Professor K

Atomic structure

Review

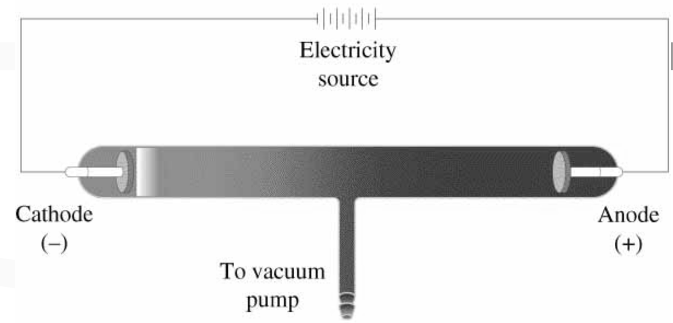
- Reaction- the formation and breaking of chemical <u>bonds</u>
- Bond- a transfer or sharing of <u>electrons</u>

Electrons

- Abbreviated e^-
- What are they?
- How were they discovered?

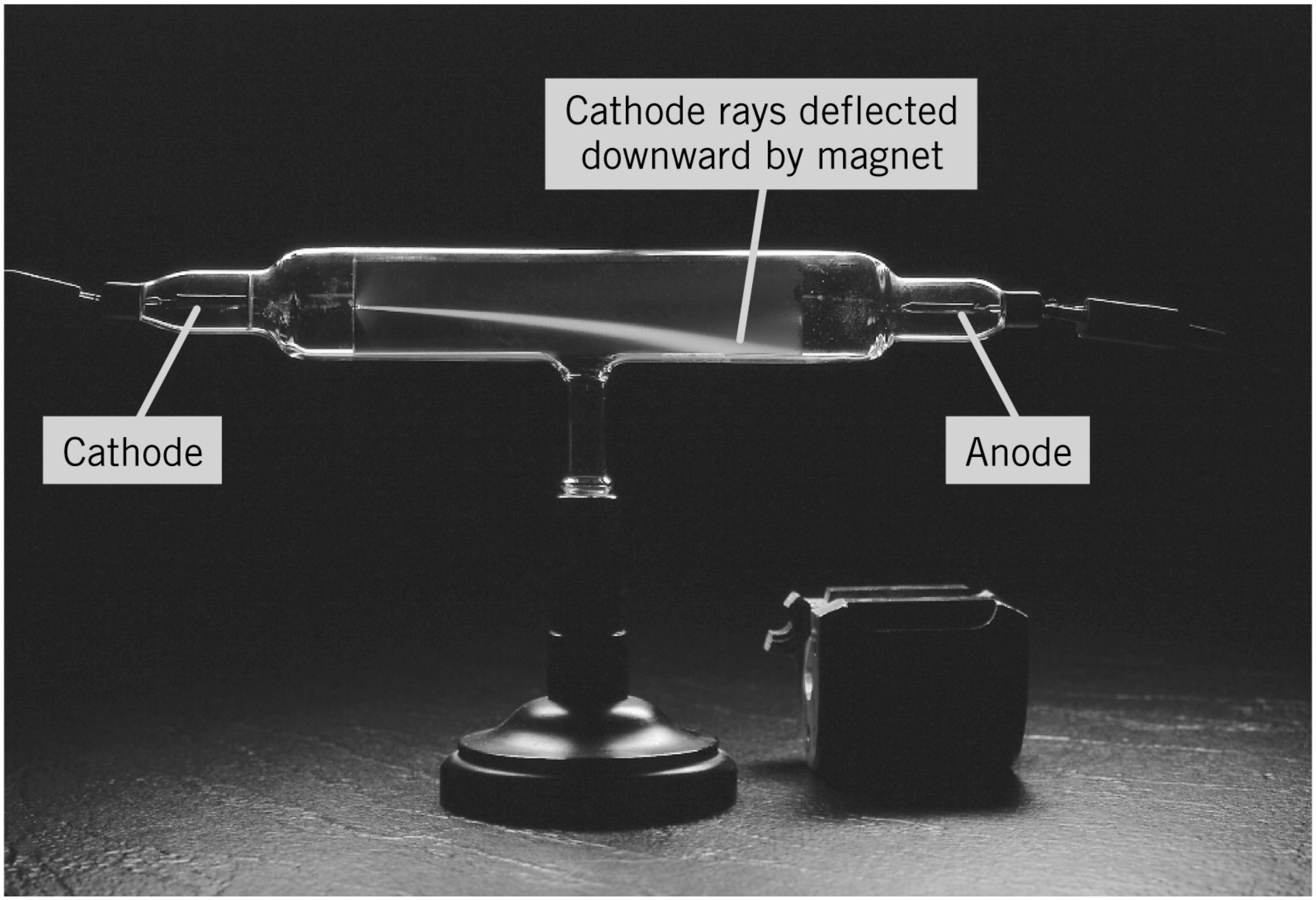
Early experiments

- William Crookes used an evacuated tube hooked up to a source of electricity (in 1879) and saw a fluorescent beam



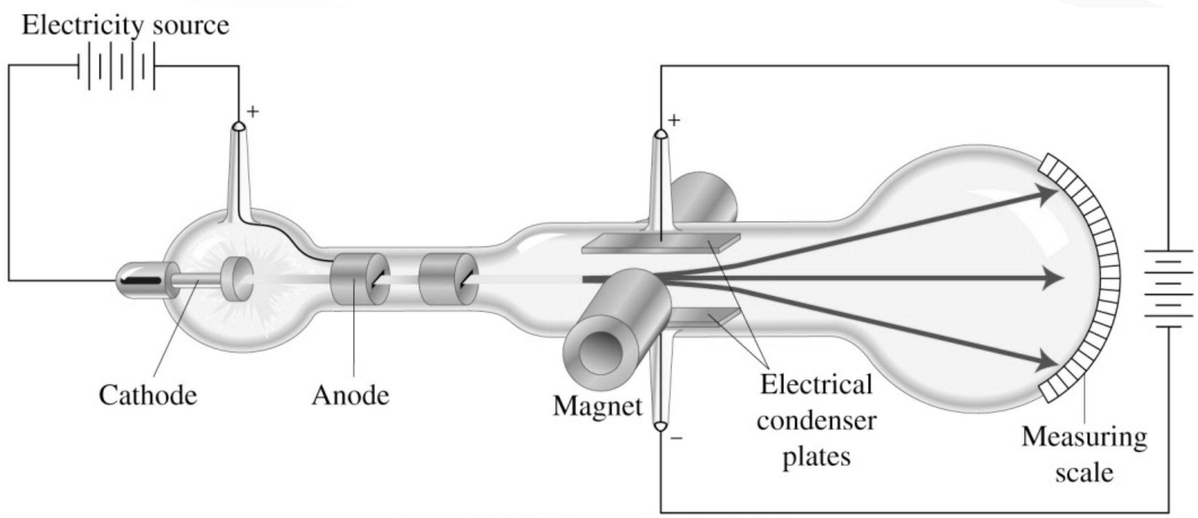
- JJ Thomson (in 1897) determined the particles causing this fluorescence were negatively charged, based on their behavior in the presence of a magnetic field
- Thomson found the fluorescence was independent of the identity of the residual gas in the tube....the particles must therefore be a property of all matter

Cathode rays



More on Thomson

- Thomson determined the mass to charge ratio ($m_e/e = -5.686 \times 10^{-12}$ kg/C) and decided (based on previous knowledge with H^+) he had one of three situations:
  - If the charge were similar to H^+, then mathematically the mass of the particle must be much less than that of H^+
  - If the mass were similar to H^+, then mathematically the charge must be much greater than that on H^+
  - Something in between the two extremes
- He suspected the first case to be true, but could not prove it



Explanations

- 1909 Millikan's oil drop experiment (next slide) showed that the rate of fall (velocity) of a charged oil drop could be varied in the presence of an electric field such that the charge could only in multiples of a fundamental unit ($e=-1.602 \times 10^{-19}$)
- Thomson knew the e^- had to be neutralized by + charges, but was unsure of the arrangement and devised the "raisin pudding" model (2 slides ahead)
- Ernest Rutherford (a student of Thomson's) studied *radioactivity*, a phenomenon of unstable heavy atoms giving off radiation during disintegration
- Rutherford bombarded metal foils with alpha particles (He^{2+})...most went through, but some were scattered at odd angles...not explained by the Thomson model of the atom...
- Can be explained with a *nuclear* model (three slides ahead)

Millikan’s oil drop experiment

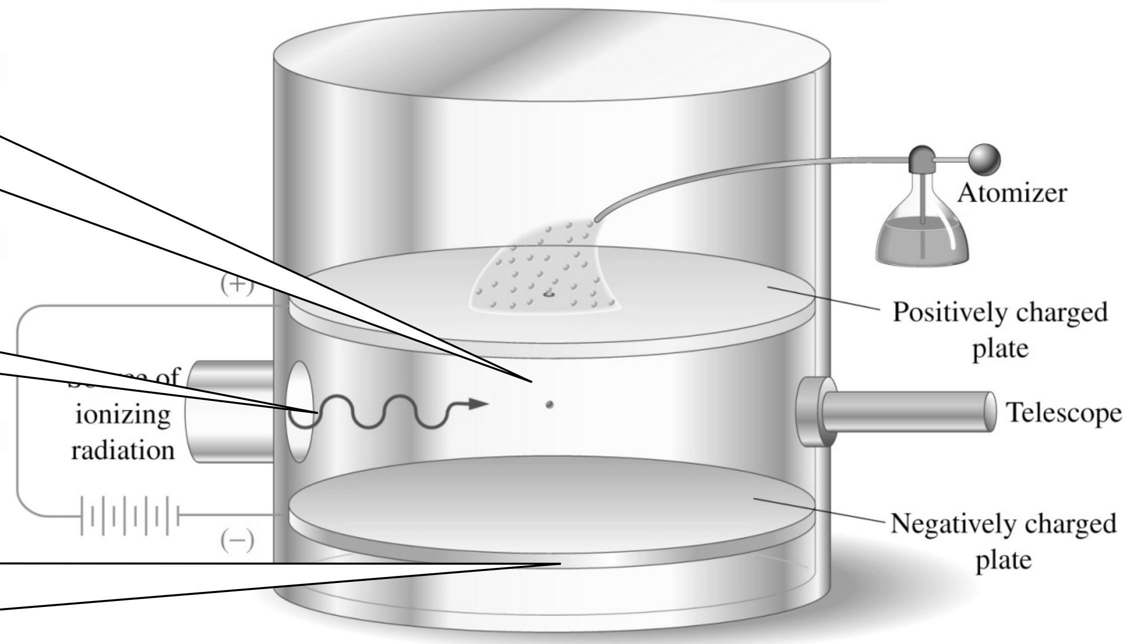
- George Stoney: names the cathode-ray particle the ***electron.***
- Robert Millikan: determines a value for the electron’s charge:

$$e = -1.602 \times 10^{-19}\ \text{C}$$

Charged droplet can move either up or down, depending on the charge on the plates.

