

# ECE 535: Introduction to Quantum Sensing

## Energies of one-electron atoms

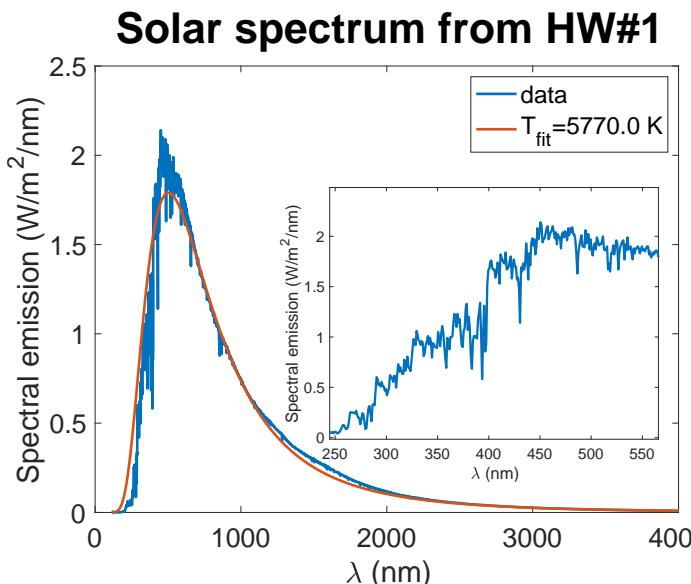
Jennifer Choy

Fall 2025

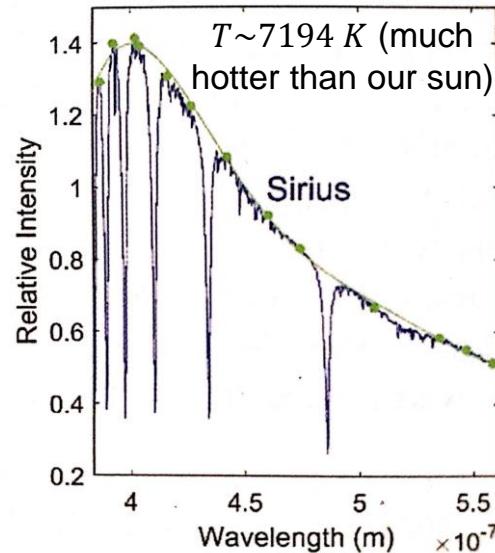


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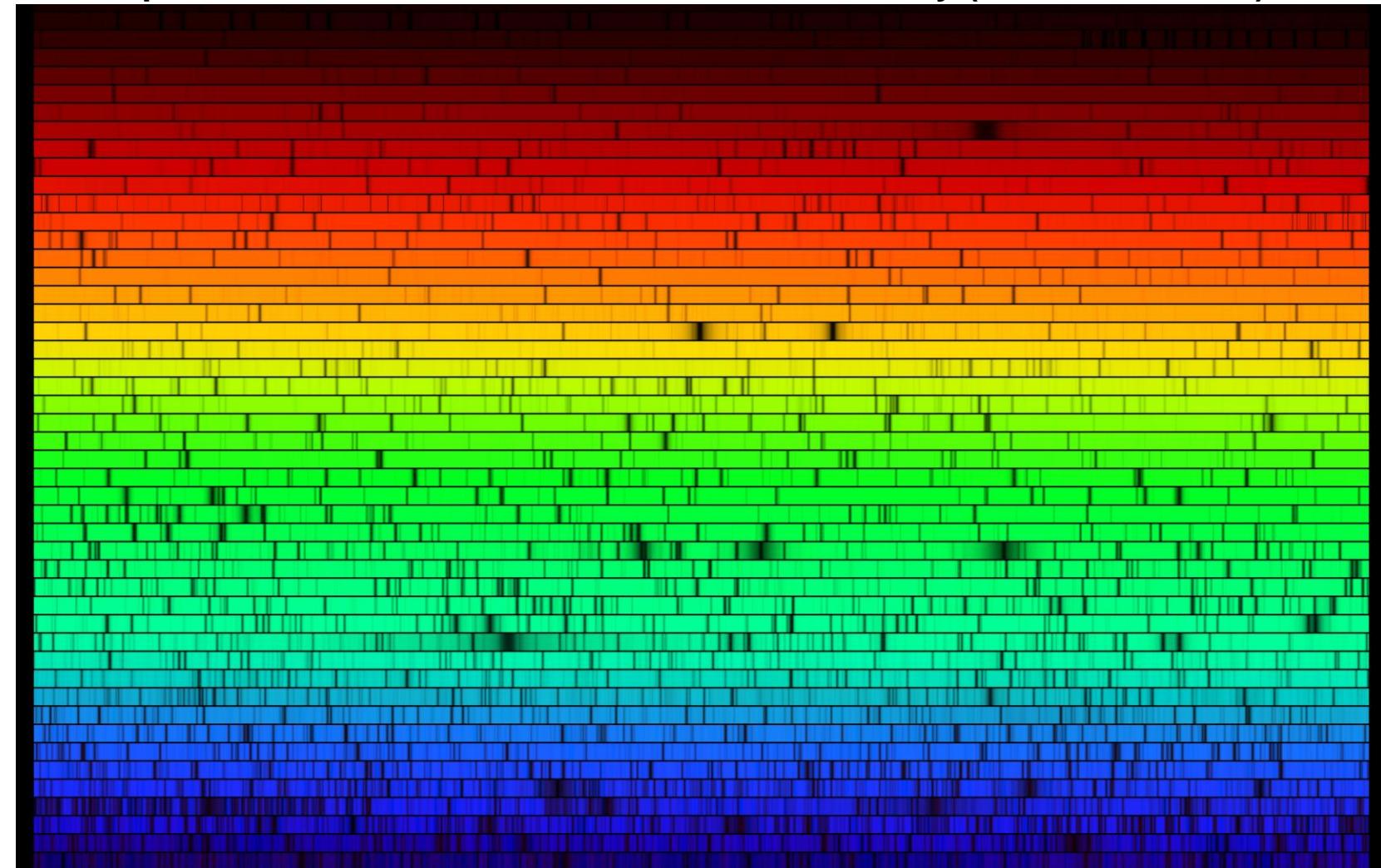
# Phenomena of atomic absorption helped motivate development of quantum mechanics



**Spectrum from a brighter star**



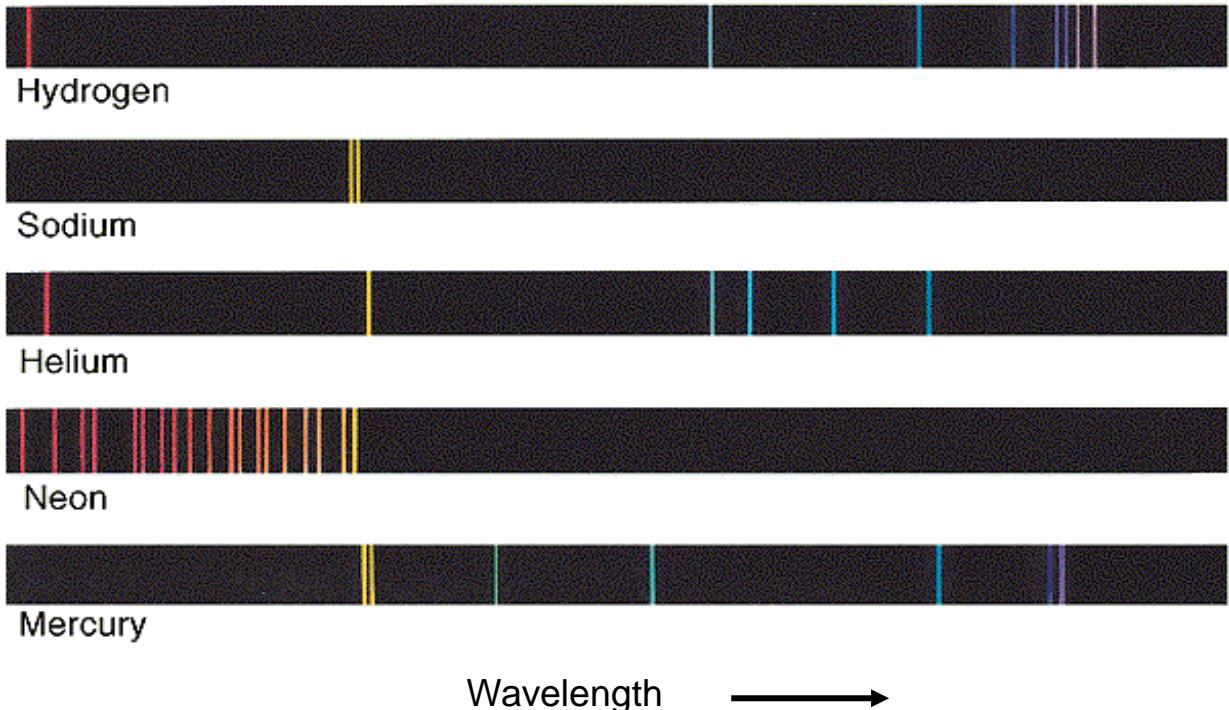
**Solar spectrum taken at the National Solar Observatory (each row ~ 6 nm)**



These dark lines (Fraunhofer lines) come from absorption of thermal emission by elements in the star's atmosphere

# Empirical formulas were developed to describe atomic spectra

Discrete and unique spectral lines from atomic gases



Here are the first 4 lines in the Balmer series, in nm. What do they physically represent?

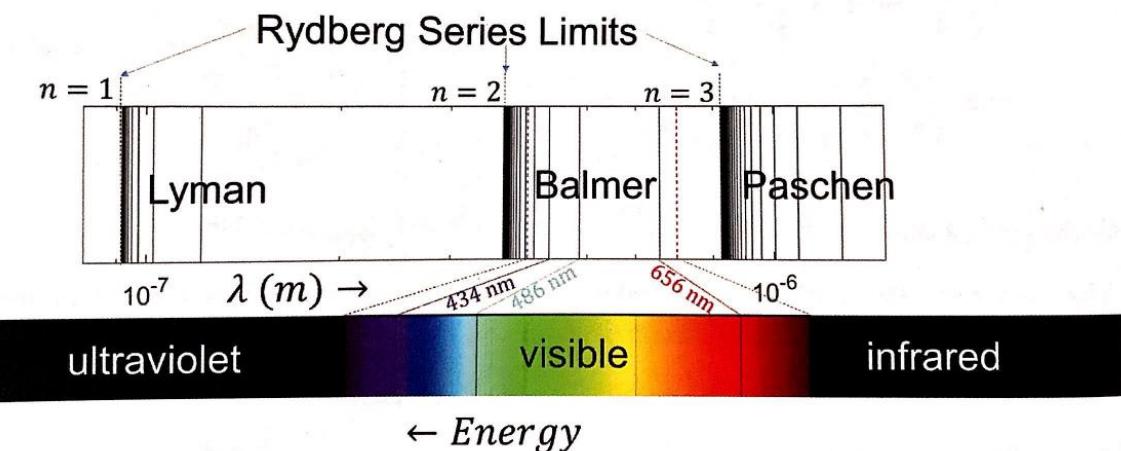
$k$	$\lambda$ (nm)
3	656
4	486
5	434
6	410

