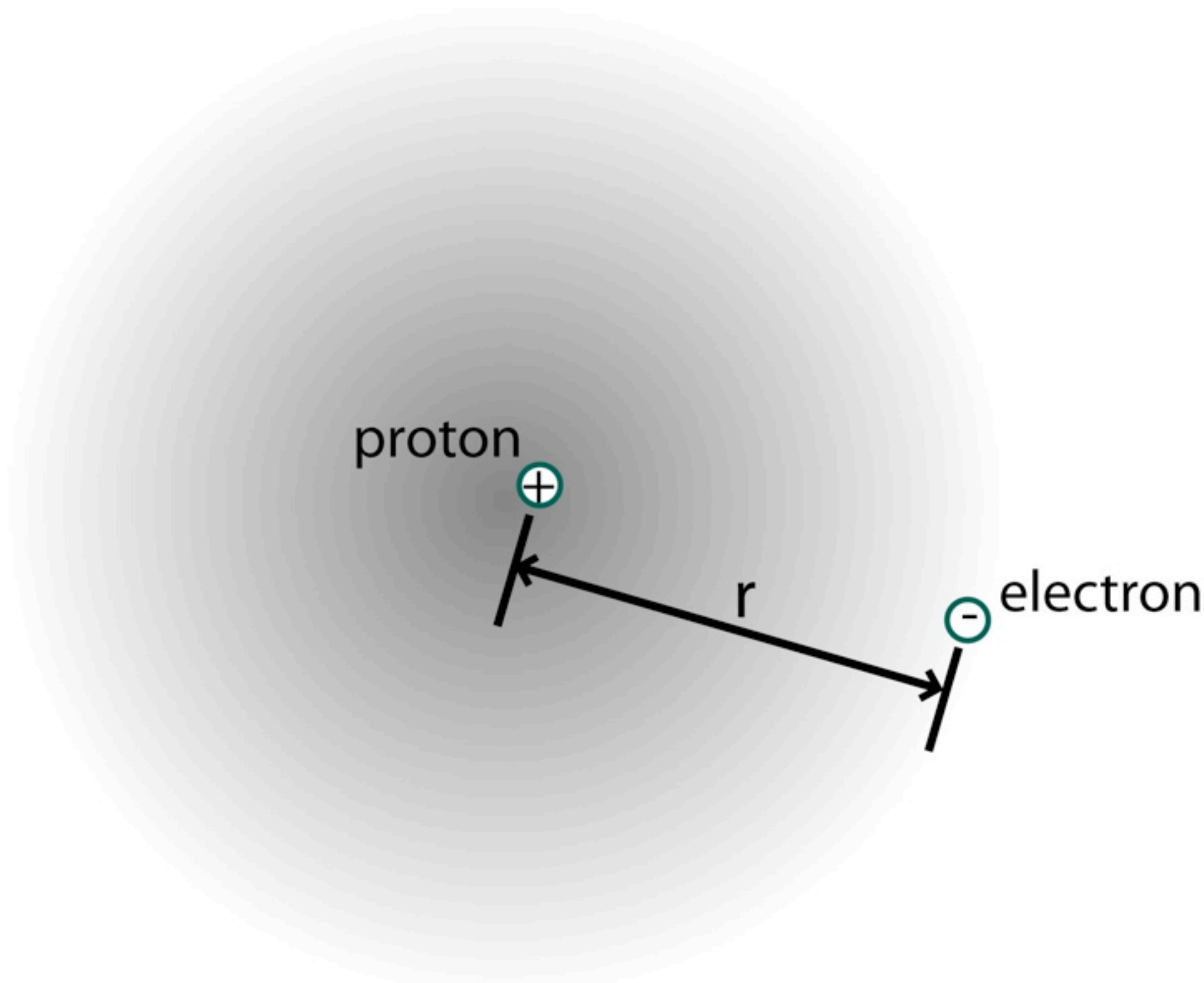
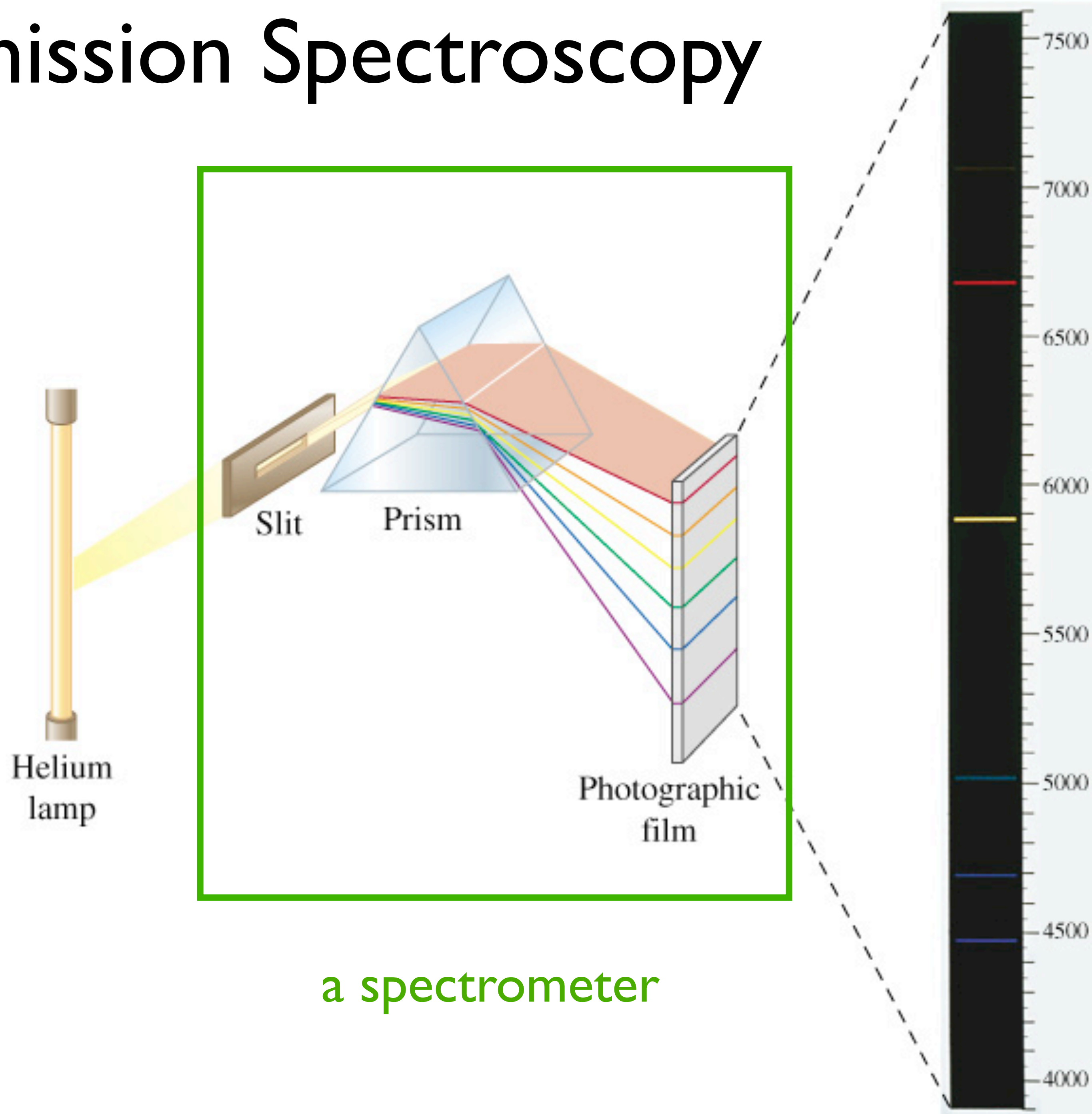
The Hydrogen atom

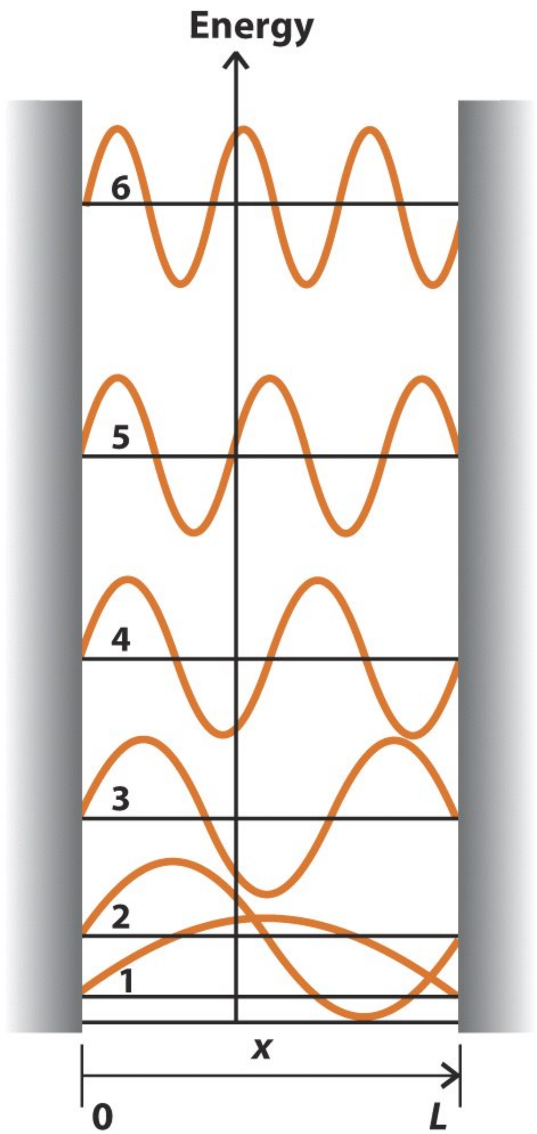


Atomic Emission Spectroscopy

the atomic emission spectrum is the result of many atoms emitting light simultaneously.



