Spectra of atoms and molecules

Classical dipole (moving/oscillating charge) emits electromagnetic wave → and looses energy!



If we have a negative classical charge moving around positive charge, its radius would gradually decrease and the system would collapse

So how comes atoms are stable?

Quantum physics → electrons in atoms can only have very specific energies, and not something in between

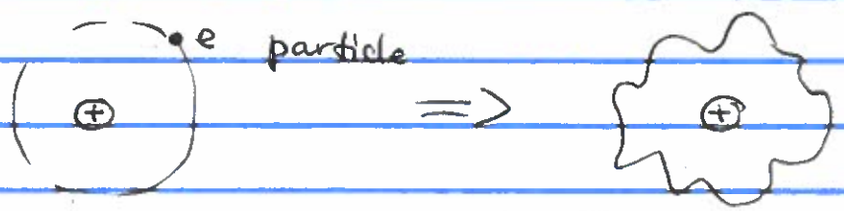
Why? Because electron is also a wave

if a particle's momentum is $\vec{p}$ ($\approx m_e \vec{v}$)

de Broigle wavelength $\lambda \approx 3-7 \cdot 10^{-10}$ m

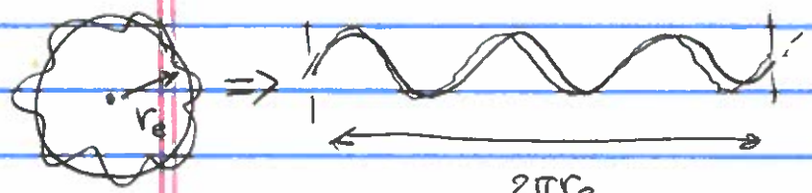
comparable to the size of electron's orbit

So rather than



and if that is a wave, we have to account for interference!

In order to have a stable orbital, the electron wave should constructively interfere with itself "unwrapped"



$$2\pi r_e = n \cdot \lambda = n \cdot \frac{2\pi\hbar}{m_e v_e}$$

$$r_e \cdot v_e = n \cdot \frac{\hbar}{m_e}$$

For circular motion

$$m_e \frac{v_e^2}{r_e} = \frac{k e^2}{r_e^2}$$

$$v_e^2 = \frac{k e^2}{m_e r_e} \qquad v_e = \sqrt{\frac{k e^2}{m_e r_e}}$$

$$r_e \cdot \sqrt{\frac{k_e e^2}{m_e r_e}} = n \cdot \frac{\hbar}{m_e}$$

$$r_e^2 \cdot \frac{k e^2}{m_e r_e} = n^2 \frac{\hbar^2}{m_e^2} \qquad \Rightarrow r_e = r_n = n^2 \frac{\hbar^2}{k e^2 m_e}$$

Electron energy in a circular motion

$$E_n = -\frac{1}{2}\frac{k e^2}{r_n} = -\frac{1}{2}\frac{(k e^2)^2 m_e}{\hbar^2 n^2}$$

This is the same answer we would get from quantum mechanics calculations

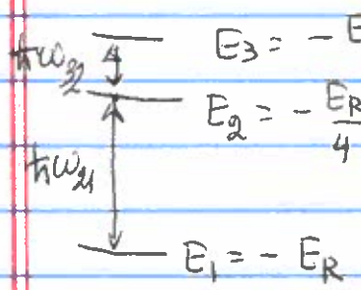
$$E_n = -\frac{E_R}{n^2}$$

Rydberg constant

$$E_R = \frac{1}{2}\frac{(k e^2)^2 m_e}{\hbar^2}$$

Bohr radius $a = \dfrac{\hbar^2}{k e^2 m_e}$ (but $r_n = n \cdot a$)

But what about light emission?



$$\hbar\omega_{21} = E_2 - E_1 = -\frac{E_R}{4} + E_R = \frac{3E_R}{4}$$

$$\hbar\omega_{32} = E_3 - E_2 = -\frac{E_R}{9} + \frac{E_R}{4} = \frac{5}{36}E_R$$