Transitions from  
 $n = k$  to  $n = 2$

Empirical formulas for describing hydrogen spectrum

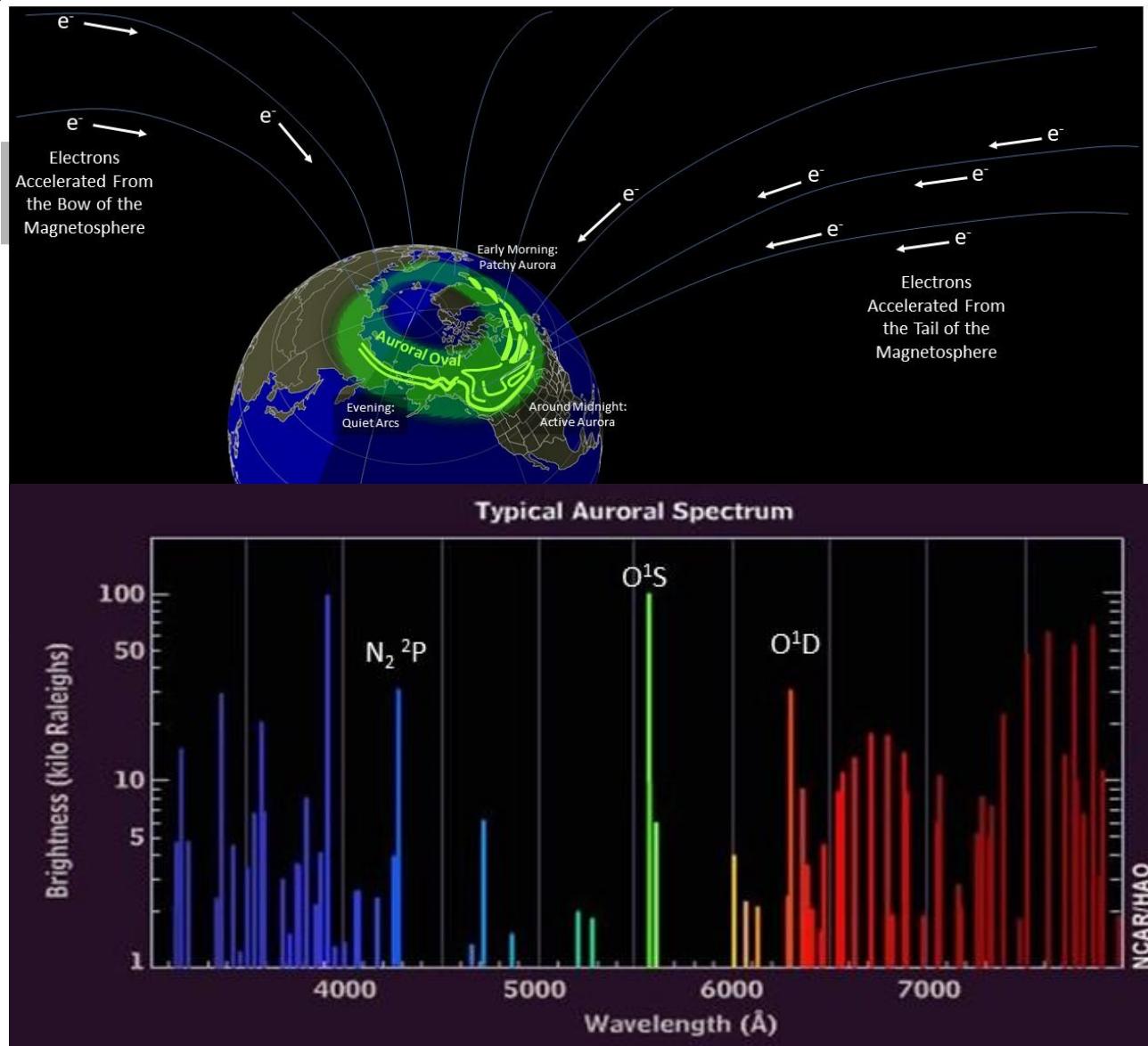
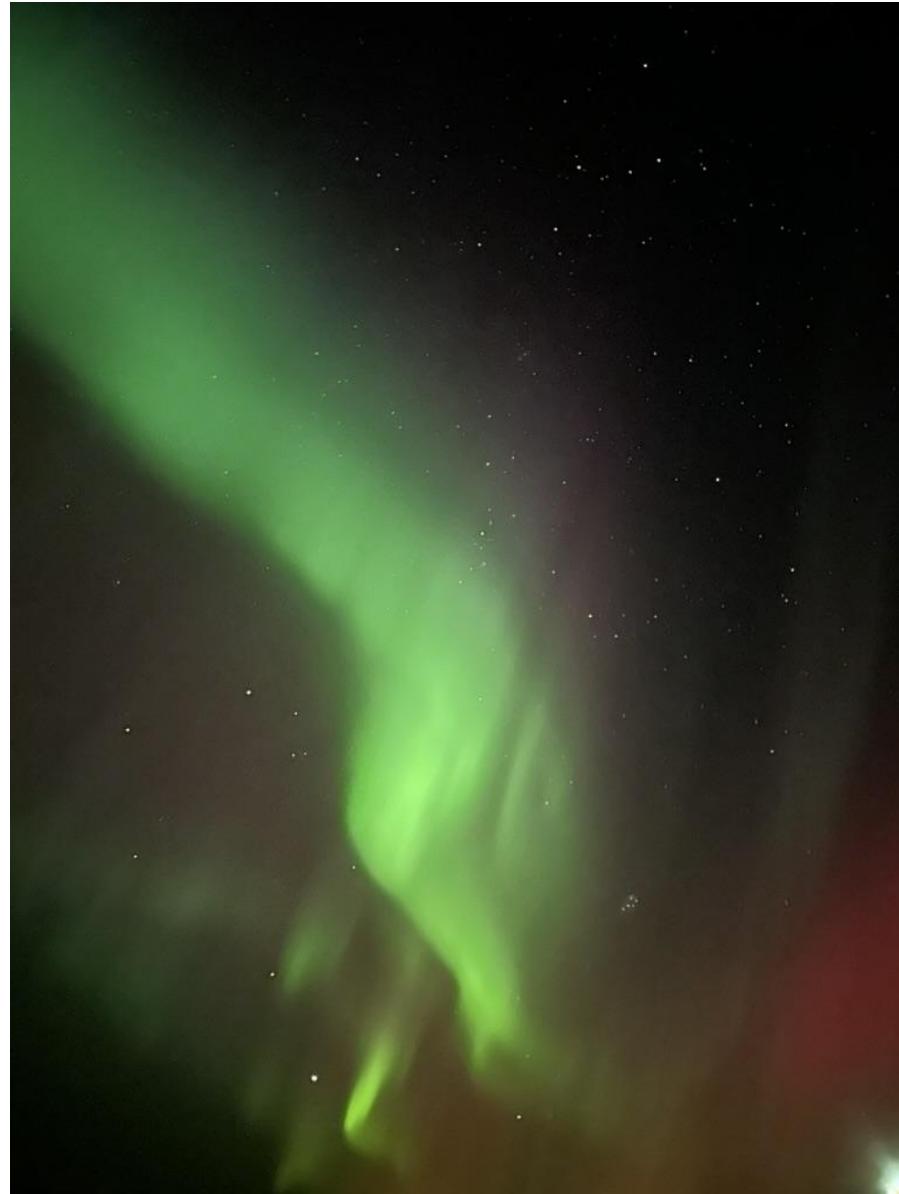
$$\text{Balmer: } \frac{1}{\lambda} = \frac{4}{364.56\text{nm}} \left( \frac{1}{2^2} - \frac{1}{k^2} \right) \quad \text{where } k = 3, 4, 5, \dots$$

$$\text{Rydberg: } \frac{1}{\lambda} = R_H \left( \frac{1}{n^2} - \frac{1}{k^2} \right) \quad R_H = 1.096776 \times 10^7 \text{ m}^{-1}$$



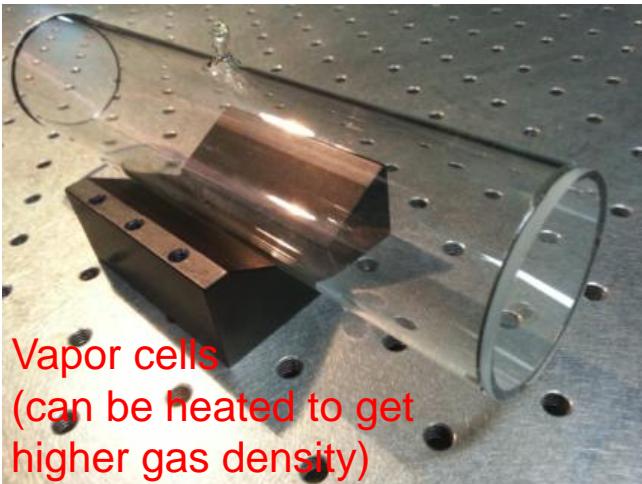
References: Demtroder, Chapter 3.4  
R. Trebino's lecture notes on Modern Physics  
Foot, "Atomic Physics", Chapter 1

# Atomic emission is responsible for the colors we see in Northern/Southern lights



<https://www.spaceweather.gov/content/aurora-tutorial>

# Atomic species



Electric discharges are used to ionize gas or generate plasma



Atomic Symbol	Name	Weight
1 H	Hydrogen	-11
2 He	Helium	
3 Li	Lithium	1
4 Be	Beryllium	2
11 Na	Sodium	1
12 Mg	Magnesium	2
19 K	Potassium	1
20 Ca	Calcium	2
21 Sc	Scandium	3
22 Ti	Titanium	4
23 V	Vanadium	5
24 Cr	Chromium	3 6
25 Mn	Manganese	2 4 7
26 Fe	Iron	2 3
27 Co	Cobalt	2 3
28 Ni	Nickel	2
29 Cu	Copper	2
30 Zn	Zinc	2
31 Ga	Gallium	3
32 Ge	Germanium	-4 2 4
33 As	Arsenic	-3 3 5
34 Se	Selenium	-2 2 4 6
35 Br	Bromine	1 1 3 5
36 Kr	Krypton	2
37 Rb	Rubidium	1
38 Sr	Strontium	2
39 Y	Yttrium	3
40 Zr	Zirconium	4
41 Nb	Niobium	5
42 Mo	Molybdenum	4 6
43 Tc	Technetium	4 7
44 Ru	Ruthenium	3 4
45 Rh	Rhodium	3
46 Pd	Palladium	2 4
47 Ag	Silver	1
48 Cd	Cadmium	2
49 In	Indium	3
50 Sn	Tin	-4 2 4
51 Sb	Antimony	-3 3 5
52 Te	Tellurium	-2 2 4 6
53 I	Iodine	-1 1 3 5 7
54 Xe	Xenon	2 4 6
55 Cs	Caesium	1
56 Ba	Barium	2
57-71		
72 Hf	Hafnium	4
73 Ta	Tantalum	5
74 W	Tungsten	4 6
75 Re	Rhenium	4
76 Os	Osmium	3 4
77 Ir	Iridium	2 4
78 Pt	Platinum	2 4
79 Au	Gold	3
80 Hg	Mercury	1 2
81 Tl	Thallium	1 3
82 Pb	Lead	2 4
83 Bi	Bismuth	3
84 Po	Polonium	-2 2 4
85 At	Astatine	-1 1
86 Rn	Radon	2
87 Fr	Francium	1
88 Ra	Radium	2
89-103		
104 Rf	Rutherfordium	4
105 Db	Dubnium	5
106 Sg	Seaborgium	6
107 Bh	Bohrium	7
108 Hs	Hassium	8
109 Mt	Meitnerium	
110 Ds	Darmstadtium	
111 Rg	Roentgenium	
112 Cn	Copernicium	
113 Nh	Nihonium	
114 Fl	Flerovium	
115 Mc	Moscovium	
116 Lv	Livermorium	
117 Ts	Tennessee	
118 Og	Oganesson	

Oxidation states are the number of electrons added to or removed from an element when it forms a chemical compound.