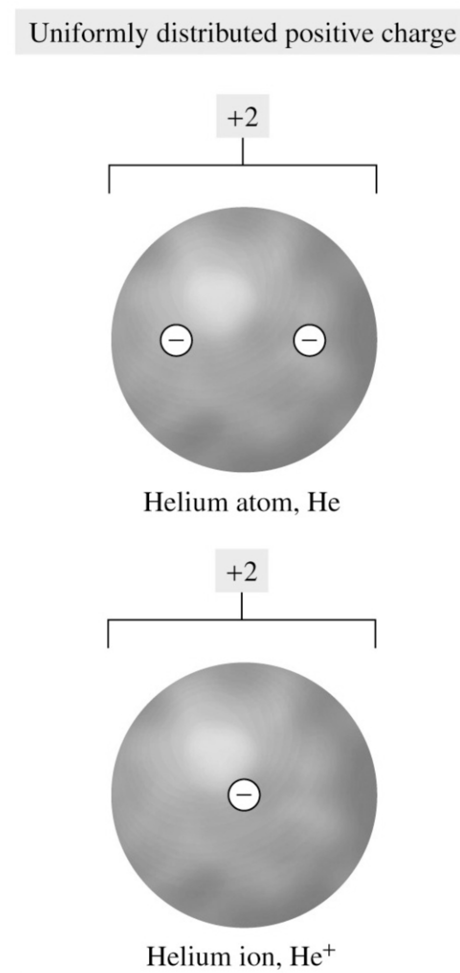
Radiation ionizes a droplet of oil.

Magnitude of charge on the plates lets us calculate the charge on the droplet.



J. J. Thomson's model of the atom

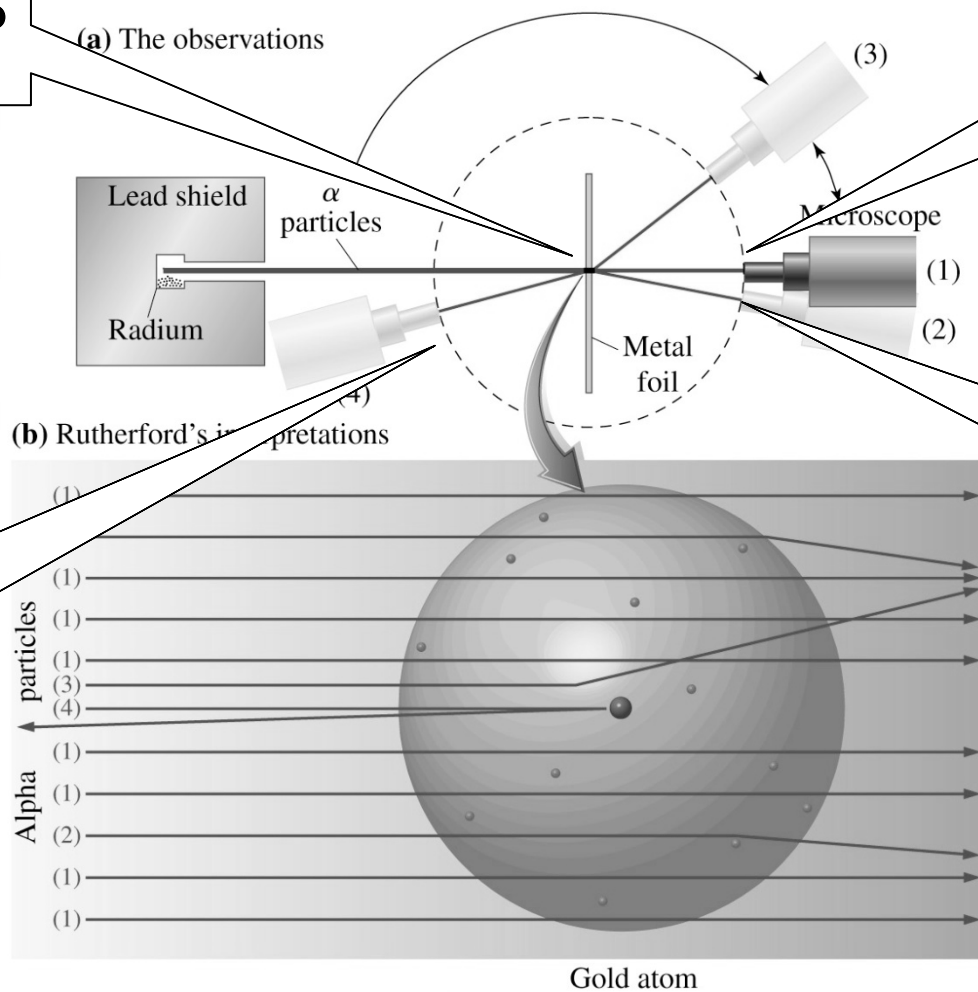
- Thomson proposed an atom with a positively charged sphere containing equally spaced electrons inside.
- He applied this model to atoms with up to 100 electrons.



Alpha scattering "gold foil expt": Rutherford's observations

Alpha particles were "shot" into thin metal foil.

Most of the alpha particles passed *through* the foil.



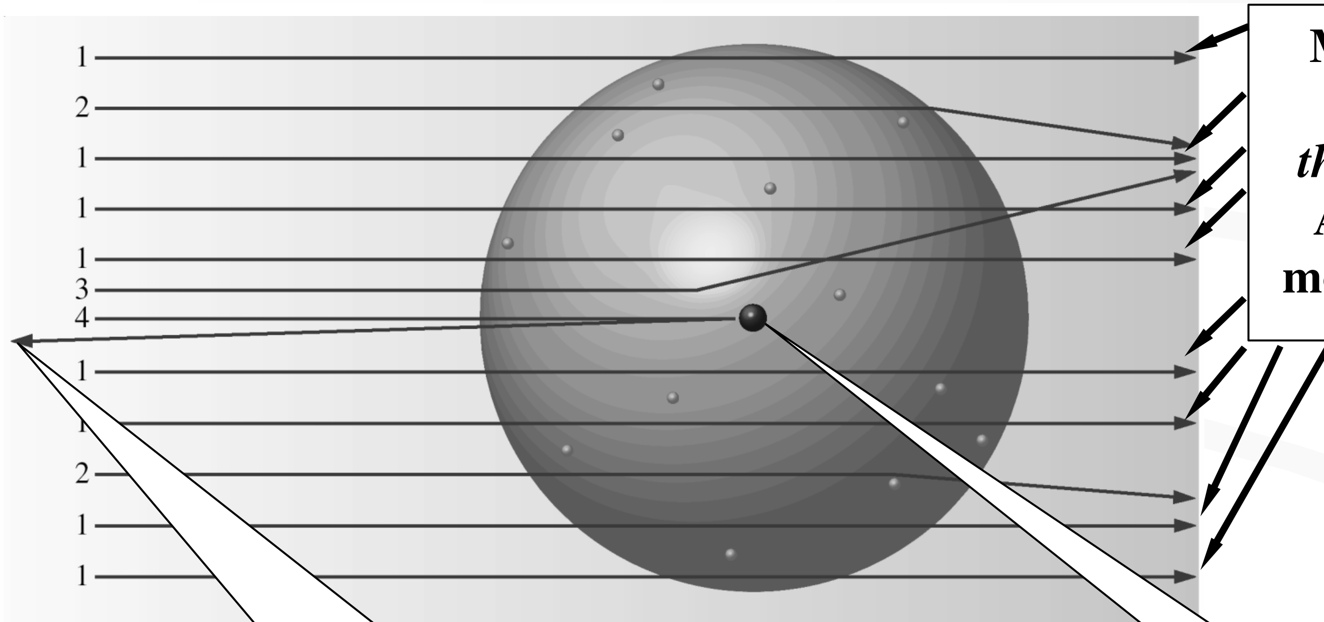
A few particles were *deflected slightly* by the foil.

A *very* few "bounced back" to the source!

Alpha scattering experiment:

Rutherford's conclusions

If Thomson's model of the atom was correct, most of the alpha particles should have been deflected a little, like bullets passing through a cardboard target.



Most of the alpha particles passed *through* the foil => An atom must be mostly empty space.

A *very* few alpha particles bounced back => The nucleus must be very small and dense.

