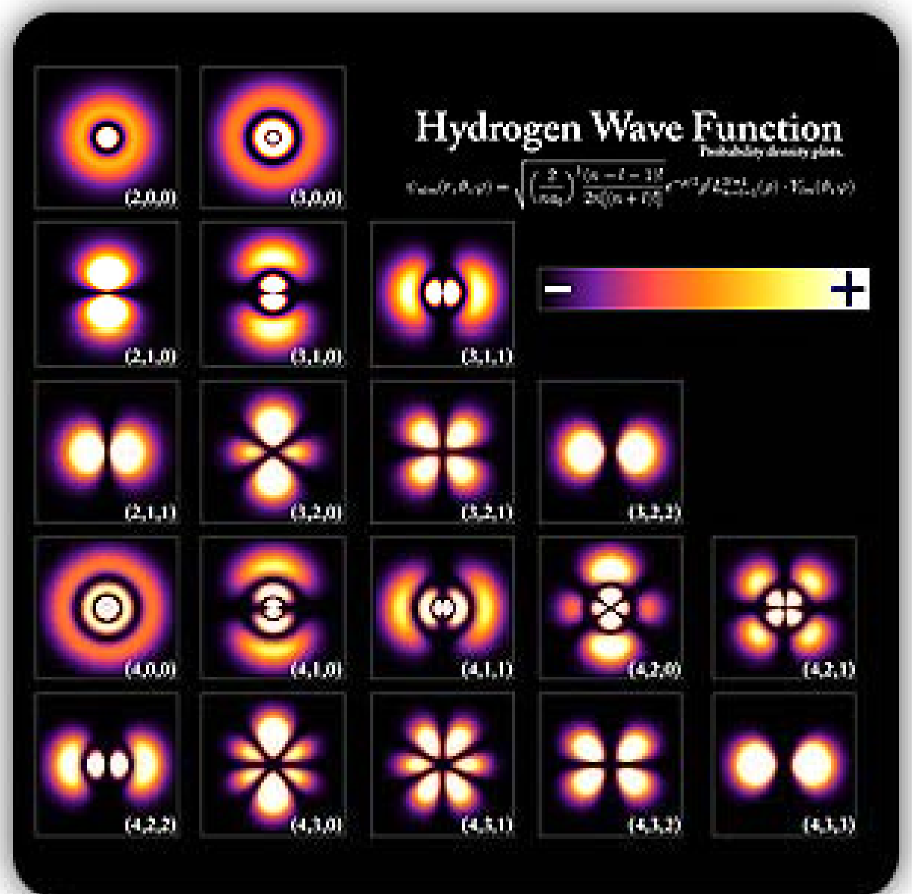
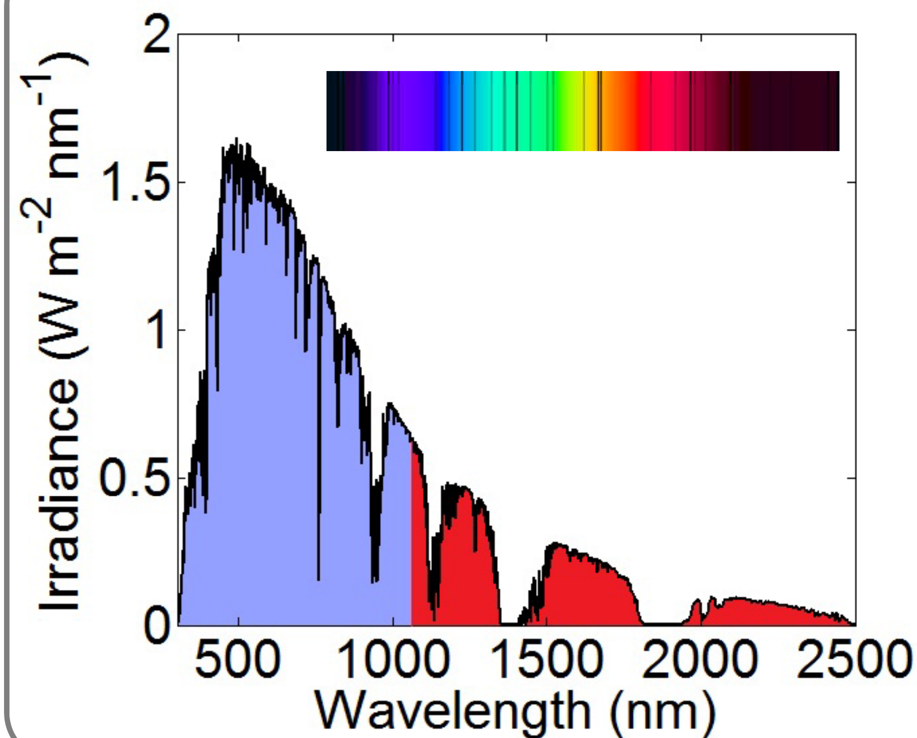
Lecture 12

Atoms, atomic transitions, & neon lighting

Atomic transitions



Absorption in Solar Spectrum



Neon Lighting

Electron Wavefunctions

Steady-state total wavefunction:

$$\Psi(x,t) = \psi(x)\exp\left(-\frac{iEt}{\hbar}\right)$$

E=energy of the electron

t=time

ψ(x) = electron wavefunction that describes only the spatially behavior

Experimentally, we measure the probability of finding an electron in a given position at time *t* (like an intensity):

$$|\Psi(x,y,z,t)|^2 = |\psi(x,y,z)|^2$$

Time independent Schrodinger equation

Schrodinger's equation for one dimension

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

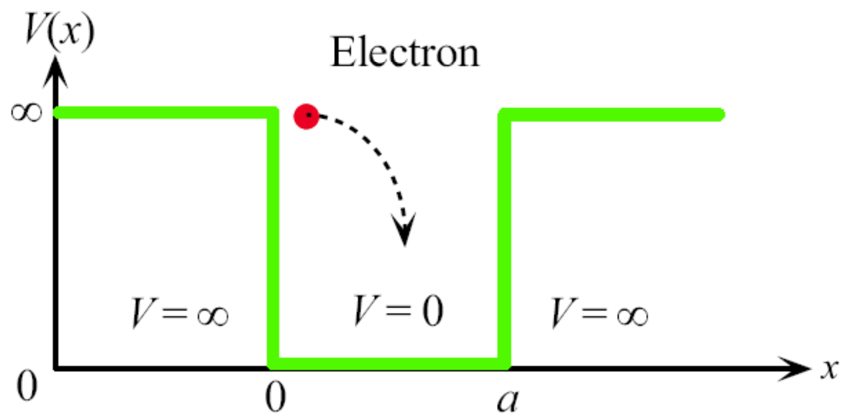
Schrondinger's equation for three dimensions

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

A mathematical "crank": we input the potential V of the electron (i.e., the 'force' it experiences, F=-dV/dx), and can obtain the electron energies E and their wavefunctions / probability distributions.