6	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
7	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Alkali metals that can be prepared in gas cells and commonly used for spectroscopy

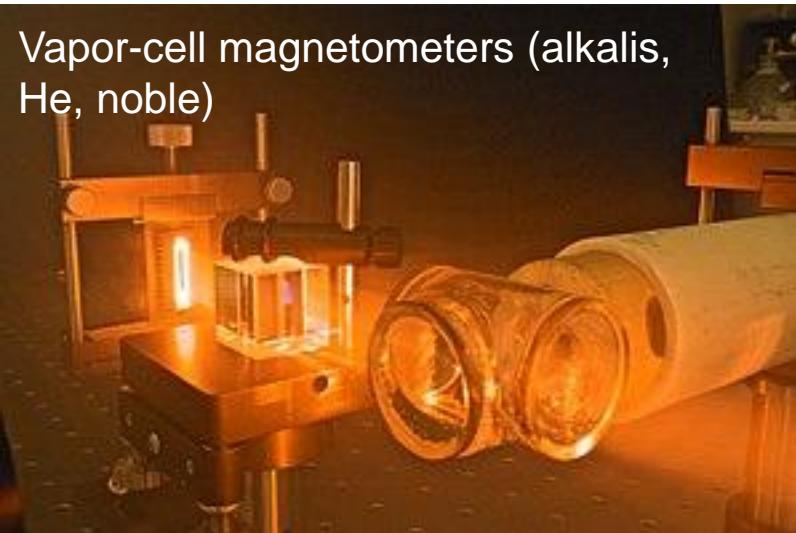
Inert (“Noble”) gases that have low reactivity and naturally exist in monoatomic form

Diatomeric molecules at room temperature (need to break bonds to get individual atoms)

# Sensing applications

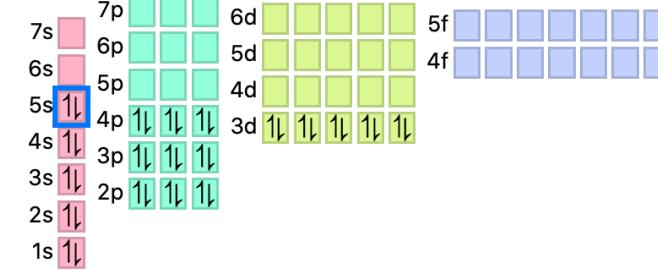


Vapor-cell magnetometers (alkalis, He, noble)

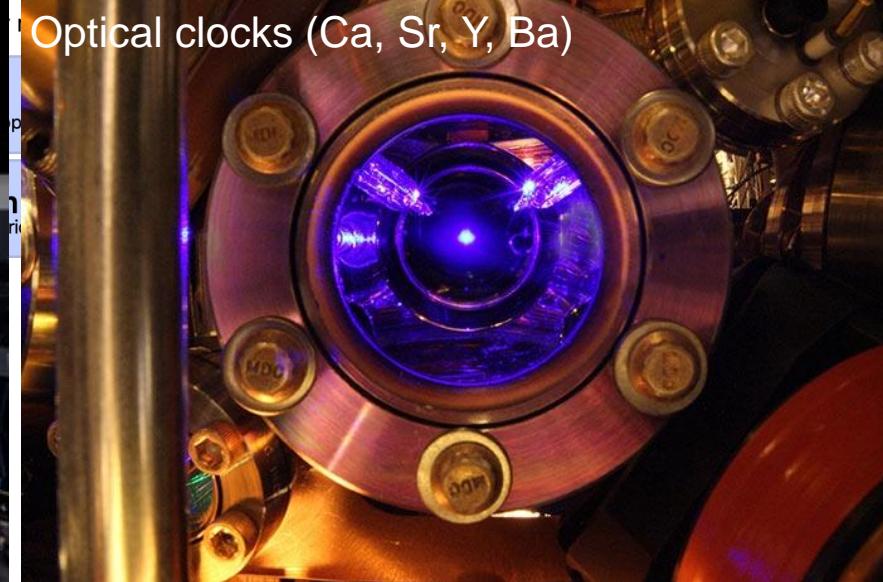
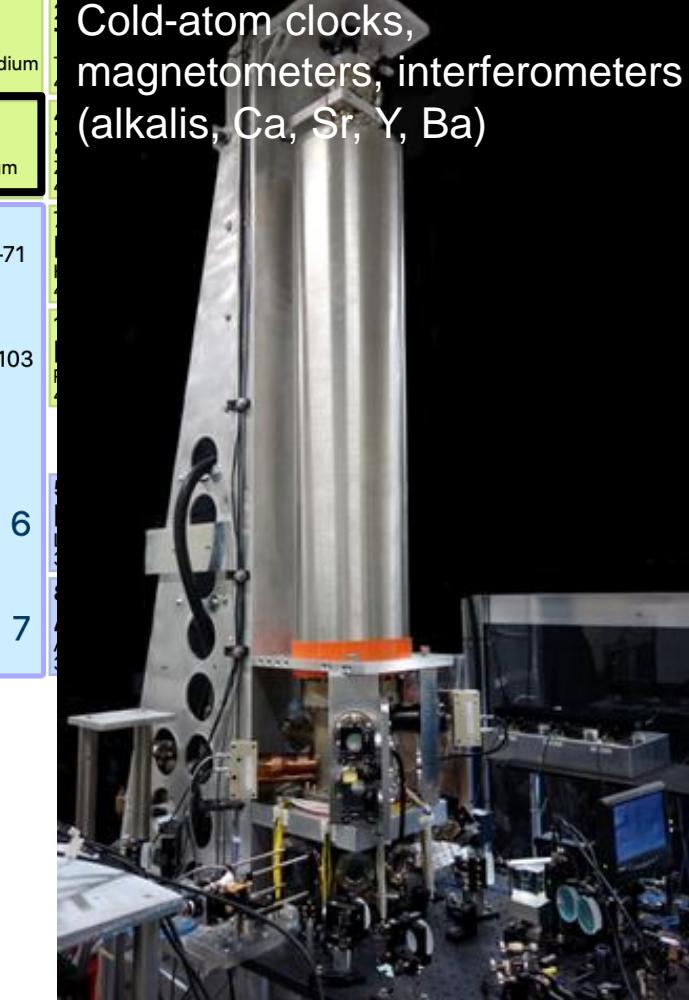


1 <b>H</b> Hydrogen -11	2 <b>He</b> Helium
3 <b>Li</b> Lithium 1	4 <b>Be</b> Beryllium 2
11 <b>Na</b> Sodium 1	12 <b>Mg</b> Magnesium 2
19 <b>K</b> Potassium 1	20 <b>Ca</b> Calcium 2
37 <b>Rb</b> Rubidium 1	38 <b>Sr</b> Strontium 2
55 <b>Cs</b> Caesium 1	56 <b>Ba</b> Barium 2
87 <b>Fr</b> Francium 1	88 <b>Ra</b> Radium 2

**s** block  
**p** block  
**d** block  
**f** block



Cold-atom clocks,  
magnetometers, interferometers  
(alkalis, Ca, Sr, Y, Ba)

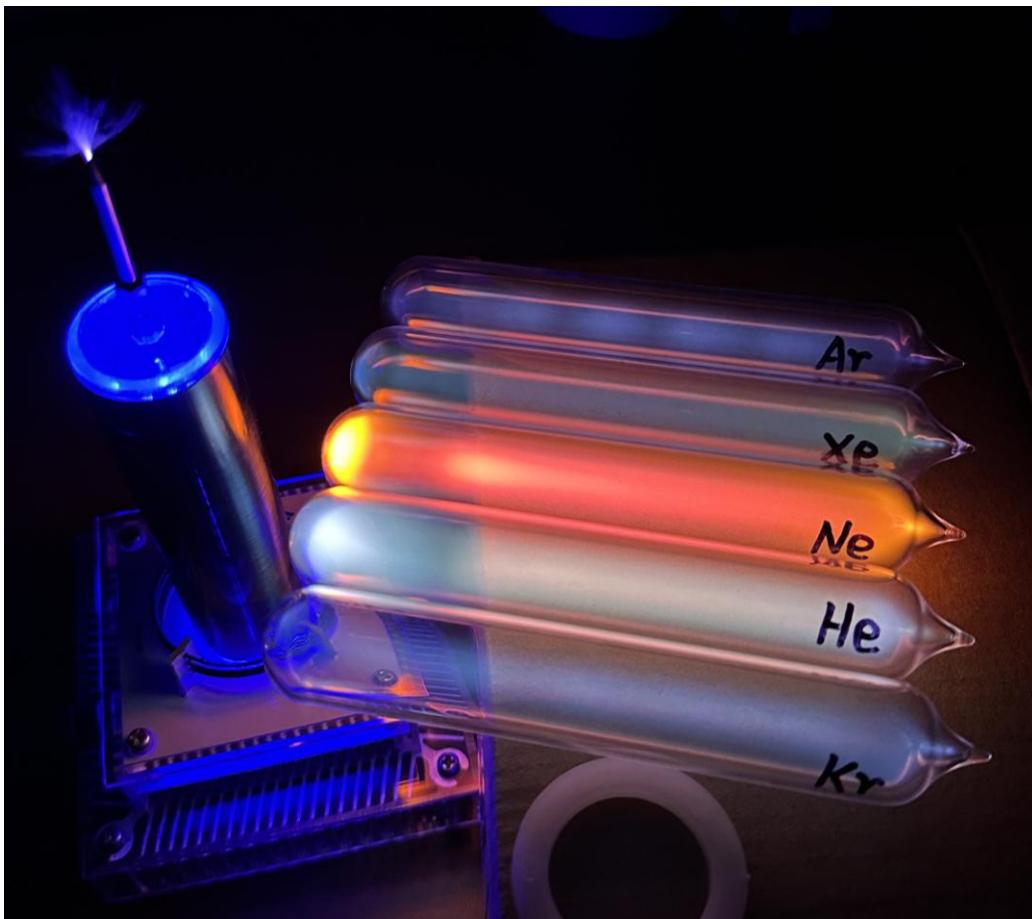


5 <b>B</b> Boron 3	6 <b>C</b> Carbon -4 4	7 <b>N</b> Nitrogen -3 3 5	8 <b>O</b> Oxygen -2	9 <b>F</b> Fluorine -1	10 <b>Ne</b> Neon
13 <b>Al</b> Aluminium 3	14 <b>Si</b> Silicon -4 4	15 <b>P</b> Phosphorus -3 3 5	16 <b>S</b> Sulfur -2 2 4 6	17 <b>Cl</b> Chlorine -1 1 3 5 7	18 <b>Ar</b> Argon
29 <b>Cu</b> Copper 2	30 <b>Zn</b> Zinc 2	31 <b>Ga</b> Gallium 3	32 <b>Ge</b> Germanium -4 2 4	33 <b>As</b> Arsenic -3 3 5	34 <b>Se</b> Selenium -2 2 4 6
47 <b>Ag</b> Silver 1	48 <b>Cd</b> Cadmium 2	49 <b>In</b> Indium 3	50 <b>Tin</b> -4 2 4	51 <b>Sb</b> Antimony -3 3 5	52 <b>Te</b> Tellurium -2 2 4 6
79 <b>Au</b> Gold 3	80 <b>Hg</b> Mercury 1 2	81 <b>Tl</b> Thallium 1 3	82 <b>Pb</b> Lead 2 4	83 <b>Bi</b> Bismuth 3	84 <b>Po</b> Polonium -2 2 4
111 <b>Rg</b> Roentgenium	112 <b>Cn</b> Copernicium	113 <b>Nh</b> Nihonium	114 <b>Fl</b> Flerovium	115 <b>Mc</b> Moscovium	116 <b>Lv</b> Livermorium
117 <b>Ts</b> Tennessine					118 <b>Og</b> Oganesson