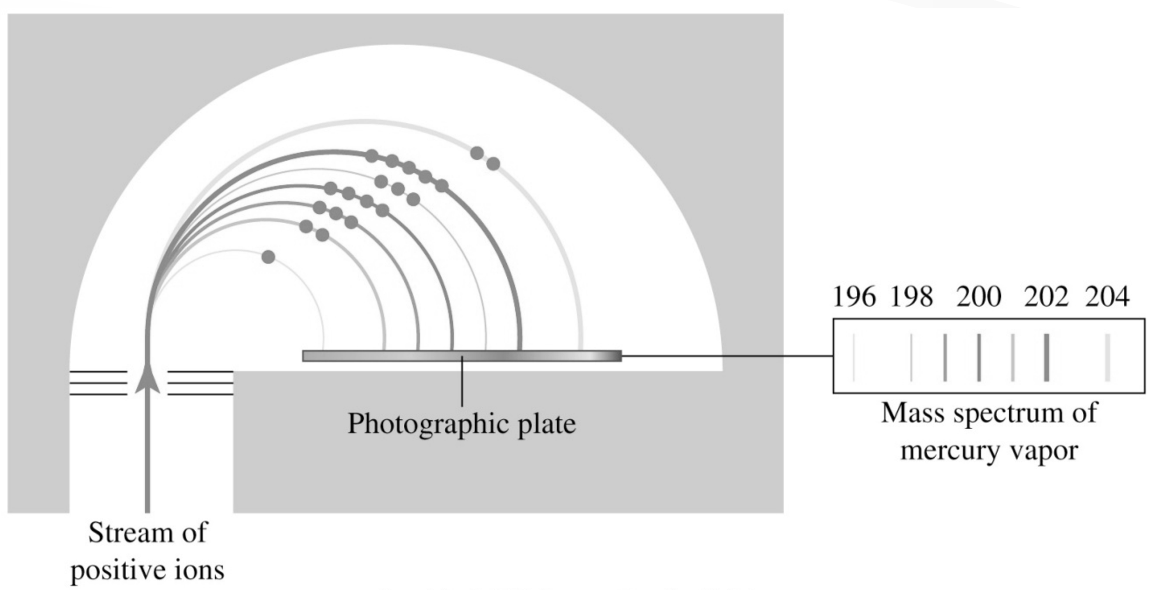
The nucleus is *far* smaller than is suggested here. (10^5)

Rearranging the periodic table

- Prior to 1914, atomic numbers were given out simply by arranging the elements in order of mass...
- Now that the number of protons and electrons could be determined and the mass of them calculated, there was some additional mass to be explained.
- A neutral particle was postulated, the existence of which was proven in **1932** by Chadwick

Proof

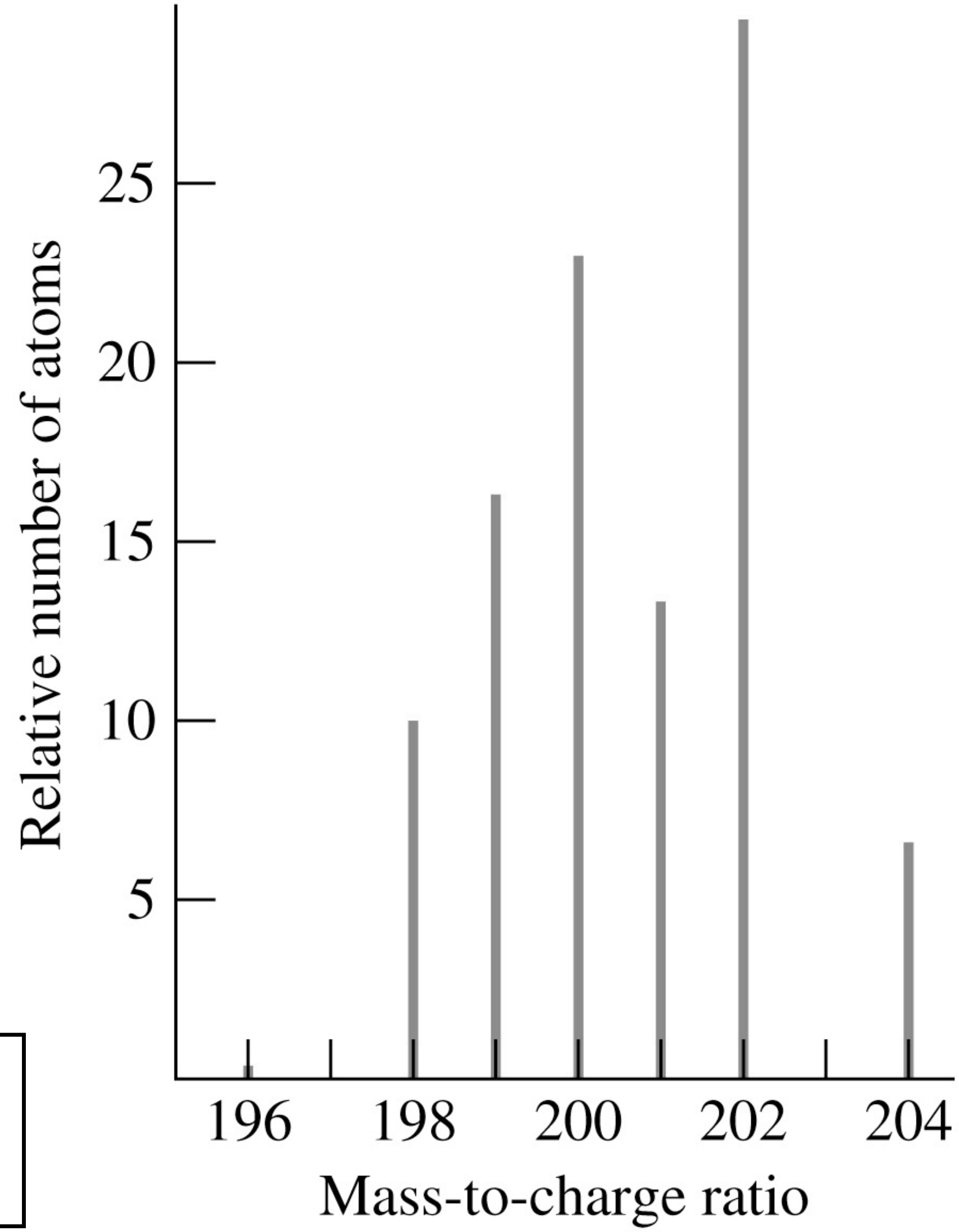
- A Crookes tube can also be constructed to detect positive ions drawn to the cathode (negative pole) or deflected away from the anode (positive pole).
- These experiments ARE matter dependent.
- A mass analyzer (mass spectrometer) is based on this concept.



A mass spectrum for mercury

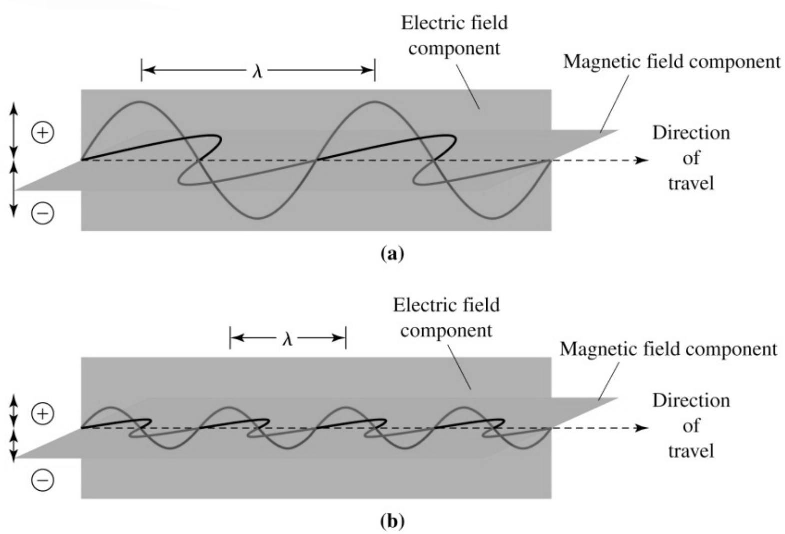
Mass spectrum of an *element* shows the abundance of its isotopes. What are the three most abundant isotopes of mercury?

Mass spectrum of a *compound* can give information about the structure of the compound.