From *Principles of Electronic Materials and Devices, Third Edition*, S.O. Kasap (© McGraw-Hill, 2005)

Example 1: electrons in a 1D box



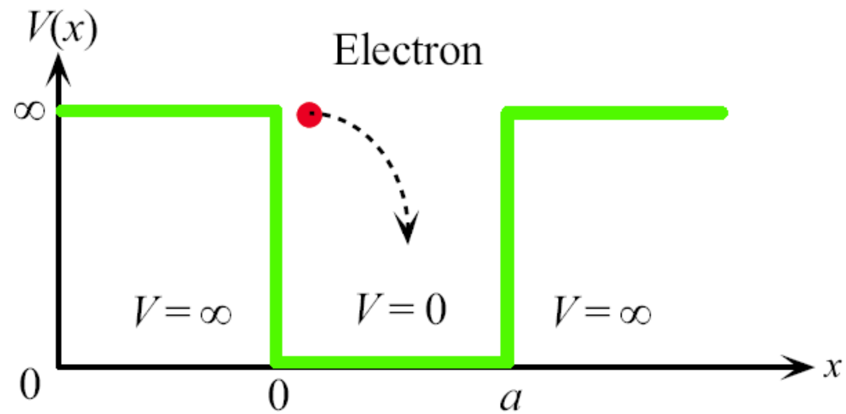
Wavefunction: $$\psi_n(x) = 2Ai\sin\left(\frac{n\pi x}{a}\right)$$

Electron energy in an infinite PE well: $$E_n = \frac{\hbar^2(\pi n)^2}{2ma^2} = \frac{h^2 n^2}{8ma^2}$$

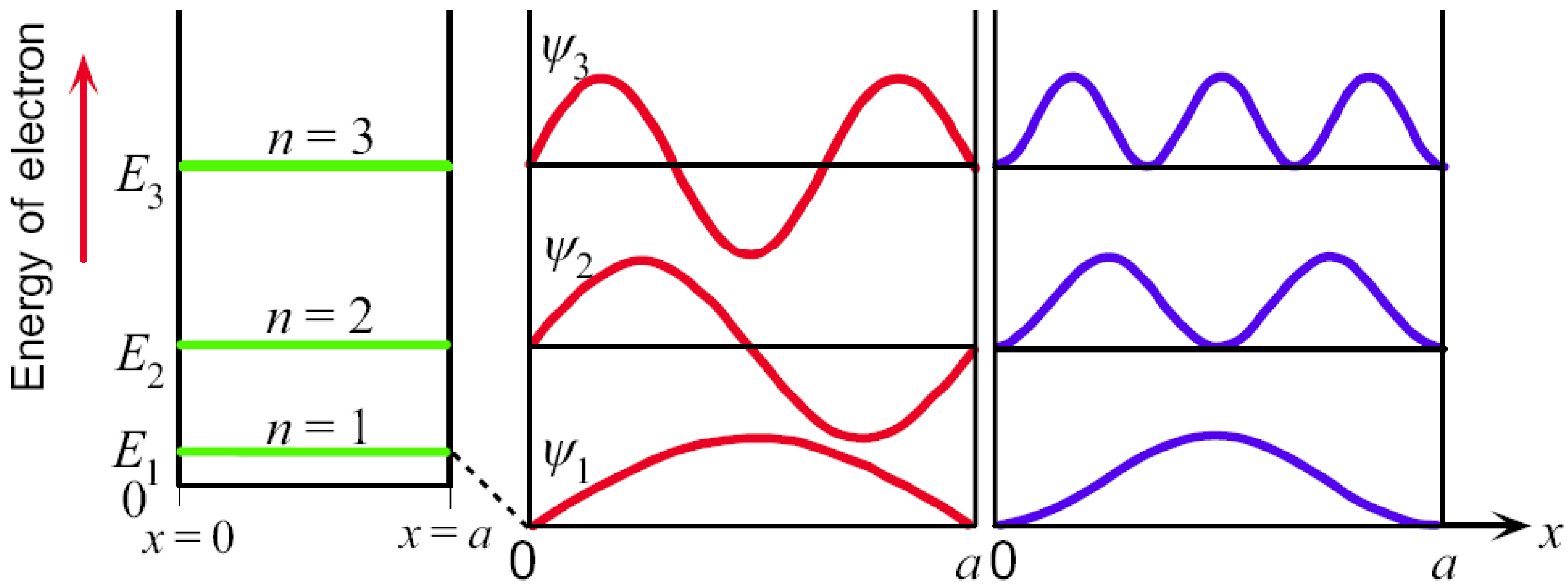
Energy separation in an infinite PE well:

