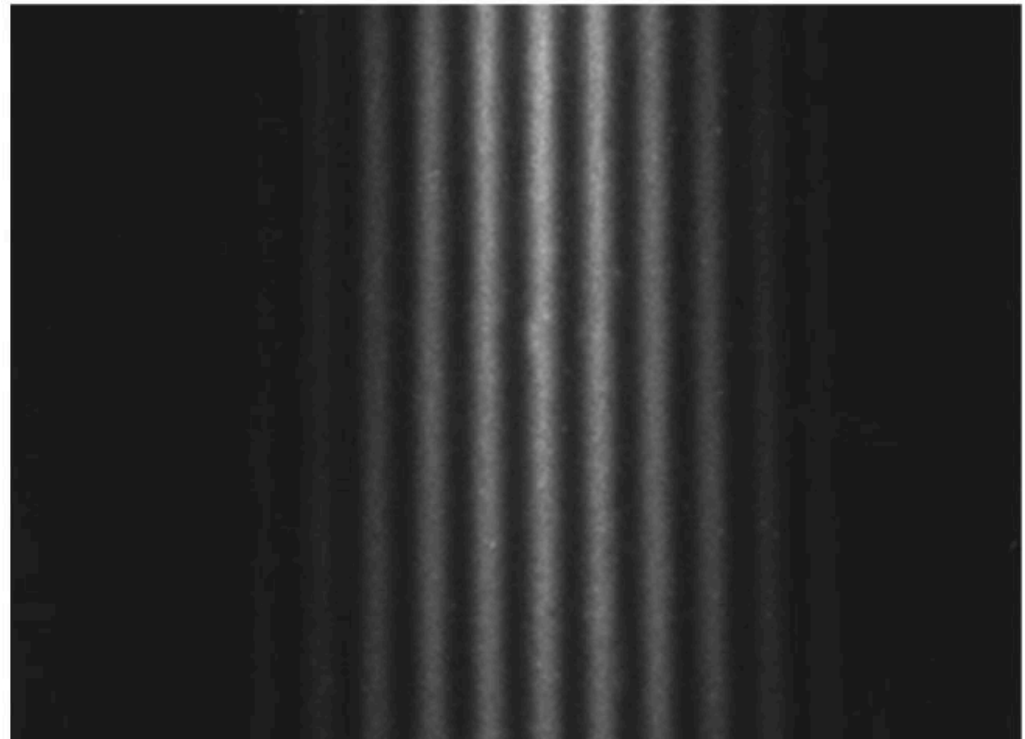## Double-Slit diffraction Experiment with electrons. – a mysterious guiding hand ?

• de Broglie's matter-wave idea predicts that particles like electrons should exhibit interference just as light does.

•Surprise! They do!

• An electron beam passing through a double slit indeed produces an interference pattern similar to that for light.

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

De Broglie wavelength for a moving particle

27.9 Electron Microscopes

Hot filament
(source of electrons)

High voltage

Condensing "lens"

Object

Objective "lens"

Projection "lens" (eyepiece)

Image (on screen, film, or semiconductor detector)
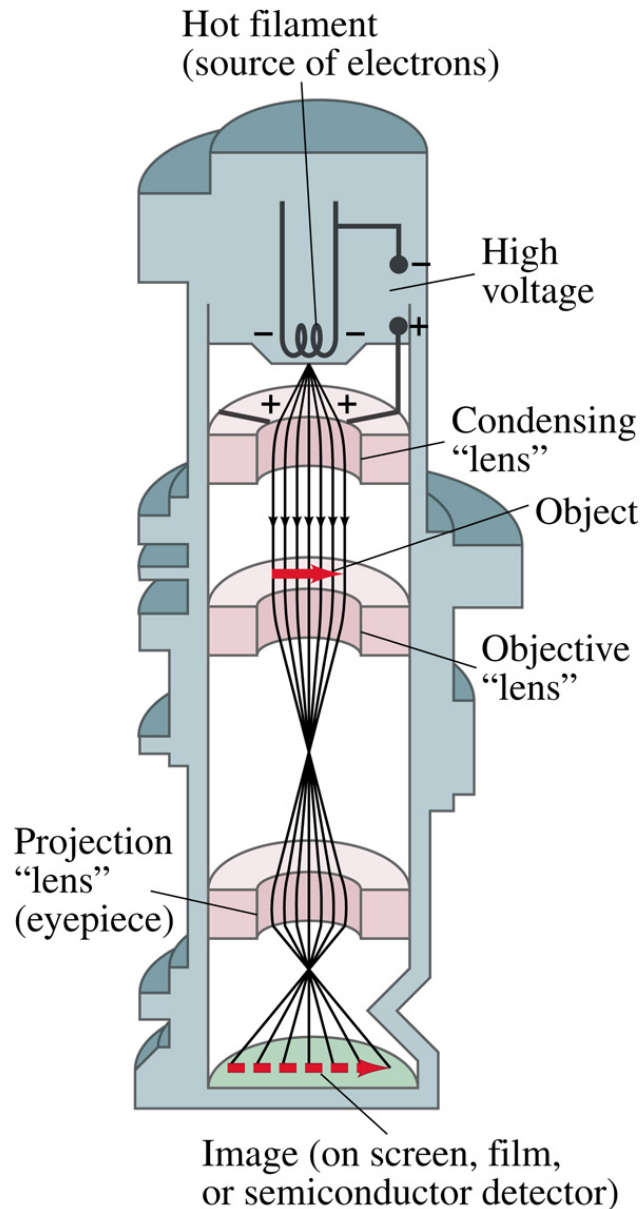
- **According to de Broglie, all the properties of optics should apply to particles!**

- **If we use the appropriate de Broglie wavelength!**

- **Transmission electron microscope – the electrons are focused by magnetic coils**

- **The magnetic coils act as lenses to focus the electron beam**

- **The resolution limit (1.22λ/D) still applies**

- **electron wavelength is tiny compared to that of light 0.004nm vs 500nm**

- **So much smaller details can be seen**

ConcepTest 27.3a   Wave-Particle Duality I

The speed of proton A is larger than the speed of proton B. Which one has the longer wavelength?