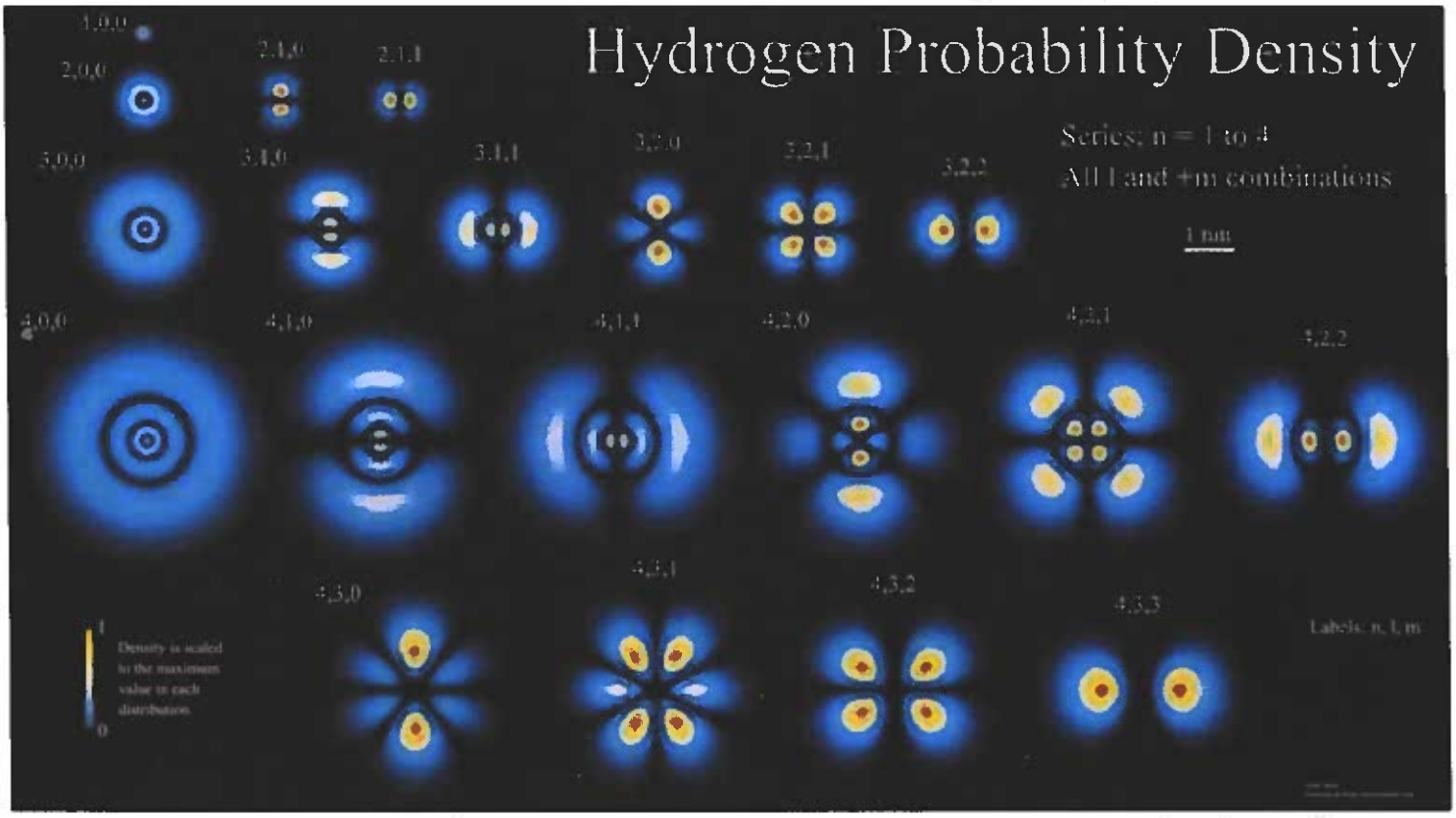
In general

$$\hbar\omega_{nm} = E_R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

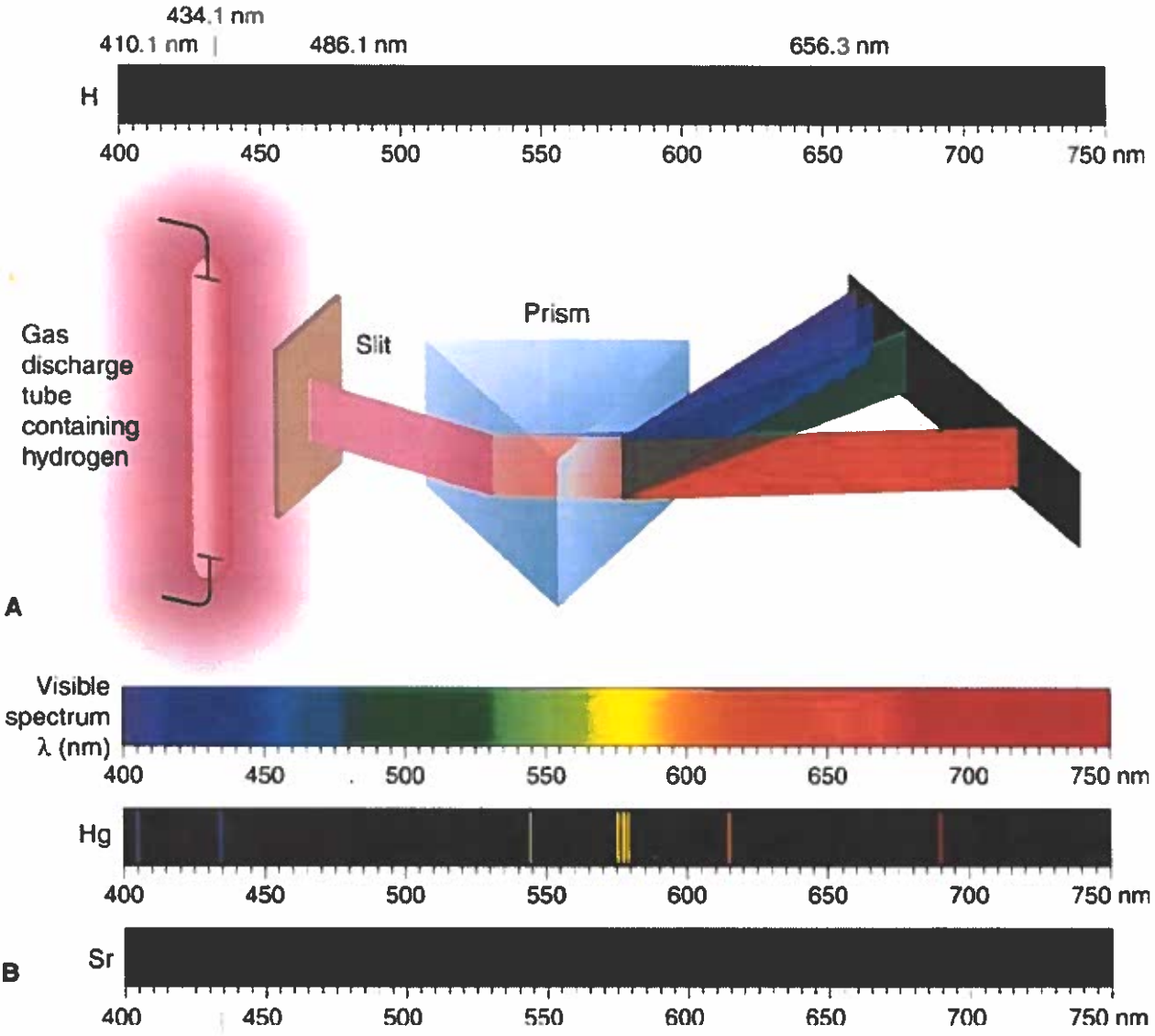
transition frequencies

The exact values of energies change depending on each atom, that is the basis of atomic spectroscopy.

Molecules also have sharp spectral line, but more complex. In addition to electron transitions, there are lines associated with vibration and rotation


Hydrogen Probability Density
Series: n = 1 to 4
All l and +m combinations
1 nm
1,0,0
2,0,0
2,1,0
2,1,1
3,0,0
3,1,0
3,1,1
3,2,0
3,2,1
3,2,2
4,0,0
4,1,0
4,1,1
4,2,0
4,2,1
4,2,2
4,3,0
4,3,1
4,3,2
4,3,3
Density is scaled to the maximum value in each distribution
1
0
Labels: n, l, m

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$$\hbar\omega_{light} = E_2 - E_1$$