$$\Delta E = E_{n+1} - E_n = \frac{h^2(2n+1)}{8ma^2}$$

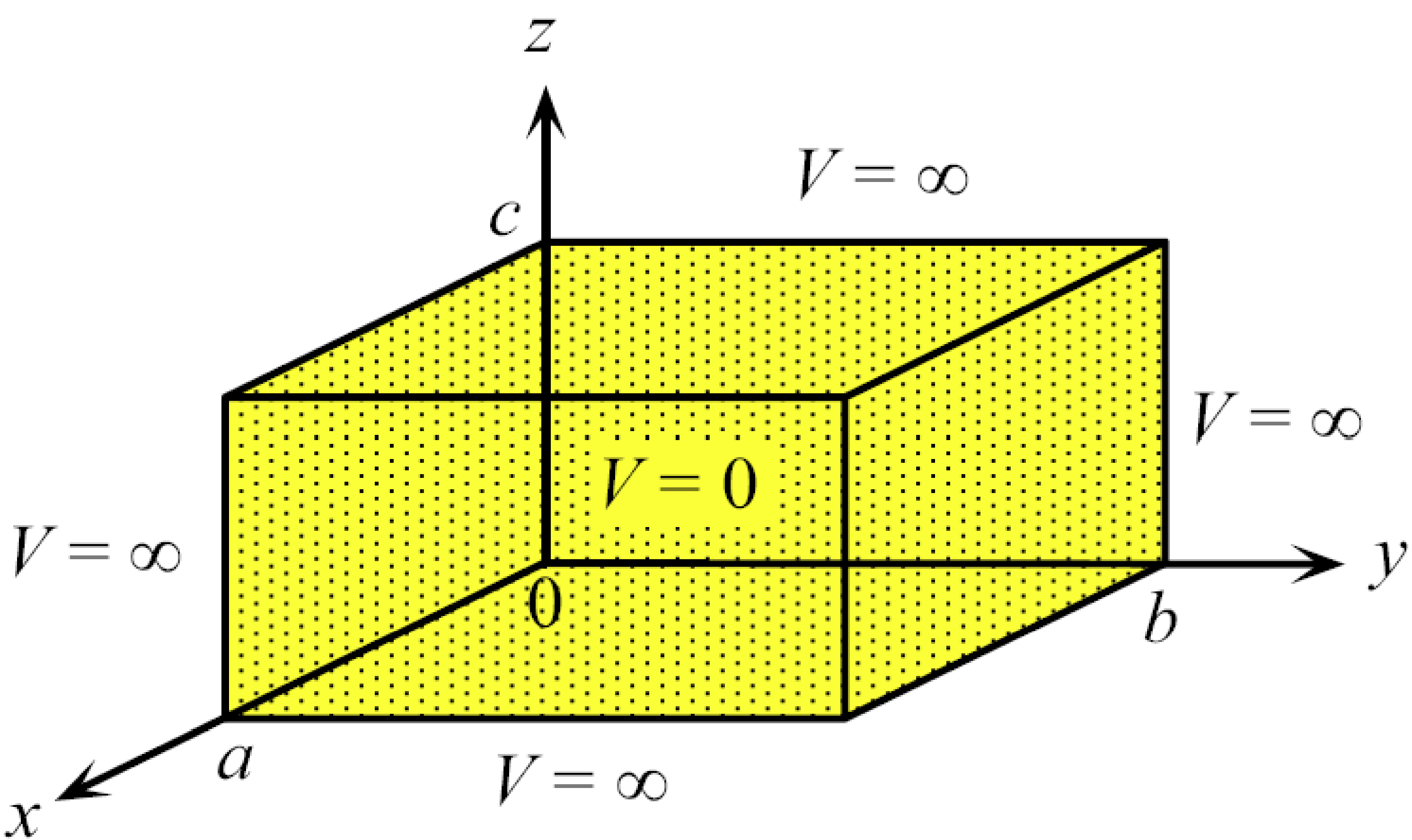
Example 1: electrons in a 1D box



Wavefunction: Probability:



Atoms: A 3D Quantum well



Electron confined in three dimensions by a three-dimensional infinite PE box. Everywhere inside the box, V = 0, but outside, V = ∞. The electron cannot escape from the box.

Quantum mechanics in 3D: 3 quantum numbers

Electron wavefunction in infinite PE well

$$\psi_{n_1 n_2 n_3}(x,y,z) = A \sin\left(\frac{n_1 \pi x}{a}\right) \sin\left(\frac{n_2 \pi y}{b}\right) \sin\left(\frac{n_3 \pi z}{c}\right)$$

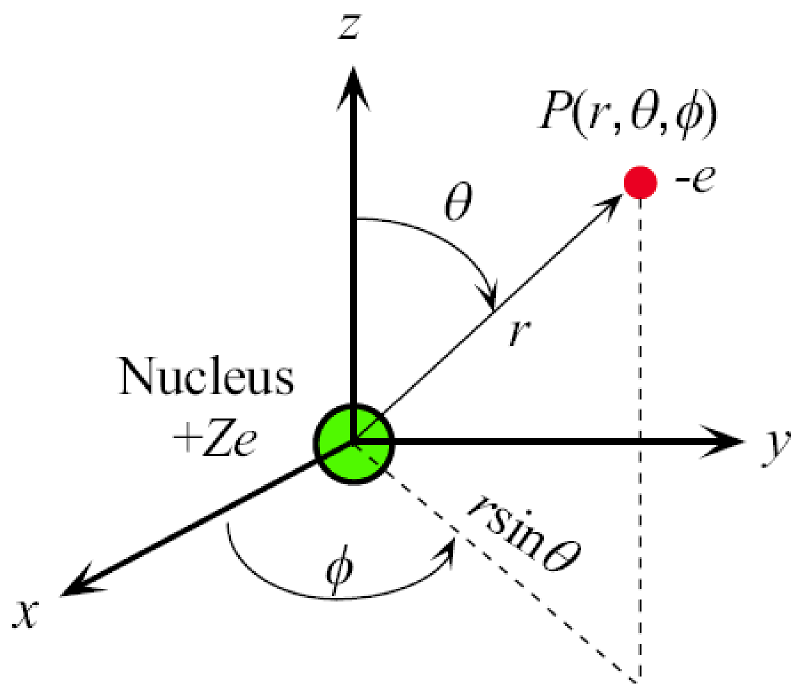
Electron energy in infinite PE box

$$E_{n_1 n_2 n_3} = \frac{h^2\left(n_1^2 + n_2^2 + n_3^2\right)}{8ma^2} = \frac{h^2 N^2}{8ma^2}$$

$$N^2 = n_1^2 + n_2^2 + n_3^2$$

Atoms: electrons in a 3D spherical box

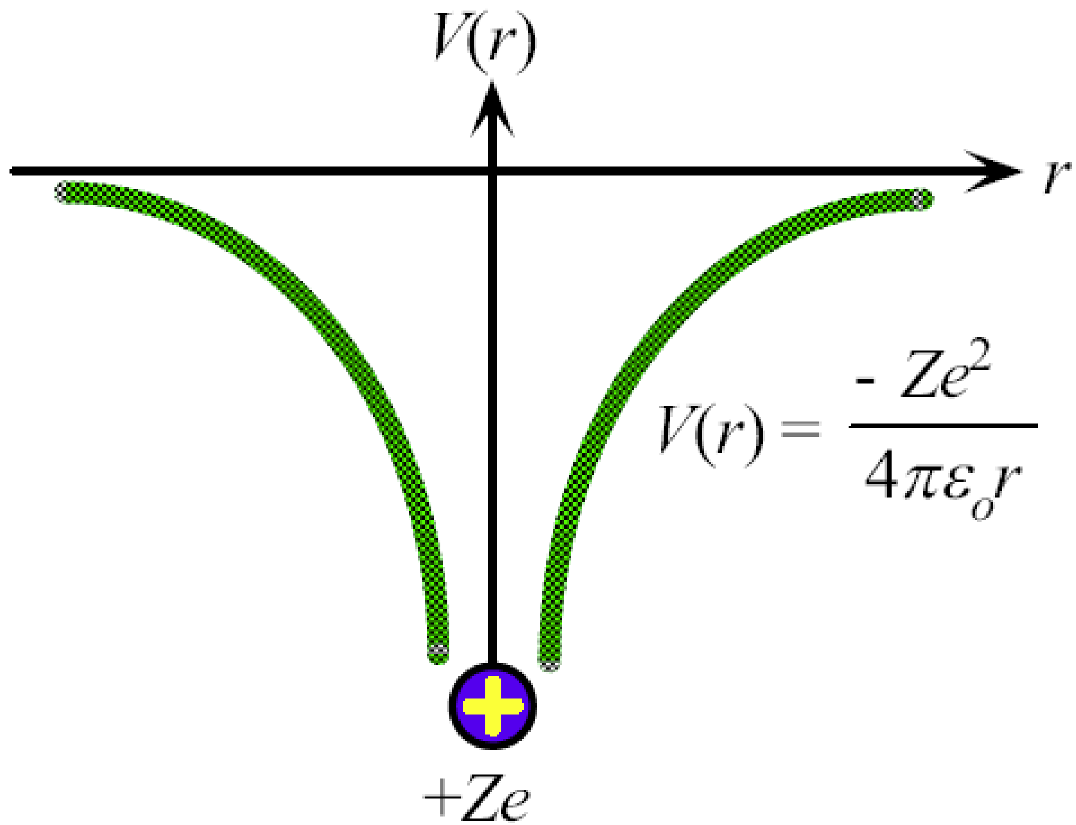
$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0$$



The electron in the hydrogenic atom is atom is attracted by a central force that is always directed toward the positive nucleus.