1) proton A

2) proton B

3) both the same

4) neither has a wavelength

ConcepTest 27.3a   Wave-Particle Duality I

The speed of **proton A** is **larger** than the speed of **proton B**. Which one has the **longer** wavelength?

1) proton A

2) proton B

3) both the same

4) neither has a wavelength

Remember that $\lambda = \dfrac{h}{mv}$ so the proton with the **smaller** velocity will have the **longer** wavelength.

27.13 de Broglie᾽s Hypothesis Applied to Atoms

$n = 2$

$n = 3$

$n = 5$
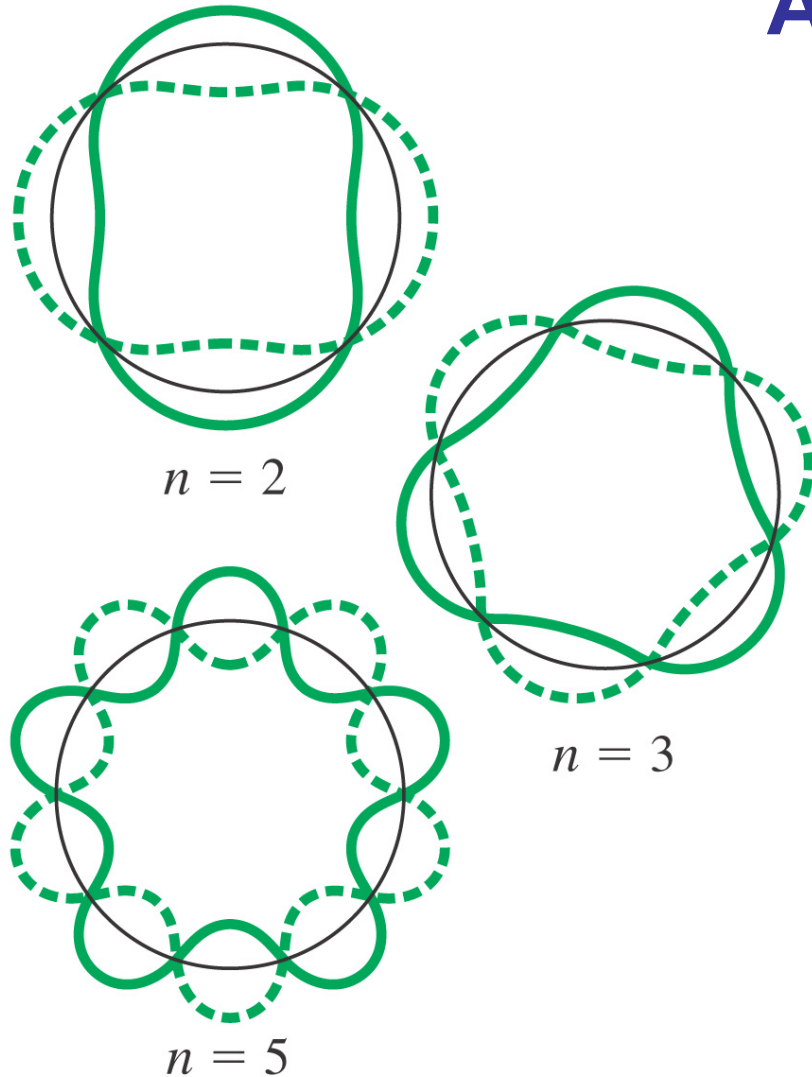
These are circular standing waves for n = 2, 3, and 5.

• De Broglie᾽s hypothesis associates a wavelength with the momentum of a particle.

• He proposed that only those orbits where the wave would be a circular standing wave will occur.

• This yields graphically the same relation that Bohr had proposed mathematically

• De Broglie᾽s model adds a physical justification to the quantum model of the atom.

• Essentially the electron waves interfere, and the allowed orbits correspond to the condition for constructive interference

•Bohr encoded this as the 2nd Quantum number: l

28.2 The Wave Function.

Double-Slit diffraction Experiment with electrons. – a mysterious guiding hand ?

• de Broglie's matter-wave idea predicts that particles like electrons should exhibit interference just as light does.

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

De Broglie wavelength for a moving particle

• An electron beam passing through a double slit indeed produces an interference pattern similar to that for light.

