CHAPTER 16:
Quantum Mechanics and the Hydrogen Atom

- Waves and Light
- Paradoxes in Classical Physics
- Planck, Einstein, and Bohr
- Waves, Particles, and the Schrödinger equation
- The Hydrogen Atom

Questions

- What is quantum mechanics?
- When do we need it?
- What does it do?
- How does it apply to the H atom?

Quantum Mechanics (QM)

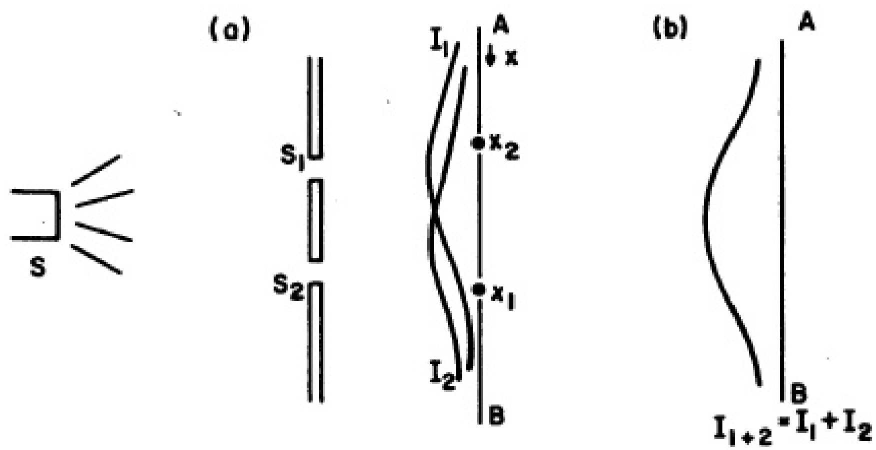
Quantum mechanics is…

- The set of rules obeyed by small systems (molecules, atoms, and subatomic particles)
- One of the two greatest achievements of 20^{th} century physics
- The basis for new research into smaller electronic devices (e.g., quantum dots)
- Required to understand chemistry

The two-slit experiment

- Fire very small particles at a barrier with two tiny slits in it… expect a result like this:

Figure 3.2. (a) Intensity pattern when S_1 or S_2 is open, due to a beam of incident particles. (b) The pattern with both slits open according to classical mechanics ($I_{1+2} = I_1 + I_2$).



R. Shankar, Principles of Quantum Mechanics

The two-slit experiment

- For very small particles, actually get something more like this…

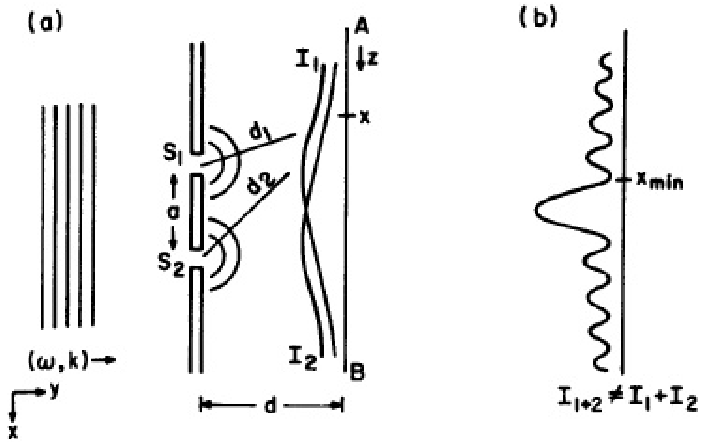
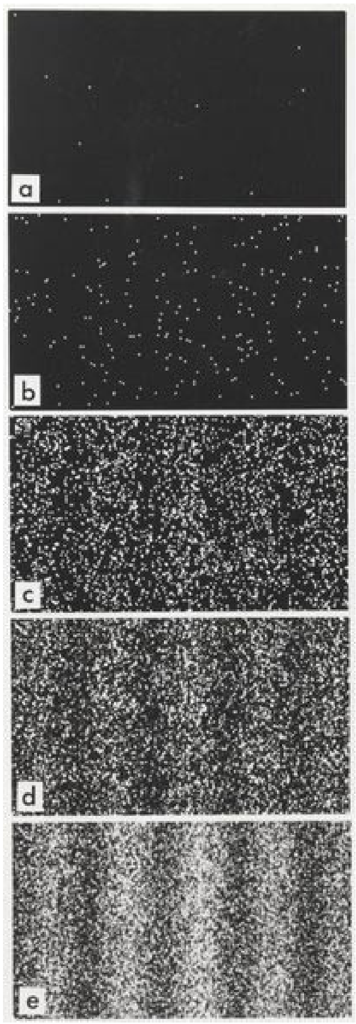


Figure 3.1. (a) When a wave $\psi = e^{i(ky-\omega t)}$ is incident on the screen with *either* slit S_1 or S_2 open, the intensity patterns I_1 and I_2, respectively, are measured by the row of detectors on AB. (b) With both slits open, the pattern I_{1+2} is observed. Note that $I_{1+2} \neq I_1 + I_2$. This is called interference.

R. Shankar, Principles of Quantum Mechanics

An interference pattern! Wavelike properties!

Actual experiment with electrons



Results of a double-slit experiment sending one electron through at a time. Numbers of electrons are
(a) 10, (b) 200, (c) 6000, (d) 40000
(e) 140000

Strange: the wave-like interference pattern happens even when we send through only one electron at a time!!!