Absorption and Emission Spectroscopy



$$\Delta E_{51} = E_5 - E_1 = h\nu$$

$$|n=5\rangle$$

$$|n=1\rangle$$

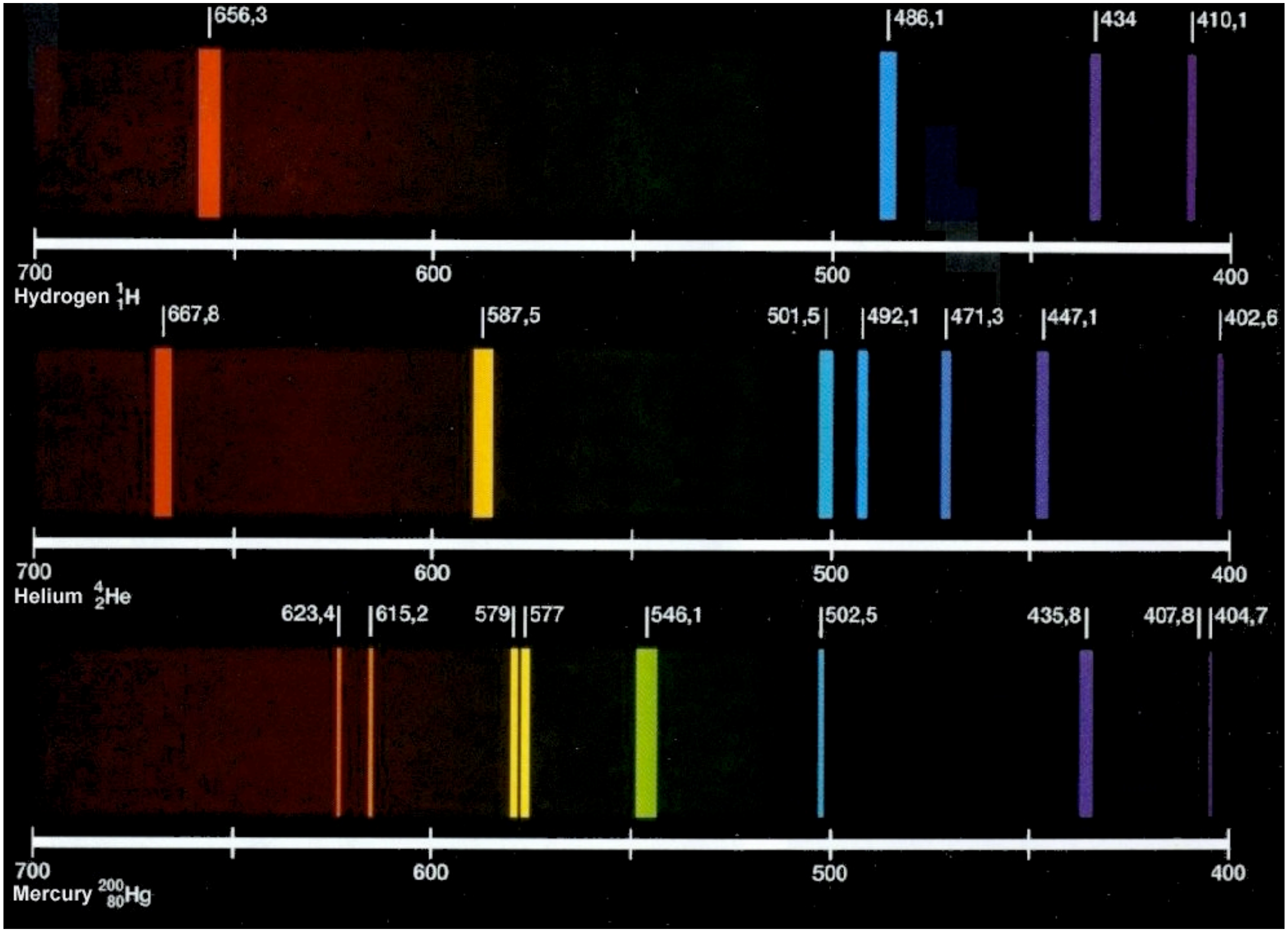
Light will be absorbed or emitted only if $\Delta E = h\nu$

The spectrum is QUANTIZED!

$\Delta E_{51}=24G$
$\Delta E_{41}=15G$
$\Delta E_{31}=8G$
$\Delta E_{21}=3G$

$G= h^2/8mL^2$

Atomic Emission Spectroscopy



The emission spectra of H, He and Hg are all quantized!

Energy eigenvectors/eigenstates

$$\hat{H}\left|\Psi_n\right\rangle = E_n\left|\Psi_n\right\rangle$$

$\left|\Psi_n\right\rangle$ is the eigenstate vector solution to the Schrödinger equation.

E_n is the energy eigenvalue associated with this eigenstate vector.

Hydrogen eigenstates/wavefunctions

$$\left|\Psi_n\right\rangle$$

State Vectors

$$\Psi_{n,l,m_l}(\mathbf{r})$$

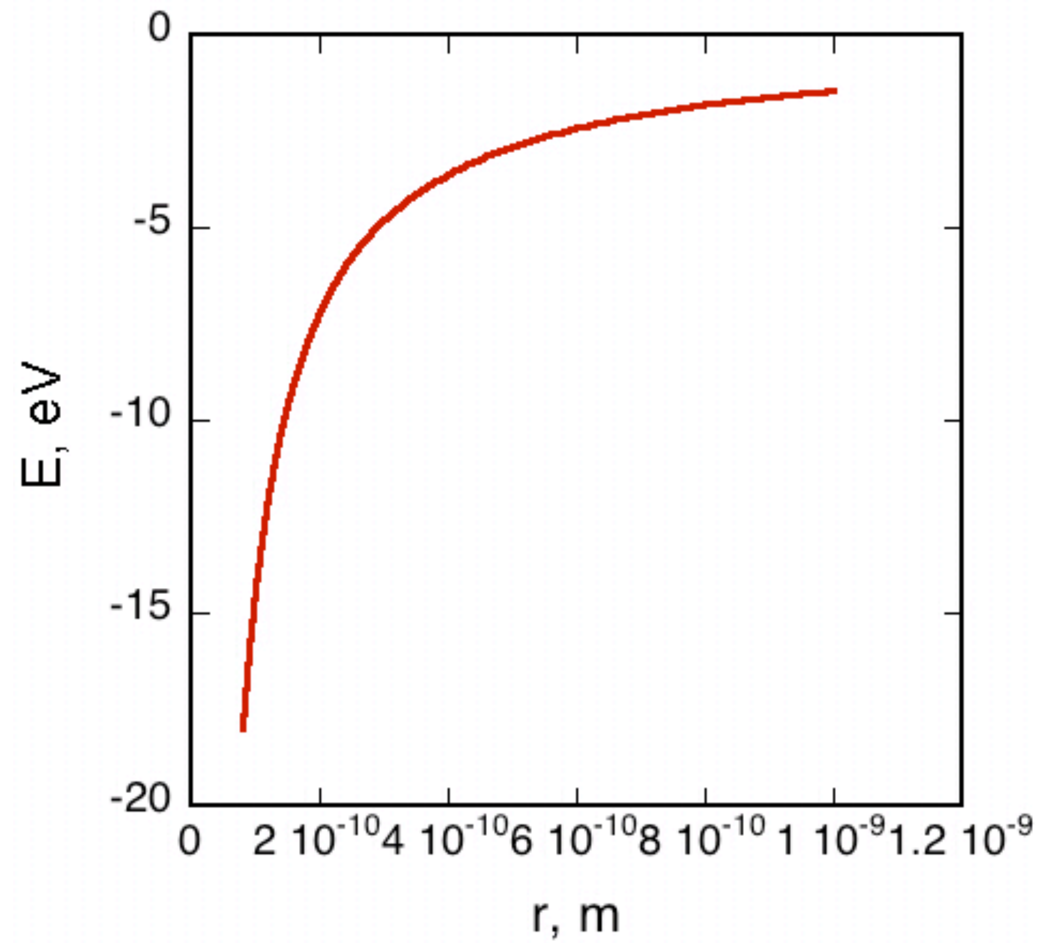
Three Dimensional Wavefunction
(Hydrogen Atom)

The spatial component of the eigenstate vector can be represented by a three dimensional wavefunction $\psi(\mathbf{r}) = \psi(x,y,z)$.

The Hydrogen Atom Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\mathbf{r})$$

$$V(\mathbf{r}) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$



V(r) is called the Coulomb potential.

WHEN we solve the Schrödinger equation, we always obtain two things:

1. a set of eigenstate energies, E_n.

Example: PIAB

$$E_n = \frac{n^2 h^2}{8mL^2} \qquad n = 1, 2, 3\ldots$$

WHEN we solve the Schrödinger equation, we always obtain two things:

1. a set of eigenstate energies, E_n.
2. a set of eigenstate vectors $|\psi_n>$.

Example: PIAB

$$E_n = \frac{n^2 h^2}{8mL^2}$$

n = 1, 2, 3...

$$\left| n = 1 \right\rangle$$

Eigenstate vectors are labeled with the quantum number n.

WHEN we solve the Schrödinger equation, we always obtain two things:

1. a set of eigenstate energies, E_n.

Hydrogen atom solution:

$$E_n = -\frac{hcR}{n^2}$$

n = 1, 2, 3...

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Hydrogen atom solution:

$$E_n = -\frac{hcR}{n^2}$$

n = 1, 2, 3...

$$\left|n, l, m_l, m_s\right\rangle$$

State vectors are labeled with the quantum number n...
AND three more: l, m_l, m_s

WHEN we solve the Schrödinger equation, we always obtain two things:

1. a set of eigenstate energies, E_n.

Hydrogen atom solution:

$$E_n = -\frac{hcR}{n^2} \qquad n = 1, 2, 3\ldots$$

Let's focus on the energies first!

WHEN we solve the Schrödinger equation, we always obtain two things:

1. a set of eigenstate energies, E_n.

Hydrogen atom solution:

$$E_n = -\frac{hcR}{n^2}$$

n = 1, 2, 3... hcR = 13.60 eV

R is the Rydberg constant.

WHEN we solve the Schrödinger equation, we always obtain two things:

1. a set of eigenstate energies, E_n.

A small aside about the Rydberg constant R:

$$R = -\frac{m_e e^4}{8h^3\varepsilon_0^2 c}$$

$1.097 \times 10^7\ m^{-1}$ in SI units

Atkins eliminates c from the definition of R, and ends up defining it in units of s^{-1} or Hz.

R(Atkins) = Rc = $(1.097 \times 10^7\ m^{-1})x(2.997 \times 10^8\ m\ s^{-1})$

= 3.288×10^{15} Hz. Oh well.

WHEN we solve the Schrödinger equation, we always obtain two things:

1. a set of eigenstate energies, E_n.

Hydrogen atom solution:

$$E_n = -\frac{hcR}{n^2}$$

n = 1, 2, 3...

hcR = 13.60 eV

13.60 eV is the Ionization Potential for Hydrogen.

Hydrogen atom energy levels

E $\geq$0 means ionization

n=∞ - - - - - - - - - - - - - - 0 eV

n=4 -0.851 eV

n=3 -1.51 eV

n=2 -3.40 eV

hcR = 13.60 eV

$$E_n = -\frac{hcR}{n^2}$$

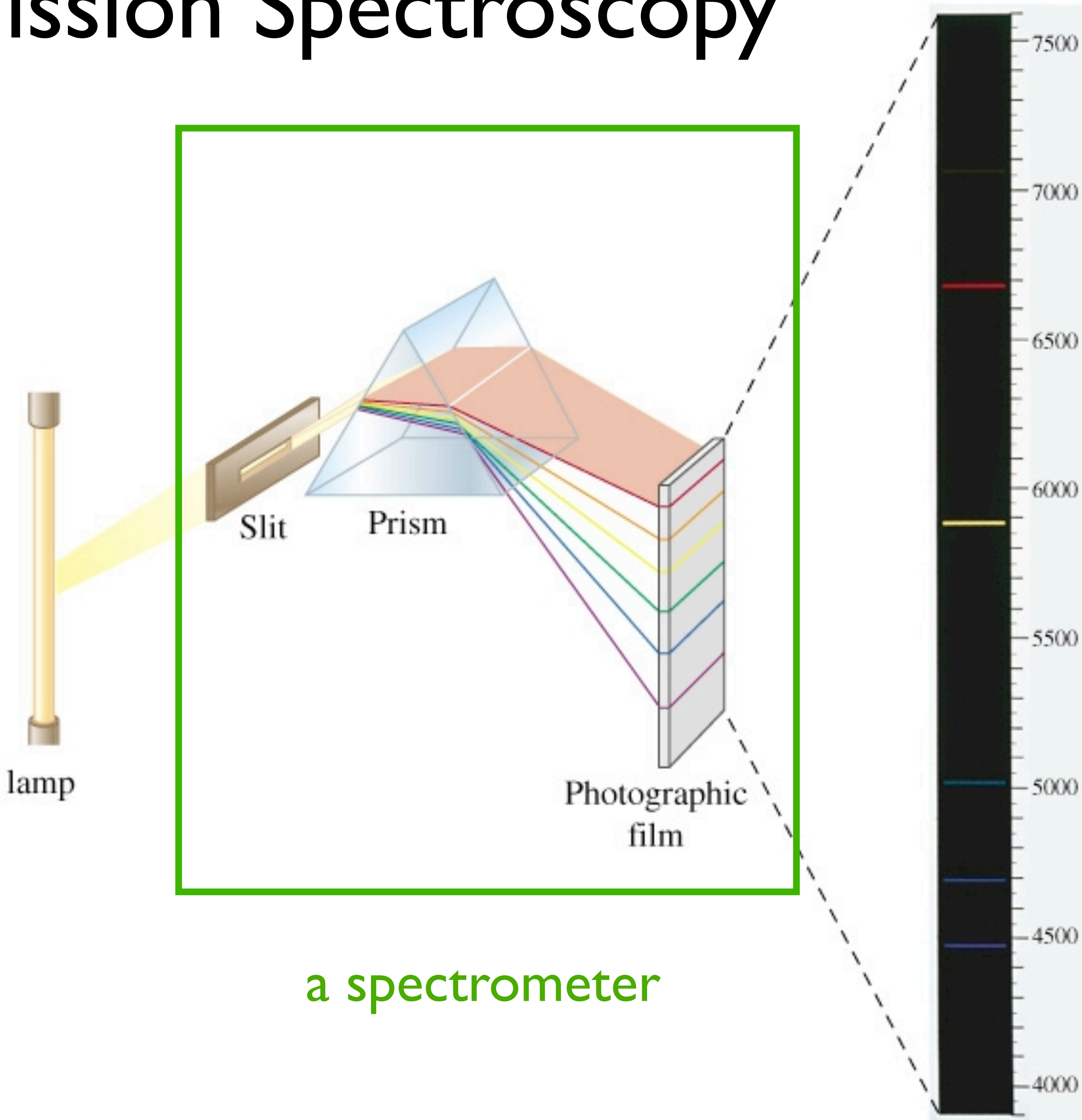
n = 1, 2, 3...