• **Bizarrely, the Interference pattern appears even if the electrons are sent through one at a time!**
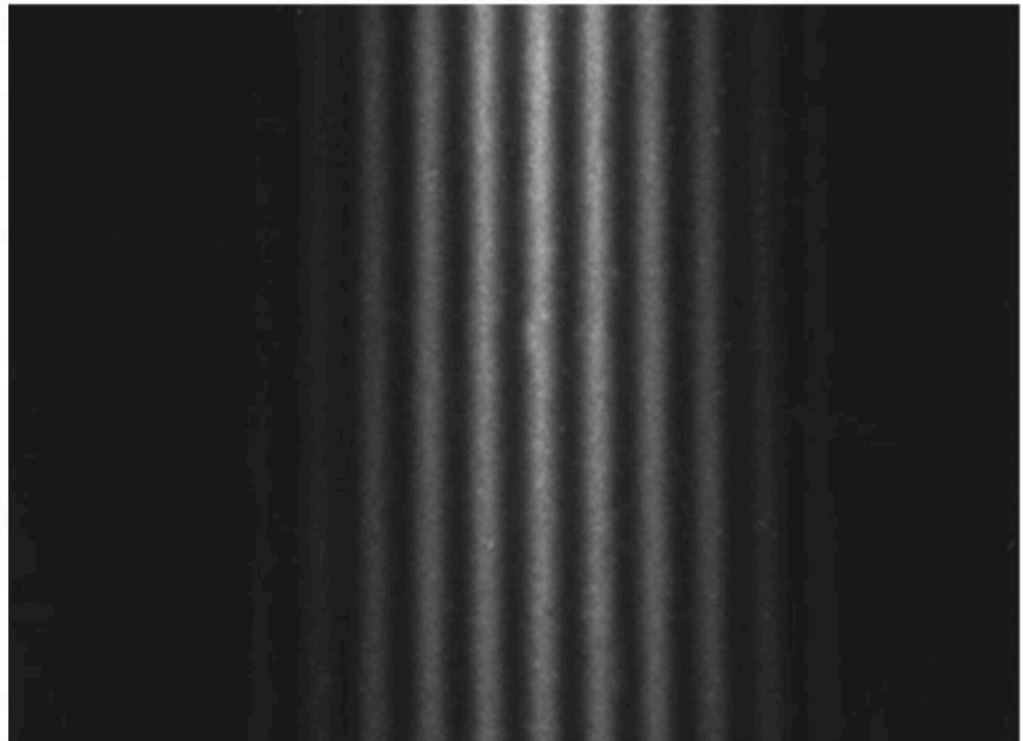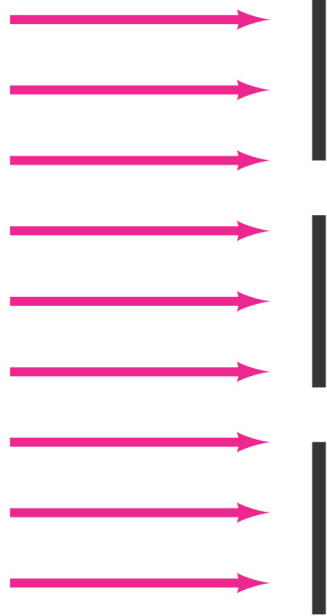
28.2 The Wave Function and Its Interpretation; the Double-Slit Experiment

The interference pattern is observed after many electrons have gone through the slits.

If we send the electrons through one at a time, we cannot predict the path any single electron will take, but we can predict the overall distribution.

Light or electrons

Intensity on screen

28.2 The Wave Function and Its Interpretation; the Double-Slit Experiment

- An electromagnetic wave has oscillating electric and magnetic fields.

- In Electromagnetism (light as a wave): $I \propto E^2$ (electric field)

- In the photon theory of light: $I \propto N$ (number of photons)

- So: $N \propto E^2$

- Which is all very well for intense beams of light or perhaps dense streams of electrons where we can imagine the particles responding to a "field" of some kind.

- But for individual particles, where there is no field to oscillate, a new interpretation is required.

- Enter the *Wavefunction* Ψ –

- Erwin Schrödinger proposed rewriting the equations that describe waves, replacing E with **Probability**

- **The Wavefunction completely describes the state of a particle (or system of particles) in terms of probability.**

28.2 The Wave Function and Its Interpretation; the Double-Slit Experiment

•For a single electron, the wave function is the probability of finding that electron at that point.

•Does this mean one could measure the wavefunction, and thus predict the future position, velocity, etc ?

•It turns out to be quite the opposite!

•Any measurement *whatsoever* changes the wavefunction in a completely unpredictable way.

•Thus it is impossible to know *which* electrons will end up where on the screen.

•Even though we know exactly what the overall picture will look like.

28.3 The Heisenberg Uncertainty Principle

Electron

Light source
(a)

Light source
(b)
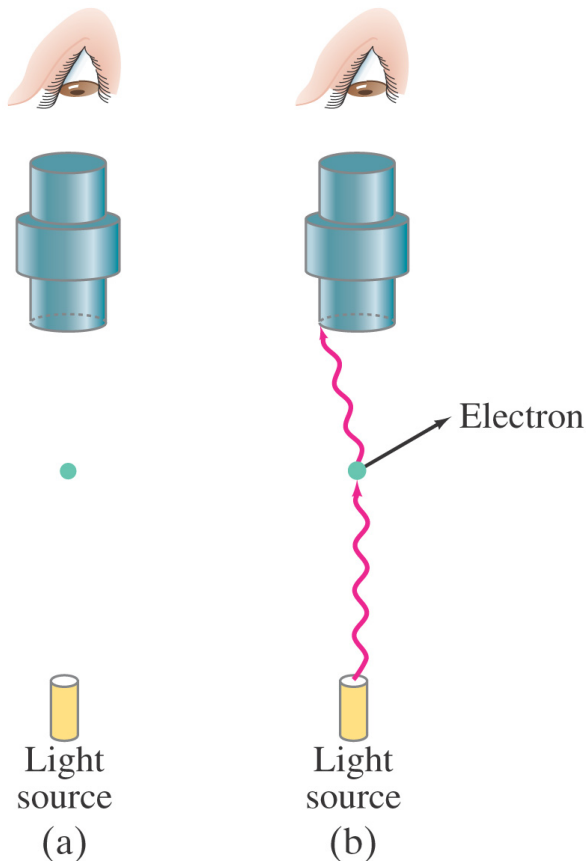
$$(\Delta x)(\Delta p_x) \approx h$$

- Imagine trying to see an electron with a powerful microscope. At least one photon must scatter off the electron and enter the microscope, but in doing so it will transfer some of its momentum to the electron.