Spherical coordinates centered at the nucleus are used to describe the position of the electron. The *PE* of the electron depends only on *r*.

Atoms: electrons in a 3D spherical box



The electron's potential energy $V(r)$ in a hydrogenic atom (i.e., just one electron) is used in the Schrödinger equation.

Recall: $r^2 = x^2 + y^2 + z^2$

Solutions to Schrodinger's equation in an atom

$$\nabla^2 \psi + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

$$\downarrow$$

$$V(r) = \frac{-Ze^2}{4\pi\varepsilon_o r}$$

$$\nabla^2 f : \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial f}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial f}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 f}{\partial \phi^2}$$

$$\downarrow$$

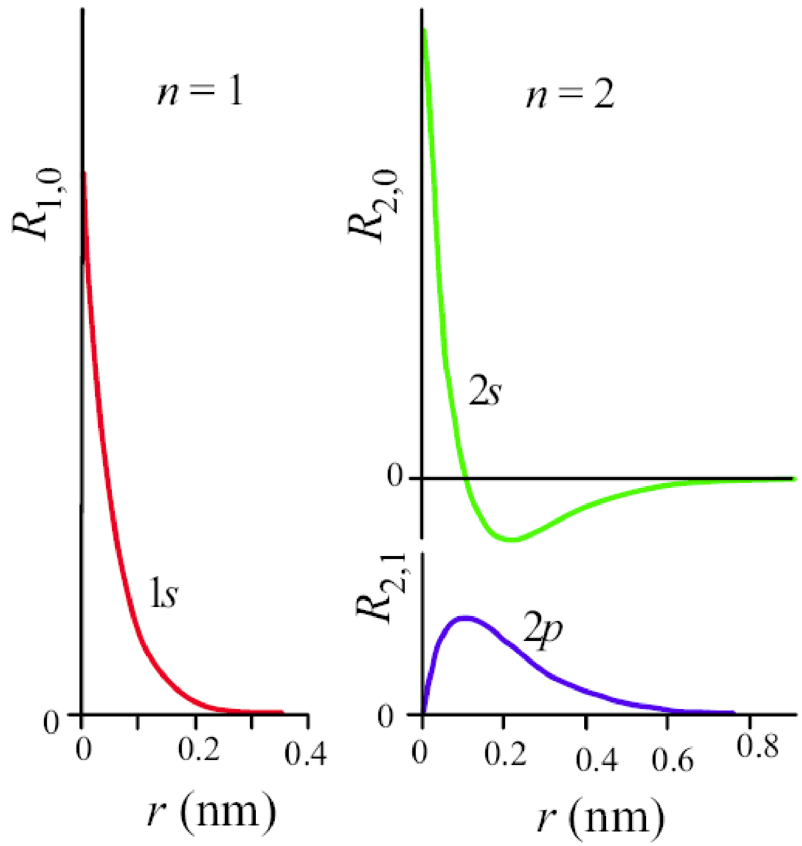
$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

R: Radial wavefunction – depends on two quantum numbers, "n" and "l"

Y: Angular wavefunction – depends on another quantum number, "m_l"

(A fourth quantum number, also in Y, arises from relativity: "m_s")

Radial wavefunctions, R(r)

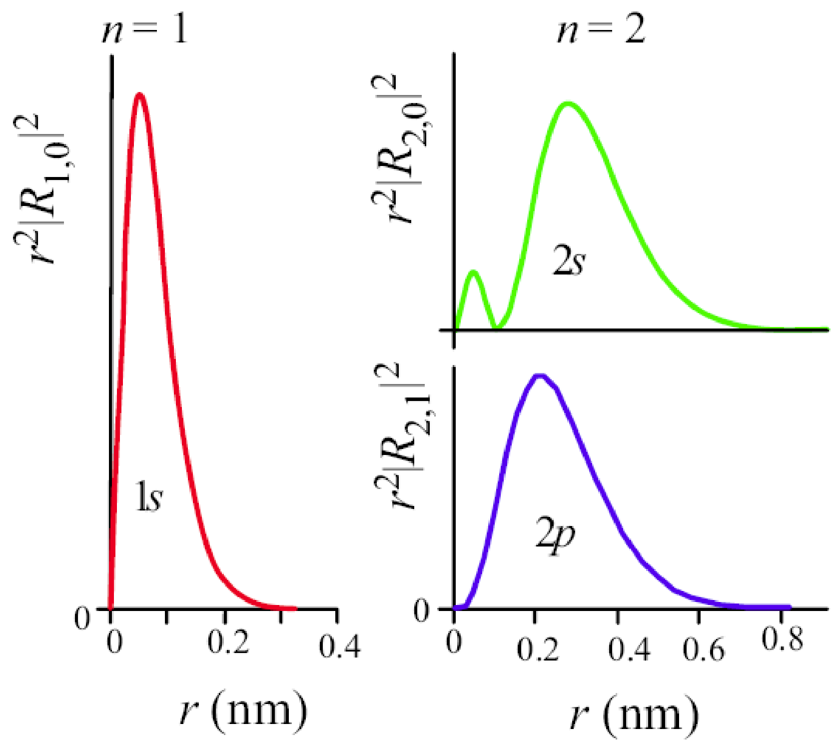


Radial wavefunctions of the electron in a hydrogenic atom for various n and ℓ values.

n=1,2,3,...(just like particle in a box)

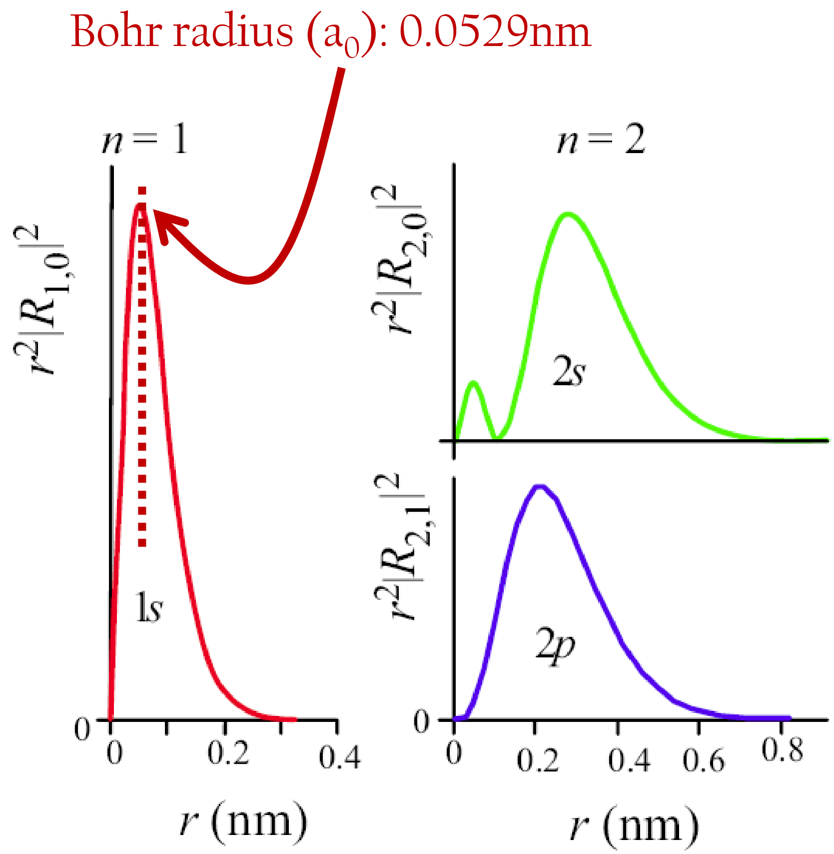
ℓ=0,1,2,3,...(n-1) ℓ=0: "s" ℓ=1: "p" ℓ=2: "d" ℓ=3: "f"