Atomic  
Symbol  
Name  
Weight

# Creating plasma discharges with a tesla coil

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Helium



Neon



Argon



Krypton



Xenon



Hydrogen



# Quantum mechanical treatment of atoms

- Simplest: One-electron / Hydrogenic atoms
  - Hydrogen (H)
  - Isoelectronic with H ( $\text{He}^+$ ,  $\text{Li}^{++}$ ,  $\text{Be}^{+++}$ )
  - Atoms with one electron more weakly bound than all others, such that the inner electrons can be considered to be part of the core (Na, K, Rb, Cs)
- One-electron atoms are the only systems for which the Schrodinger equation can be exactly solved; others have to be approximated
- Notation:

The diagram features a standard periodic table with several additional elements and annotations:

- Orbitals:** A central column displays atomic orbitals for each element. Orbitals are represented by colored boxes (pink for s, teal for p, yellow for d, blue for f) containing numbers indicating electron spin. The s block has 1s, 2s, and 3s subshells. The p block has 2p, 3p, 4p, and 5p subshells. The d block has 3d, 4d, and 5d subshells. The f block has 4f, 5f, and 6f subshells.
- Oxidation States:** Below the periodic table, a statement reads: "Oxidation states are the number of electrons added to or removed from an element when it forms a chemical compound."
- Notation:** The symbol  $A_Z X$  is shown at the bottom left, with arrows pointing to its components:
  - An arrow from "Mass number = Z + number of neutrons" points to the mass number  $A$ .
  - An arrow from "Chemical symbol for the element" points to the element symbol  $X$ .
  - An arrow from "Atomic number = number of protons" points to the atomic number  $Z$ .

# Schrödinger equation for one-electron atoms

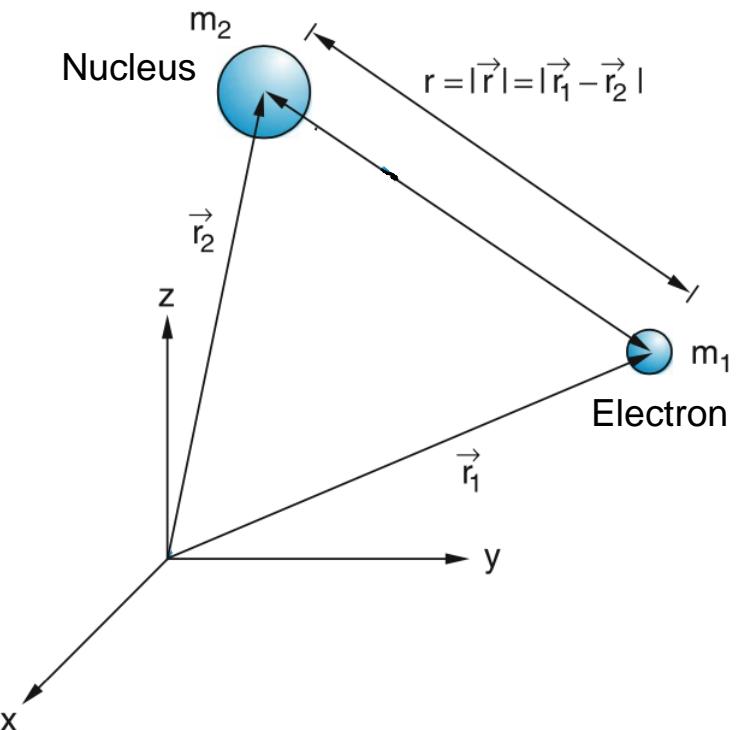
- A system of one electron (with mass  $m_1$ , charge  $q = -e$  and at position  $\vec{r}_1$ ) and a nucleus (with mass  $m_2$ , charge  $q = +Ze$  and at position  $\vec{r}_2$ )
  - Electron is separated from the nucleus by distance  $r = |\vec{r}_1 - \vec{r}_2|$
- The potential energy of the electron-nucleus system is electrostatic:

$$V(\vec{r}_1, \vec{r}_2) = -\frac{Ze^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|}$$

- Time-dependent Schrödinger equation  $\hat{H}(\vec{r}_1, \vec{r}_2)\Psi(\vec{r}_1, \vec{r}_2, t) = i\hbar \frac{\partial\Psi(\vec{r}_1, \vec{r}_2, t)}{\partial t}$  has solutions  $\Psi(\vec{r}_1, \vec{r}_2, t) = e^{-\frac{iE_n t}{\hbar}}\psi_n(\vec{r}_1, \vec{r}_2)$ , where  $n$  represents the quantum numbers needed to describe the state.
- Since  $\hat{H}(\vec{r}_1, \vec{r}_2)$  is time-independent,  $\hat{H}(\vec{r}_1, \vec{r}_2)\psi_n(\vec{r}_1, \vec{r}_2) = E_n\psi_n(\vec{r}_1, \vec{r}_2)$

$$\hat{H}(\vec{r}_1, \vec{r}_2) = -\frac{\hbar^2}{2m_1}\nabla_{r_1}^2 - \frac{\hbar^2}{2m_2}\nabla_{r_2}^2 - \frac{Ze^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|}$$

$$\hat{H}(r) = -\frac{\hbar^2}{2m_1}\nabla_r^2 - \frac{\hbar^2}{2m_2}\nabla_r^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$



Reference: Demtroder, Chapter 5

# Let's gain some intuitions through the Bohr atom model

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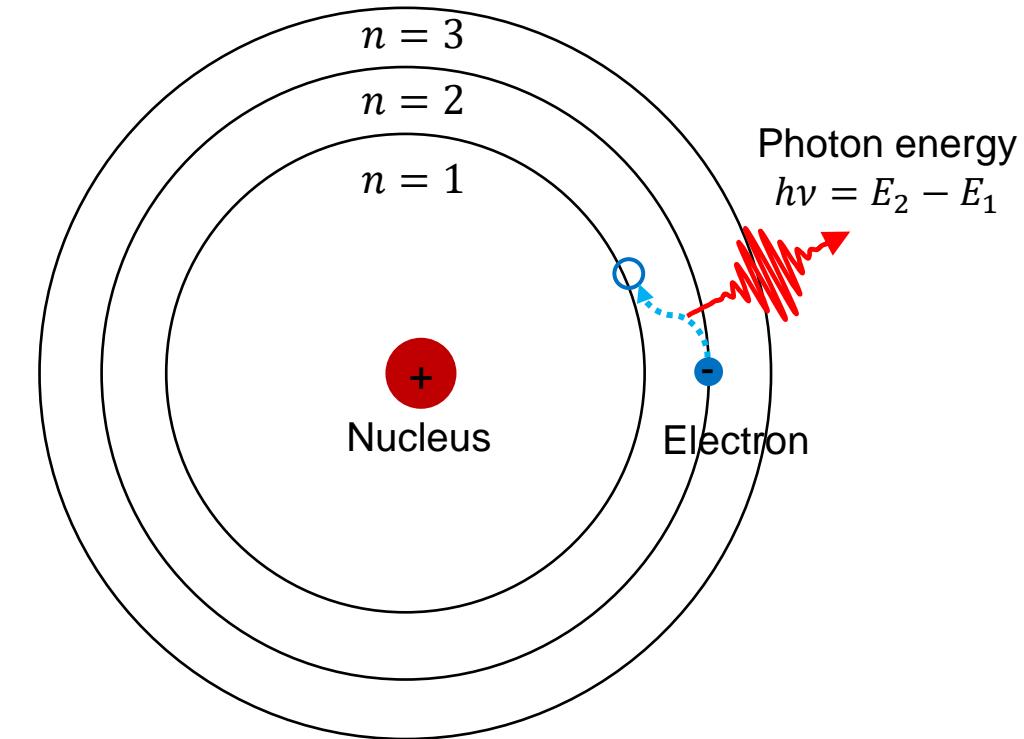
## Assumptions:

- Electrons are in stationary states and do not radiate. They have well-defined energies  $E_n$ , where  $n = 1, 2, 3 \dots$
- Transitions between energy levels lead to light absorption and emission
- Classical laws of physics can account for all behavior except for transitions between discrete states:
  - Newton's second law balances Coulomb force on the electron ( $F_e$ ) with orbital motion

$$F_e = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} = \frac{mv^2}{r}$$

$$v = \frac{e}{\sqrt{4\pi\epsilon_0 mr}}$$

- Angular momentum of the electron is also quantized and is  $n\hbar$  where  $n$  is the principal quantum number and  $\hbar$  is a constant (specifically, the reduced Planck's constant)



$\epsilon_0$  = permittivity of free space

$e$  = electric charge

$m$  = mass of electron

$v$  = tangential velocity of electron

$r$  = distance between electron and nucleus

References: Demtroder, Chapter 3.4

R. Trebino's lecture notes on Modern Physics  
Foot, "Atomic Physics", Chapter 1

# Angular momentum of the electron

- Imposing quantization on the classical formula for angular momentum:

$$L = mvr = n\hbar$$

- The velocity of the electron in terms of the quantized angular momentum is  $v_n = \frac{n\hbar}{mr}$
- Since  $v = \frac{e}{\sqrt{4\pi\epsilon_0 mr}}$  (classical result)  $\rightarrow \frac{e}{\sqrt{4\pi\epsilon_0 m r_n}} = \frac{n\hbar}{m r_n}$
- Solve for  $r_n = n^2 a_0$ , where  $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$

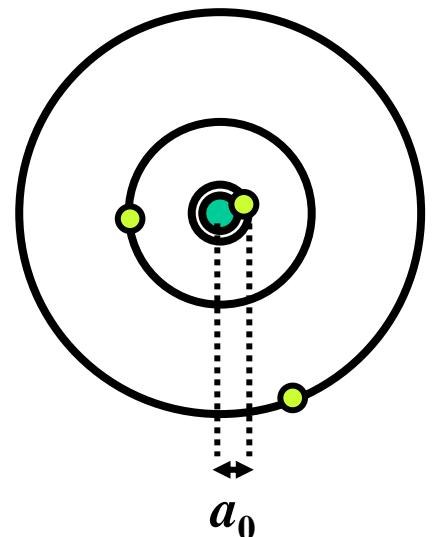
$a_0$  is the Bohr radius,  $\frac{1}{2}$  the diameter of the Hydrogen atom in its lowest-energy (or ground) state.

$$a_0 = \frac{4\pi\epsilon_0 \hbar}{me^2} = \frac{(1.055 \times 10^{-34} \text{ J}\cdot\text{s})^2}{(8.99 \times 10^9 \text{ N}\cdot\text{m}^2/\text{C}^2)(9.11 \times 10^{-31} \text{ kg})(1.6 \times 10^{-19} \text{ C})^2} = 0.53 \times 10^{-10} \text{ m}$$

The ground state of the Hydrogen atom has diameter  $2r_1 = 2a_0 \approx 10^{-10} \text{ m}$

States with  $n > 1$  are called excited states and have larger diameters.