- The uncertainty in the momentum of the electron is roughly the momentum of the photon – it could have transferred anywhere from none to all of its momentum.

- In addition, the position can only be measured to about one wavelength of the light used.

- You could use shorter wavelengths, but in doing so the photon momentum increases, and consequently makes that measurement worse!

- Werner Heisenberg showed that the more you pin down one quantity, the more another will altered.

- Surprisingly the product of these uncertainties has a finite value: Plank's constant.

When you measure the pressure in your car tires, the gauge works by allowing some air to escape. Does this change the pressure in the tire?

A. Yes, by a significant amount
B. Yes, but only by a tiny amount
C. No, not at all

28.3 The Heisenberg Uncertainty Principle

The Uncertainty principle can also be written as a relation between the uncertainty in time and the uncertainty in energy:

$$(\Delta E)(\Delta t) \approx h$$

This says that if an energy state only lasts for a limited time, its energy will be uncertain.

In a high pressure gas, frequent collisions stimulate atoms in excited states to de-excite and emit photons almost immediately. This shortening of the lifetime produces an small variation in the emitted photon's energy.

As a consequence, the width of spectral lines can directly reveal gas pressure, for example in stars and gas clouds in outer space!

This effect is called Pressure Broadening

Think about how the situation of photographing a moving vehicle is analogous to the uncertainty principle….

A motion-blurred photo can be used to measure the speed of an object, but not its accurate position.

A faster shutter speed would freeze the motion giving an accurate position, but it would not reveal the speed

….And how it differs.

When you "see" an object, light must have bounced off it, and then entered your eye.

Does the force of the light photons move the object, so that it might no longer be where you "saw" it?

A. No, light cannot exert a force
B. Yes, all we see is an illusion
C. Yes, but everyday objects are too massive to be affected significantly.

28.5 Quantum-Mechanical View of Atoms

Since we cannot say exactly where an electron is, the Bohr picture of the atom, with electrons in neat orbits, cannot be correct.

Quantum theory describes an electron probability distribution; this figure shows the distribution for the ground state of hydrogen:
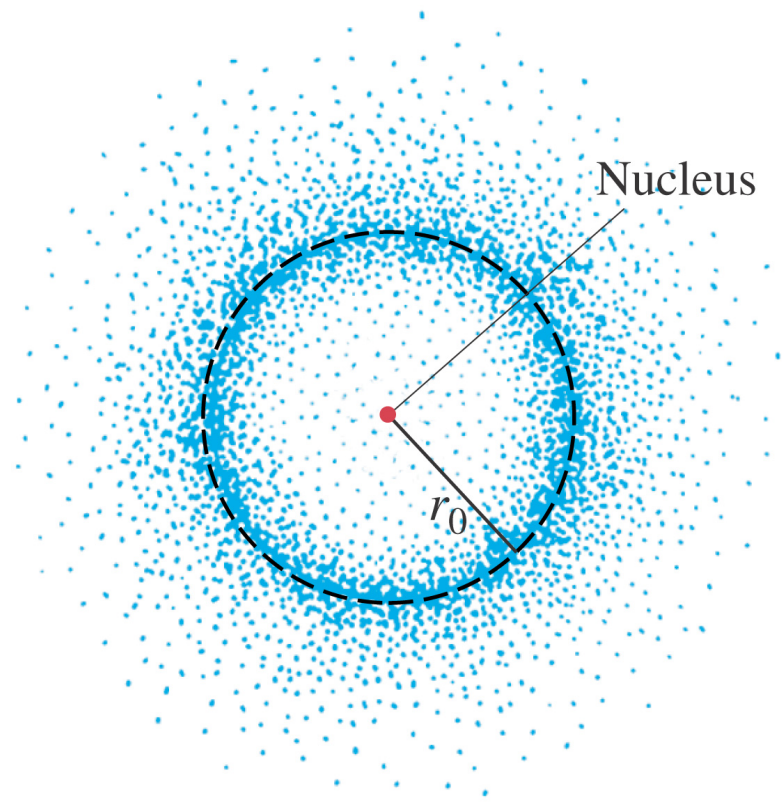
# 28.6 Quantum Numbers and Pauli Exclusion Principle

There turn out to be exactly 4 attributes, known as quantum numbers, needed to specify the state of an electron in an atom.

n Principal quantum number n gives the total energy associated with a state or energy level. (n = 1,2,3,....)

l Orbital quantum number l gives the angular momentum. l can take on integer values from 0 to (n-1)

m_l Magnetic quantum number m_l gives the direction of the electron's angular momentum, and can take on integer values from $-l$ to $+l$

s Spin quantum number s

Exclusion Principle: No two electrons in an atom can occupy the same quantum state.