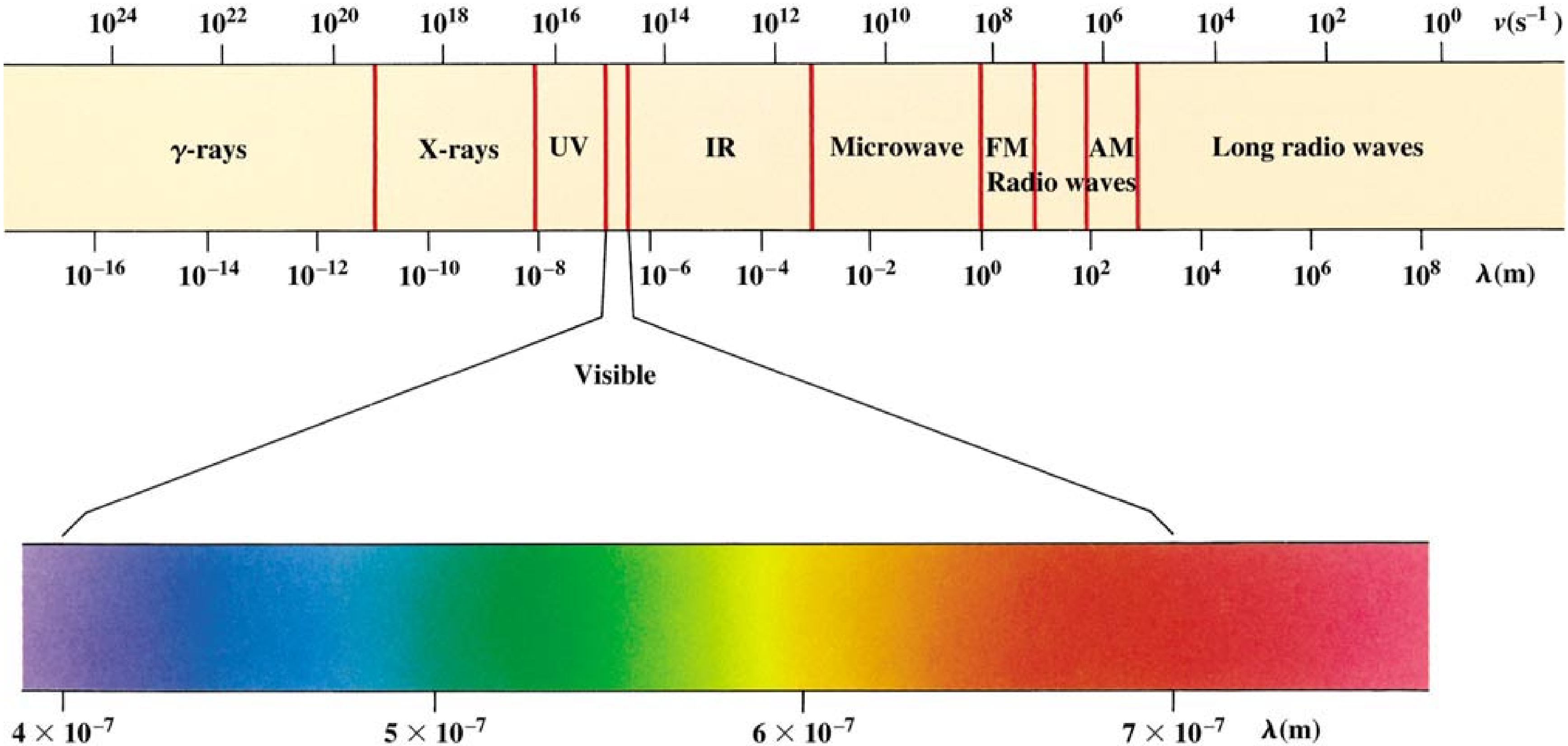
Even stranger…

- If we watch to see which slit a particle goes through, the interference pattern disappears and we see the “expected” pattern! The experiment changes depending on how we observe it!
- Richard Feynman (Nobel Prize in Physics, 1965): “I think it is safe to say that no one understands quantum mechanics. Do not keep saying to yourself, if you can possibly avoid it, 'but how can it be like that?' … Nobody knows how it can be like that." (The Character of Physical Law, 1965, p.129).

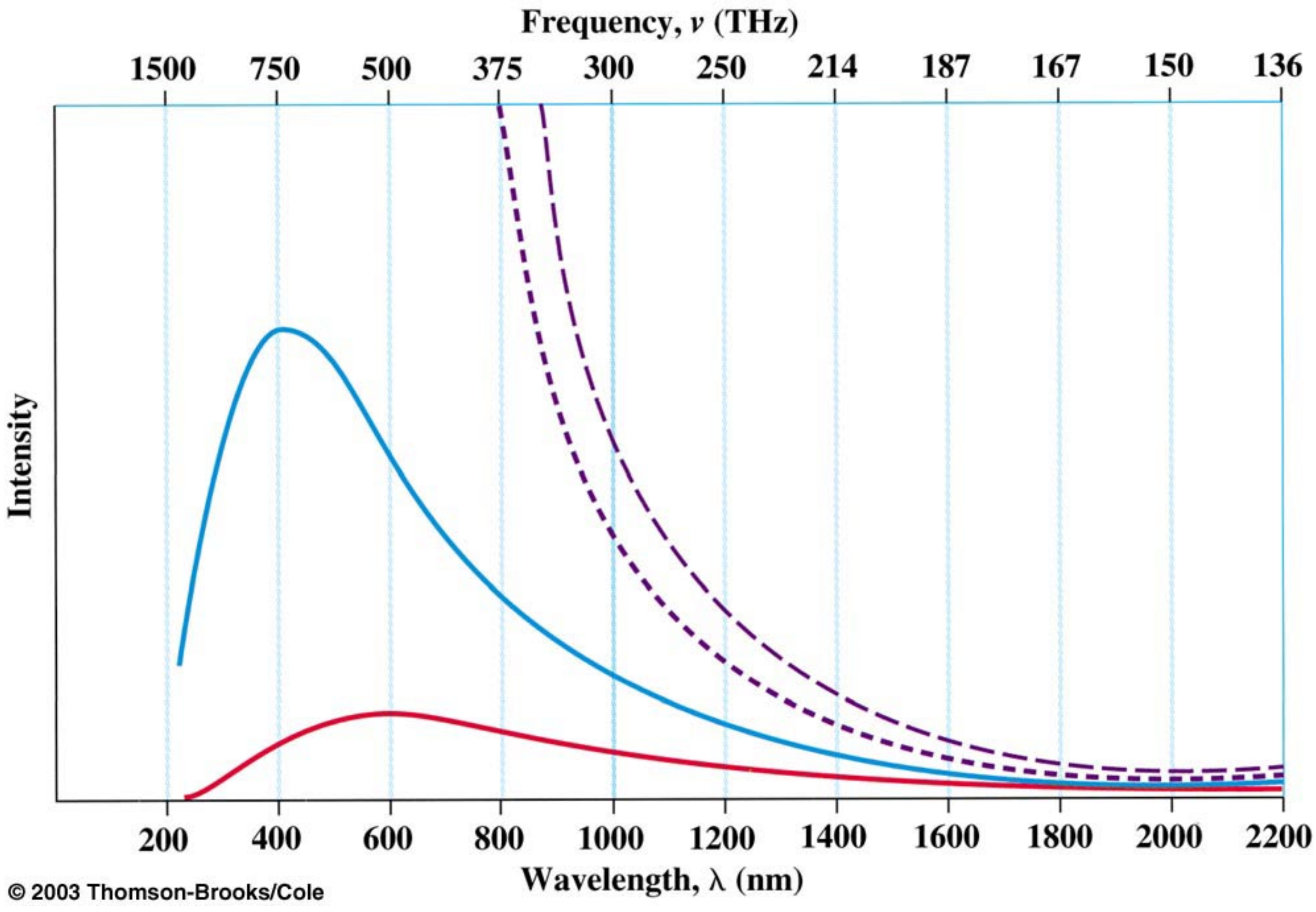
QM: Historical Background

- Near the end of the 19th century, physicists thought they knew everything
- Several key experiments showed something really unknown was going on
- QM developed to explain these unusual experiments in early 1900’s (~1900-1930’s)
- Developed around same time as theory of relativity