References: Demtroder, Chapter 3.4  
R. Trebino's lecture notes on Modern Physics  
Foot, "Atomic Physics", Chapter 1



# Hydrogen atom energies

- Bohr atom energy:  $E = -\frac{e^2}{8\pi\epsilon_0 r_n}$

$$r_n = n^2 a_0$$

- Energies of stationary states:

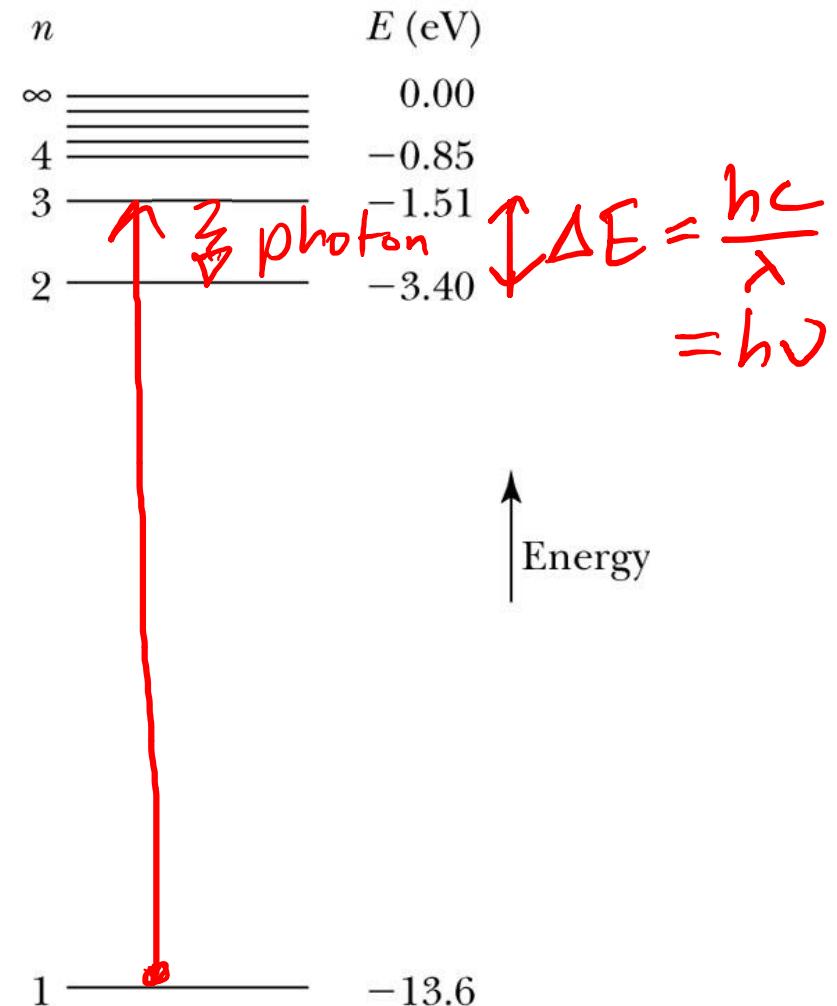
$$E_n = -\frac{e^2}{8\pi\epsilon_0 n^2 a_0} = -\frac{E_0}{n^2}$$

$$E_0 = \frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} = 13.6 \text{ eV}$$

- Light is emitted when electron goes from higher to lower energy states ( $n_u$  to  $n_l$ ):  $h\nu = E_u - E_l$ , where  $\nu$  is the frequency of the photon

$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{h\nu}{hc} = \frac{E_u - E_l}{hc} = R_\infty \left( \frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

Rydberg equation, with  $R_\infty \equiv \frac{me^4}{(4\pi\hbar)^3 c \epsilon_0^2}$



References: Demtroder, Chapter 3.4  
R. Trebino's lecture notes on Modern Physics  
Foot, "Atomic Physics", Chapter 1

# Rydberg constant and reduced mass correction

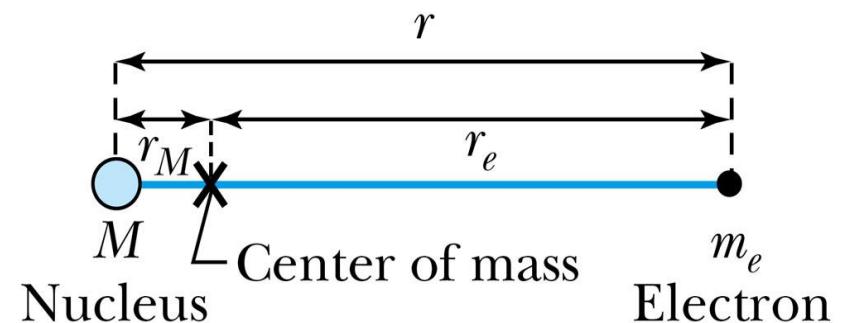
- $R_\infty$  is calculated to be  $10\ 973\ 731.568\ 525\ m^{-1}$ 
  - Uses our underlying assumption of the electron orbiting a fixed nucleus (ok if the nucleus is infinitely massive)
  - A little different from the constant derived from empirical results
- Revised picture: electron and nucleus both orbiting around their center of mass
  - Introduce the reduced mass of the electron

$$\mu_e = \frac{Mm_e}{M+m_e} = \frac{m_e}{1+m_e/M}$$

- Correct Rydberg constant with reduced mass:

$$R = \frac{\mu_e}{m_e} R_\infty = \frac{1}{1+m_e/M} R_\infty$$

- Improved agreement with empirical results
- For hydrogen:  $R_H = R_\infty \frac{1}{1+m_e/M_{proton}} \approx R_\infty \left(1 - \frac{m_e}{M_{proton}}\right)$ , where  $\frac{m_e}{M_{proton}} \approx 1/1836$
- Note that reduced mass correction is not the same for different isotopes of an element (accounts for small observable difference in frequency of light emission known as **isotope shift**)



References: Demtroder, Chapter 3.4  
R. Trebino's lecture notes on Modern Physics  
Foot, "Atomic Physics", Chapter 1

## Fine structure constant

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- The electron's velocity in the Bohr model:

$$v_n = \frac{n\hbar}{mr_n} = \frac{1}{n} \frac{e^2}{4\pi\epsilon_0\hbar}$$

- In the ground state,  $v_1 = 2.2 \times 10^6 \text{ m/s} \sim 1\% c$ .
- Ratio of  $v_1$  to  $c$  is called the **fine structure constant**,  $\alpha$ .

$$\alpha = \frac{v_1}{c} = \frac{\hbar/m a_0}{c} = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}$$

Generally  $\frac{v}{c} = \frac{\alpha}{n}$

- Useful for estimating relativistic corrections to the Bohr model
- What energy resolution ( $\Delta E/E$ ) do we need to resolve relativistic effects in hydrogen that cause line-splitting in the Balmer lines?

$\lambda \sim 656 \text{ nm} \sim 1.9 \text{ eV}$  ( $n=3 \rightarrow n=2$ )

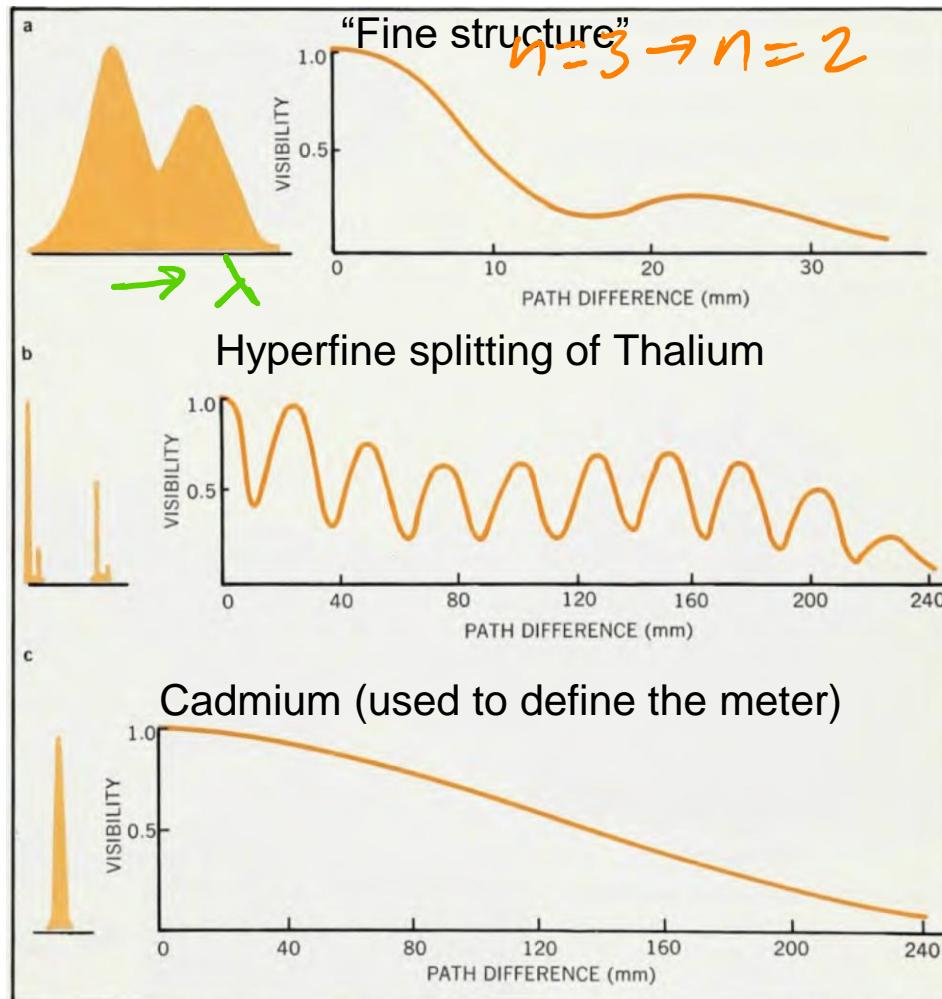
$$\Delta E = \frac{1}{2} \alpha^2 (E) \sim 5 \times 10^{-5} \text{ eV}$$

$$\begin{aligned} E &= \gamma m_e c^2 = E_{\text{kin}} + m_e c^2 \\ \gamma &= \frac{1}{\sqrt{1 - (\frac{v}{c})^2}} \approx 1 + \frac{1}{2} \frac{v^2}{c^2} \\ E_{\text{kin}} &= \Delta E = (\gamma - 1) m_e c^2 \\ &= \frac{1}{2} \frac{v^2}{c^2} m_e c^2 \\ \frac{\Delta E}{m_e c^2} &\approx \frac{1}{2} \frac{v^2}{c^2} = \frac{1}{2} \alpha^2 \end{aligned}$$