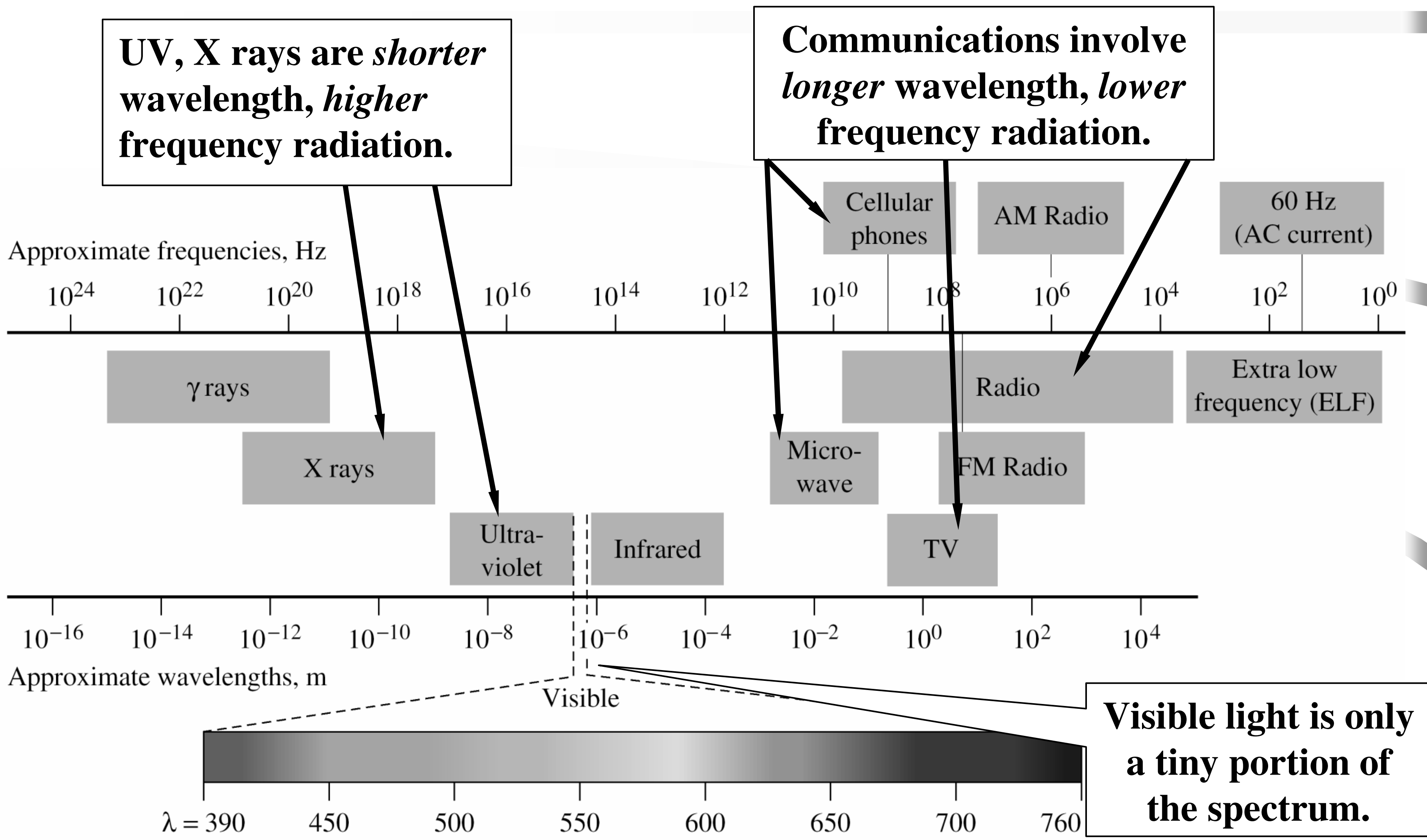


Electromagnetic (EM) radiation

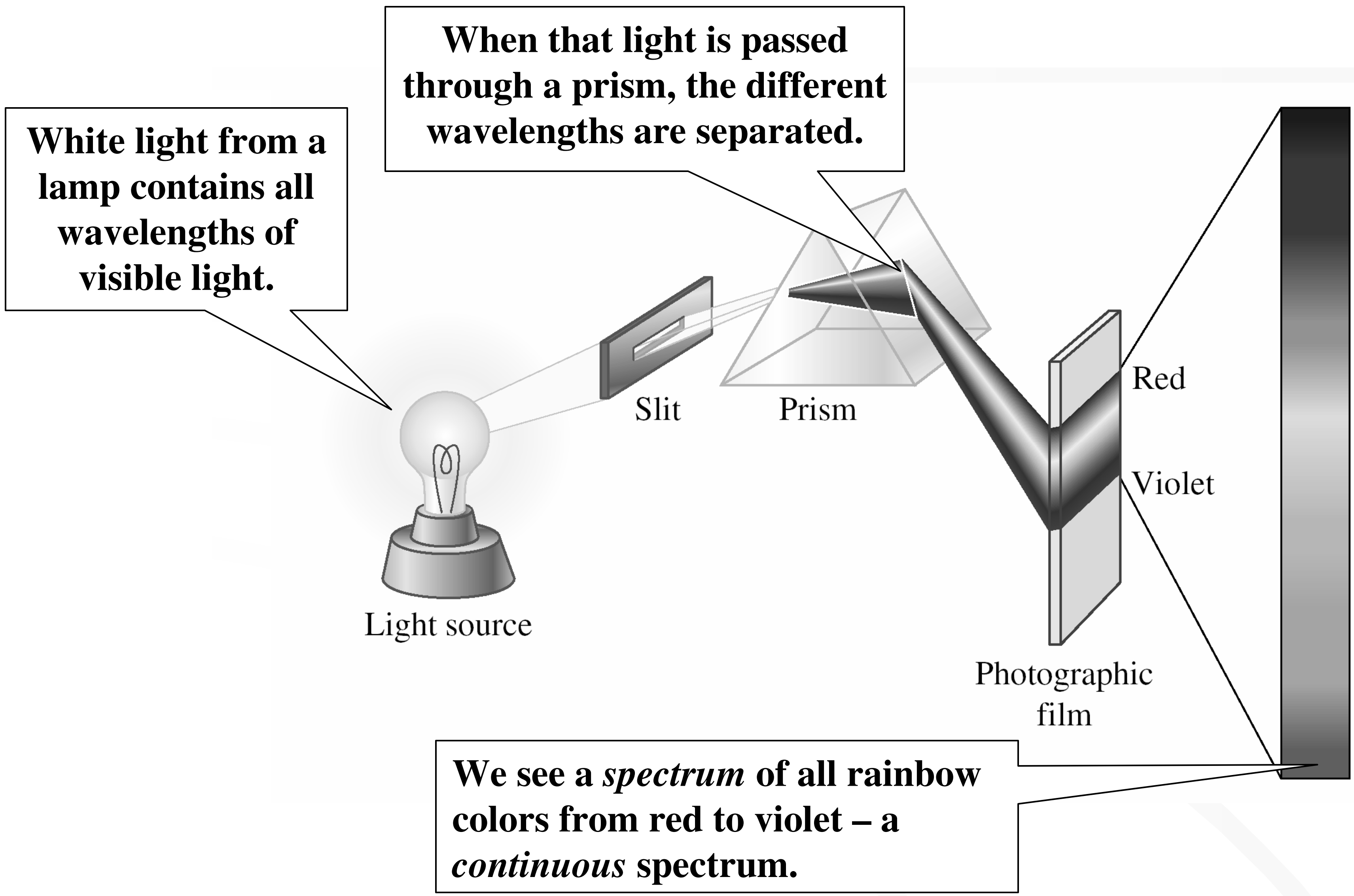
- Composed of perpendicular electric and magnetic field waves (something that repeats as it progresses through space)
- The region of the full spectrum which WE call light is only a small portion (next slide)
- Wavelength (λ) is the distance between equivalent wave points on adjacent peaks, expressed in meters



Electromagnetic (EM) radiation



A continuous *spectrum*

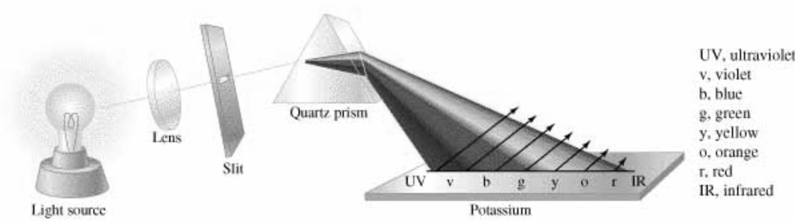


Frequency

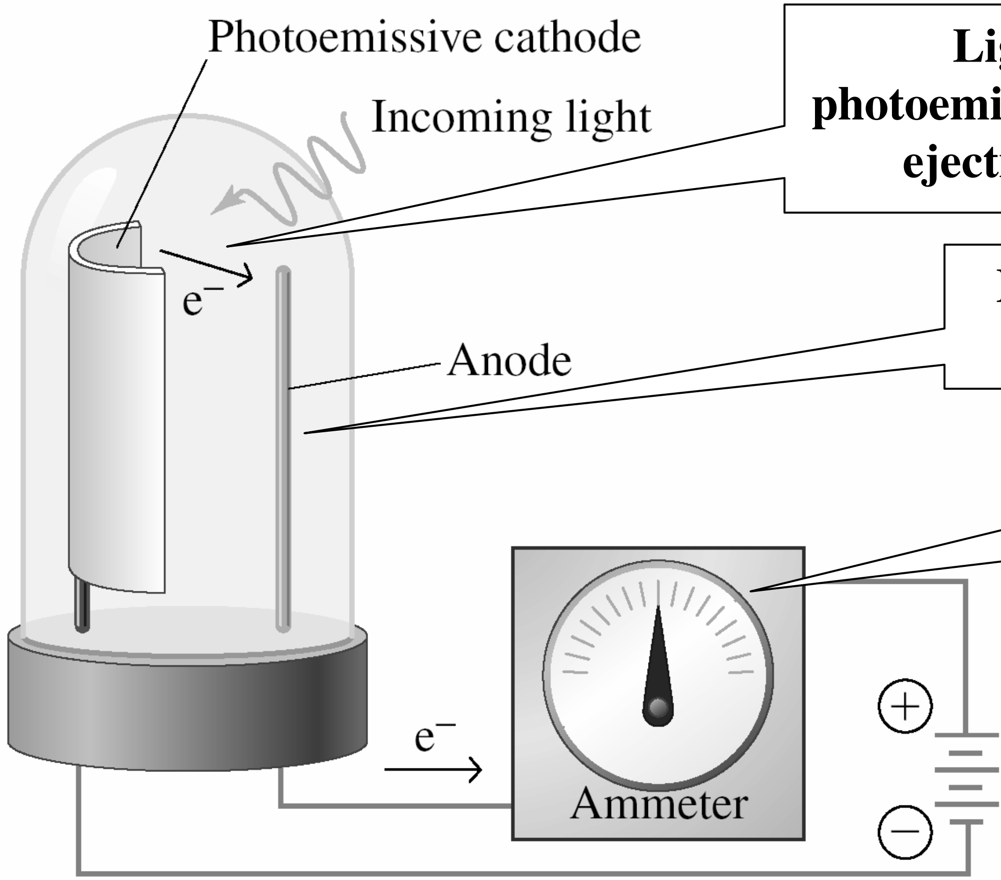
- Frequency (ν) is how many waves pass a fixed point per unit time, expressed in hertz (Hz, s-1)
- Frequency times wavelength = speed, c= 2.99792458 x 10^8 m/s (or just 3 x 10^8 m/s)
- In 1900, Max Planck explained the behavior of both high and low frequency radiation by equating energy with frequency and a constant, $E=h\nu$, where h is Planck's constant = 6.626 x 10^{-34} (think how small this number is)
- Planck's equation demonstrates that light comes only in discrete "packets" called quanta (singular = "quantum")

Einstein

- In 1905, Einstein used Planck's theories to explain how electrons can result from bombarding a sample with light...
- This plus the observation of line spectra when elements were heated lead to...