n is called the
principal quantum number.

n=1 -13.60 eV

H atom Emission Spectroscopy

the atomic emission spectrum is the result of many excited atoms emitting light simultaneously.



H atom Emission Spectrum

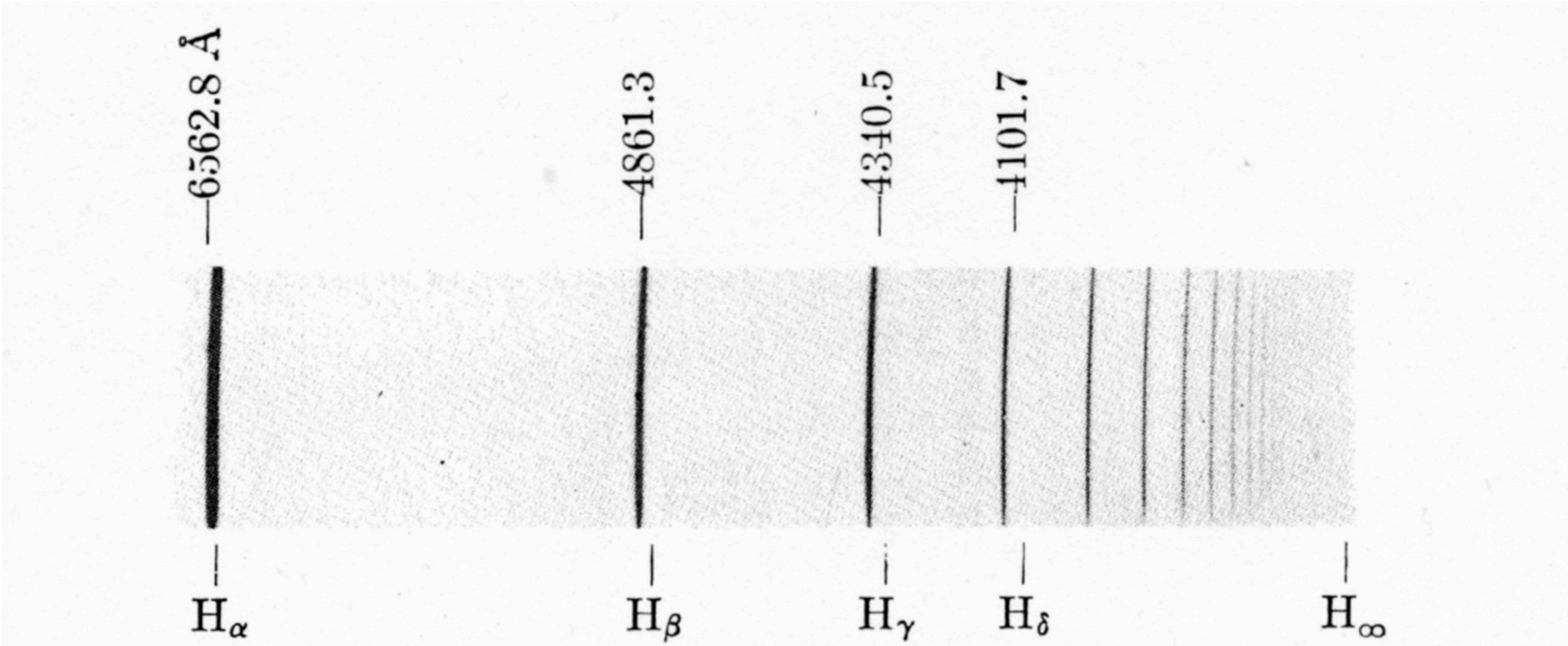
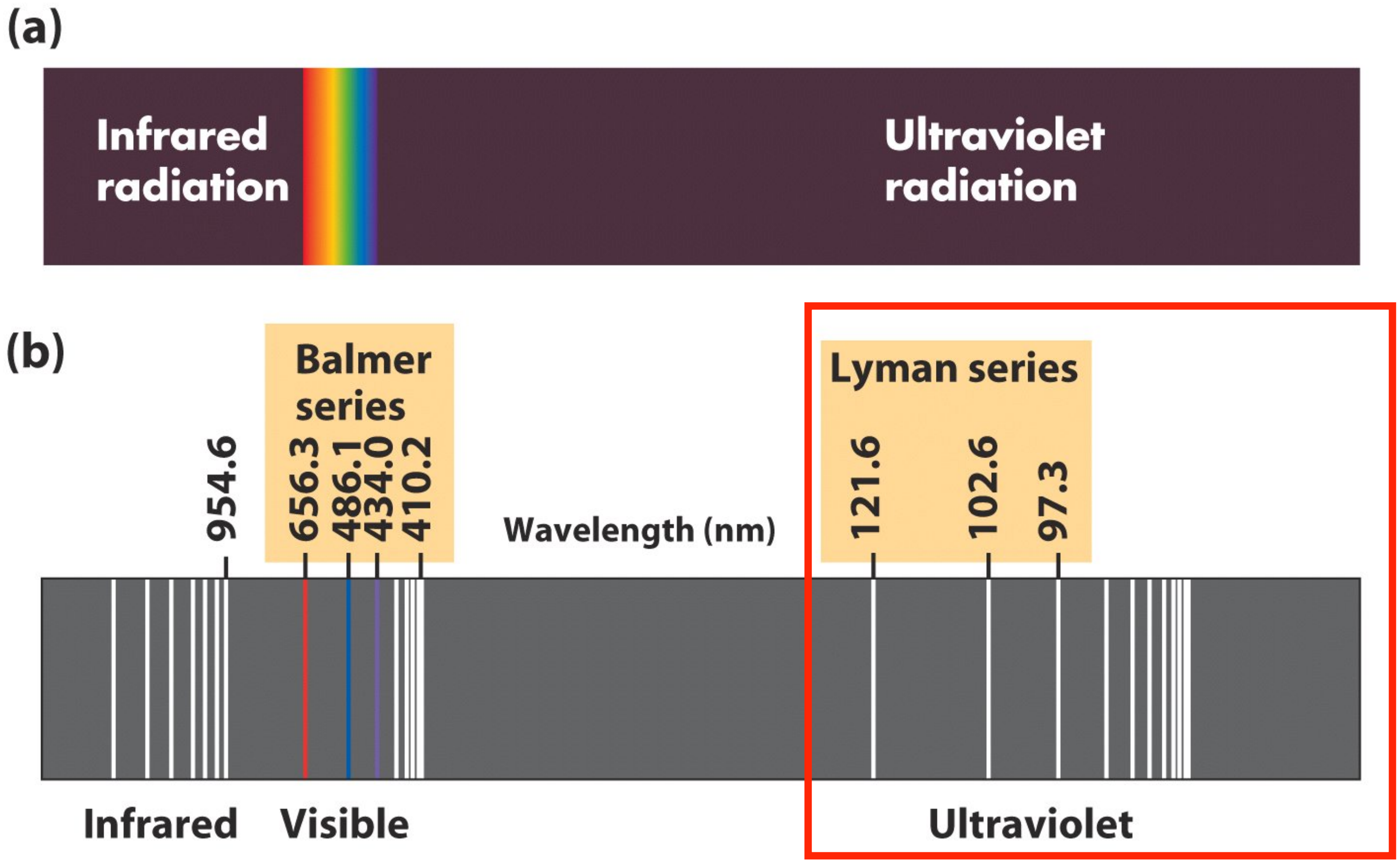


Fig. 1. Emission Spectrum of the Hydrogen Atom in the Visible and Near Ultraviolet Region [Balmer series, Herzberg (41)]. H_∞ gives the theoretical position of the series limit.

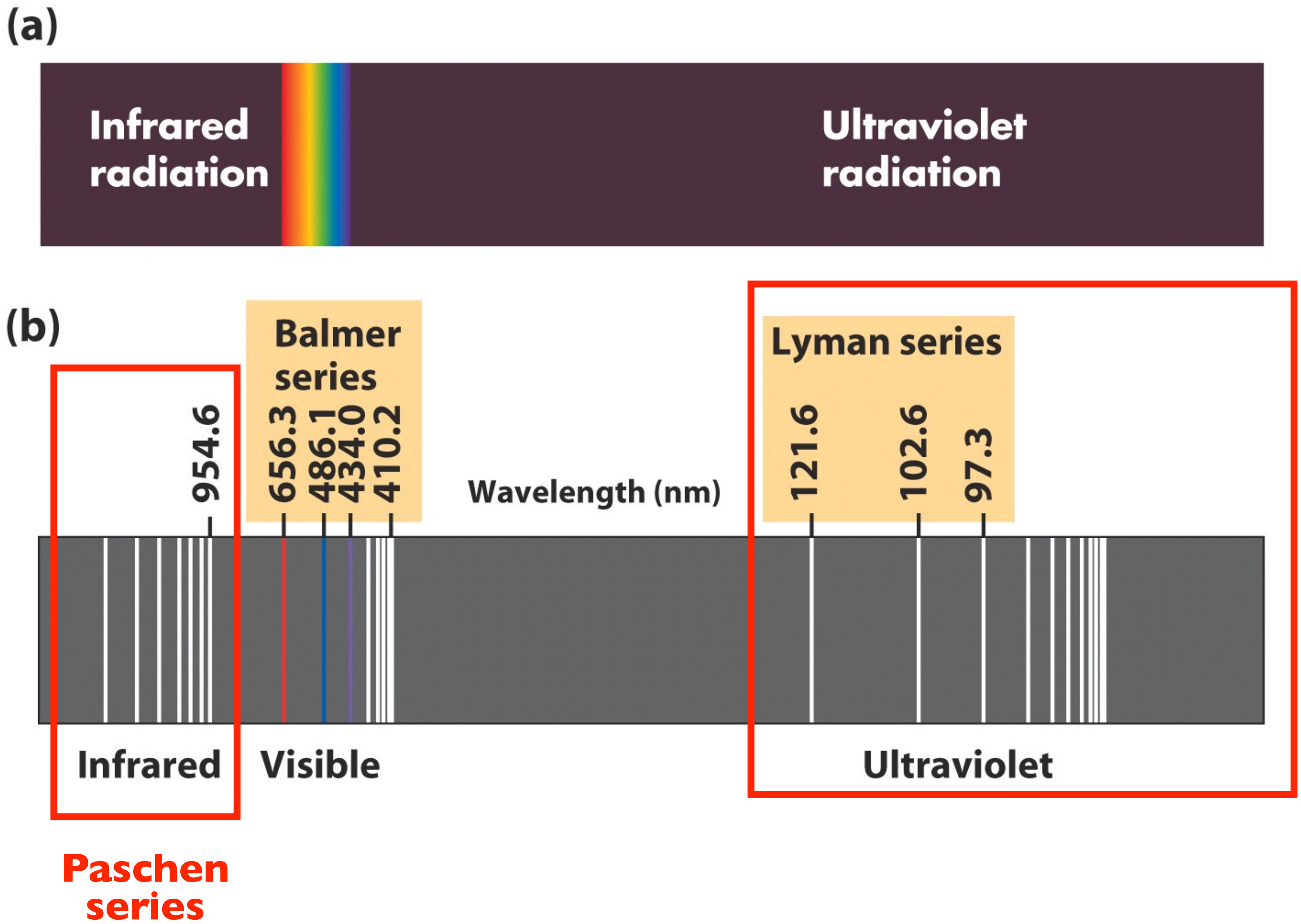
From "*Atomic Spectra and Atomic Structure*" by G. Herzberg, 1937.