Electromagnetic spectrum



“Ultraviolet catastrophe”



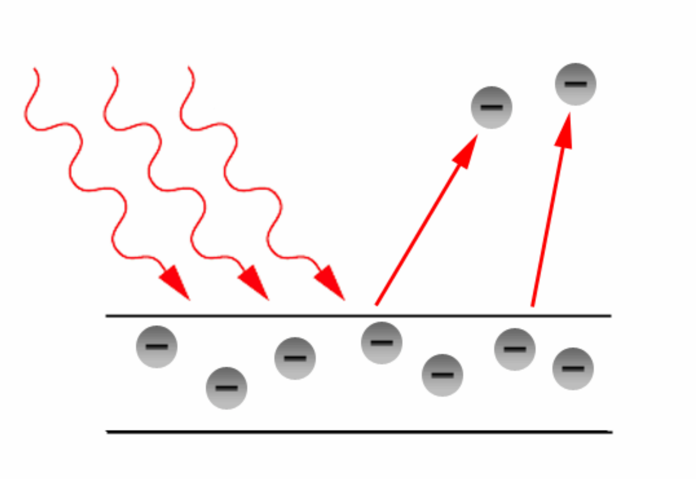
Planck to the rescue

- In 1900, Planck postulated that the blackbody is made of tiny oscillators with energies proportional to the frequency of oscillation, $E = n h \nu$, where h is a constant (Planck's constant, 6.626E-34 J s)
- The equation means not just any energies are allowed. Only certain values are allowed. *Energy is quantized*.
- Using this hypothesis, blackbody radiation curves can be predicted accurately

Max Planck

Nobel Prize in Physics, 1918

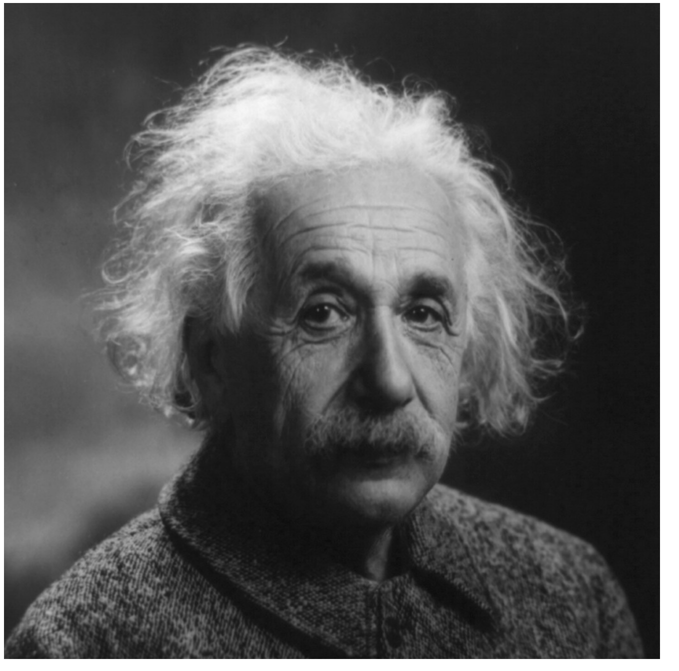
The Photoelectric Effect



- Light can cause electrons to be ejected from a metal surface
- Would expect electrons to be ejected with greater KE if greater light intensity
- Problem: KE of electrons does not depend on intensity, but does depend on frequency ν

Einstein to the rescue

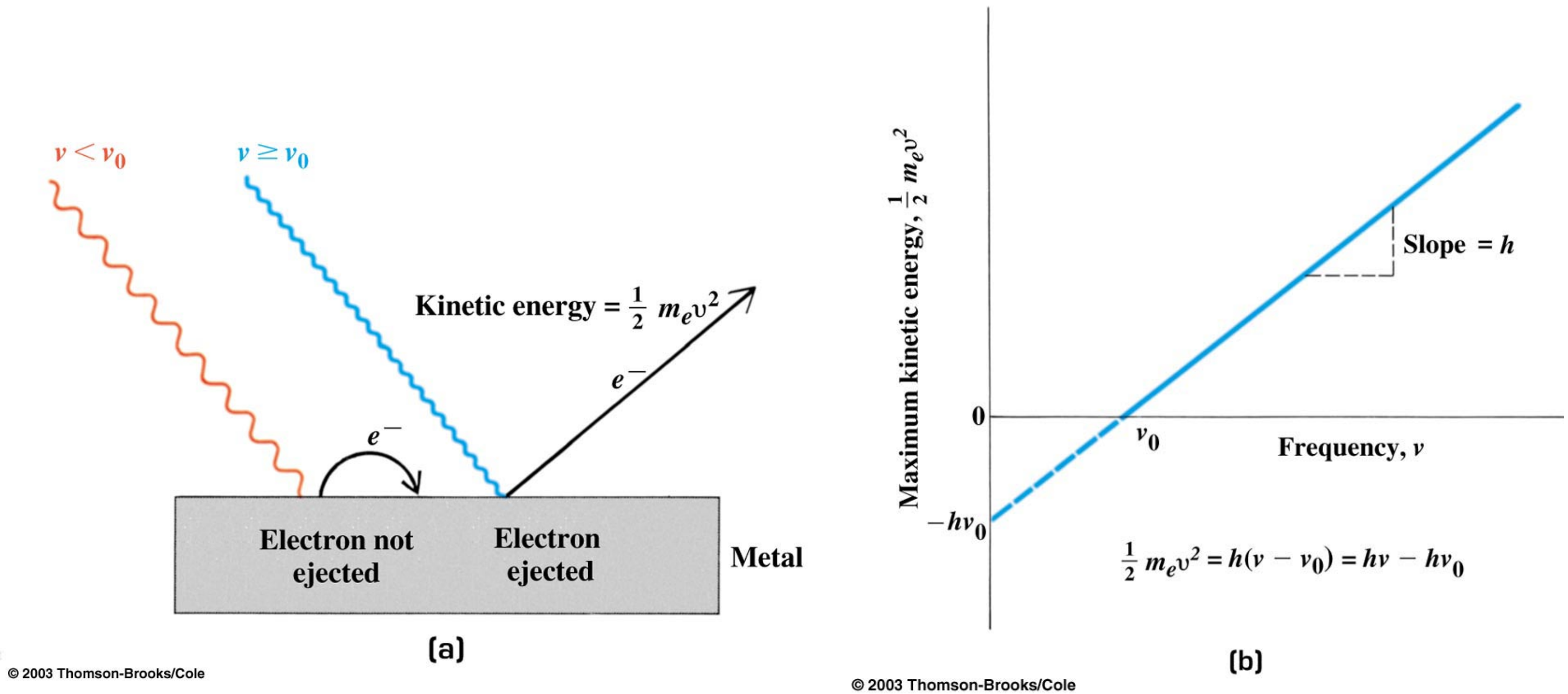
- Borrowed Planck's "quantum" idea --- maybe *light* might have quantized energy levels, too!
- Light comes in "packets" of energy $E = h\nu$, called "photons"
- Explains the photoelectric effect --- higher ν, more energy in each light packet (photon), kicks out electron with more KE