The photoelectric effect



(a)

Light striking a photoemissive cathode causes ejection of electrons.

Ejected electrons reach the anode, and the result is …

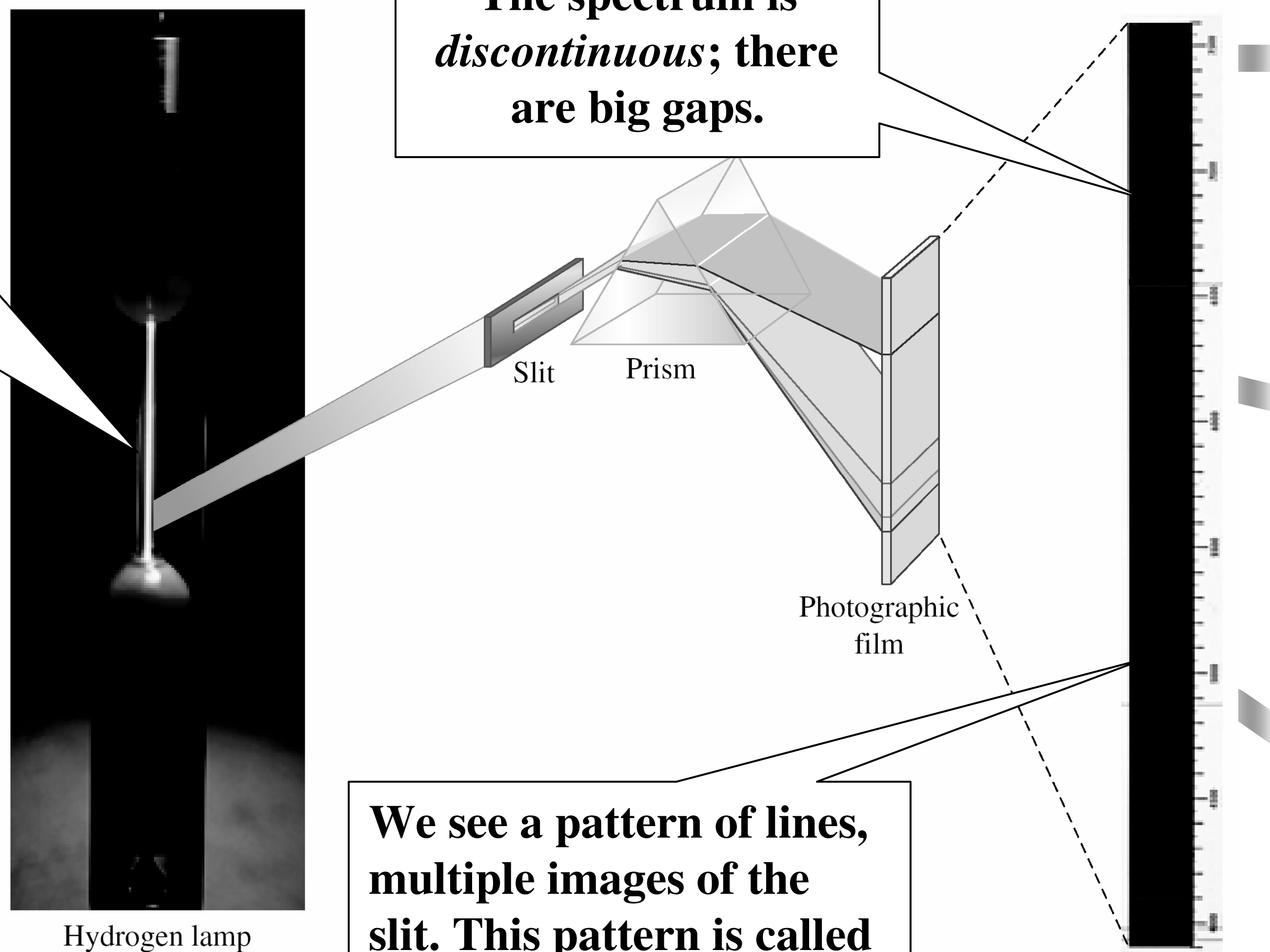
… current flow through an external circuit.

But not "any old" light will cause ejection of electrons …

A line *spectrum*

Light from an electrical discharge through a gaseous element (e.g., neon light, hydrogen lamp) does *not* contain all wavelengths.

The spectrum is *discontinuous*; there are big gaps.



We see a pattern of lines, multiple images of the slit. This pattern is called a *line spectrum*. (duh!)

The Bohr model of the atom

- Combined classical physics and quantum theory
- Different energy levels of electrons correspond to orbits of different distances from the nuclei of atoms
- The lowest energy level (that nearest the nucleus) is level 1, the next is level 2, and so on
- The electron energy levels $E_n = -B/n^2$, where n is the energy level (an integer) and B is a constant related to Planck's and the mass and charge of an electron (negative energy for an attractive force)

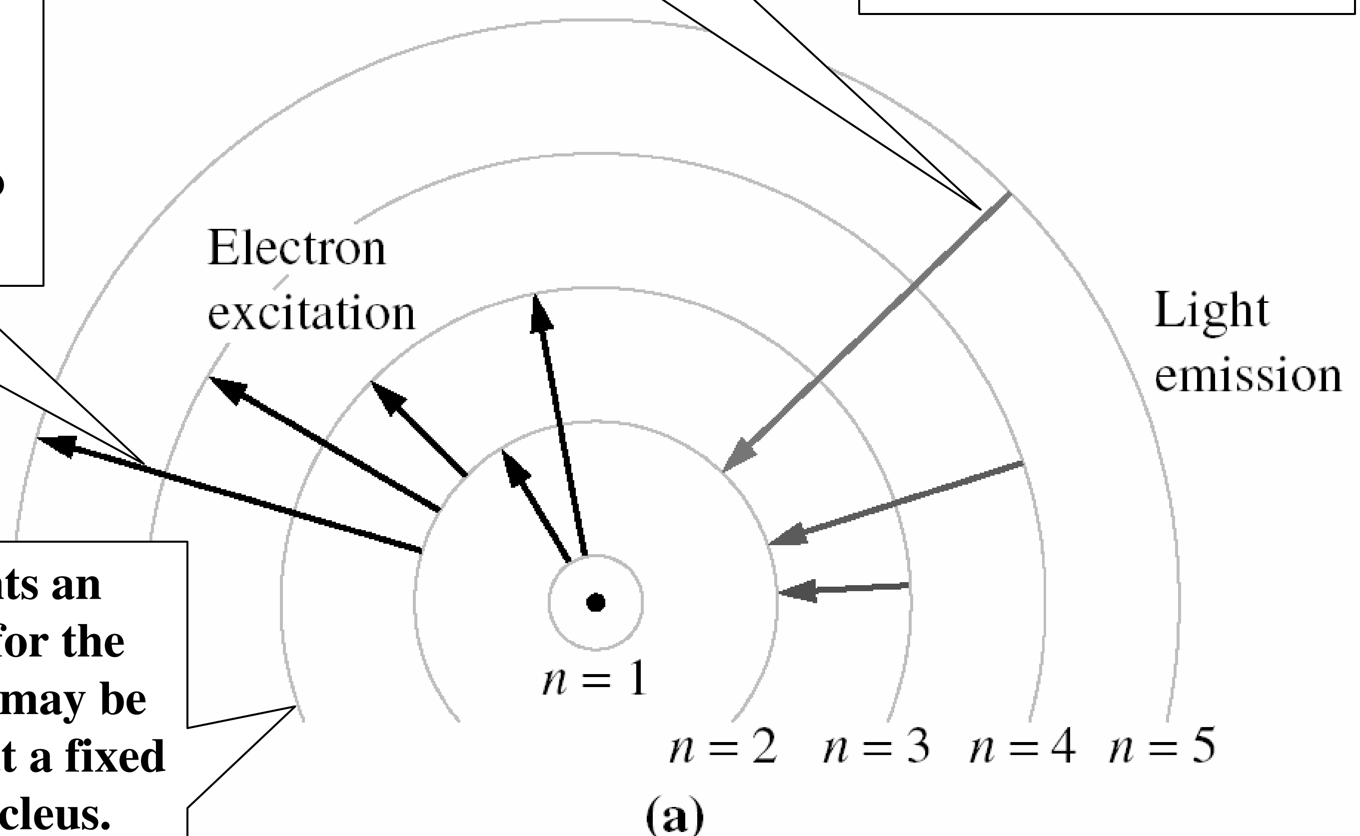
The Bohr model of hydrogen

When excited, the electron is in a *higher* energy level.