The quantum state is completely specified by the four quantum numbers; and nature doesn't allow two electrons to have the same set.

m : The 3rd Quantum Number
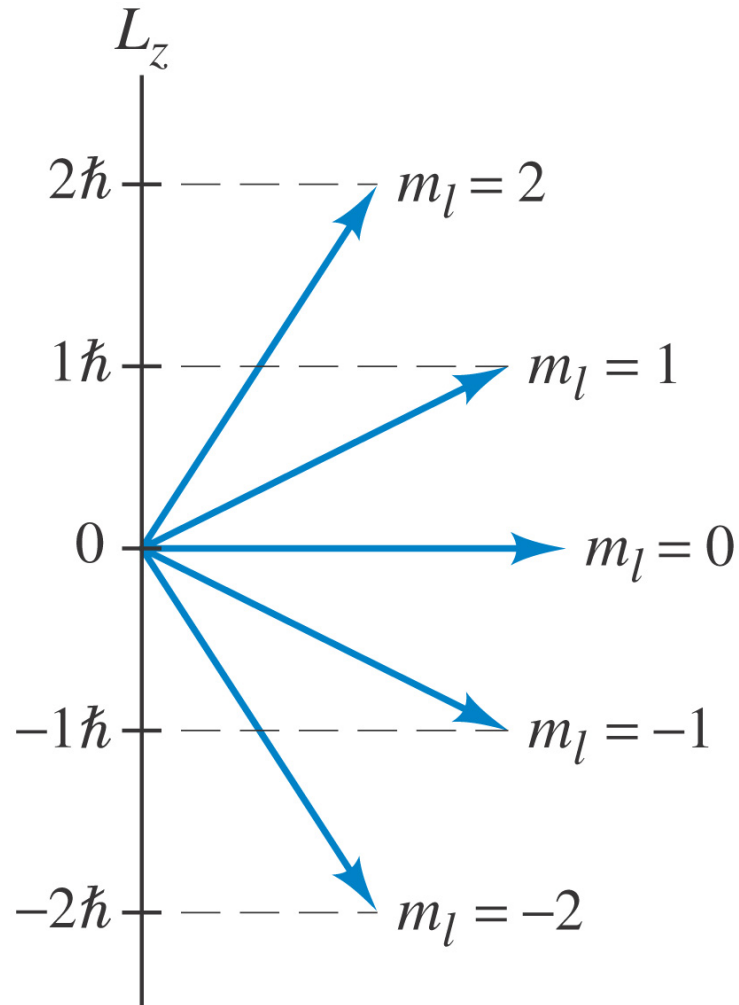
The magnetic quantum number, m

M_l gives the direction of the electron's angular momentum, and can take on integer values from $-l$ to $+l$.

This plot indicates the quantization of angular momentum direction for $l = 2$.

You can visualize it as the inclination of the electron's orbit.

Or the projection of the total angular momentum along the z axis

$$L_z = m_l \hbar$$

This behavior is responsible for para-magnetism, dia-magnetism, ferro-magnetism

28.6 Quantum Numbers and the Exclusion Principle: Selection Rules

The uncertainty principle tells us that only one electron per atom can have the same quantum state

This establishes a finite set of permutations of *n, l, m,* and *s* summarized in the table below.

TABLE 28–1 Quantum Numbers for an Electron

| Name	Symbol	Possible Values
Principal	n	$1, 2, 3, \cdots, \infty.$
Orbital	l	For a given n: l can be $0, 1, 2, \cdots, n-1.$
Magnetic	m_l	For given n and l: m_l can be $l, l-1, \cdots, 0, \cdots, -l.$
Spin	m_s	For each set of $n, l,$ and m_l: m_s can be $+\frac{1}{2}$ or $-\frac{1}{2}.$

28.6 Quantum Mechanics of the Hydrogen Atom; Quantum Numbers

The angular momentum quantum numbers do not affect the energy level much, but they do change the spatial distribution of the electron cloud.

(a) $n = 2$, $l = 0$, $m_l = 0$

(b) $n = 2$, $l = 1$, $m_l = 0$

(c) $n = 2$, $l = 1$, $m_l = \pm 1$
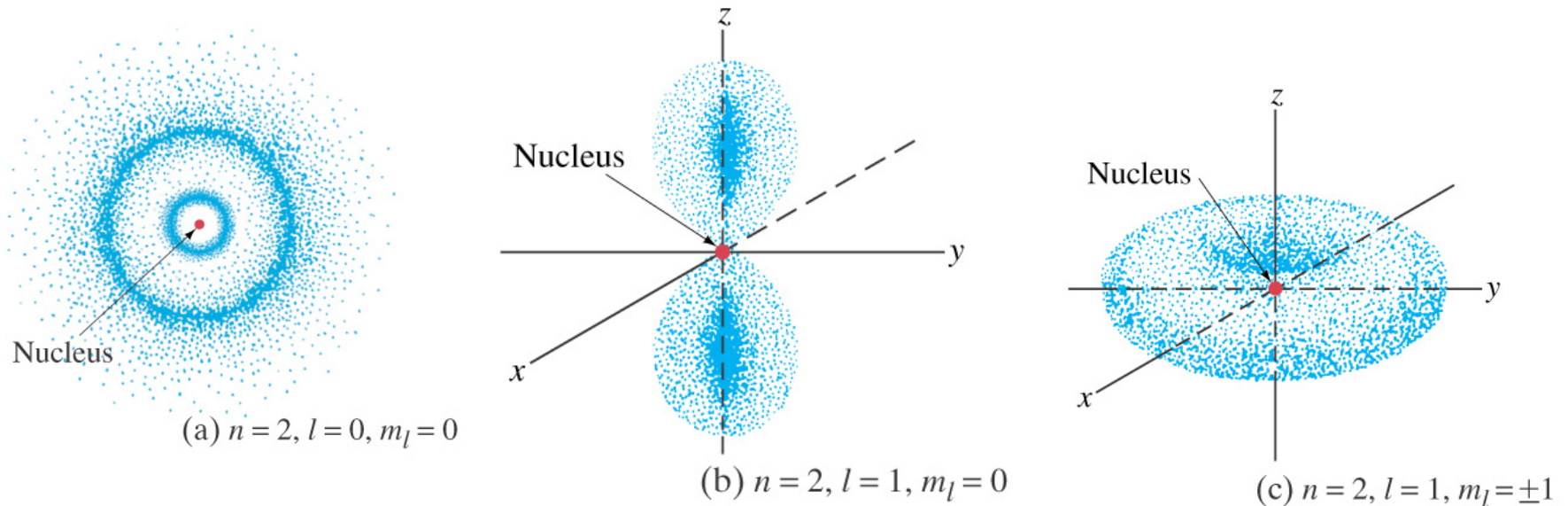
The need for these additional "degrees of freedom" originated in the discovery that many more lines are seen in spectra than can be accounted for by Bohr's initial quantum model that only considered energy and L.