Albert Einstein

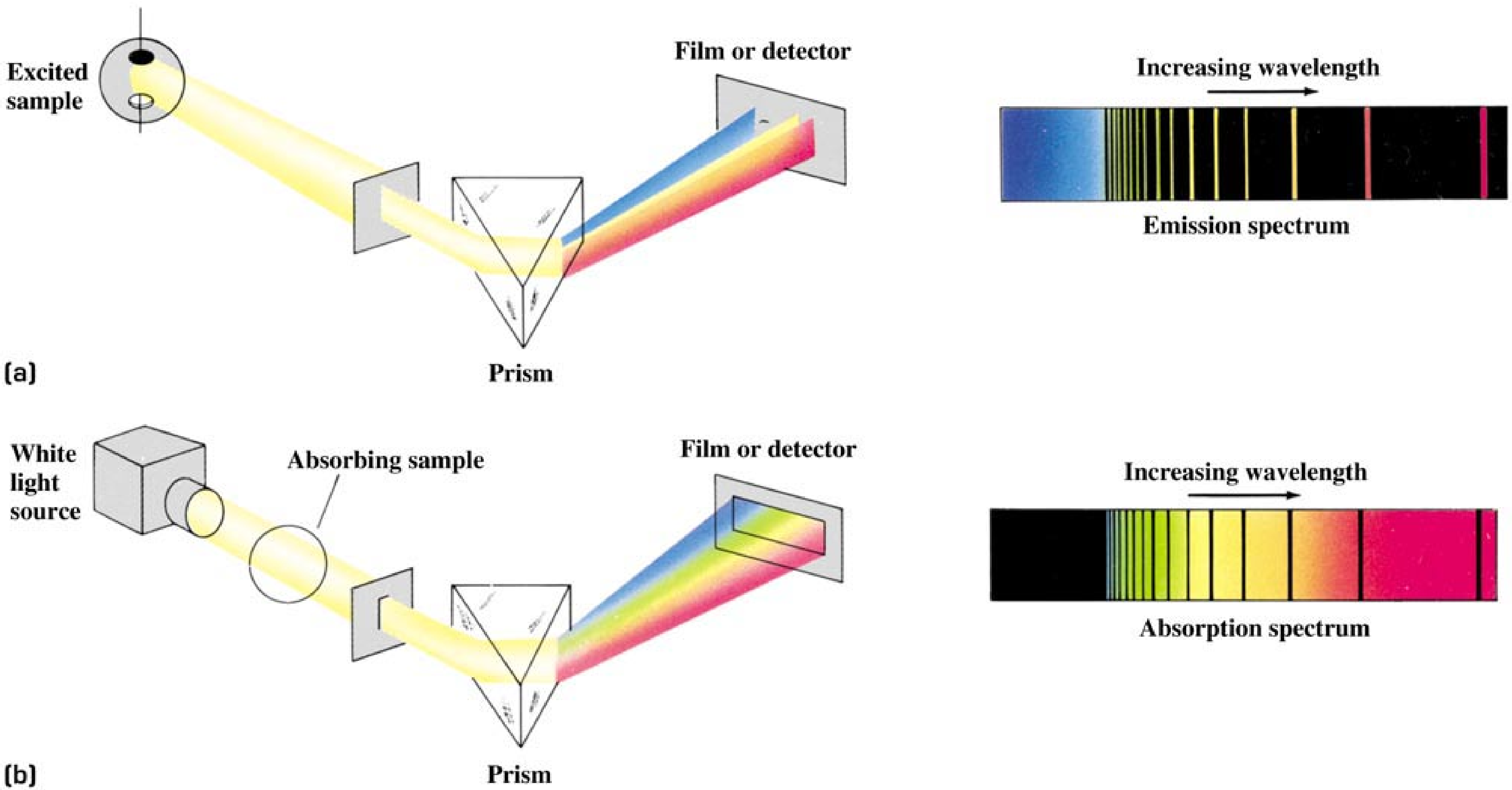
Nobel Prize in Physics, 1905, for explaining the Photoelectric Effect

Photoelectric effect explained



Minimum energy to remove an electron is $h\nu_0$, the "work function" of the metal

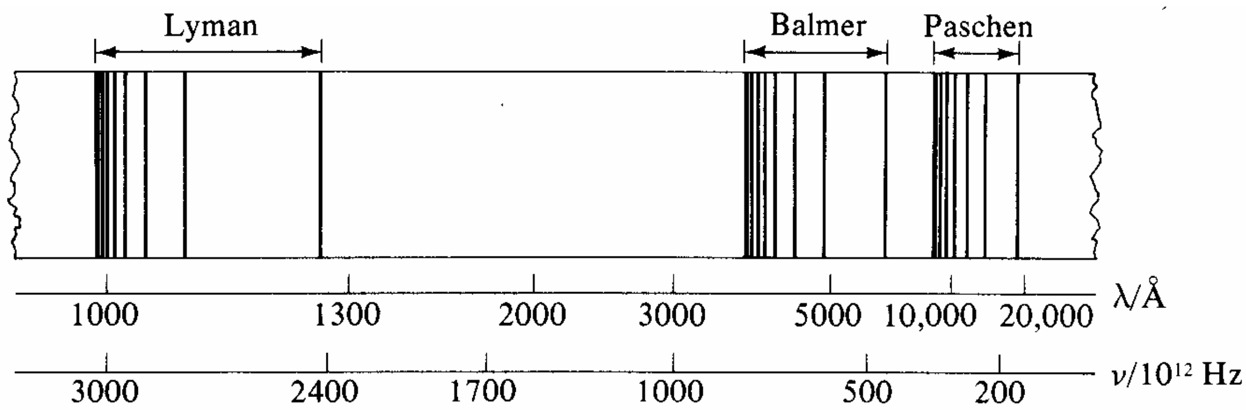
Atomic/molecular Spectra



Individual lines. Why???