Emission: The atom gives off energy—as a photon.

Upon emission, the electron drops to a *lower* energy level.

Excitation: The atom absorbs energy that is exactly equal to the *difference* between two energy levels.



Each circle represents an allowed energy level for the electron. The electron may be thought of as orbiting at a fixed distance from the nucleus.

Experimental

- Bohr then explained line spectra as being due to the energy difference between 2 levels

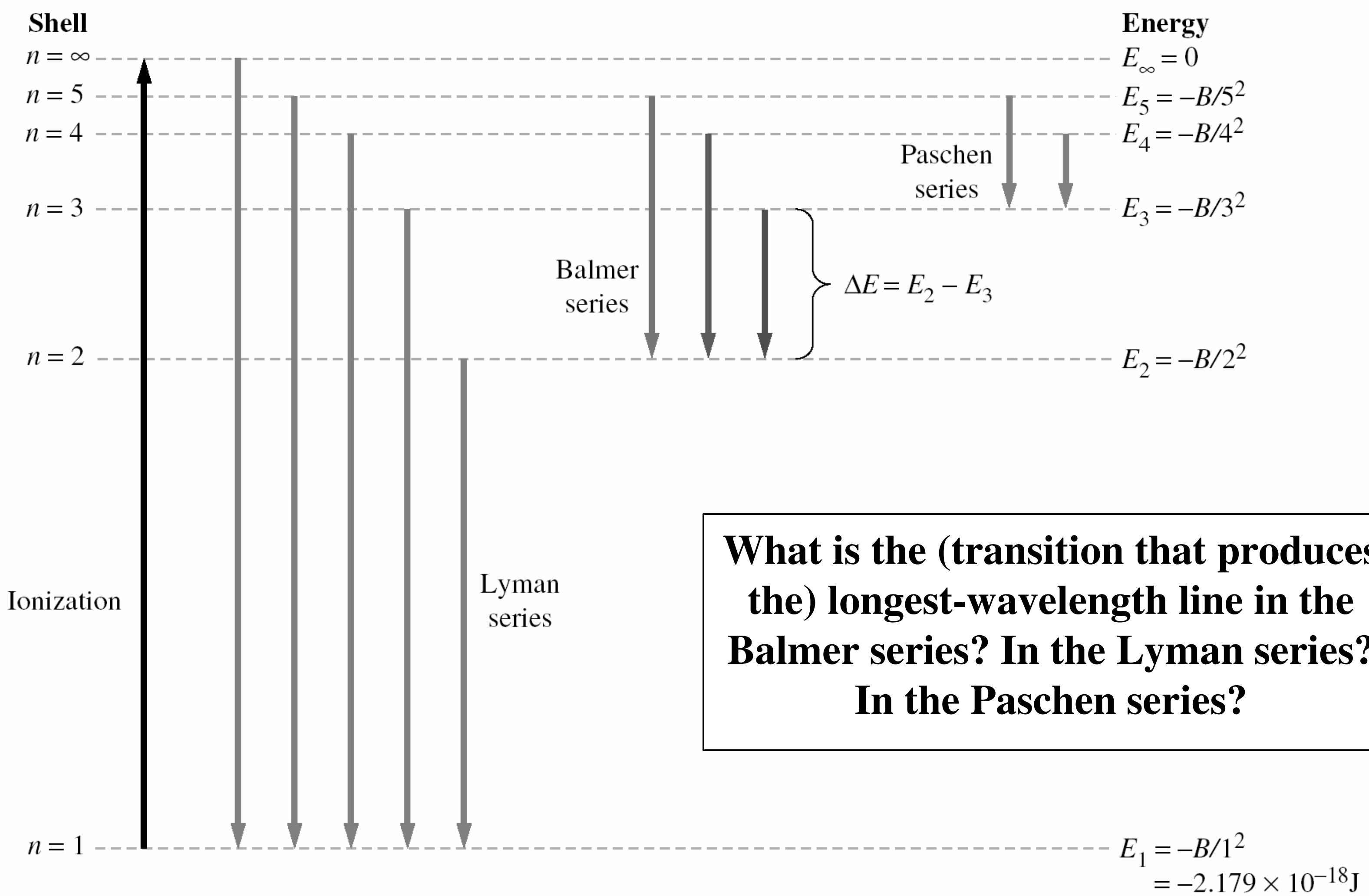
$$E_f = \frac{-B}{n_f^2} \quad and \quad E_i = \frac{-B}{n_i^2} \quad so \quad \Delta E = B\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

- (That should be n_i-n_f)

Atoms

- When an atom has all its electrons in their lowest possible energy levels, the atom is in its GROUND STATE
- If energy has been supplied sufficient to promote an electron to a higher level, the atom is in an EXCITED STATE

Energy levels and spectral lines for hydrogen



What is the (transition that produces the) longest-wavelength line in the Balmer series? In the Lyman series? In the Paschen series?

Wave-particle duality

- If light can act like particles of matter, can particles act like waves?
- According to DeBroglie's theories, yes!

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

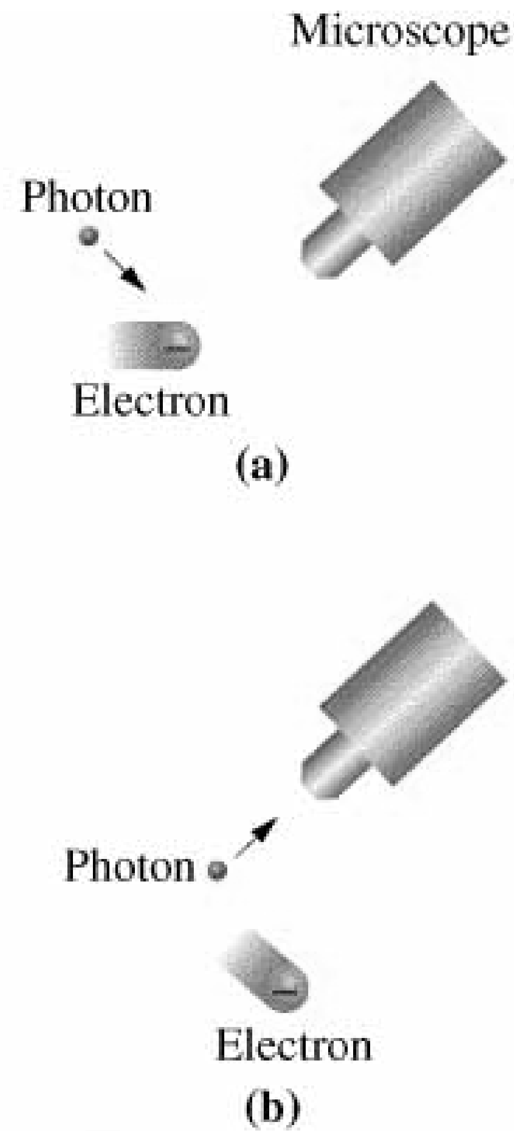
Particles as waves

- The Bohr model is mostly classical, but if the particles are treated as waves, *quantum* or *wave mechanics* are needed
- In 1926 Erwin Schrodinger developed a mathematical equation to describe the hydrogen atom (a *wave equation*, the solution to which is called a *wave function*
- According to Max Born, the square of the wave function (ψ^2) gives the probability of finding an electron in a particular volume of space in an atom

Particles as waves (cont'd)

- According to Werner Heisenberg, in fact, we *cannot* know both the *exact* position and motion of a tiny particle like an electron *simultaneously*... think of it this way- the act of measuring its position changes its motion, and vice versa

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$



Quantum numbers

- Integral value parameters from the wave function of the hydrogen atom...
- A set of these three wave function quantum numbers (there is a fourth) is called an *atomic orbital*, a mathematical expression which allows us to visualize a 3D region in an atom where there is a significant *probability* of finding an electron

Quantum numbers: n

The ***principal quantum number (n)***:

- Is independent of the other two quantum numbers.
- Can only be a positive integer (n = 1, 2, 3, 4, …)
- The ***size*** of an orbital and its electron energy depend on the value of n.
- Orbitals with the same value of n are said to be in the same ***principal shell***.

Quantum numbers: 1

The ***orbital angular momentum quantum number (l)***:

- Determines the ***shape*** of the orbital.
- Can have positive integer values from 0,1,2…(*n* – 1)
- Orbitals having the same values of *n* and of *l* are said to be in the same ***subshell***.

Value of *l*	0	1	2	3
Subshell	*s*	*p*	*d*	*f*

- Each orbital designation represents a different region of space and a different shape.

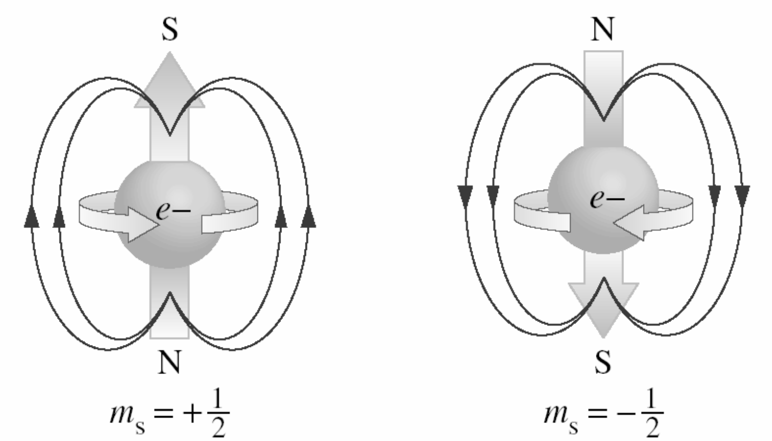
Quantum numbers: m_l

The ***magnetic quantum number (m_l)***:

- Determines the ***orientation*** in space of the orbitals of any given type in a subshell.
- Can be any integer from $-l$ to $+l$
- The number of possible values for m_l is $(2l + 1)$, and this determines the number of orbitals in a subshell.