Radial Probability



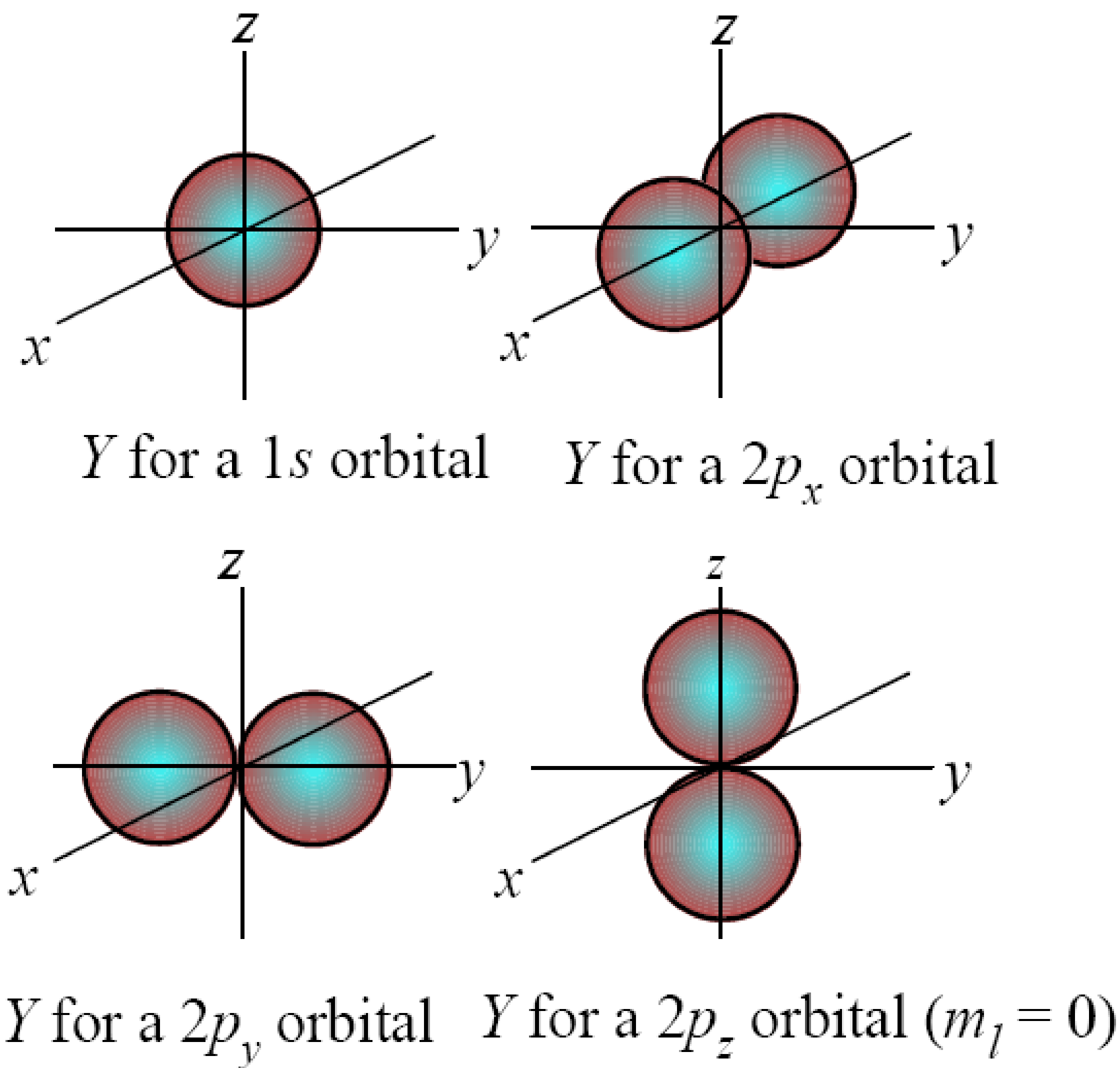
$r^2\ |R_{n,\ell}{}^2|$ gives the radial probability density., i.e., where are we most likely to find the electron around the nucleus

Radial Probability



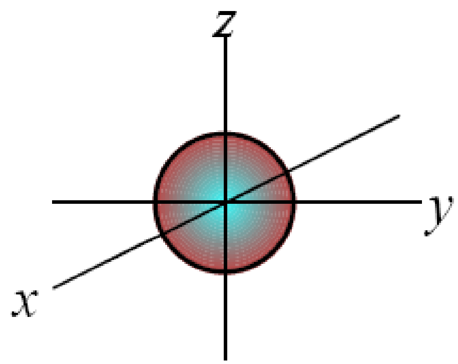
$r^2\ |R_{n,\ell}{}^2|$ gives the radial probability density., i.e., where are we most likely to find the electron around the nucleus

Angular Wavefunctions, Y(θ,φ)

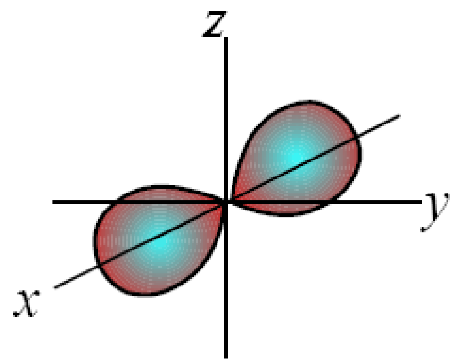


The polar plots of Y(θ, ϕ) for 1s and 2p states.