28.7 Complex Atoms; the Exclusion Principle

This chart shows the occupied – and some unoccupied – states in He, Li, and Na.

Helium (He, $Z = 2$)   Lithium (Li, $Z = 3$)   Sodium (Na, $Z = 11$)
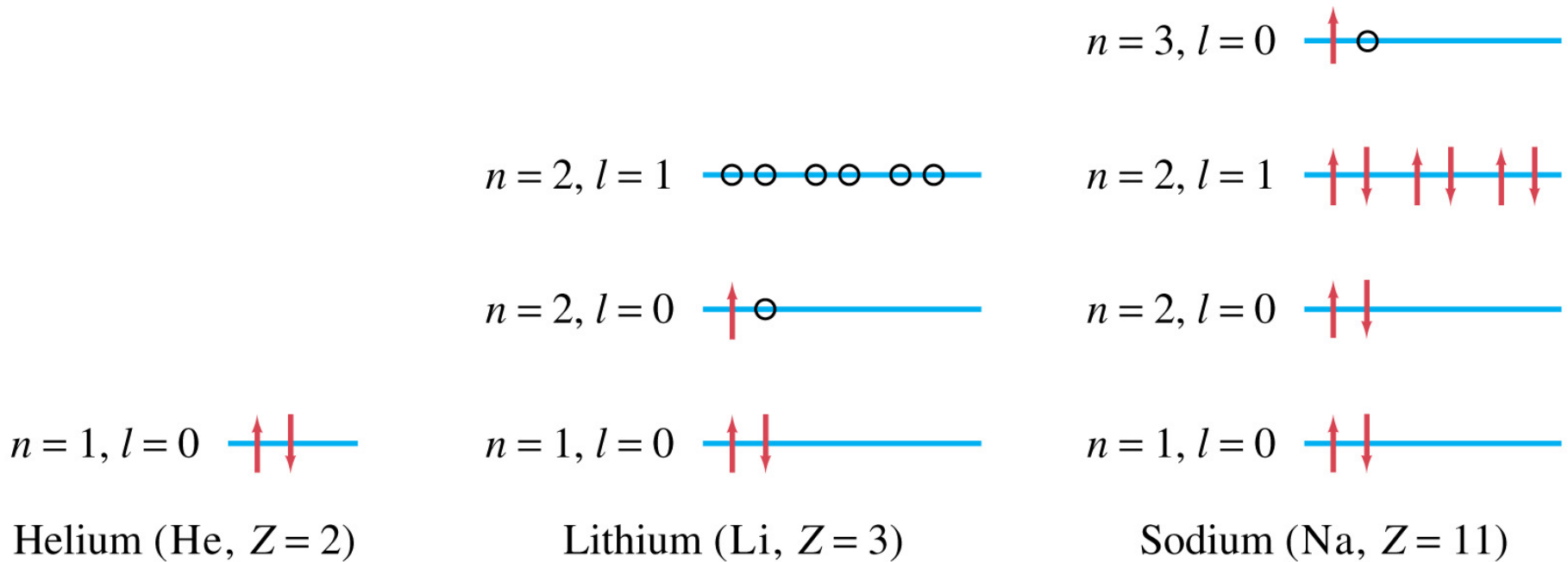
Quantum explanation for the the periodic table