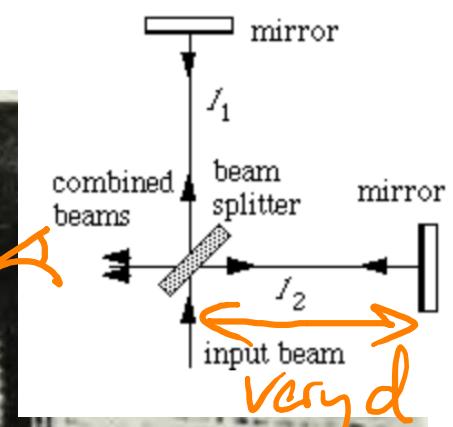
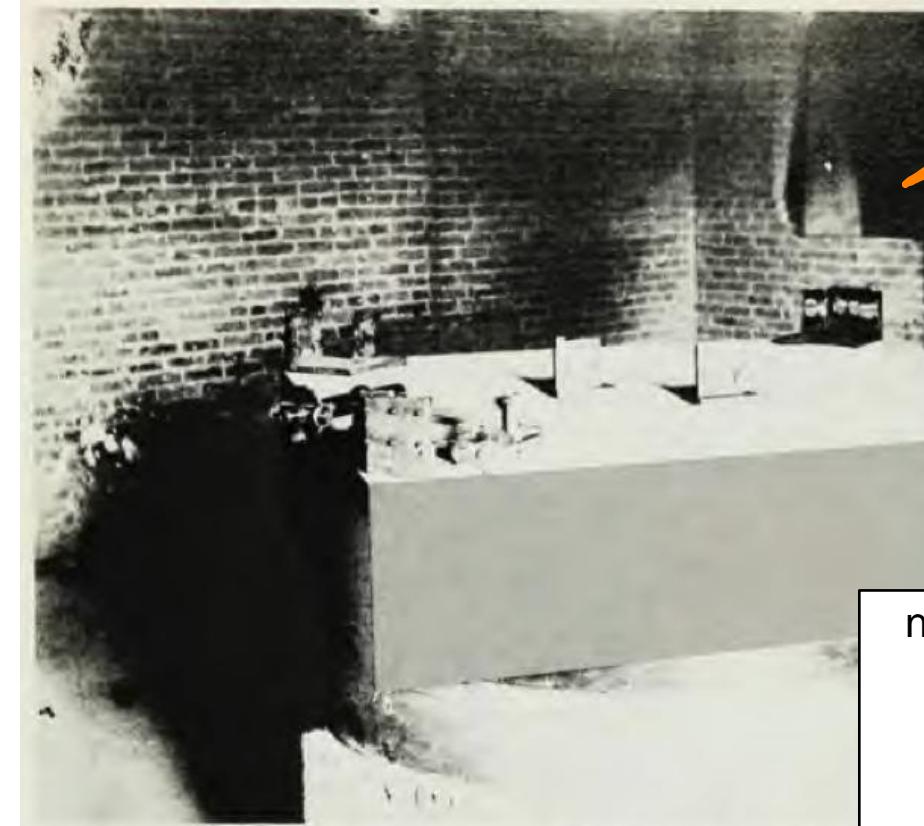
Reference: R. Trebino's lecture notes on Modern Physics  
Foot, "Atomic Physics", Chapter 1

# Observations of line splitting in atomic spectra, thanks to improved resolution in spectroscopy

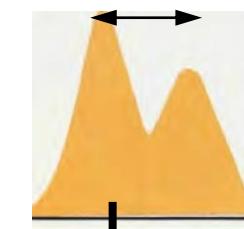
H-alpha line of hydrogen splitting ( $0.33 \text{ cm}^{-1}$ )



Michelson interferometer



$n = 3$  to  $n = 2$  transition in the Balmer series for H  
 $0.33 \text{ cm}^{-1} \sim 4.5 \times 10^{-5} \text{ eV}$



$656.281 \text{ nm} \rightarrow$   
 $\sim 1.1889 \text{ eV}$

<https://physicstoday.scitation.org/doi/pdf/10.1063/1.3128534>

See also: [https://en.wikisource.org/wiki/Light\\_waves\\_and\\_their\\_uses/Lecture\\_IV](https://en.wikisource.org/wiki/Light_waves_and_their_uses/Lecture_IV)

## Excitation of hydrogen atom

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- An electron is initially in the ground state of a hydrogen atom. Using the Bohr model, which is the highest excited state for that electron if the excitation energy is 13.387 eV?

$$\Delta E = 13.6 \text{ eV} \left(1 - \frac{1}{n^2}\right) = 13.387 \text{ eV}$$
$$n = 8$$

- What is the radius of the atom at the excited state?

$$r_8 = 8^2 a_0 = 64 a_0$$

- Which emission lines might you expect?

$$n=8 \rightarrow n=1$$

$$n=8 \rightarrow 7, 6, \dots$$

$$7 \rightarrow 6, \dots$$

## Problem with the Bohr model: atoms should be unstable!

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- According to classical electrodynamics: accelerating charges emit radiation, with power given by the Larmor formula  $P = \frac{2}{3} \frac{e^2 a^2}{c^3}$ , where  $a$  is the charge's acceleration
- What is the power radiated by an accelerating charge for a ground-state electron in the Bohr model? Approximately much time would it take to dissipate all of its energy?

$$a = \frac{v_1^2}{a_0} \approx 9.1 \times 10^{22} \frac{m}{s^2} \rightarrow P = 10^{-13} W$$

$$\Delta t = \frac{P}{E_1} \sim 2 \times 10^{-5} s$$

- In the Bohr model, the electron is orbiting the nucleus in circular motion → This should mean that the electron is always radiating and eventually will spiral into the nucleus!
- Since atoms are stable, **the description of the electron's motion in the Bohr model is incorrect.**

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References: Demtroder, Chapter 3.4

## What is the Bohr model good for?

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- Predicting electron energies for one-electron or hydrogenic atoms (neutral or charged atoms that have a nucleus and a single electron)
- We get physical intuitions for important constants (you can ignore everything else, like electron velocity and acceleration, that comes with the model):

- Bohr radius  $a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 5.29 \times 10^{-11} m$

- Hydrogen ground state energy  $E_0 = -hcR_\infty = -m \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 / (2\hbar^2) = -13.6 \text{ eV}$

- Fine structure constant  $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}$

# Quantum mechanical treatment of one-electron atoms

- One-electron / Hydrogenic atoms
  - Hydrogen (H)
  - Isoelectronic with H (He+, Li++, Be+++)
  - Atoms with one electron far more weakly bound than all others, such that the inner electrons can be considered to be part of the core (Na, K, Rb, Cs)

- Potential energy is determined by the Coulomb interaction between the particles  $V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$

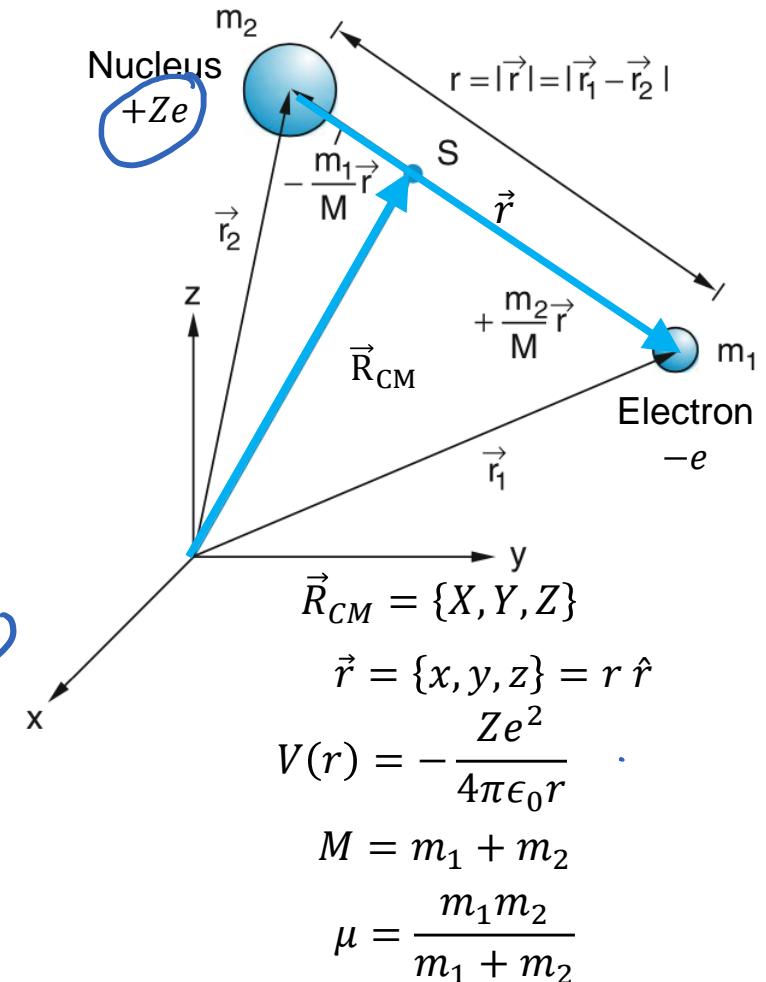
$$\hat{H}(\vec{r}_1, \vec{r}_2) = -\frac{\hbar^2}{2m_1} \nabla_{r_1}^2 - \frac{\hbar^2}{2m_2} \nabla_{r_2}^2 - \frac{Ze^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

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

$\sum_i -\frac{\hbar^2}{2m_i} \nabla_{r_i}^2 + V(r)$

- Approach to solve the Schrödinger equation:
  - Separate center-of-mass and relative motions between the nucleus and electron (we care about the latter to derive electron energies)
  - Use spherical coordinate system  $r, \theta, \phi$
  - Find separable solutions for azimuthal, polar, and radial components

$$\psi(r, \theta, \phi) = \psi_r \psi_\theta \psi_\phi$$



References: Demtröder, Chapter 5

# Separating the center of mass and relative motion

Reference

- Define:  $\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{M}$ , with  $M = m_1 + m_2$   
 $\vec{R} = \{X, Y, Z\}; \vec{r}_i = \{x_i, y_i, z_i\}$   
 $\vec{r} = \{x_1 - x_2, y_1 - y_2, z_1 - z_2\} = \{x, y, z\}$

- Write  $\vec{r}_1$  and  $\vec{r}_2$  in terms of  $\vec{R}$  and  $\vec{r}$ :  
 $\vec{r}_1 = \vec{R} + \frac{m_2}{M}\vec{r}$   
 $\vec{r}_2 = \vec{R} - \frac{m_1}{M}\vec{r}$

- The Hamiltonian can be rewritten as

$$\hat{H} = -\frac{\hbar^2}{2M} \left( \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) - \frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(r)$$

C.O.M.  
kinetic energy

where  $\mu = \frac{m_1 m_2}{m_1 + m_2}$

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 + V(r)$$

relative motion

- Assume separable solutions:  $\psi(\vec{R}, \vec{r}) = f(\vec{r})g(\vec{R})$

relative motion:  
internal electron energies

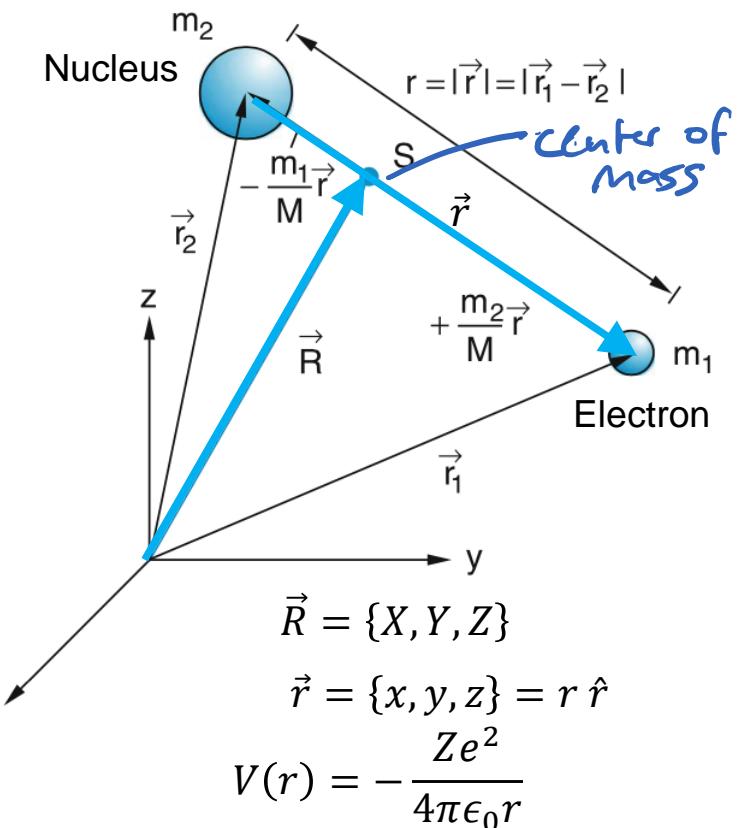
atom's motion

wavefunction w/  
 $k = \frac{2\pi}{\lambda_{dB}}$

$$\lambda_{dB} = \frac{h}{\sqrt{2ME_g}} e^{ikR}$$

kinetic energy of particle

Reference: Demtroder, Chapter 5



# Schrödinger equation for center-of-mass coordinate system

Reference

- Separable equations for (1) the center-of-mass motion of the atom and (2) the relative motion of the electron and nucleus

$$(1): \quad -\frac{\hbar^2}{2M} \nabla_R^2 g(R) = E_g g(R)$$

$$(2): \quad -\frac{\hbar^2}{2\mu} \nabla_r^2 f(r) + V(r)f(r) = E_f f(r)$$

reduced mass

- In (1),  $E_g$  describes the kinetic energy of the motion of the atom. Its solution is similar to that of a free particle

$$g(R) = A e^{ikR}$$

$$\Psi_R(R, t) = g(R) e^{-iE_g t/\hbar}$$

- Can define the de Broglie wavelength associated with the atom's (center-of-mass) motion