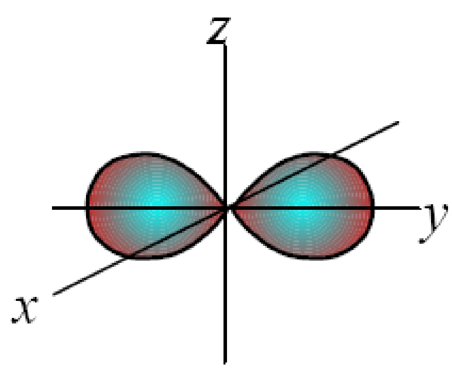
Angular Probability Distribution



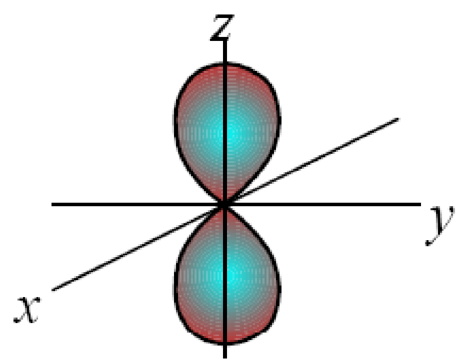
$|Y|^2$ for a $1s$ orbital



$|Y|^2$ for a $2p_x$ orbital



$|Y|^2$ for a $2p_y$ orbital



$|Y|^2$ for a $2p_z$ orbital

The angular dependence of the probability distribution, which is proportional to $|\,Y(\theta, \phi)|^2$.

Total Wavefunction: $\psi(r, \theta, \varphi)=R(r)Y(\theta,\varphi)$

n	ℓ	$R(r)$	m_ℓ	$Y(\theta, \phi)$		
1	0	$\left(\frac{1}{a_o}\right)^{3/2} 2\exp\left(-\frac{r}{a_o}\right)$	0	$\frac{1}{2\sqrt{\pi}}$		
2	0	$\left(\frac{1}{2a_o}\right)^{3/2} \left(2-\frac{r}{a_o}\right)\exp\left(-\frac{r}{2a_o}\right)$	0	$\frac{1}{2\sqrt{\pi}}$		
2	1	$\left(\frac{1}{2a_o}\right)^{3/2} \left(\frac{r}{\sqrt{3}a_o}\right)\exp\left(-\frac{r}{2a_o}\right)$	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$		
			1	$\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{j\phi}$	$\propto \sin\theta\cos\phi$	Correspond to $m_\ell = -1$ and $+1$.
			-1	$\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{-j\phi}$	$\propto \sin\theta\sin\phi$	

n=1,2,3,...(just like particle in a box)

ℓ=0,1,2,3,...(n-1) ℓ=0: "s" ℓ=1: "p" ℓ=2: "d" ℓ=3: "f"

$m_\ell = -\ell \ldots, 0, \ldots \ell$

Electron energies

Knowing ψ, we can use the Schrodinger equation to find the electron energies.

Just like electrons in a 1D or 3D quantum well, the electron energy in the hydrogenic atom is quantized.

$$E_n = -\frac{me^4 Z^2}{8\varepsilon_o^2 h^2 n^2}$$

(Z is atomic number, n is the quantum number, 1,2,3,...)

Ionization energy of hydrogen: energy required to remove the electron from the ground state in the H-atom

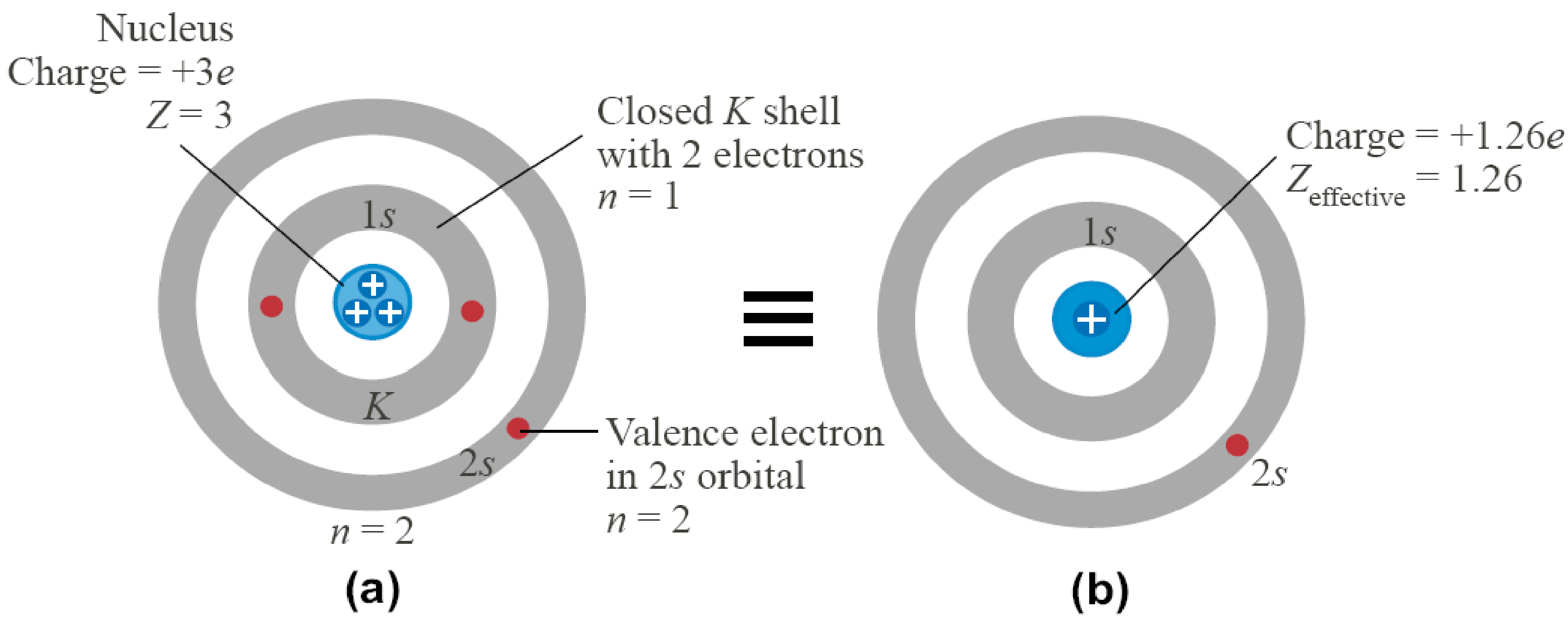
$$E_I = \frac{me^4}{8\varepsilon_o^2 h^2} = 2.18\times10^{-18}\,\mathrm{J} = 13.6\,\mathrm{eV}$$