H atom spectrum

- The lines follow a particular pattern…



- Lines fit the "Rydberg formula"
  $\nu = (1/n^2 - 1/m^2)(3.29 \times 10^{15}\ s^{-1})$
  where n and m are *integers*. Amazing!

Bohr to the rescue

- Bohr (1913) borrowed ideas of quantization from Planck and Einstein and explained the H atom spectrum
- Bohr argued that *angular momentum* was quantized --- leads to quantization of H atom energy levels
- Bohr frequency condition:
  $\Delta E = h\nu$
- Equations match the Rydberg formula to an accuracy not seen previously in all of science

Niels Bohr

Nobel Prize in Physics, 1922, for explaining H atom spectrum

Bohr's solution

$$
\begin{aligned}
m_e v r &= \frac{nh}{2\pi} \\
&\vdots \\
r_n &= \frac{n^2}{Z} a_0 \\
&\vdots \\
E_n &= -\frac{Z^2}{n^2}\left(\frac{h^2}{8\pi^2 m_e a_0^2}\right) \\
&= -\left(\frac{Z^2}{n^2}\right) R_y \\
\Delta E &= h\nu \\
h\nu &= -Z^2\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) R_y
\end{aligned}
$$

- Quantization of angular momentum…
- Leads to quantization of radii ("Bohr orbits")
- Leads to quantization of energies
- Assume the "Bohr frequency condition"
- Yields the same "Rydberg formula" for allowed energy levels!!!

a_0 = 1 bohr (0.529 Å), R_y = 1 Rydberg = 2.17987 x 10^{-18} J

H atom spectrum explained

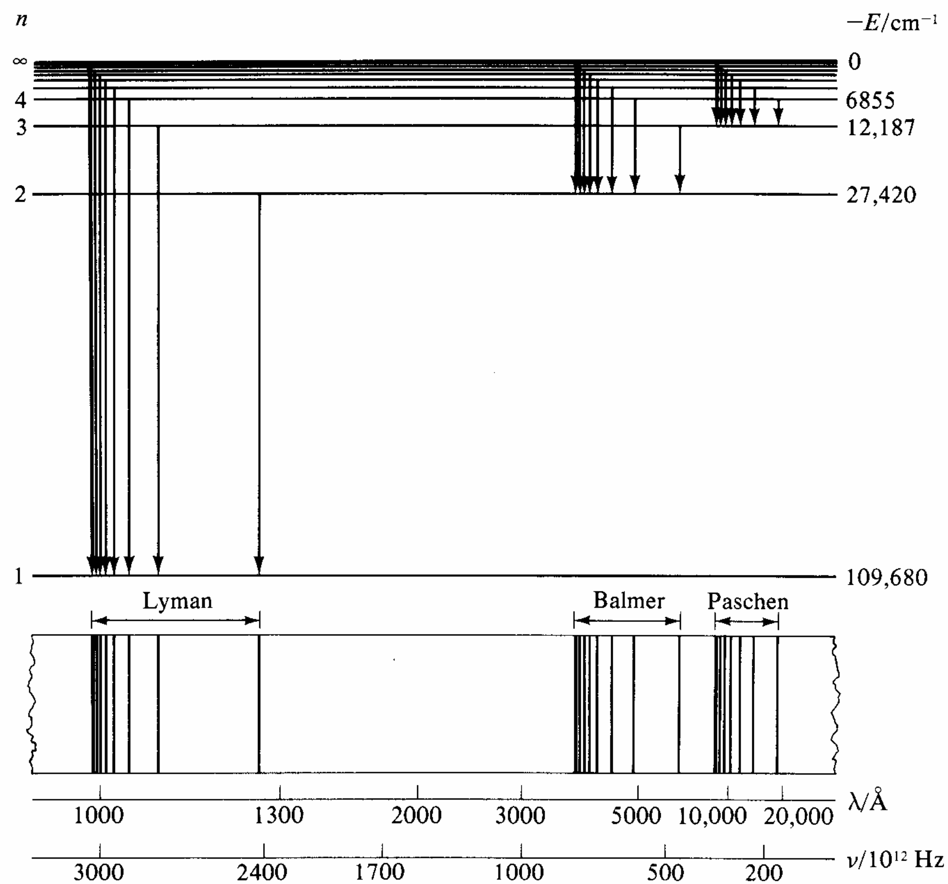


Figure 1-10. The energy-level diagram for the hydrogen atom, showing how transitions from higher states into some particular state lead to the observed spectral series for hydrogen.

McQuarrie, "Quantum Chemistry"

“New quantum theory”

- The “quantization” idea was groundbreaking, but it did not have a firm foundation
- De Broglie (1924) realized that if light can act as a wave and a particle, then maybe particles like electrons can also act like waves! (Recall 2-slit experiment…) “Wave/particle duality” also works for matter!
- Can relate momentum (particle property) to wavelength (wave property) via the de Broglie relation

$$\lambda = h / p \qquad (p = mv)$$

Proof of de Broglie relation for a photon (Einstein)

The Schrödinger Equation

- 1925: Schrödinger developed new mechanics for "matter waves" shown by de Broglie. Quantum mechanics!

$$i\frac{h}{2\pi}\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$$

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

Austrian 1000 Schilling bank note

Erwin Schrödinger

Nobel Prize in Physics, 1933, for the Schrödinger equation, the foundation of quantum mechanics

The Schrödinger Equation

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

$$\begin{aligned}\hat{H} = & -\sum_{A}^{\text{nuc}} \frac{\hbar^2}{M_A}\nabla_A^2 \\ & - \sum_{i}^{\text{elec}} \frac{\hbar^2}{m_e}\nabla_i^2 \\ & - \frac{1}{4\pi\epsilon_0}\sum_{i}^{\text{elec}}\sum_{A}^{\text{nuc}} \frac{Z_A e}{r_{iA}} \\ & + \frac{1}{4\pi\epsilon_0}\sum_{A}^{\text{nuc}}\sum_{B>A}^{\text{nuc}} \frac{Z_A Z_B}{R_{AB}} \\ & + \frac{1}{4\pi\epsilon_0}\sum_{i}^{\text{elec}}\sum_{j>i}^{\text{elec}} \frac{e^2}{r_{ij}}\end{aligned}$$