2   10   18   36   54
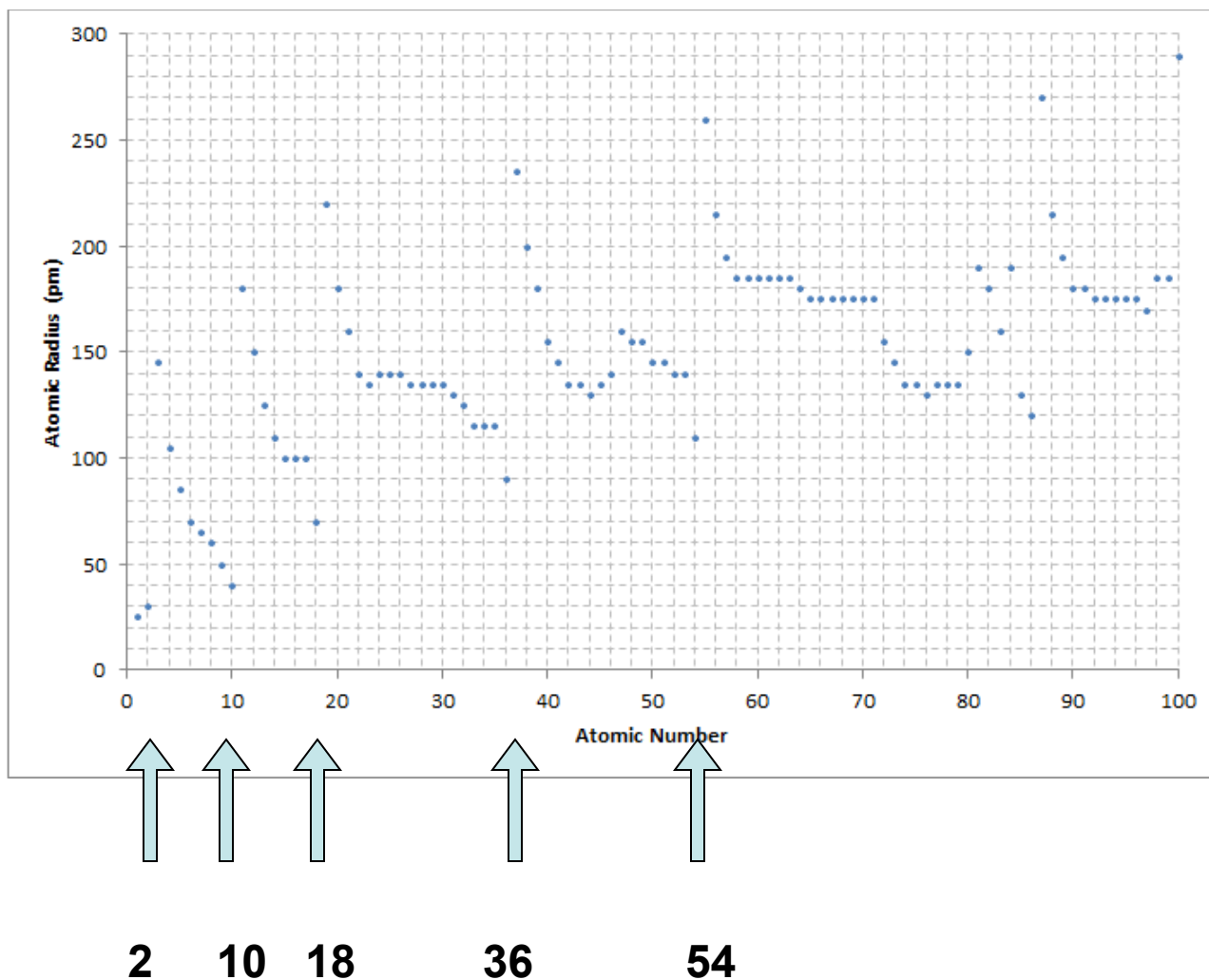
28.8 The Periodic Table of the Elements

TABLE 28–2 Value of l		
Value of l	Letter Symbol	Maximum Number of Electrons in Subshell
0	s	2
1	p	6
2	d	10
3	f	14
4	g	18
5	h	22
⋮	⋮	⋮

We can now understand the organization of the periodic table.

Electrons with the same n are in the same shell. Electrons with the same n and l are in the same subshell.

The exclusion principle limits the maximum number of electrons in each subshell to $2(2l + 1)$.

Each value of l is given its own letter symbol.

28.8 The Periodic Table of the Elements

Electron configurations are written by giving the value for n, the letter code for l, and the number of electrons in the subshell as a superscript.

For example, here is the ground-state configuration of sodium:

$$1s^2 2s^2 2p^6 3s^1$$
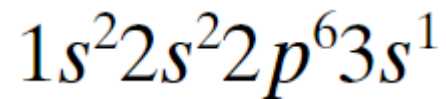
28.8 The Periodic Table of the Elements

This table shows the configuration of the outer electrons only.

TABLE 28–3
Electron Configuration of Some Elements

| Z (Number of Electrons)	Element†	Ground State Configuration (outer electrons)
1	H	$1s^1$
2	He	$1s^2$
3	Li	$2s^1$
4	Be	$2s^2$
5	B	$2s^2 2p^1$
6	C	$2s^2 2p^2$
7	N	$2s^2 2p^3$
8	O	$2s^2 2p^4$
9	F	$2s^2 2p^5$
10	Ne	$2s^2 2p^6$
11	Na	$3s^1$
12	Mg	$3s^2$
13	Al	$3s^2 3p^1$
14	Si	$3s^2 3p^2$
15	P	$3s^2 3p^3$
16	S	$3s^2 3p^4$
17	Cl	$3s^2 3p^5$
18	Ar	$3s^2 3p^6$
19	K	$4s^1$
20	Ca	$4s^2$
21	Sc	$3d^1 4s^2$
22	Ti	$3d^2 4s^2$
23	V	$3d^3 4s^2$
24	Cr	$3d^5 4s^1$
25	Mn	$3d^5 4s^2$
26	Fe	$3d^6 4s^2$

28.8 The Periodic Table of the Elements

Atoms with the same number of electrons in their outer shells have similar chemical behavior. They appear in the same column of the periodic table.

The outer columns – those with full, almost full, or almost empty outer shells – are the most distinctive.

The inner columns, with partly filled shells, have more similar chemical properties.