Radial electron 'position' & ionization energies in a hydrogenic atom (Z≥1)

$$r_{\max} = \frac{n^2 a_o}{Z}$$

$$E_{I,n} = \frac{Z^2_{\mathrm{effective}}(13.6\,\mathrm{eV})}{n^2}$$

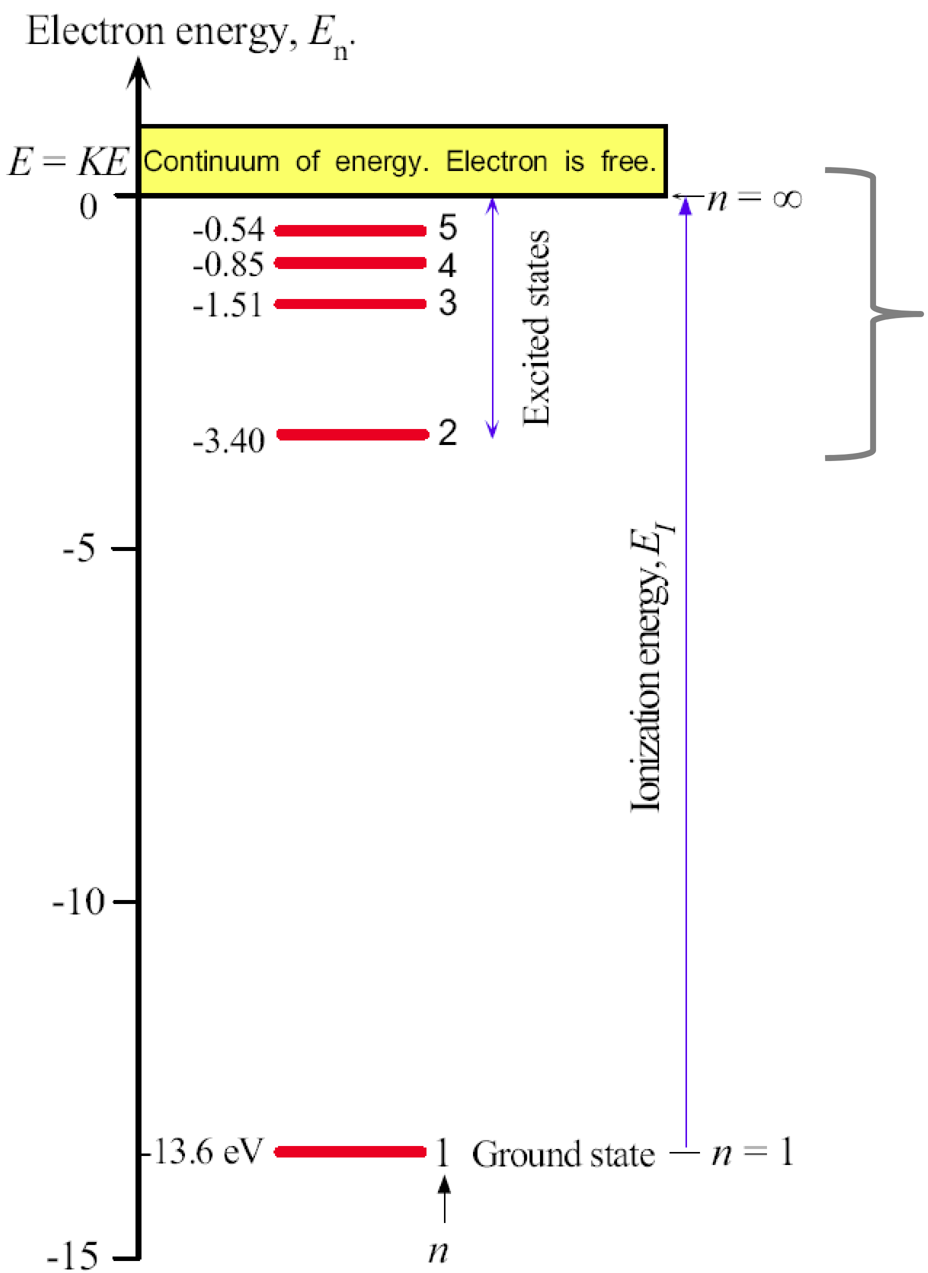
Example of Z_{eff}: Li as a 'hydrogenic atom'



The Li atom has a nucleus with charge +3e, 2 electrons in the *K* shell , which is closed, and one electron in the 2*s* orbital. (b) A simple view of (a) would be one electron in the 2s orbital that sees a single positive charge, $Z = 1$

The simple view $Z = 1$ is not a satisfactory description for the outer electron because it has a probability distribution that penetrates the inner shell. We can instead use an effective Z, $Z_{effective} = 1.26$, to calculate the energy of the outer electron in the Li atom.