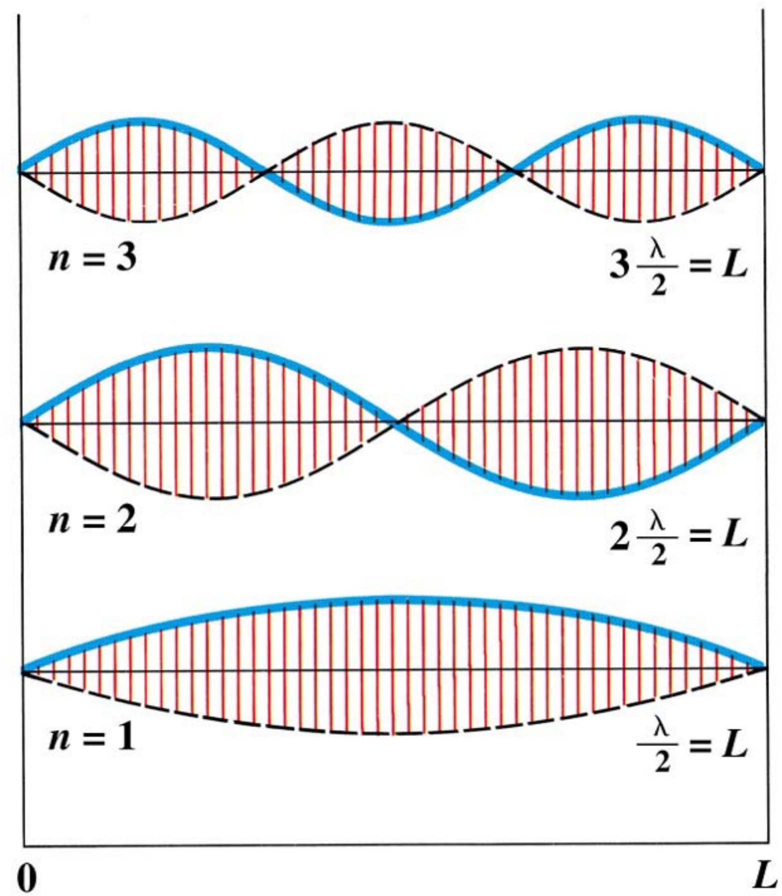
- Nuclear kinetic energy
- Electron kintetic energy
- Nuclear/electron attraction
- Nuclear/nuclear repulstion
- Electron/electron repulsion

The Schrödinger Equation

- Ψ is the *wave function.* It gives the *amplitude* of the matter wave at any position in space (for more than 1 electron, need the coordinates $\mathbf{x}_i = \{x_i, y_i, z_i\}$ for each particle i)
- $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n)$ for n particles
- Focus on wave function for a single particle (like an electron) for now…

Classical standing waves

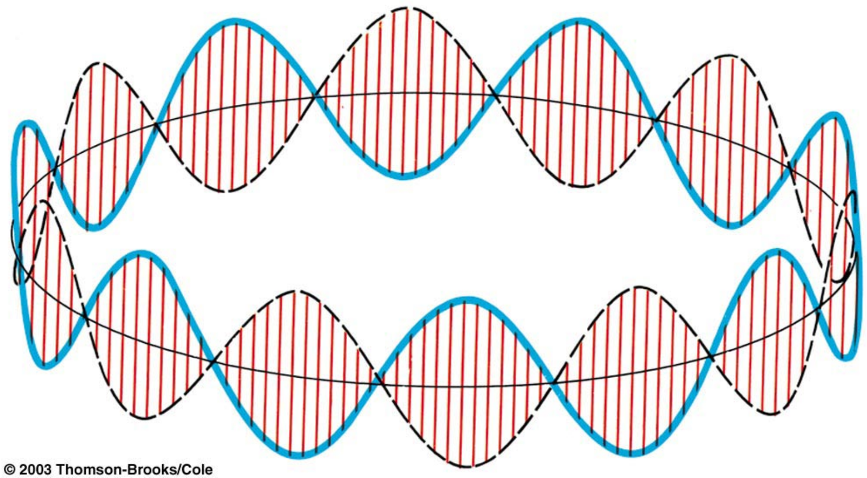
- String tied to the wall at both ends (x=0 and x=L)
- Have to fit a half-integer number of wavelengths λ in the length L
- Number the standing waves n=1, n=2, …
- Max amplitude for standing wave n is $u_n(x) = A_n \sin(n\pi x/L)$
- # of nodes increases with n; energy also increases with n (more nodes -> higher energy)
- Just like $u_n(x)$ gives amplitude of vibration at a given point x, $\Psi_n(x)$ gives the "amplitude" of the matter wave



Interpretation of Ψ

- Most commonly accepted interpretation due to Max Born
- Assume only one particle for now
- $\Psi^*(x, y, z)\, \Psi(x, y, z)\, \Delta x\, \Delta y\, \Delta z$ is the probability that the particle will be found in a box of size $\Delta x\, \Delta y\, \Delta z$ centered at point x,y,z
- Seems crazy – we never actually know where the particle is, only the probability of finding it there. Even worse – these “probability waves” can interfere constructively/destructively!

Wave picture justifies Bohr's assumption for H atom!



- To avoid destructive interference, an electron in a Bohr orbit must have its wavefunction match itself after going around once
- $2 \pi r = n \lambda$
- But also $\lambda = h / mv$
- … and so $2 \pi r = nh / mv$, or $mvr = nh / 2 \pi$, as Bohr assumed!