28.10 Fluorescence and Phosphorescence

If an electron is excited to a higher energy state, it may emit two or more photons of longer wavelength as it returns to the lower level.

One photon absorbed

Two photons emitted
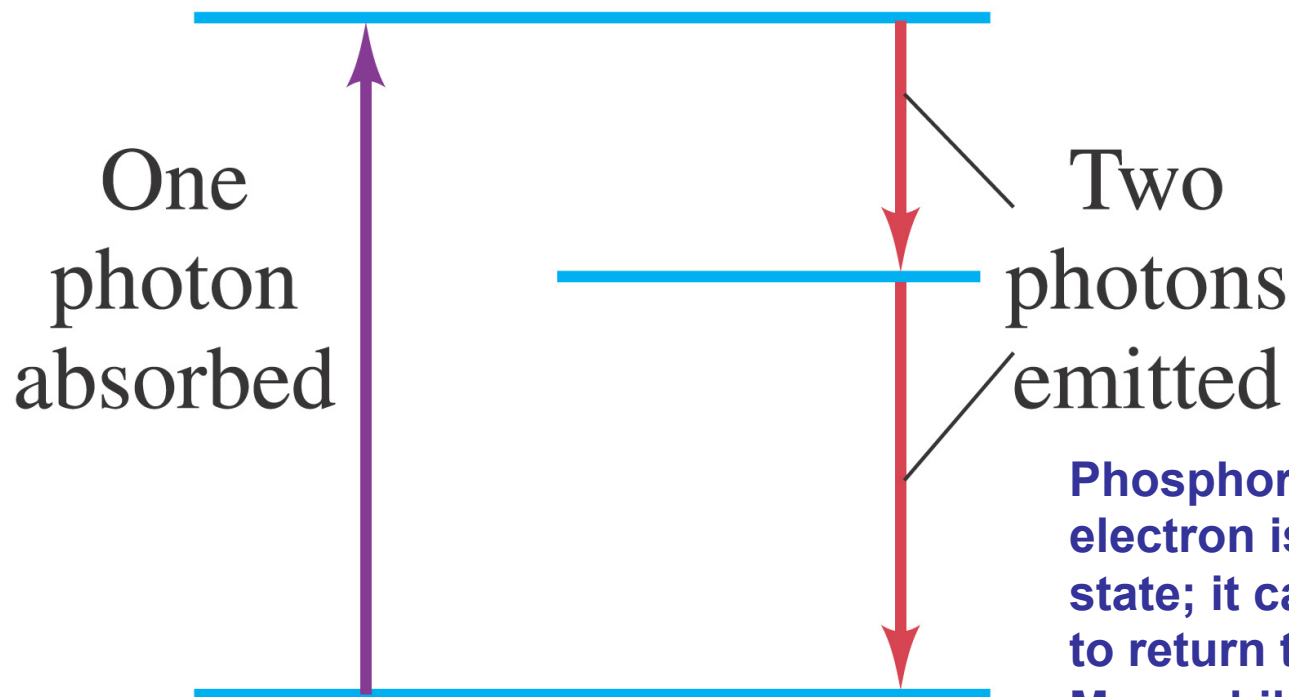
Fluorescence occurs when the absorbed photon is ultraviolet and the emitted

photons are in the visible range.

Phosphorescence occurs when the electron is excited to a metastable state; it can take seconds or more to return to the lower state. Meanwhile, the material glows

27.12 The Correspondence Principle

• **The correspondence principle states that the <u>same</u> laws of physics should apply everywhere: from the inside of the atom, to molecules, bacteria, rocks, humans, the solar system, the universe.**

• **Should be <u>no dividing line</u> between quantum and classical reality**

• **Yet everyday objects don′t appear to exhibit quantum or relativistic properties.**

• **When the differences between quantum levels are small compared to the energies, quantization should be imperceptible.**

• **When velocities are much smaller than the speed of light, relativistic effects are imperceptible.**

• **The laws of quantum physics and relativity simply reduce to the classical theory at "everyday" speeds, energies, sizes, etc.**

• **In other words, just as relativity is always in effect, so is quantization, but we often don′t notice it on the scale of "our world".**

Test your understanding: Why does quantization not apply to orbits of planets in the solar system?

The Size of Atoms

Atomic Radii range from 25-300 pico meters (10^{-12} m)

Typical size for C, O, Fe etc is 100 pm

ConcepTest 27.3b   **Wave-Particle Duality II**

An **electron** and a **proton**
have the **same speed**.
Which has the longer
wavelength?

1) electron

2) proton

3) both the same

4) neither has a wavelength

An **electron** and a **proton** have the **same speed**. Which has the **longer** wavelength?

1) electron
2) proton
3) both the same
4) neither has a wavelength

Remember that $\lambda = \dfrac{h}{mv}$ and the particles both have the same velocity, so the particle with the **smaller** mass will have the **longer** wavelength.

ConcepTest 27.3d   Wave-Particle Duality IV

An **electron** and a **proton**
have the **same momentum**.
Which has the **longer**
wavelength?

1) electron

2) proton

3) both the same

4) neither has a wavelength

ConcepTest 27.3d   Wave-Particle Duality IV

An **electron** and a **proton** have the **same momentum**. Which has the **longer** wavelength?

1) electron
2) proton
3) both the same
4) neither has a wavelength

Remember that $\lambda = \dfrac{h}{mv}$ and *p = mv*, so if the particles have the **same** momentum, they will also have the **same** wavelength.