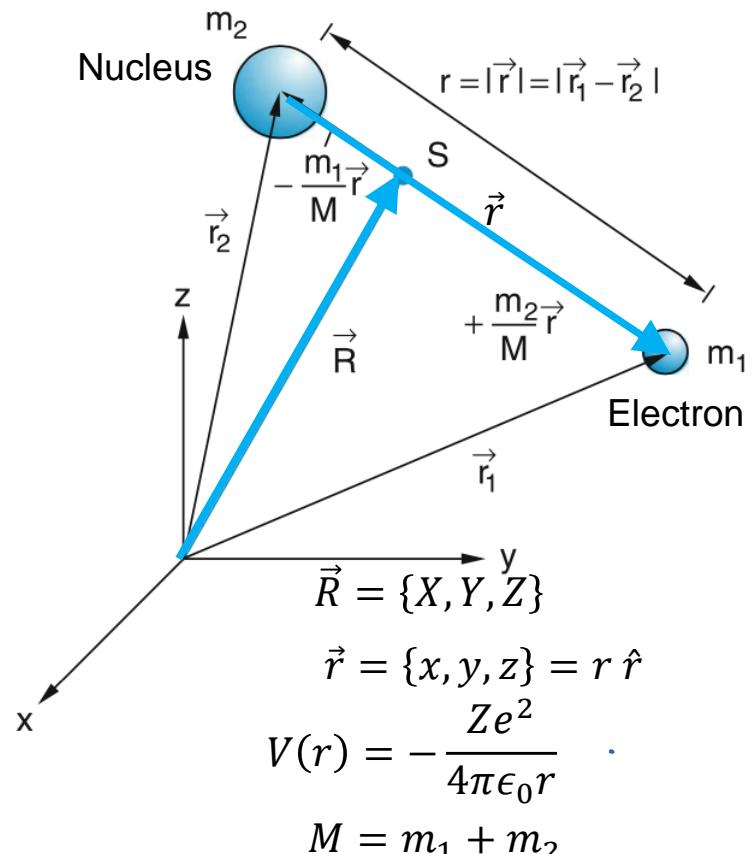
$$\lambda_{CM} = \frac{\hbar}{\sqrt{2ME_g}} = \frac{2\pi}{k}$$

- Use wave packets to describe atom's motion
- Write (2) as a Schrödinger equation with a spherically symmetric potential

$$f(r) \equiv \psi_r; E_f \equiv E$$

$$\left[ -\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \psi_r = E \psi_r$$

What it means: Relative motion of the electron and nucleus is equivalent to a particle with reduced mass  $\mu$  in a spherically symmetric potential



$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$$M = m_1 + m_2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\nabla_R^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}$$

$$\nabla_r^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

- Since the system is radially symmetric, we use spherical coordinates:

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

with the inverse relations:

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

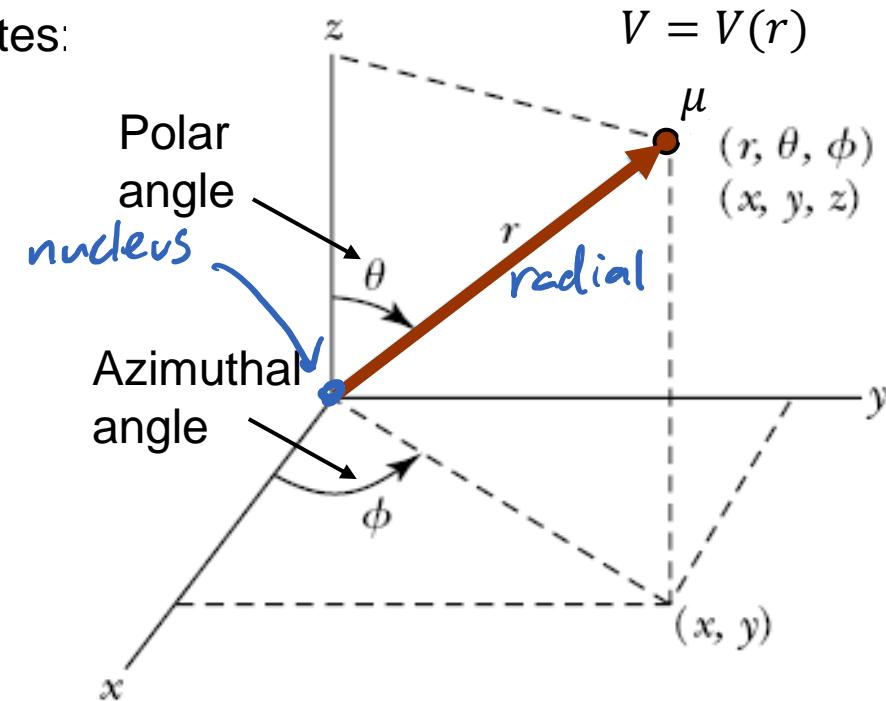
$$\cos \theta = z / r$$

$$\tan \phi = y / x$$

- The transformed Schrödinger equation is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi_r}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi_r}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi_r}{\partial \phi^2} + \frac{2\mu}{\hbar^2} (E - V) \psi_r = 0$$

- Assume separable solutions:  $\psi_r(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$ 
  - Sorry for the confusing use of the function  $R(r)$  by convention, which refers to some function of  $r$  and has nothing to do with the coordinate  $\vec{R}$



References: Demtroder, Chapters 4.3.2 and 5.1.2

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi_r}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi_r}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi_r}{\partial \phi^2} + \frac{2\mu}{\hbar^2} (E - V) \psi_r = 0$$

$$\psi_r(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

$$\left[ \frac{\Theta \Phi}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{R \Phi}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{R \Theta}{r^2 \sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} (E - V) R \Theta \Phi = 0 \right] \left( -\frac{r^2 \sin^2 \theta}{R \Phi \Theta} \right)$$

$$\frac{\partial \psi_r}{\partial r} = \Theta \Phi \frac{\partial R}{\partial r}$$

$$\frac{\partial \psi_r}{\partial \theta} = R \Phi \frac{\partial \Theta}{\partial \theta}$$

$$\frac{\partial^2 \psi_r}{\partial \phi^2} = R \Theta \frac{\partial^2 \Phi}{\partial \phi^2}$$

$$-\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) - \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) - \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} - \frac{2\mu}{\hbar^2} (E - V) r^2 \sin^2 \theta = 0$$

$$-\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) - \frac{2\mu}{\hbar^2} (E - V) r^2 \sin^2 \theta - \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) = \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = \text{constant}$$

Azimuthal component:  $\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} \equiv -m^2$  where  $m$  is an integer

$$\frac{\partial^2 \Phi}{\partial \phi^2} = -m^2 \Phi \quad \rightarrow \Phi \propto e^{-im\phi}$$

References: Demtroder, Chapters 4.3.2 and 5.1.2

- Same idea: separate radial and polar components and set to a constant

$$\left[ \frac{-\sin^2 \theta}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{2\mu}{\hbar^2} (E - V) r^2 \sin^2 \theta - \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) = -m^2 \right] \left( -\frac{1}{\sin^2 \theta} \right)$$

$$\underbrace{\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} (E - V) r^2}_{\text{Radial component only}} + \underbrace{\frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right)}_{\text{Polar component only}} = \frac{m^2}{\sin^2 \theta}$$

Radial component only

Polar component only

$$\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} (E - V) r^2 = -\frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{m^2}{\sin^2 \theta} = \text{constant} \equiv l(l+1)$$

$\ell = 0, 1, 2, \dots$

$$\text{Radial equation: } \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} (E - V) R = \frac{R}{r^2} l(l+1)$$

$$\text{Polar equation: } -\frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{m^2}{\sin^2 \theta} = l(l+1)$$

Gives  $\Theta$  which depends on  $\theta$  and is a set of solutions defined by  $l$

Gives  $R$  which depends on  $r$ , and is a set of solutions defined by  $n$  (another quantum number) and  $l$

References: Demtroder, Chapters 4.3.2 and 5.1.2 and  $m$

$$\frac{1}{r^2} \frac{d}{dr} \left( \frac{r^2 dR}{dr} \right) + \frac{2\mu}{\hbar^2} \left( E + \frac{Ze^2}{4\pi\epsilon_0 r} \right) R - \frac{l(l+1)}{r^2} R = 0$$

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left( \frac{2\mu}{\hbar^2} \left( E + \frac{Ze^2}{4\pi\epsilon_0 r} \right) - \frac{l(l+1)}{r^2} \right) R = 0$$

- Consider the asymptotic case with  $r \rightarrow \infty$ :  $\frac{Ze^2}{4\pi\epsilon_0 r}$  and  $\frac{l(l+1)}{r^2}$  vanish

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} = -\frac{2\mu}{\hbar^2} E R$$

$$W = r \cdot R$$

$$\frac{d^2 W}{dr^2} = -k^2 W, \text{ with } k = \sqrt{2\mu E} / \hbar$$

$$W(r \rightarrow \infty) = A e^{ikr} + B e^{-ikr}$$

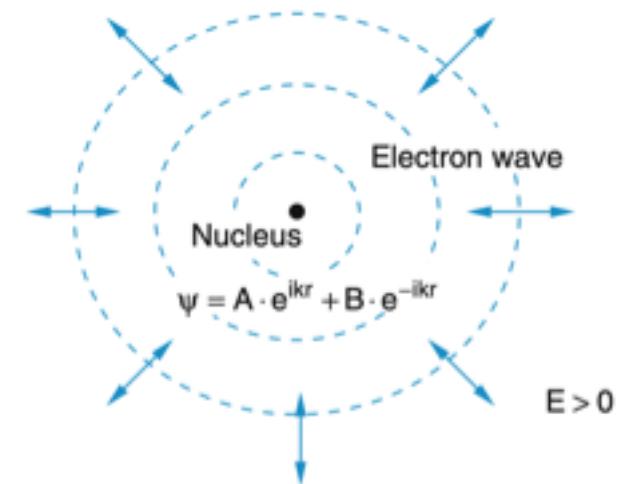
$$R(r \rightarrow \infty) = \frac{A}{r} e^{ikr} + \frac{B}{r} e^{-ikr}$$

- $E > 0; k$  is real

$$R(r \rightarrow \infty) e^{-i\omega t} = \frac{A}{r} e^{i(kr - \omega t)} + \frac{B}{r} e^{-i(kr + \omega t)}$$

[ ] Electron spherical wave leaving the atom      
 [ ] Electron spherical wave approaching the nucleus