H atom Emission Spectrum



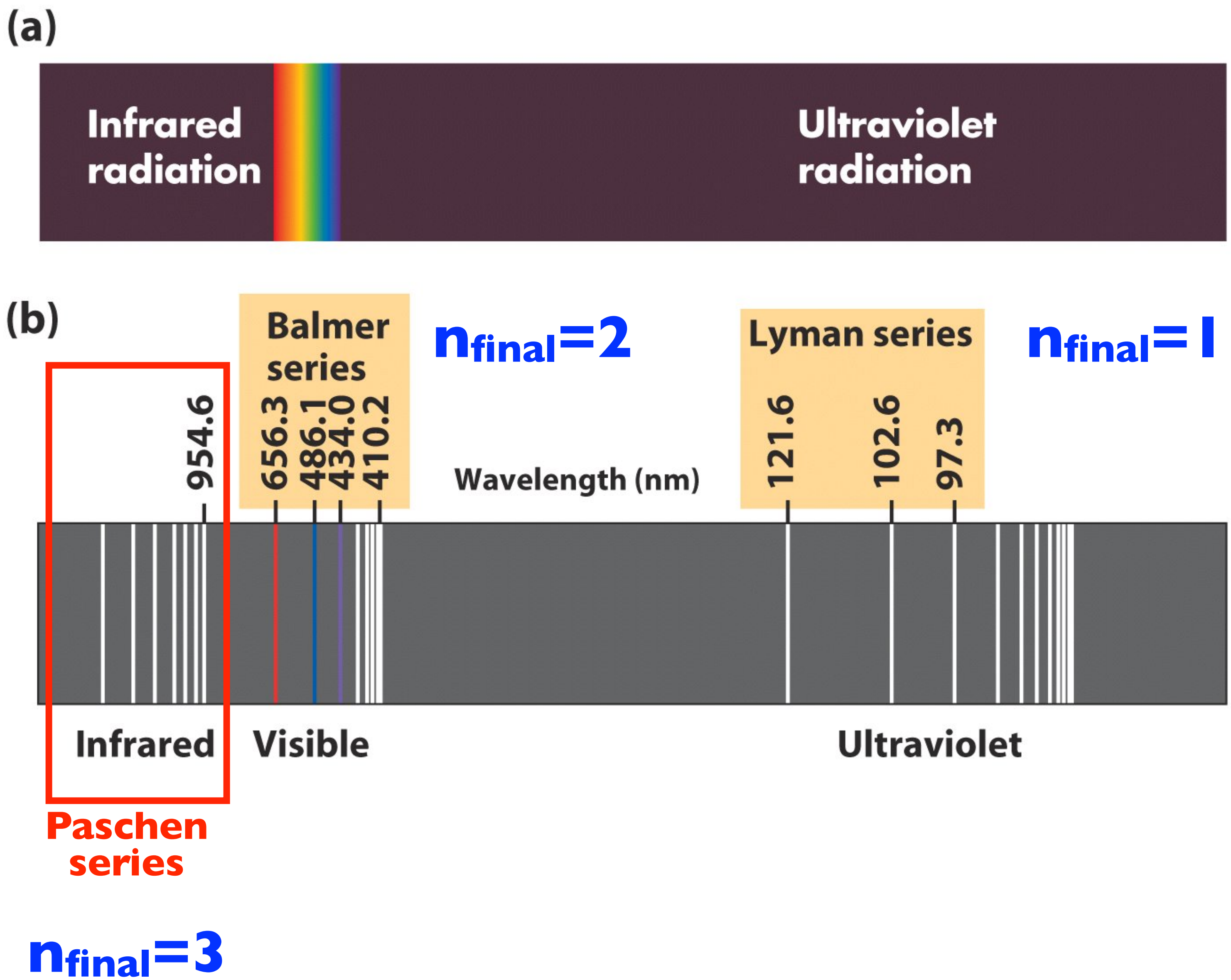
There are two more series in the UV and IR

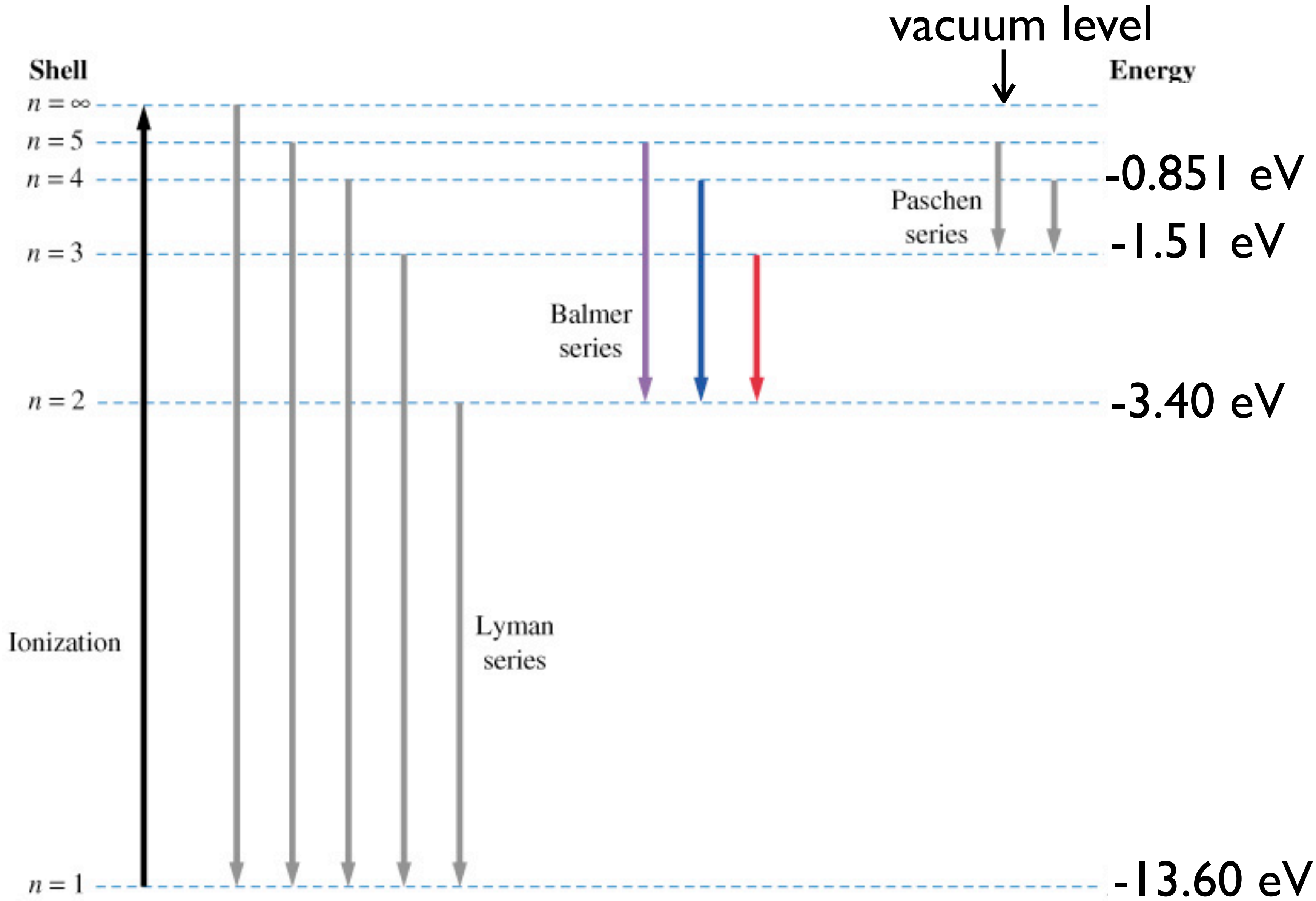
H atom Emission Spectrum



There are two more series in the UV and IR

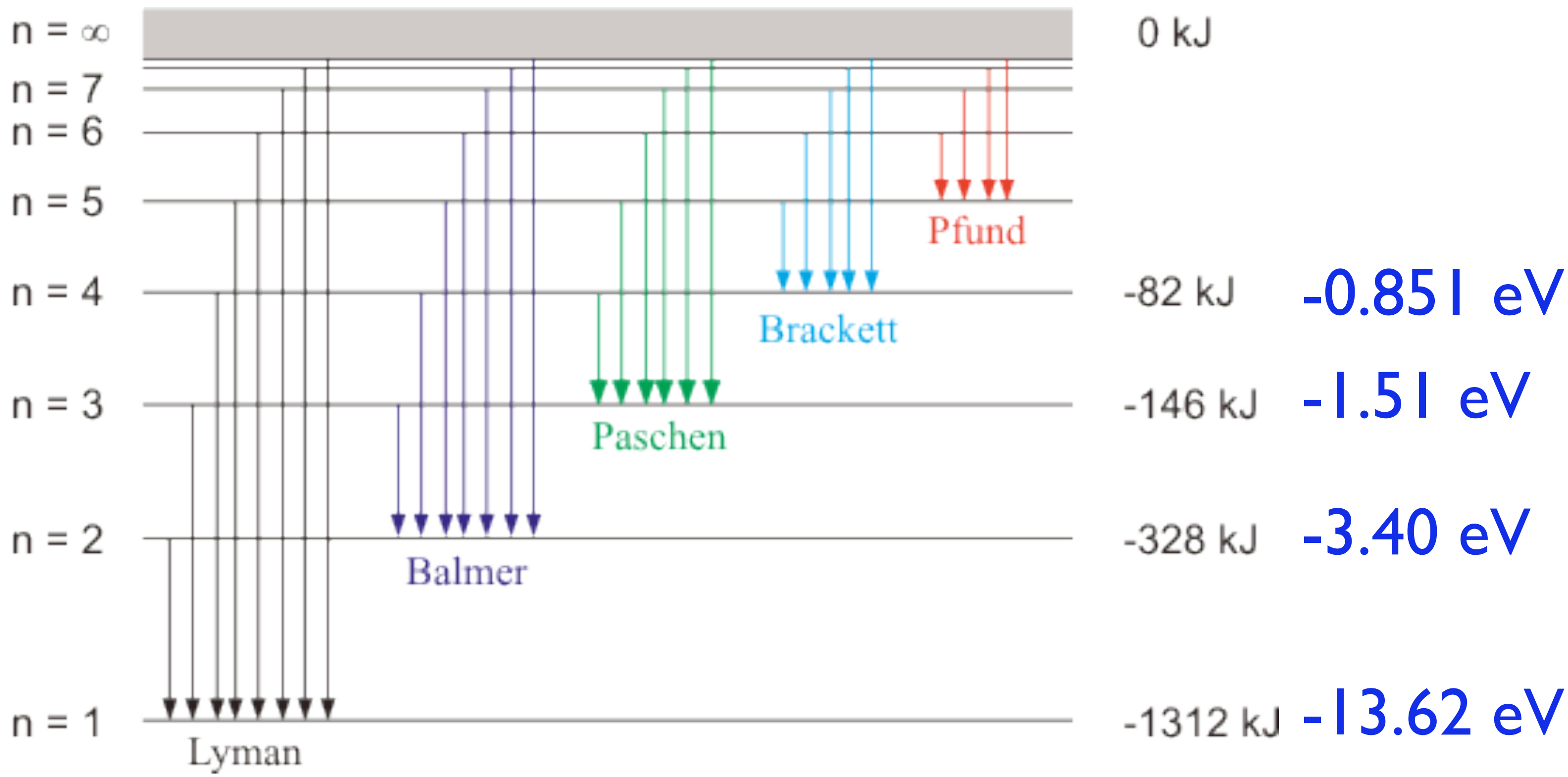
All of the lines within each of the 3 named spectroscopic “series” share the same n_{final}.