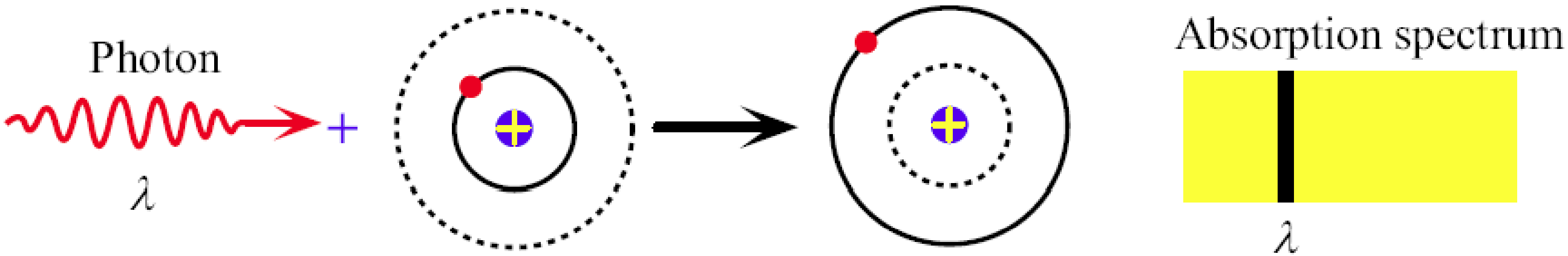
Electron energies in 1-electron atoms



Energies are more closely spaced for higher n

Energy transitions can occur via photons

Absorption of a photon



Energy transitions can occur via photons

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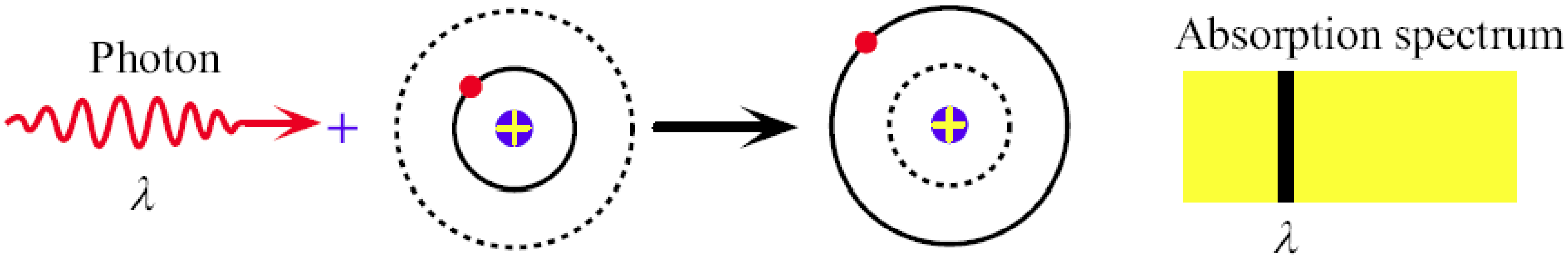
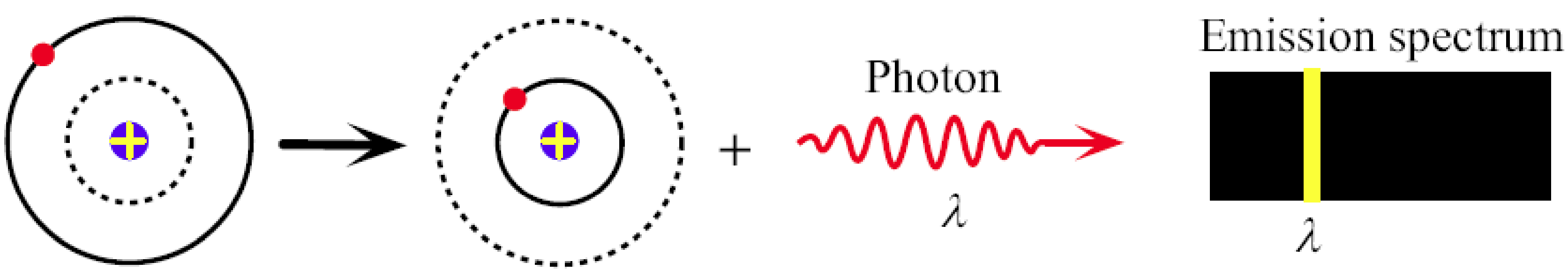
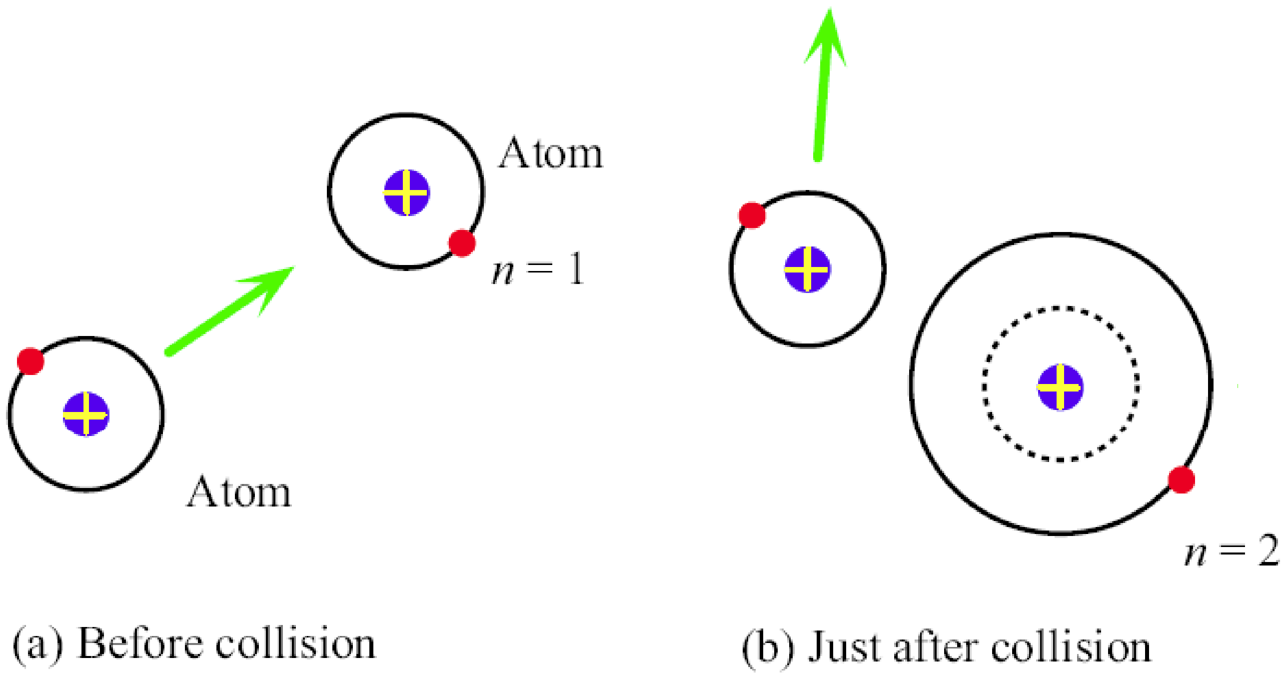


Emission of a photon

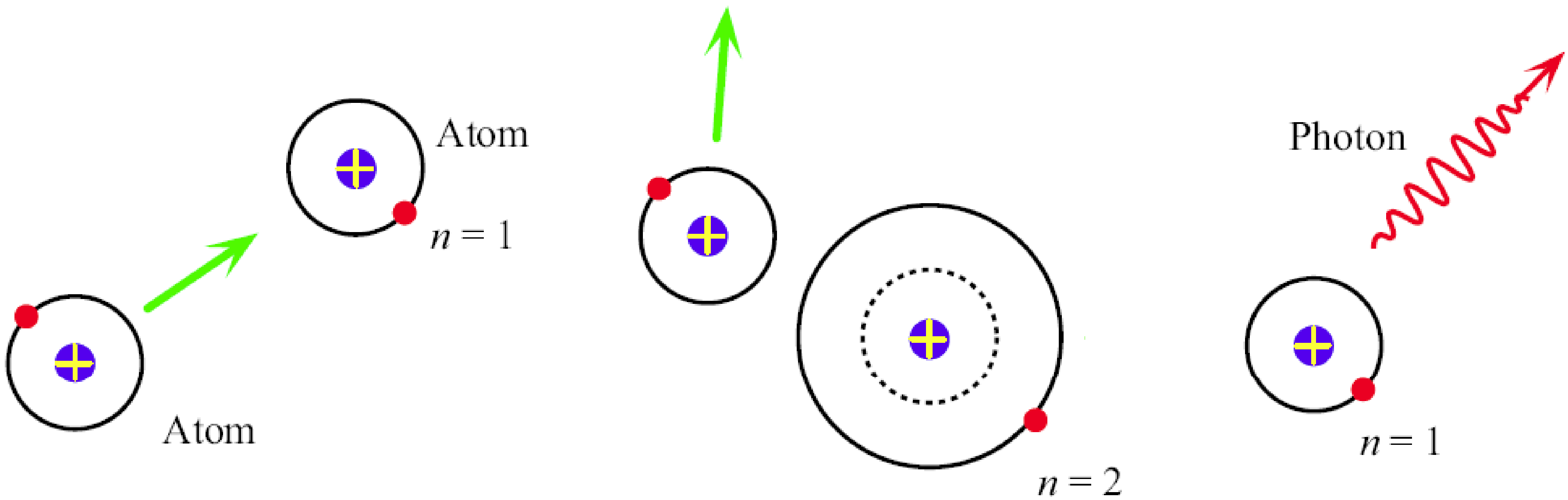


Energy transitions can also occur via collisions



An atom can become excited by a collision with another atom.

Energy transitions can also occur via collisions



(a) Before collision (b) Just after collision (c) Photon emission

An atom can become excited by a collision with another atom. When it returns to its ground energy state, the atom emits a photon.

Neon lighting occurs via quantum transitions!