Electron spin: m_s

- The ***electron spin quantum number (m_s)*** explains some of the finer features of atomic emission spectra.
- The number can have two values: +½ and –½.



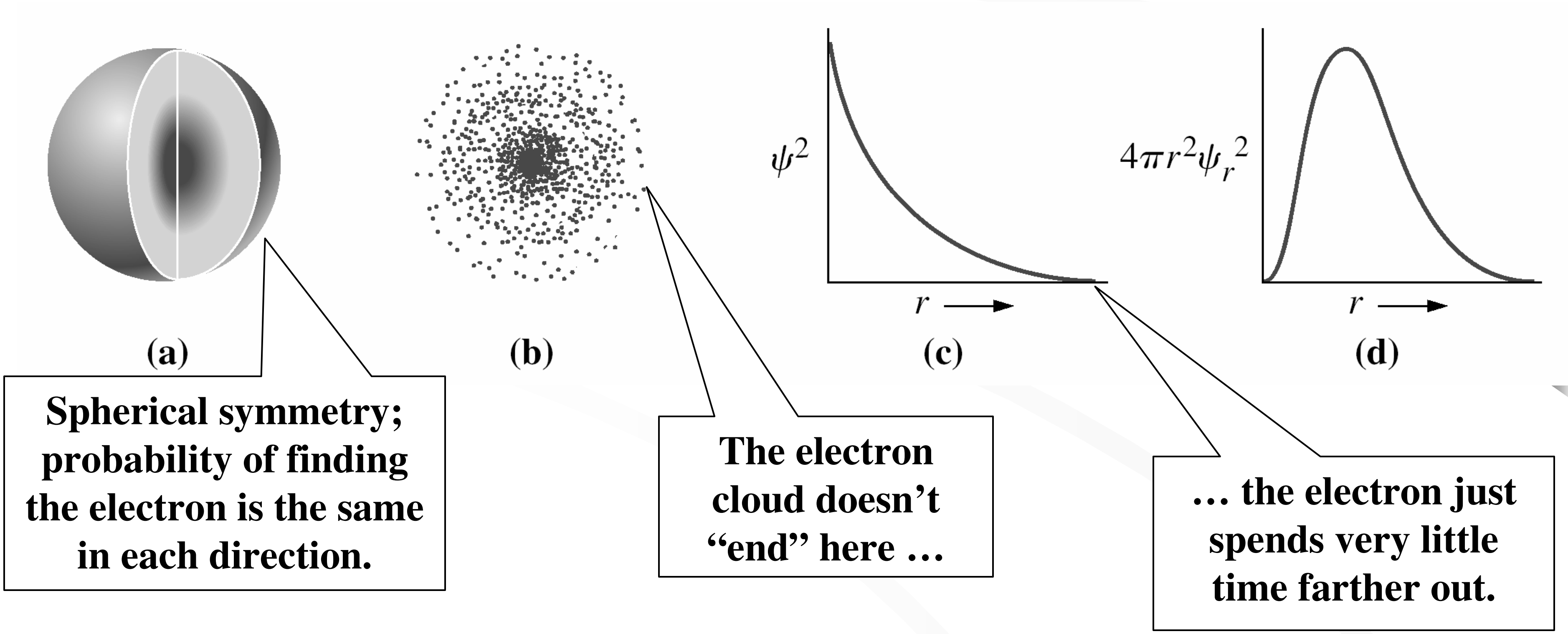
- The spin refers to a magnetic field induced by the moving electric charge of the electron as it spins.
- The magnetic fields of two electrons with opposite spins cancel one another; there is no net magnetic field for the pair.

Quantum numbers (summary)

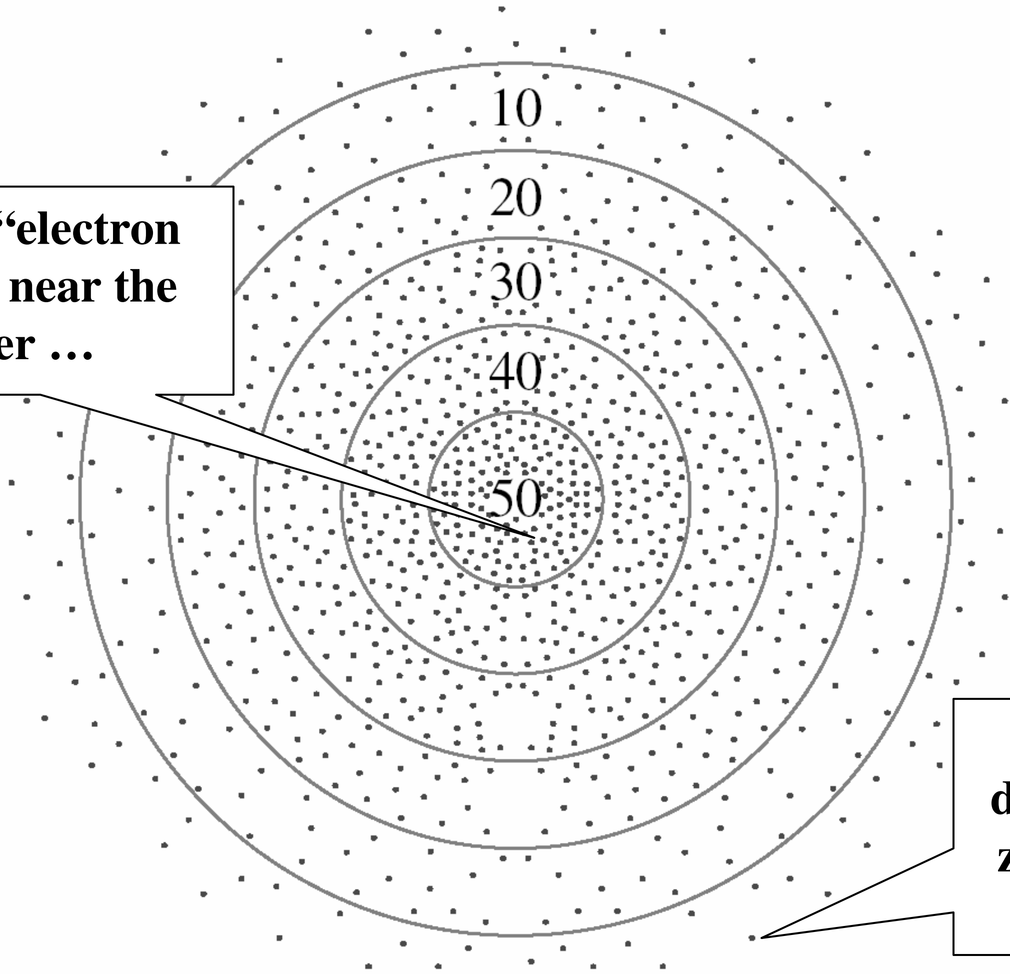
- Principal quantum number (n)
  - energy level
  - 1,2,3,4,5,....
- Orbital angular momentum (azimuthal) quantum number (l)
  - shape
  - 0,1,2,3,...(n-1) (s,p,d,f)
- Magnetic quantum number (m_l)
  - direction
  - 0, +/-1, +/-2,...+/-l
- Spin quantum number (m_s)
  - + ½, - ½

The 1s orbital

- The 1*s* orbital ($n = 1$, $l = 0$, $m_l = 0$) has *spherical* symmetry.
- An electron in this orbital spends most of its time near the nucleus.



Analogy to the 1s orbital

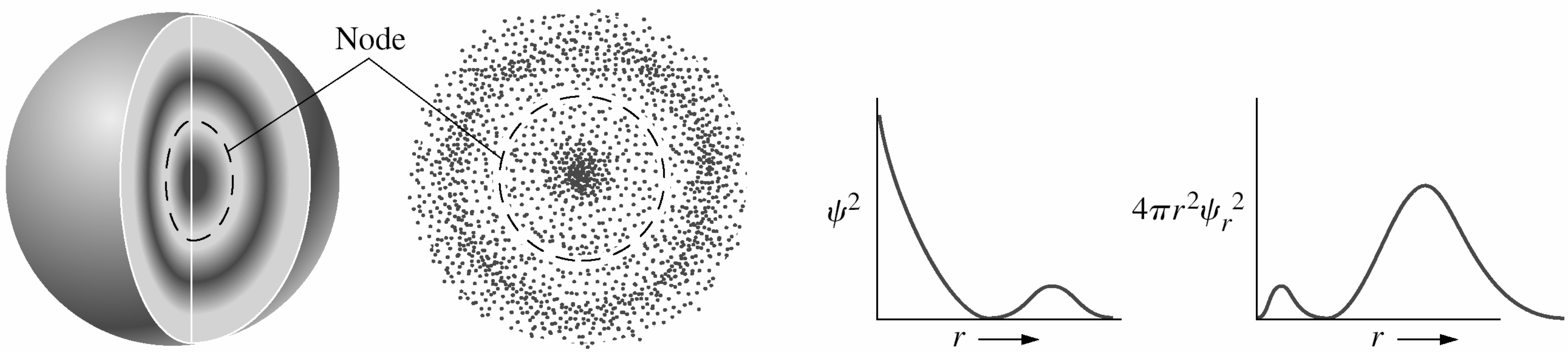


Highest "electron density" near the center …

… but the electron density never drops to zero; it just decreases with distance.