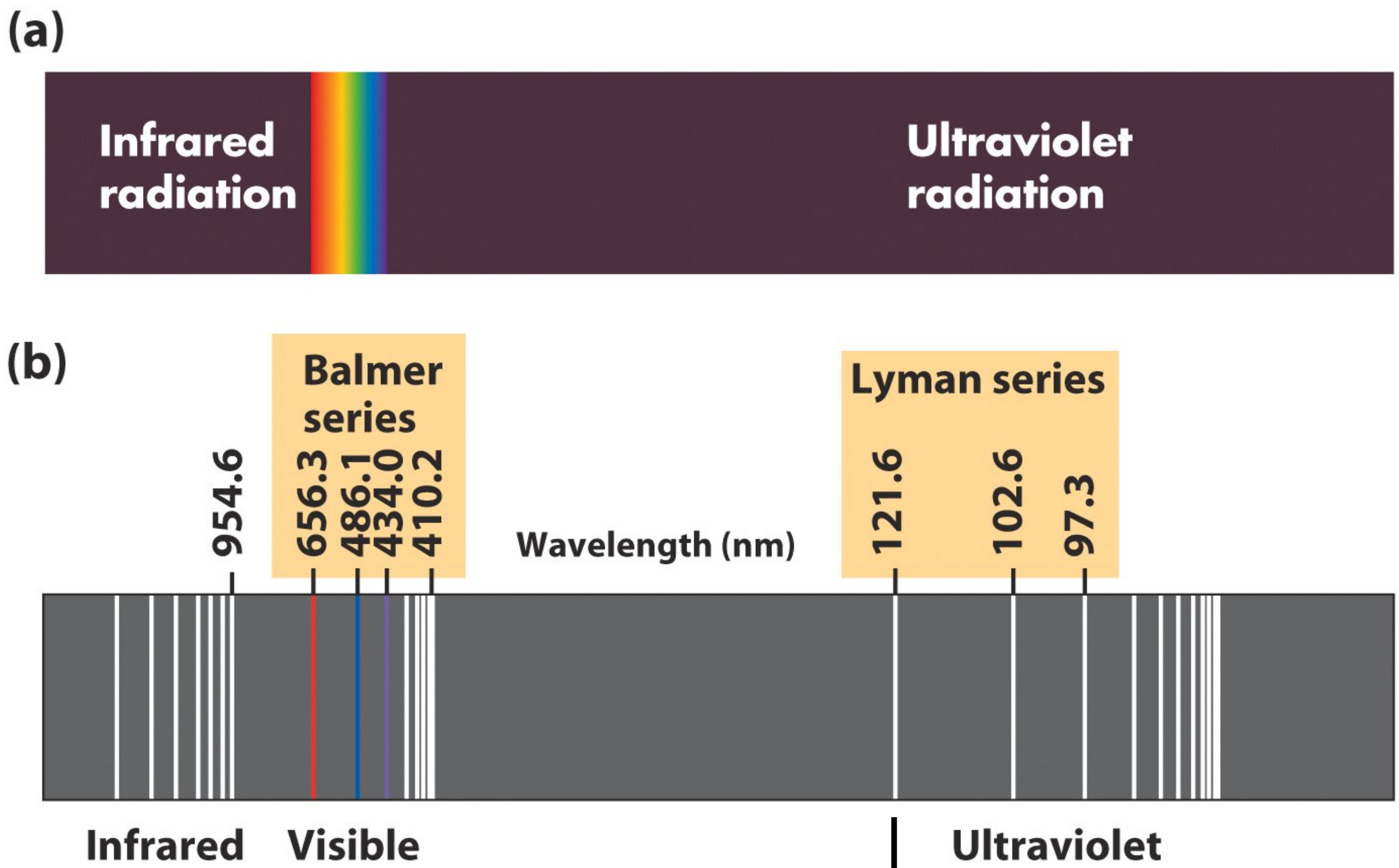


All of the lines within each of the 3 named spectroscopic “series” share the same n_{final}.

Actually, there are more series further in the IR.

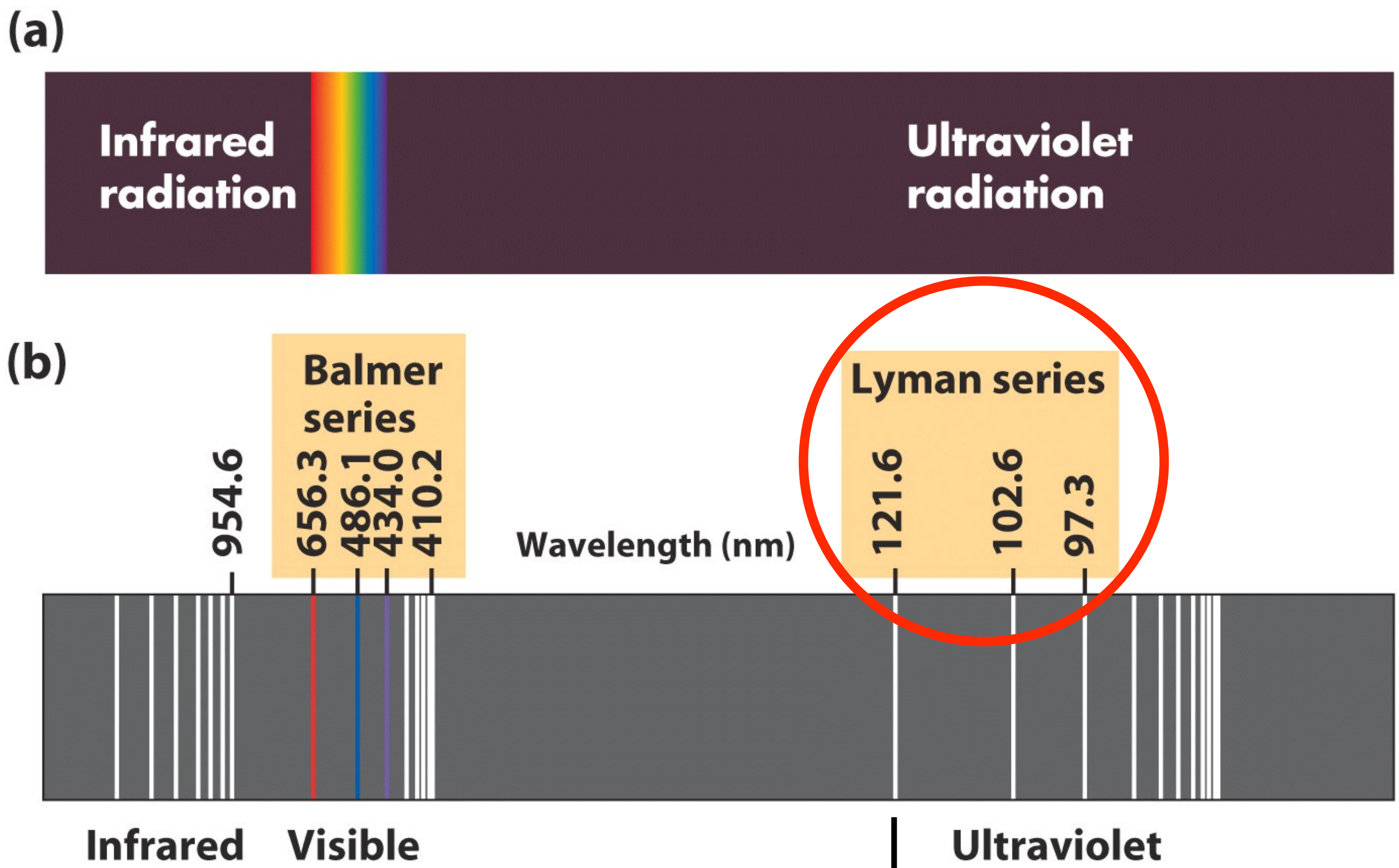


...let's do a few examples:



$$\begin{array}{ccc} n_{initial} & & n_{final} \\ 2 & \longrightarrow & 1 \end{array}$$

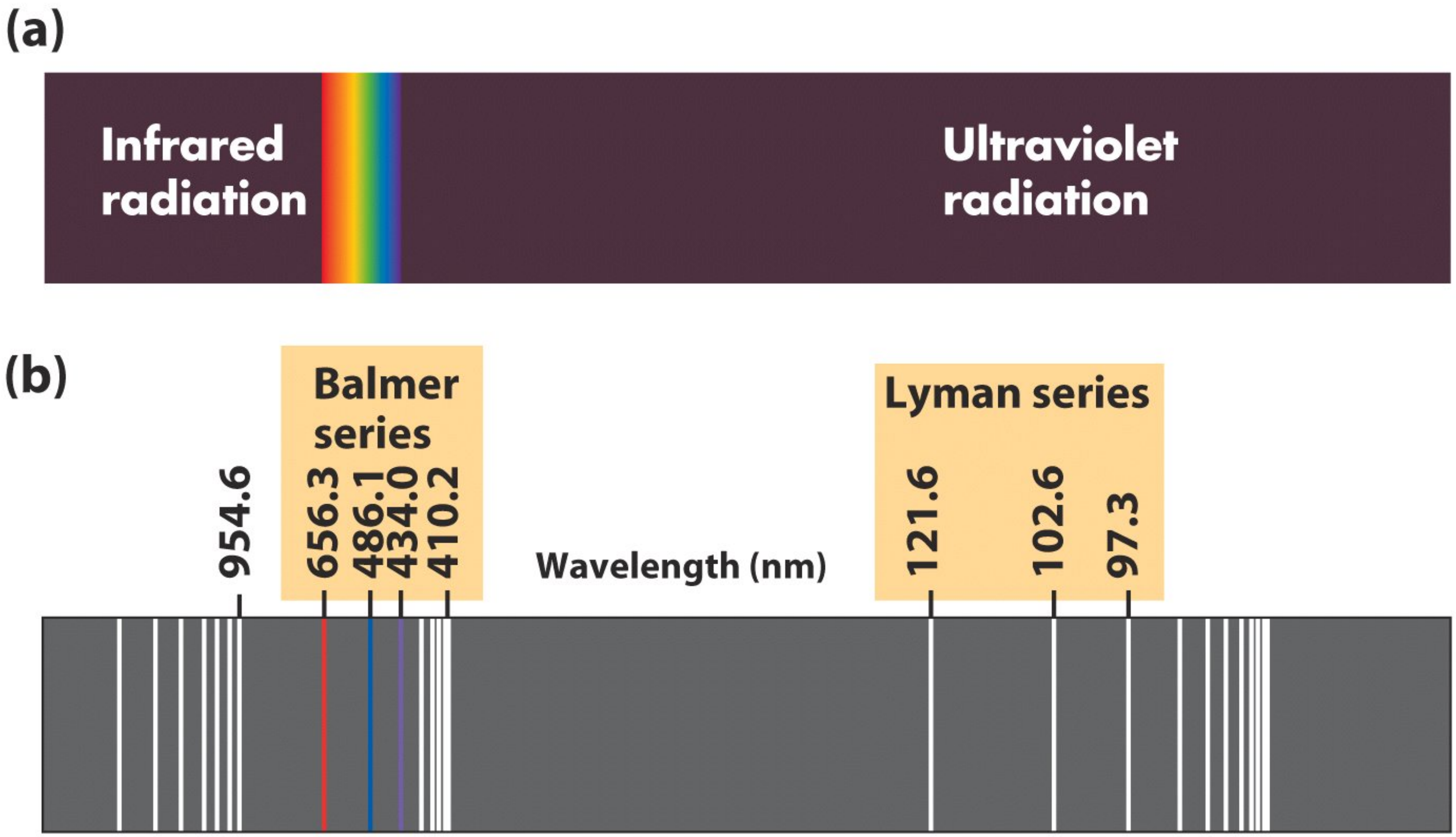
...let's do a few examples:



$n_{initial}$ → n_{final}
2 → 1

step 1 - look at series to get n_{final}

...let's do a few examples:

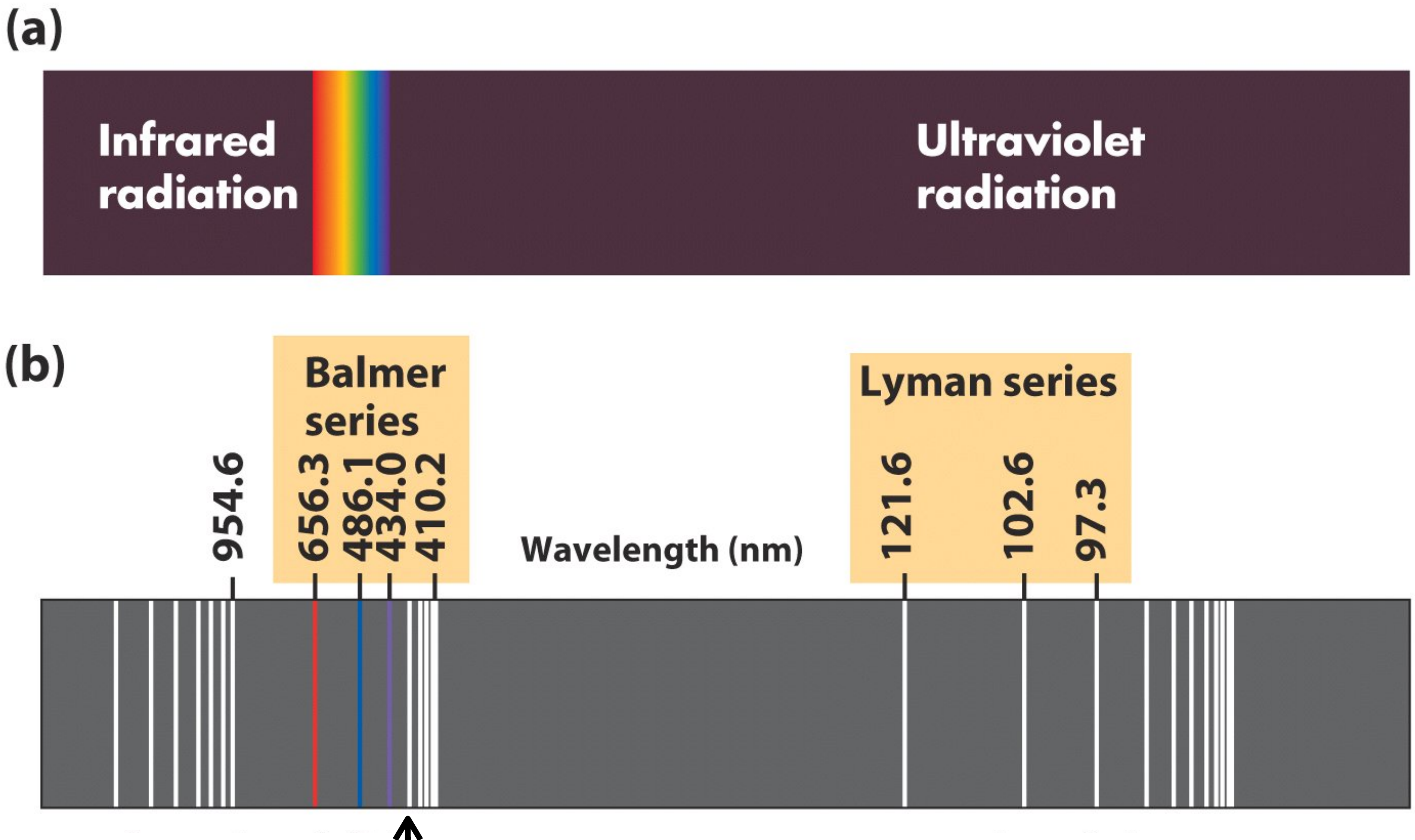


step 2 - count up from last line to get $n_{initial}$ starting at n_{final} +1.

$n_{initial} \rightarrow n_{final}$

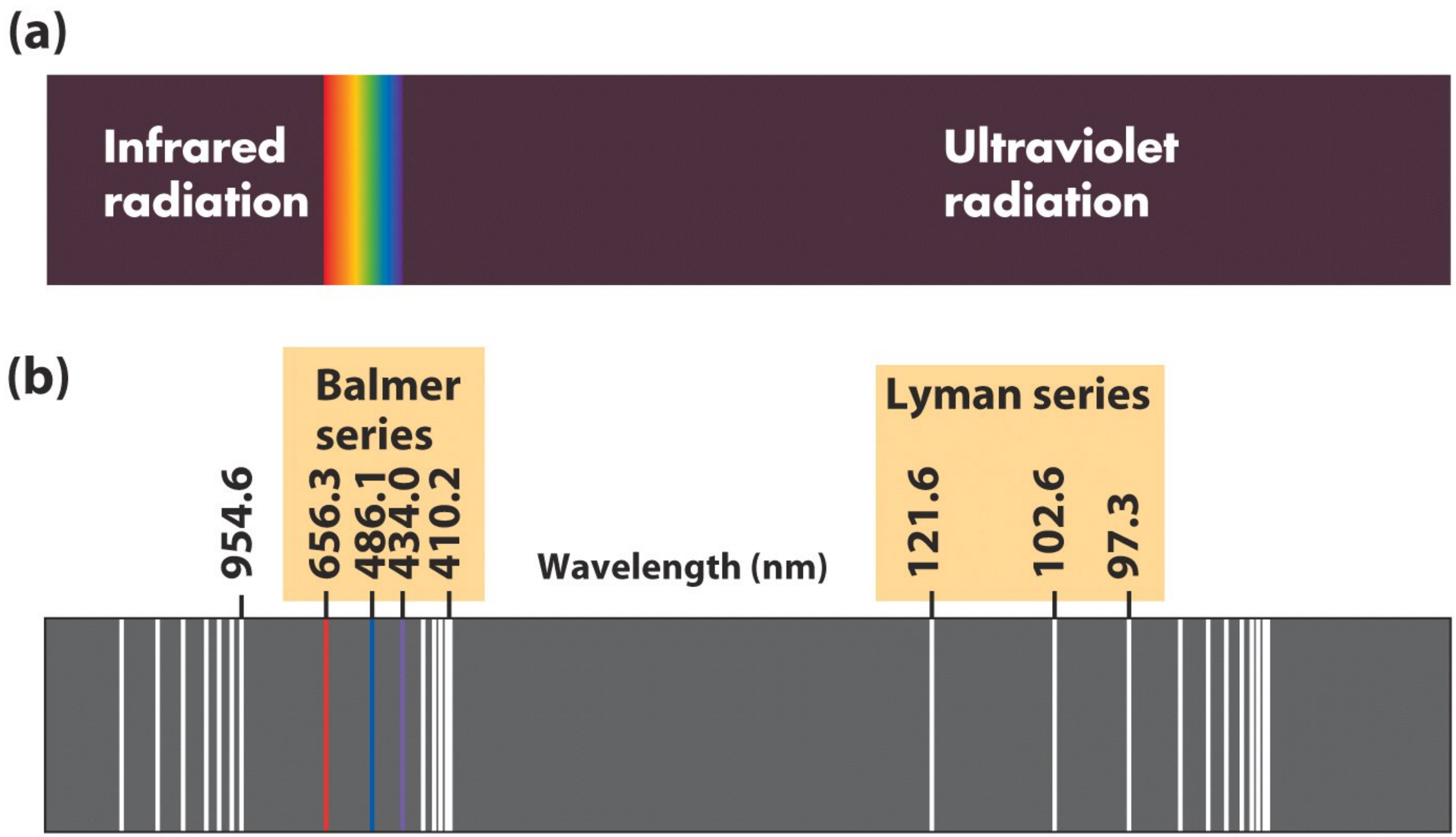
$2 \quad\quad 1$

...another example...



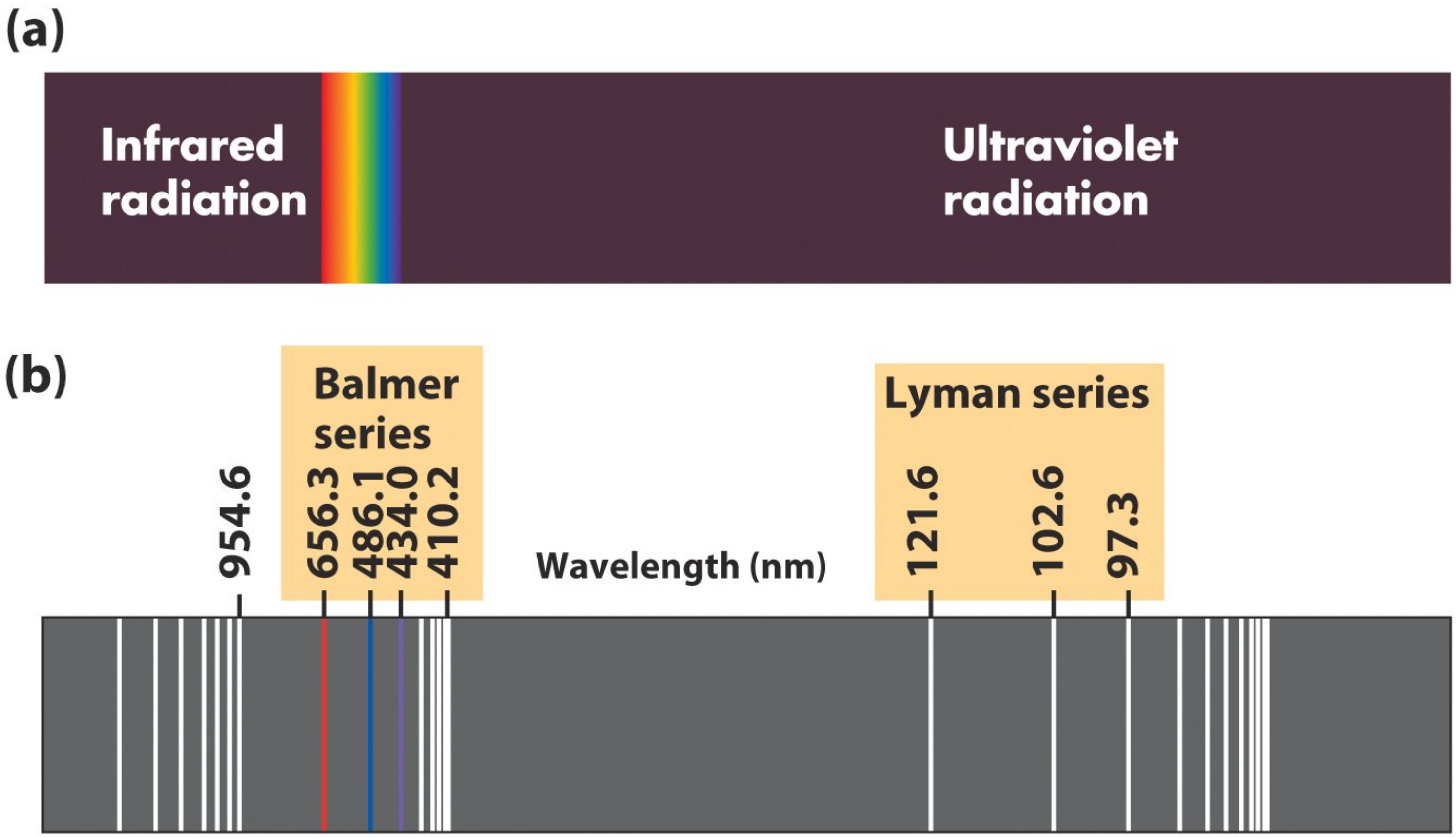
specify the initial and final states responsible for this emission line.