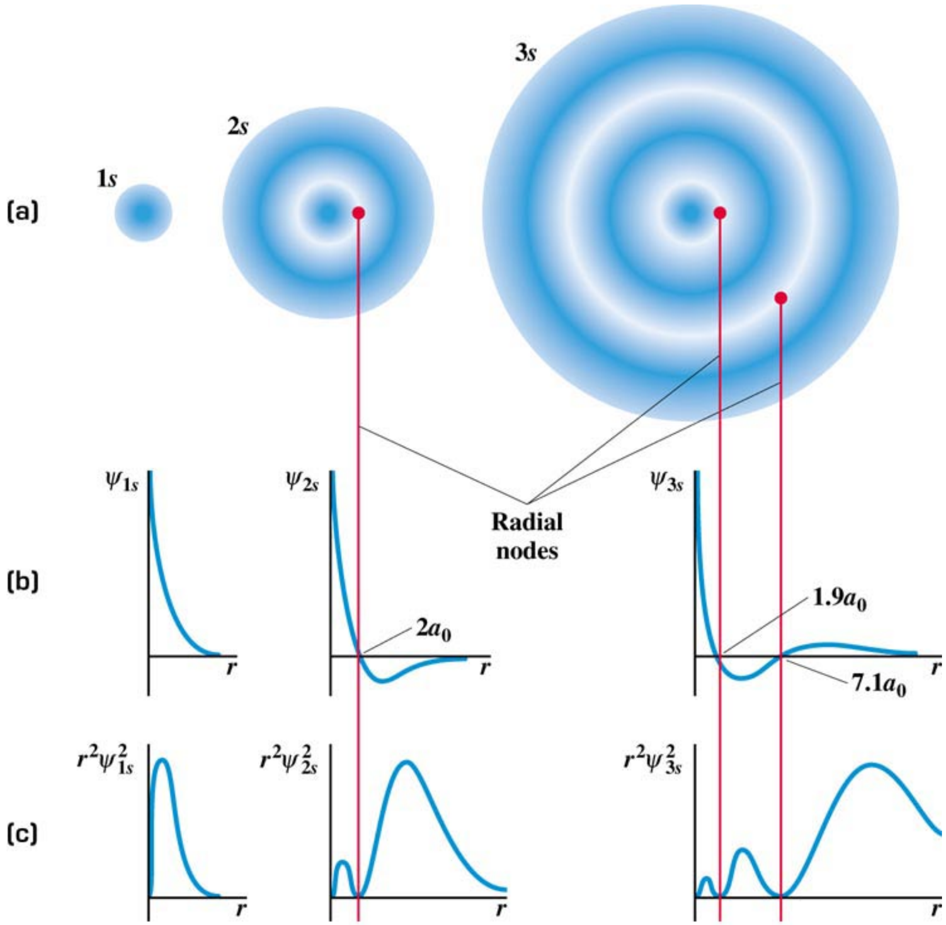
Schrödinger Equation for H atom

- Can solve and obtain same energy equation as Bohr found. But now we also get the wave function $\Psi_{nlm}(x, y, z)$, depending on three integers n, l, and m
- n = "principal quantum number" (the same n in energies E_n), starts counting from 1
- l = "angular quantum number"
  l = 0, 1, …, n-1
- m = "magnetic quantum number"
  m = -l, -l+1, …, 0, 1, …, l
- Actually there's also a 4th quantum number, m_s, giving the spin (1/2 for "up" spin α, -1/2 for "down" spin β)

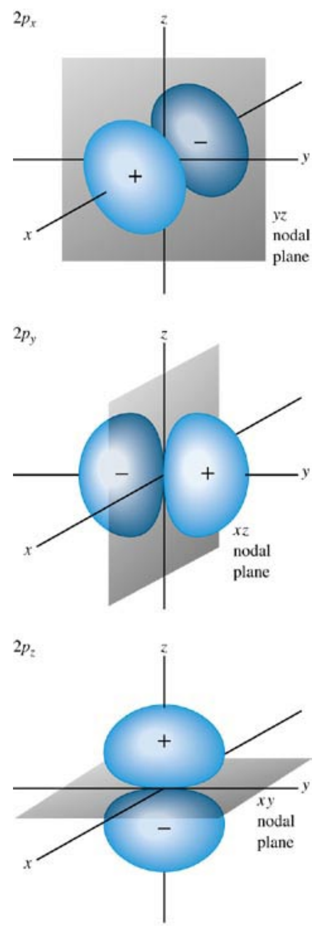
Wave functions for H atom

- Energy depends only on n for H atom, not on l or m
- Shape of wave function depends on n, l, and m
- A function of one particle is called an “orbital”
- l=0 is an s orbital
- l=1 is a p orbital (m=-1, 0, 1 => p_x, p_y, p_z)
- l=2 is a d orbital (m=-2, -1, 0, 1, 2 => d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, d_{z^2})
- l=3 is an f orbital (7 of these)… etc…
- All these functions are 3D functions; hard to plot…