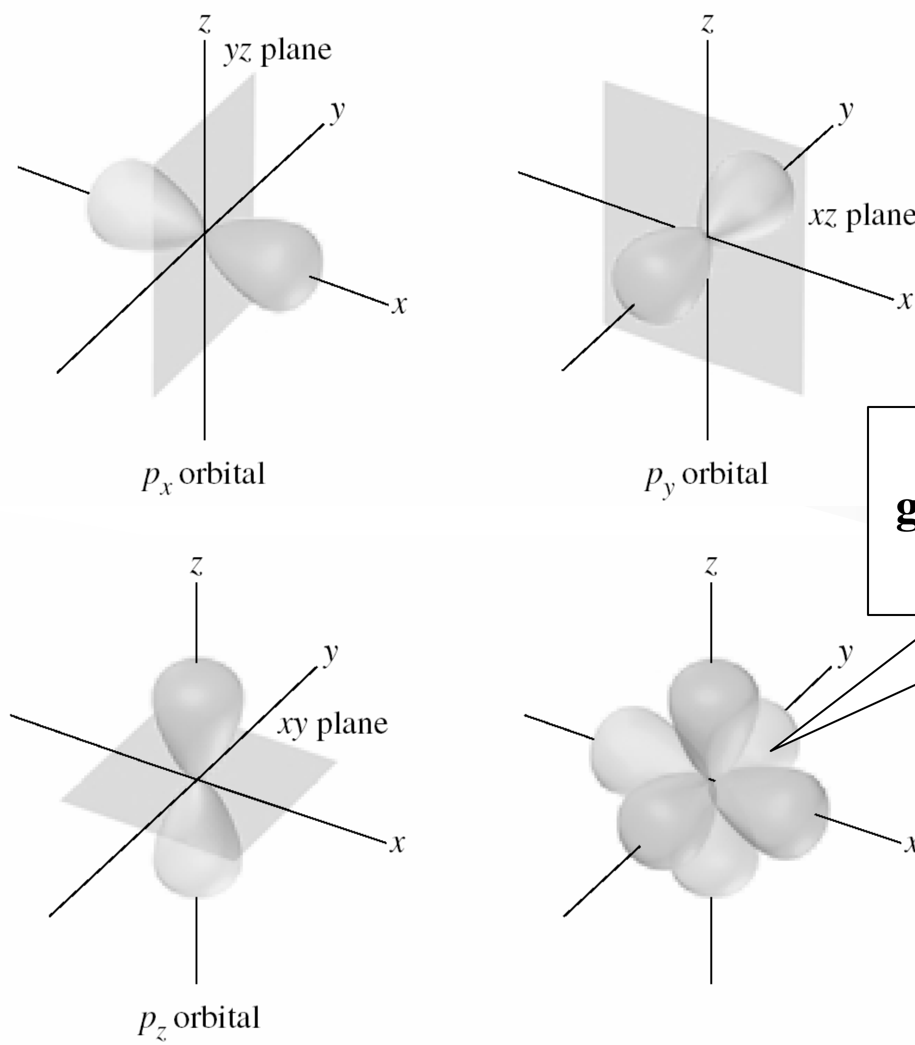
The 2s orbital

- The 2*s* orbital has two concentric, spherical regions of high electron probability.
- The region near the nucleus is separated from the outer region by a ***node***—a region (a spherical shell in this case) in which the electron probability is zero.



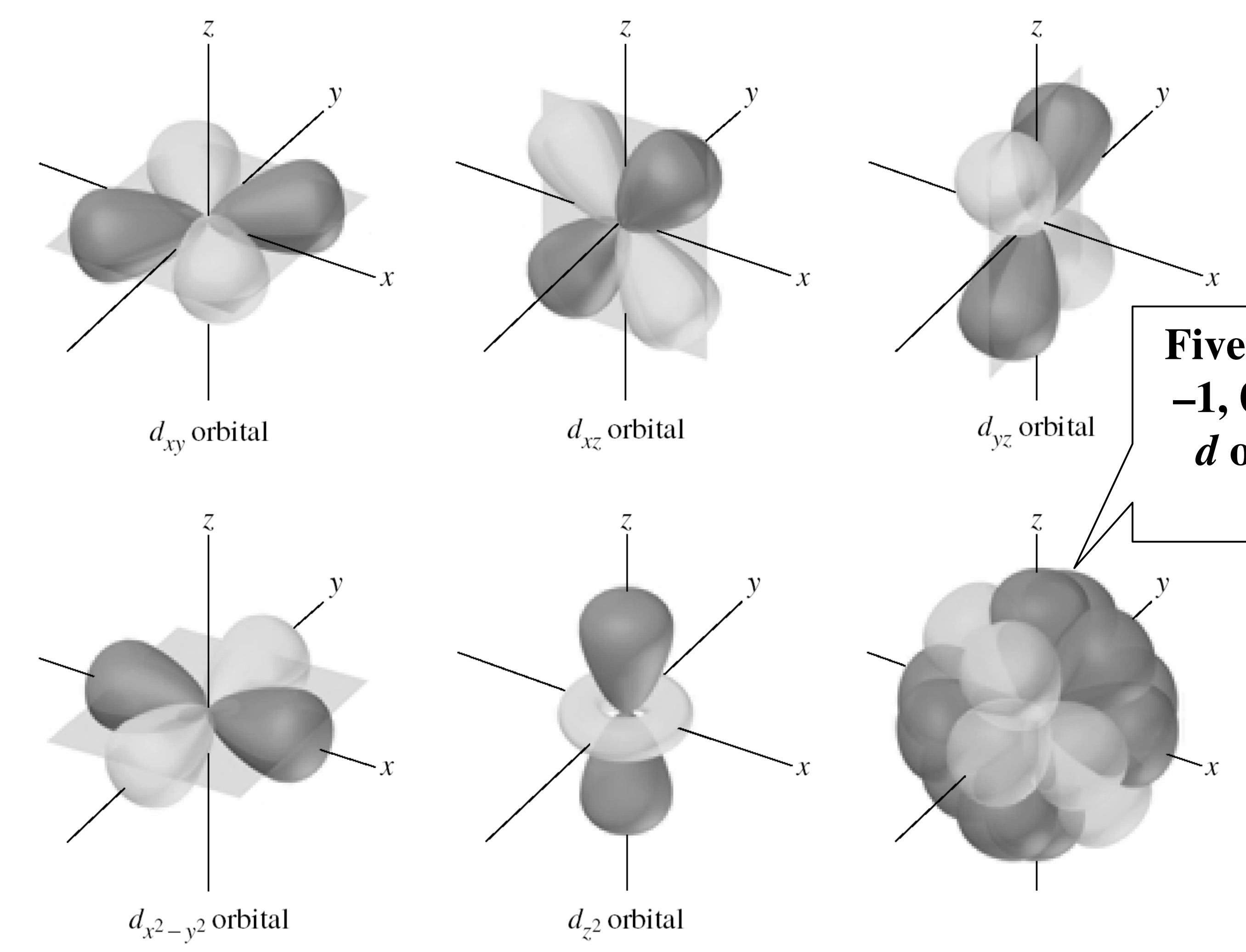
(a) (b) (c) (d)

The three p *orbitals*



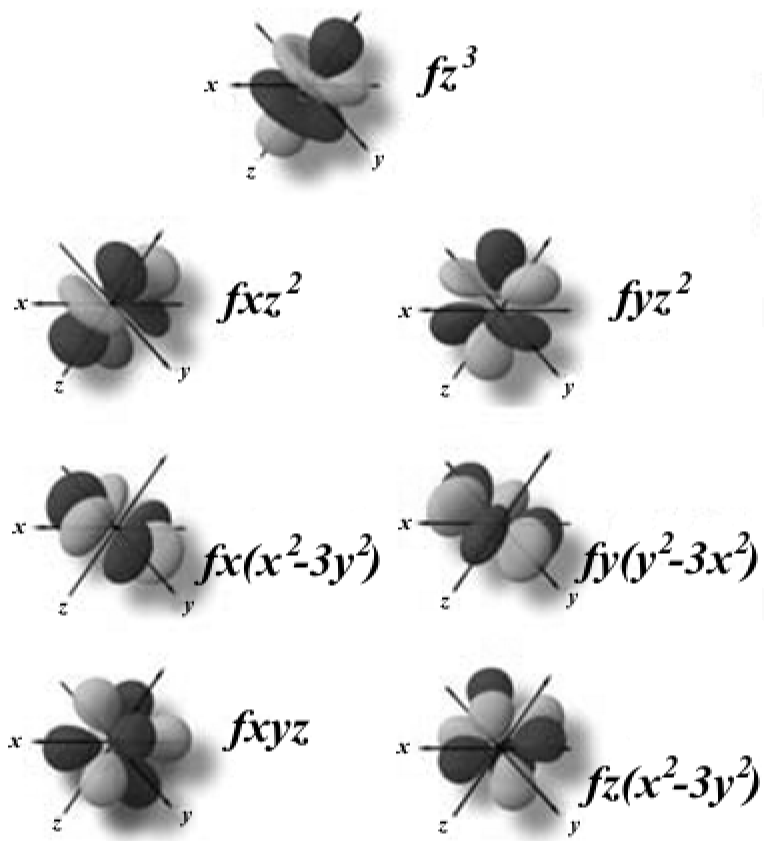
Three values of m_l gives three *p* orbitals in the *p* subshell.

The five d *orbitals*



Five values of m_l (–2, –1, 0, 1, 2) gives five *d* orbitals in the *d* subshell.

The seven f *orbitals*



Seven values of m_l (-3, -2, -1, 0, 1, 2, 3) gives seven *f* orbitals in the *f* subshell.