...another example...



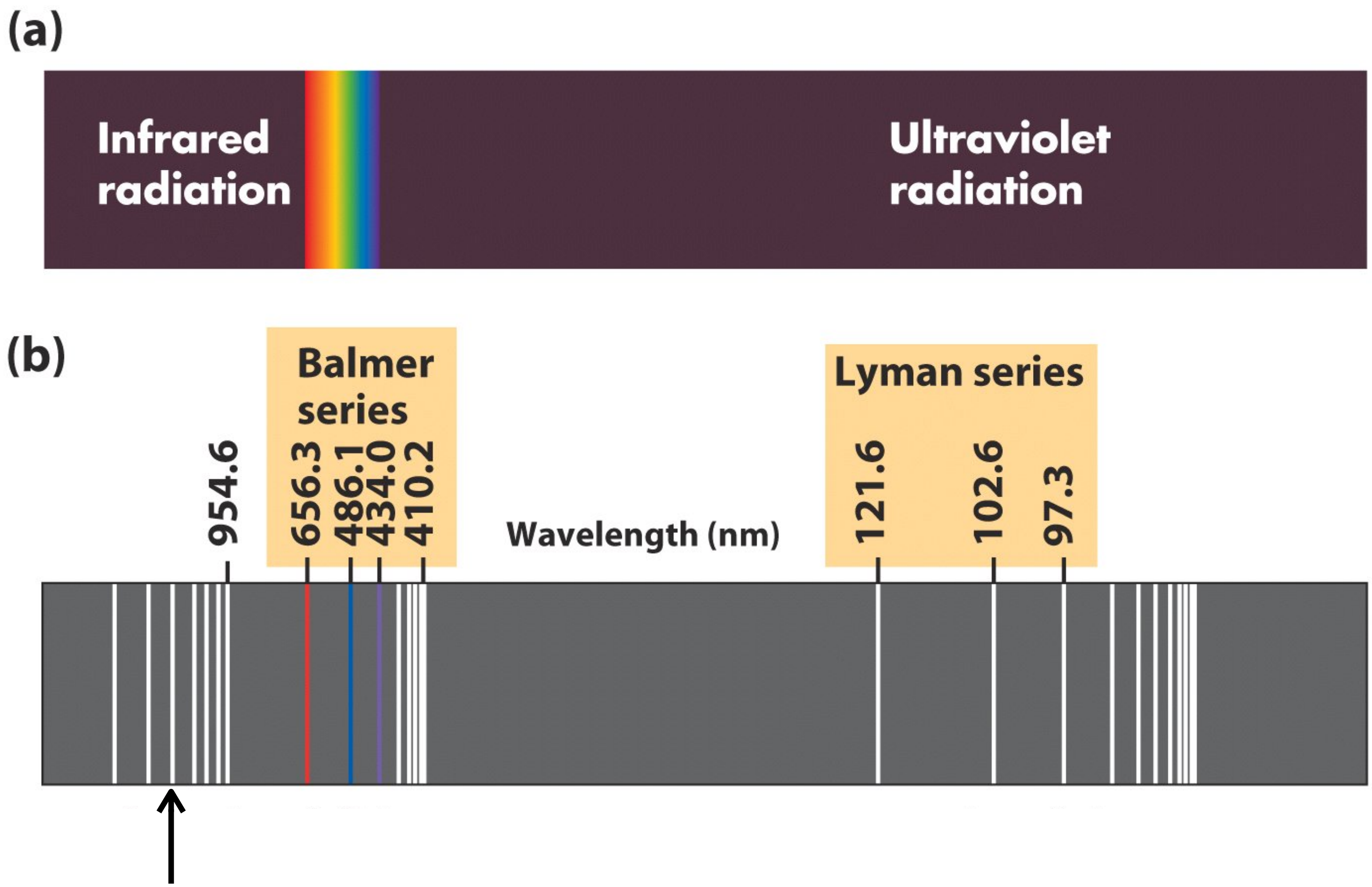
? $\longrightarrow$ $n_{final} = 2$

...another example...



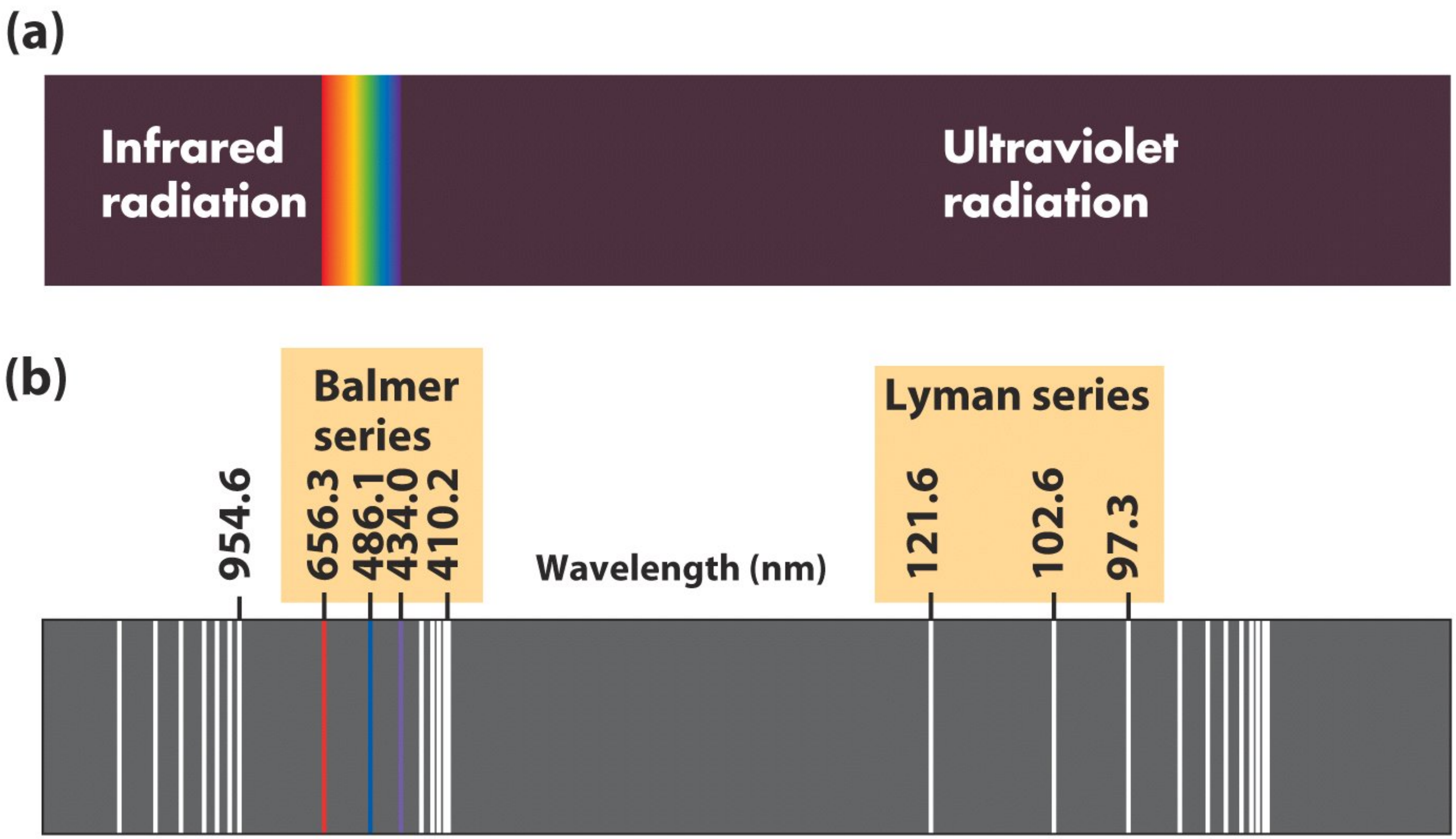
$n_{initial} = 6 \longrightarrow n_{final} = 2$

...another example...



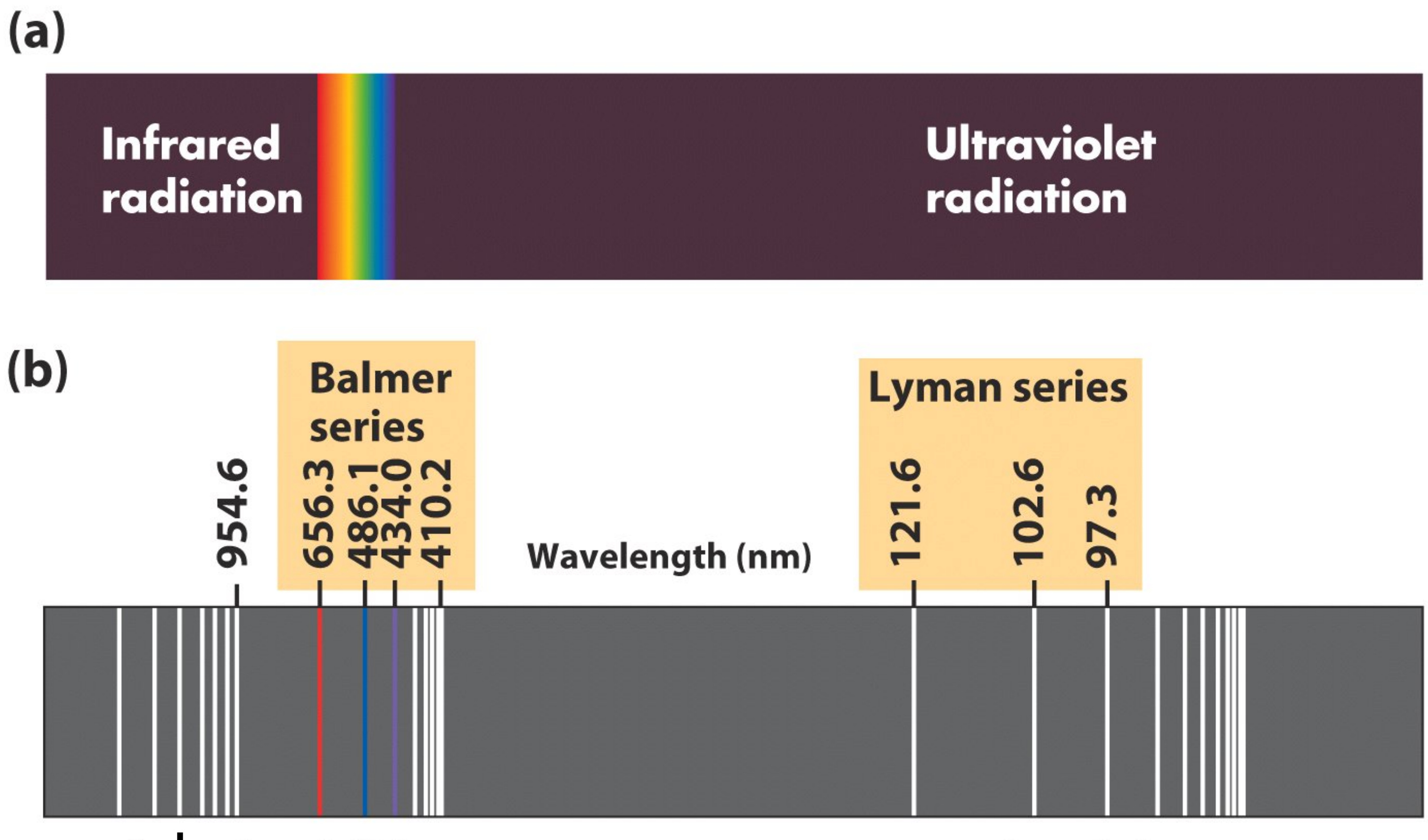
specify the initial and final states responsible for this emission line.