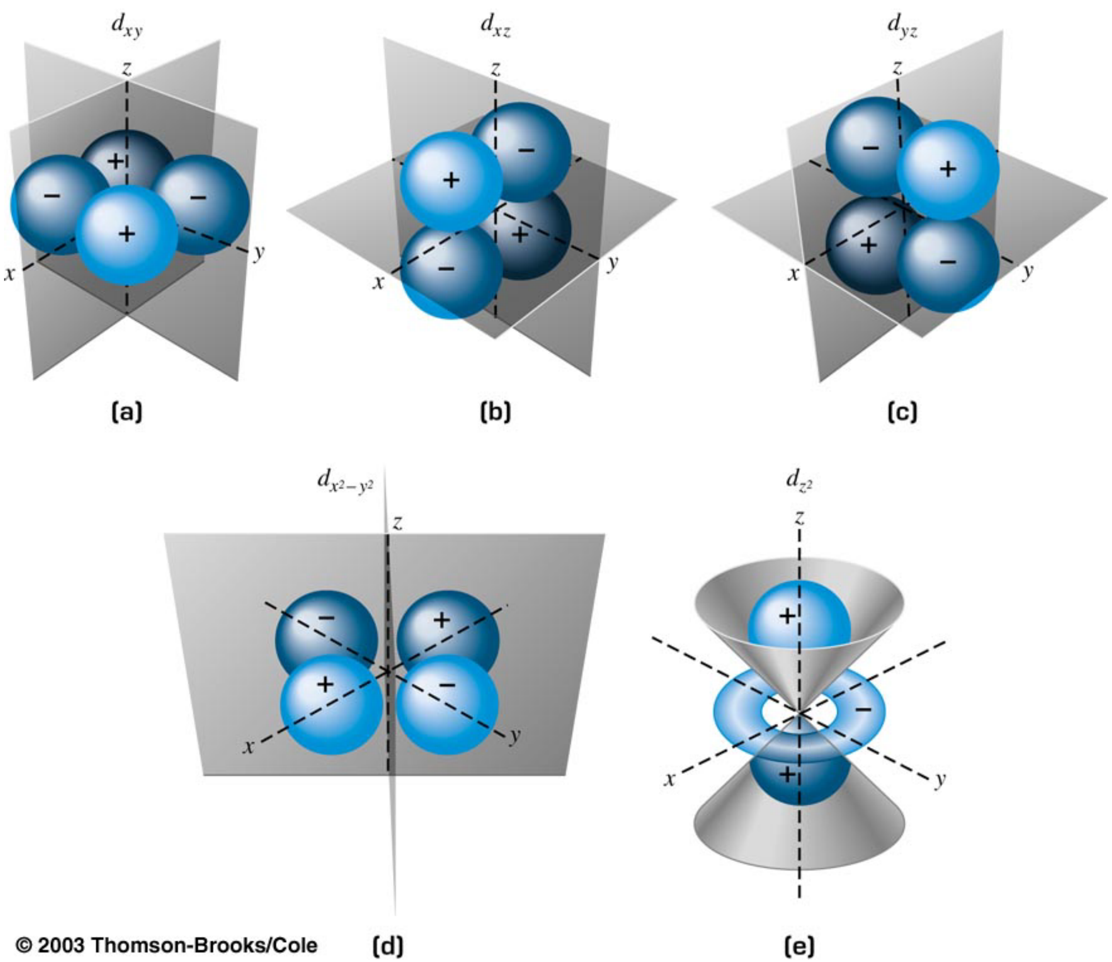
H atom S orbitals



H atom p orbitals



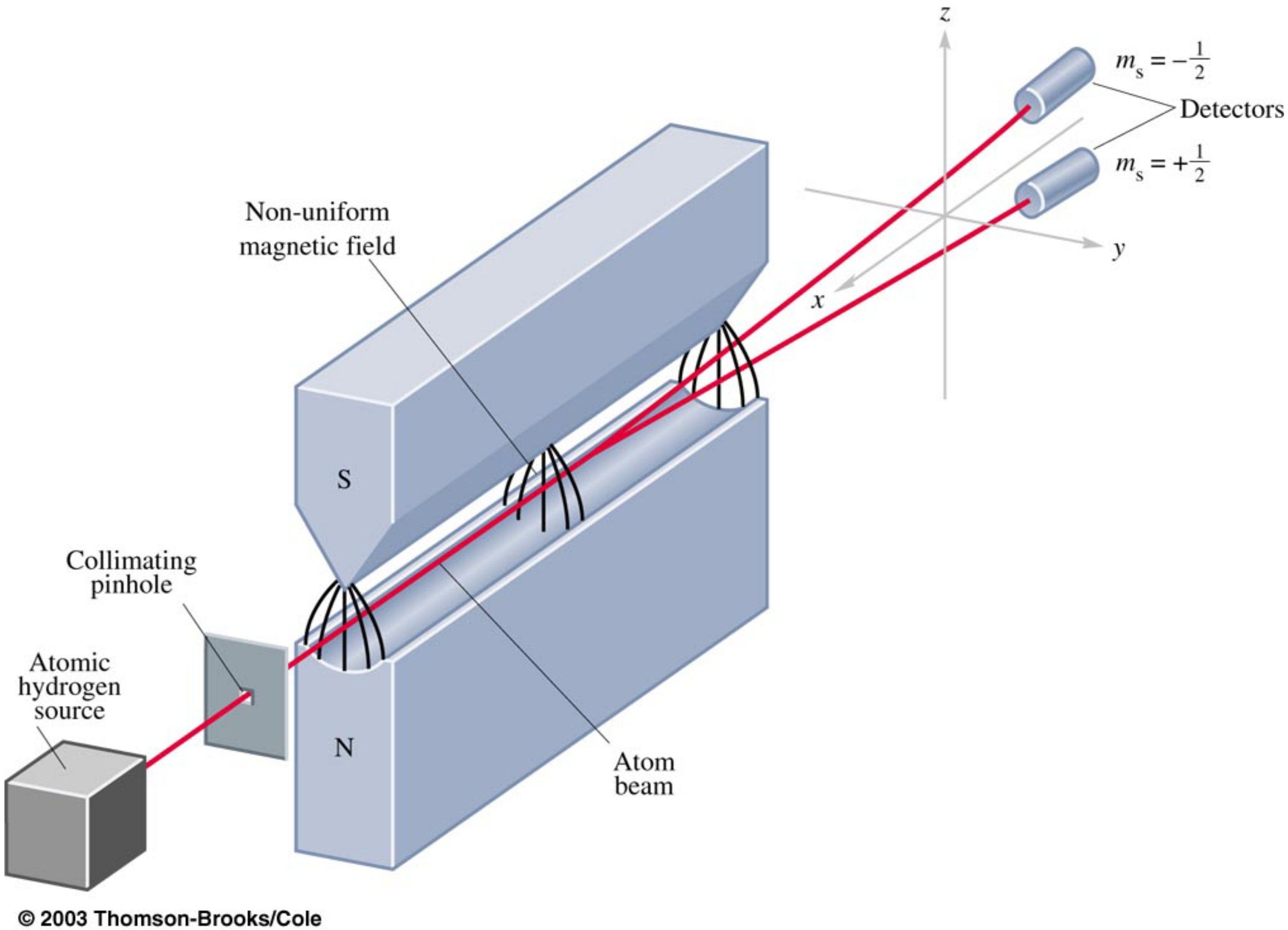
H atom d orbitals



Summary of H atom orbitals

- Energy depends only on n
- For a given l, increasing n increases the average distance of electrons from the nucleus (& the size of the orbital). 3s larger than 2s.
- Ψ_{nlm} has l angular nodes and n-l-1 radial nodes (total of n-1 nodes)
- Only for s orbitals does Ψ_{nlm} remain nonzero as $r \rightarrow 0$. Only s orbitals "penetrate to the nucleus"
- Note: orbitals are only rigorous for H atom or other 1-electron atoms! For multiple electrons, need molecular orbital theory (even for atoms). Solve multi-electron Schrödinger equation

Separation of spin components



Heisenberg uncertainty principle

- “Bohr orbit” idea violates the uncertainty principle!
- Certain pairs of variables (e.g., x and p_x; E and t; r and L) can’t be known exactly at the same time
- E.g., $(\Delta x)(\Delta p_x) \geq h/4\pi$, where Δx denotes an uncertainty in x, etc. Clearly both uncertainties can’t be zero if RHS is nonzero…
- Deep result, *NOT* a mere technical problem with measurement

Werner Heisenberg

Nobel Prize in Physics, 1932, for creating quantum mechanics (not for the uncertainty principle). Matrix mechanics came before wave mechanics.