...another example...



? $\longrightarrow$ $n_{final} = 3$

...still another example...



$n_{initial}$ = 6 $\longrightarrow$ n_{final} 3

...if we were asked, we could go one step further:
we could calculate the energies of $n_{initial}$ and n_{final} and get the energy of the emitted photon.

Let's do one:

Question: Calculate the wavelength of the photon emitted when a hydrogen atom in n=7 undergoes a transition to n=3.(what is the name of this series?).

Key equation:

$$E_n = -\frac{hcR}{n^2}$$

hcR = 13.60 eV

Question: Calculate the wavelength of the photon emitted when a hydrogen atom in n=7 undergoes a transition to n=3 (what is the name of this series?).

Key equation:

$$E_n = -\frac{hcR}{n^2}$$

$$hcR = 13.60 \text{ eV}$$

Step 1: Calculate $E_{n=7}$ and $E_{n=3}$.

$$E_7 = -13.60/7^2 = -0.2776 \text{ eV}$$

$$E_3 = -13.60/3^2 = -1.511 \text{ eV}$$

Question: Calculate the wavelength of the photon emitted when a hydrogen atom in n=7 undergoes a transition to n=3.

Step 1: Calculate $E_{n=7}$ and $E_{n=3}$.

$E_7 = -13.60/49 = -0.2776$ eV

$E_3 = -13.60/9 = -1.511$ eV

Step 2: Calculate ΔE...

$\Delta E = E_7 - E_3 = (-0.2776) - (-1.511) = 1.233$ eV

Step 3: Calculate ΔE...

$\Delta E = 1240./\lambda$

$\lambda = 1240./\Delta E = 1006$ nm

Hydrogen-like atoms

These energies work not only for hydrogen, but also to all **hydrogen-like atoms** (i.e., ANY atom with just one electron) with a nuclear charge of Z:

example: **He**$^{+}$ (Z = 2),
Li^{2+} (Z = 3),
Be^{3+} (Z = 4),
Cs^{54+} (Z = 55).
etc.

$$E_n = -\frac{Z^2 hcR}{n^2}$$

WHEN we solve the Schrödinger equation, we always obtain two things:

1. a set of eigenstates $|\psi_n>$.
2. a set of eigenstate energies, E_n.

Hydrogen atom solution:

$$E_n = -\frac{hcR}{n^2}$$

$n = 1, 2, 3...$

$hcR = 13.60$ eV

$$\left| n, l, m_l, m_s \right\rangle$$

State vectors are labeled with the quantum number n...
AND three more: l, m_l, m_s

Hydrogen atom quantum numbers

$$\left|n, l, m_l, m_s\right\rangle$$

n is called the principal quantum number.

- $n = 1, 2, 3....$

l is called the orbital angular momentum quantum number.

- $l = 0, 1, 2...(n-1) = s, p, d, f...$

m_l is called the magnetic quantum number.

- $m_l = l, l-1, ...-l$

m_s is called the spin magnetic quantum number.

- $m_s = 1/2, -1/2$ we'll deal with this one later.

Hydrogen atom wavefunctions

The three dimensional H atom wavefunction can be defined by the three quantum numbers n, l, and m_l.

$$\Psi_{n,l,m_l}(\mathbf{r})$$

Three Dimensional Wavefunction (Hydrogen Atom)

$$|n,l,m_l,m_s\rangle$$

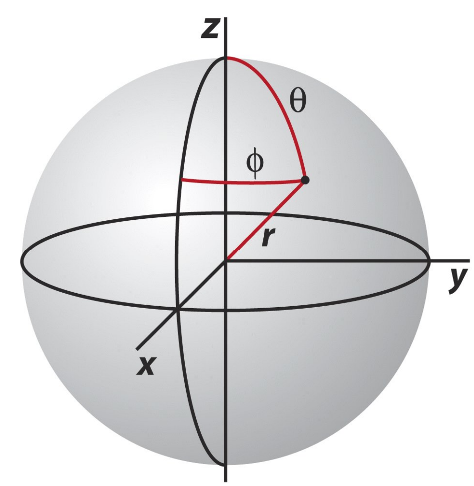
The spin magnetic quantum number doesn't appear in the wavefunction.

Hydrogen atom wavefunctions

The three dimensional H atom wavefunction can be defined by the three quantum numbers n, l, and m_l.

$$\Psi_{n,l,m_l}(\mathbf{r}) = R_{n,l}(r)Y_{l,m_l}(\theta,\phi)$$

ψ is a function of r, θ and Φ (spherical coordinates)



Hydrogen atom wavefunctions

The three dimensional H atom wavefunction can be defined by the three quantum numbers n, l, and m_l.

$$\Psi_{n,l,m_l}(\mathbf{r}) = \boxed{R_{n,l}(r)}\,Y_{l,m_l}(\theta,\phi)$$

$R_{n,l}(r)$ is the radial component of the wavefunction.

$R_{n,l}$ depends on the two quantum numbers n and l.

Hydrogen atom wavefunctions

The three dimensional H atom wavefunction can be defined by the three quantum numbers n, l, and m_l.

$$\Psi_{n,l,m_l}(\mathbf{r}) = R_{n,l}(r)\boxed{Y_{l,m_l}(\theta,\phi)}$$

$Y_{l,ml}(\theta,\phi)$ is the angular component of the wavefunction.

$Y_{l,ml}$ depends on the two quantum numbers l and m_l.

Hydrogen atom wavefunctions

TABLE 1.2 Hydrogen Wavefunctions (Atomic Orbitals), $\psi = RY$

(a) Radial wavefunctions, $R_{nl}(r)$

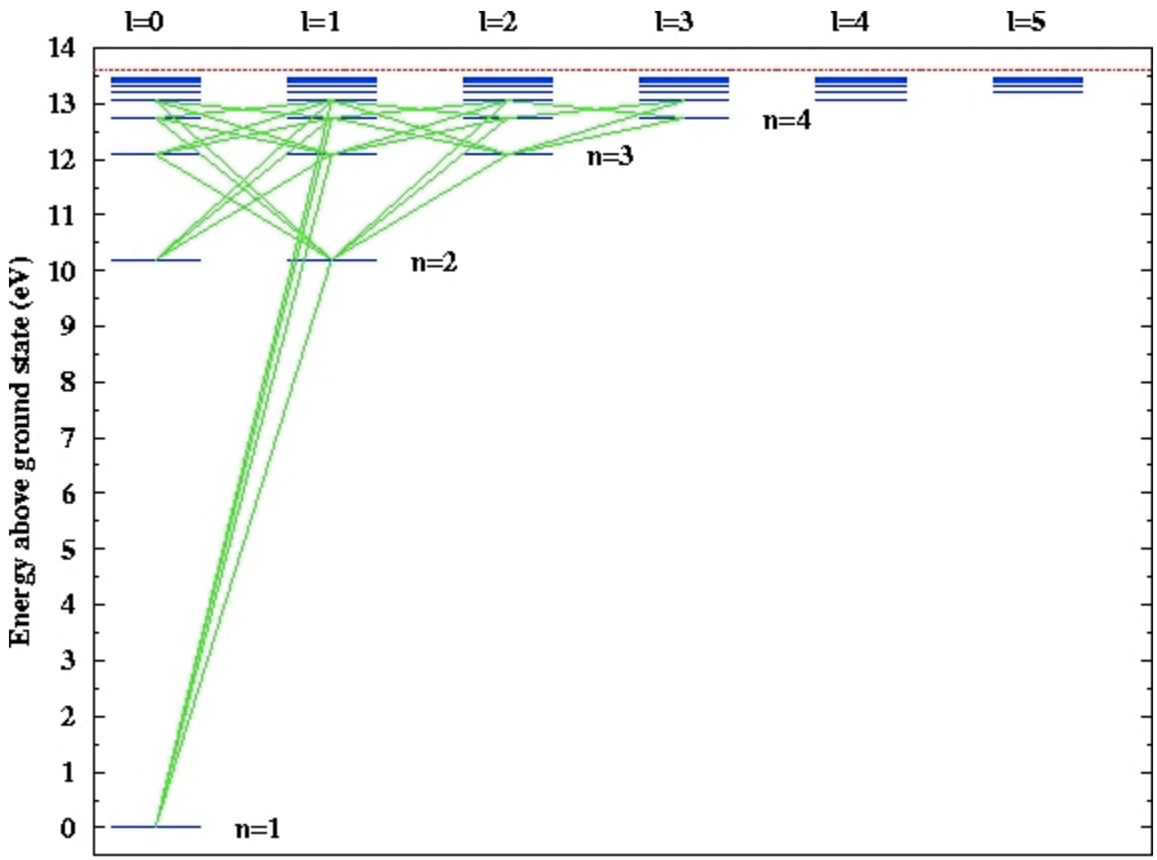
n	l	$R_{nl}(r)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
3	0	$\frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(3-\frac{2Zr}{a_0}+\frac{2Z^2r^2}{9{a_0}^2}\right)e^{-Zr/3a_0}$
	1	$\frac{2}{27\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{3a_0}\right)e^{-Zr/3a_0}$
	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$

(b) Angular wavefunctions, $Y_{lm_l}(\theta,\phi)$

l	"m_l"*	$Y_{lm_l}(\theta,\phi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	x	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
	y	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
	z	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
2	xy	$\left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\cos 2\phi$
	yz	$\left(\frac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\sin\phi$
	zx	$\left(\frac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\cos\phi$
	x^2-y^2	$\left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\sin 2\phi$
	z^2	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$

Note: In each case, $a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$, or close to 52.9 pm; for hydrogen itself, $Z = 1$.
*In all cases except $m_l = 0$, the orbitals are sums and differences of orbitals with specific values of m_l.

Hydrogen atom quantum numbers



s p d f g h

principal quanta n

angular momentum quanta l

A Grotrian diagram is what spectroscopists use to analyze their line spectra. Each column is for a different l quantum number. Note that only certain transitions are observed. These are called selection rules.

Still to come:

- ...Probability Densities for H atom orbitals.
- ...Spin!
- ...Aufbau principle for multielectron atoms.
- ...electron configurations of multielectron atoms.
- ...AES and Grotrian diagrams for different atoms.