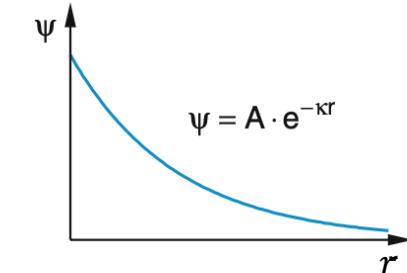
This describes the electron either leaving the atom or coming in from  $r \rightarrow \infty$  on a collision course with the nucleus



- $E < 0; \kappa = \frac{\sqrt{-2\mu E}}{\hbar} = ik$

$$R(r \rightarrow \infty) = A e^{-\kappa r} + B e^{\kappa r}$$

$B = 0$  due to normalization



$$\frac{d^2R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left( \frac{2\mu}{\hbar^2} \left( E + \frac{Ze^2}{4\pi\epsilon_0 r} \right) - \frac{l(l+1)}{r^2} \right) R = 0 \quad \kappa = \frac{\sqrt{-2\mu E}}{\hbar}$$

- General solution for confined electrons:  $R(r) = u(r)e^{-\kappa r}$

$$\frac{d^2u}{dr^2} + 2\left(\frac{1}{r} - \kappa\right) \frac{du}{dr} + \left[ \frac{2a - 2\kappa}{r} - \frac{l(l+1)}{r^2} \right] u = 0$$

where  $a = \frac{\mu Ze^2}{4\pi\epsilon_0\hbar^2}$

- Writing  $u(r)$  as a power series  $u(r) = \sum_j b_j r^j$

$$b_j = 2b_{j-1} \frac{\kappa j - a}{j(j+1) - l(l+1)}$$

- $R(r)$  must be finite (to be normalizable), so  $j$  cannot go to infinity: set  $b_{j \geq n} = 0$
- At  $j = n$ ,  $b_j = 0 \rightarrow \kappa n - a = 0$

$$\frac{\sqrt{-2\mu E}}{\hbar} n = a$$

$$E_n = -\frac{a^2\hbar^2}{2\mu n^2} = -\frac{a^2\hbar^2}{2\mu n^2} = -\frac{\mu Z^2 e^4}{32\pi^2\epsilon_0^2\hbar^2 n^2}$$

Note: to keep  $u(r)$  finite,  $b_j$  needs to be zero for  $l \geq j$   
 $l < j < n \rightarrow l \leq n-1$

Bohr model result for hydrogen, when  $Z = 1$

# Normalized radial wave functions

The solutions  $R$  to the radial equation are called the **Associated Laguerre polynomials** of the form:

$$L_n^l(x) = \sum_{m=0}^n (-1)^m \frac{(n+l)!}{(n-m)!(l+m)!m!} x^m$$

where  $n = 1, 2, 3 \dots$   
 $l \leq n - 1$

According to this solution, energy only depends on  $n$ :

$$E_n = -\frac{\mu Z^2 e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$$

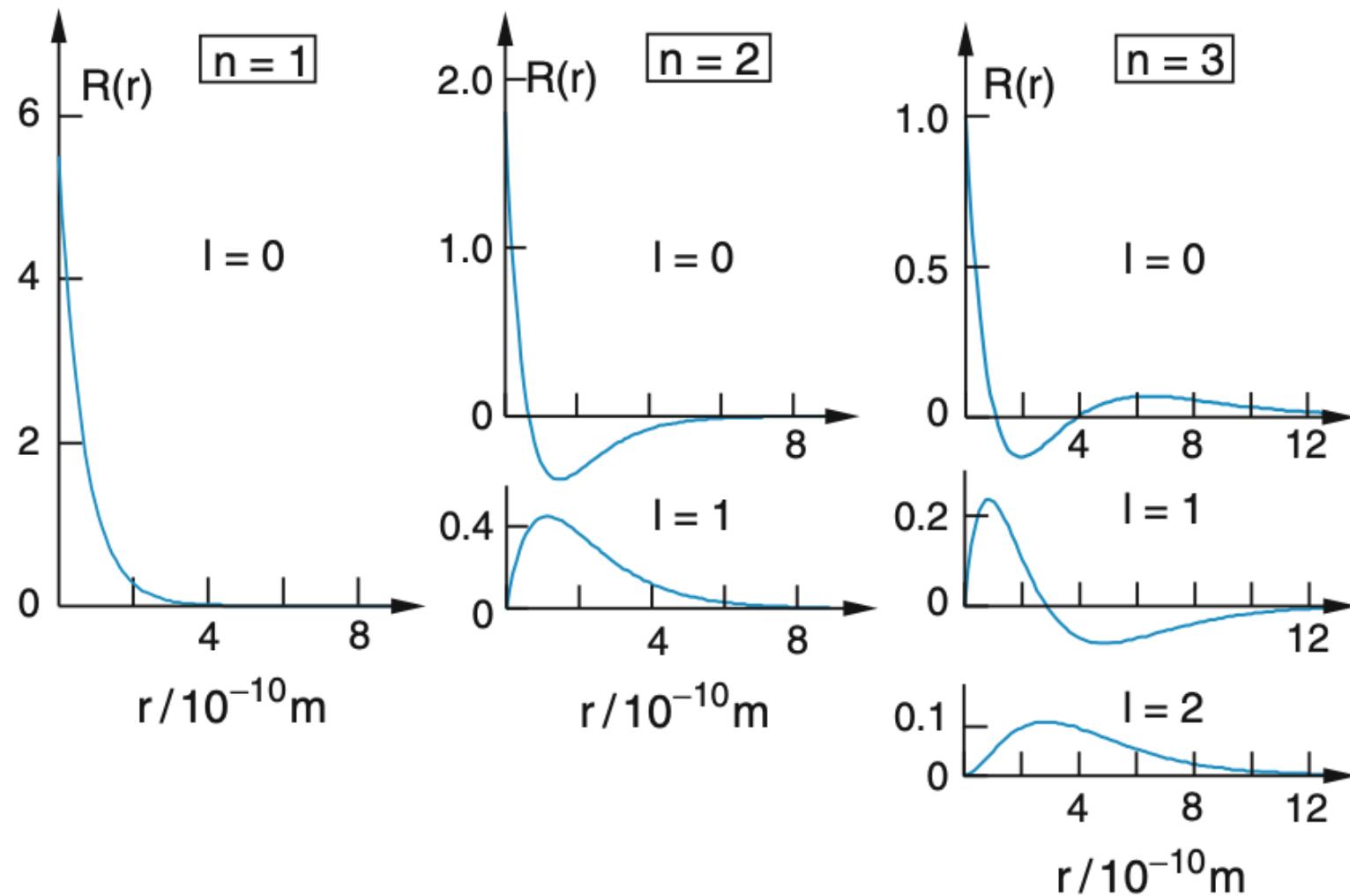
**Table 5.1** Normalized radial wave functions  $R(r)$  (Laguerre-Polynomials) of an electron in the Coulomb potential of the nucleus with charge  $Ze$  ( $N = (Z/n a_0)^{3/2}$ ;  $x = Zr/n a_0$ ;  $a_0 = 4\pi \epsilon_0 \hbar^2 / (Z \mu e^2)$ )

$n$	$l$	$R_{n,l}(r)$
1	0	$2Ne^{-x}$
2	0	$2Ne^{-x} (1-x)$
2	1	$\frac{2}{\sqrt{3}} Ne^{-x} x$
3	0	$2Ne^{-x} \left(1 - 2x + \frac{2x^2}{3}\right)$
3	1	$\frac{2}{3}\sqrt{2} Ne^{-x} x(2-x)$
3	2	$\frac{4}{3\sqrt{10}} Ne^{-x} x^2$
4	0	$2Ne^{-x} \left(1 - 3x + 2x^2 - \frac{x^3}{3}\right)$
4	1	$2\sqrt{\frac{5}{3}} Ne^{-x} x \left(1 - x + \frac{x^2}{5}\right)$
4	2	$2\sqrt{\frac{1}{5}} Ne^{-x} x^2 \left(1 - \frac{x}{3}\right)$
4	3	$\frac{2}{3\sqrt{35}} Ne^{-x} x^3$

References: Demtröder, Chapters 4 and 5

# Plots of the radial wave functions for hydrogen

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References: Demtröder, Chapters 4 and 5

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# Solutions to the polar-angle equation

$$\frac{1}{\sin \theta} \frac{d}{d\theta} (\sin \theta \frac{d\Theta}{d\theta}) + \left[ l(l+1) - \frac{m^2}{\sin^2 \theta} \right] \Theta = 0$$

Letter names for the various $l$ values						
$l$	0	1	2	3	4	5 ...
s		$p$	$d$	$f$	$g$	$h ...$

- This is an Associated Legendre equation, with sinusoidal solutions.
- Since equation has  $m$ , the polar- and azimuthal-angle equations are linked.
- $\Theta$  and  $\Phi$  can be grouped together and are known as spherical harmonics

$$\Phi(\phi) \propto e^{im\phi}$$

- Independent of  $r$
- $l$  is an integer
- $P_l^m$  are the associated Legendre polynomials

$$P_l^m(x) = \frac{(-1)^m}{2^l l!} (1-x^2)^{\frac{m}{2}} \frac{d^{l+m}}{dx^{l+m}} (x^2 - 1)^l$$

- To make sure that the  $(m+l)$ -th derivative is defined:  $|m| \leq l$ , or  $-l \leq m \leq l$

**Table 4.2** Spherical surface harmonics

$l$	$m$	$y_l^m$
0	0	$\frac{1}{2\sqrt{\pi}}$
	$\pm 1$	$\mp \frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin \vartheta e^{\pm i\varphi}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}} \cos \vartheta$
	$\pm 2$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}} \sin^2 \vartheta e^{\pm 2i\varphi}$
	$\pm 1$	$\mp \frac{1}{2}\sqrt{\frac{15}{2\pi}} \cos \vartheta \sin \vartheta e^{\pm i\varphi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}} (2\cos^2 \vartheta - \sin^2 \vartheta)$
	$\pm 3$	$\mp \frac{1}{8}\sqrt{\frac{35}{\pi}} \sin^3 \vartheta e^{\pm 3i\varphi}$
	$\pm 2$	$\frac{1}{4}\sqrt{\frac{105}{2\pi}} \cos \vartheta \sin^2 \vartheta e^{\pm 2i\varphi}$
	$\pm 1$	$\mp \frac{1}{8}\sqrt{\frac{21}{\pi}} \sin \vartheta (5\cos^2 \vartheta - 1) e^{\pm i\varphi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}} (5\cos^3 \vartheta - 3\cos \vartheta)$

References: Demtroder, Chapters 4.3.2 and 5.1.2

## Visualization of spherical harmonic functions $|Y_l^m|^2$ (see MATLAB code SphHarm.m)

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- Constraints on quantum numbers  $n, l, m$ :

$$n = 1, 2, 3, \dots$$

$$l = 0, 1, 2, \dots, n - 1$$

$$m = -l, -l + 1, \dots, 0, 1, \dots, l - 1, l$$

- According to the Schrodinger equation, how many number of degenerate states, meaning states with the same energy, does a hydrogen atom with  $n = 3$  have? (Answer on Top Hat)

$$\begin{array}{cccc} n=3 & l=0 & l=1 & l=2 \\ m=0 & m=0, \pm 1 & m=0, \pm 1, \pm 2 & \end{array} \quad \text{total \# of states} = 9 \quad (n^2)$$

- Try different combinations of  $l$  and  $m$  for  $l = 0, 1$  and evaluate the following:

- When is  $|Y_l^m|^2$  spherically symmetric?  $l=0, m=0$

- When is  $|Y_l^m|^2$  rotationally symmetric around the z axis?

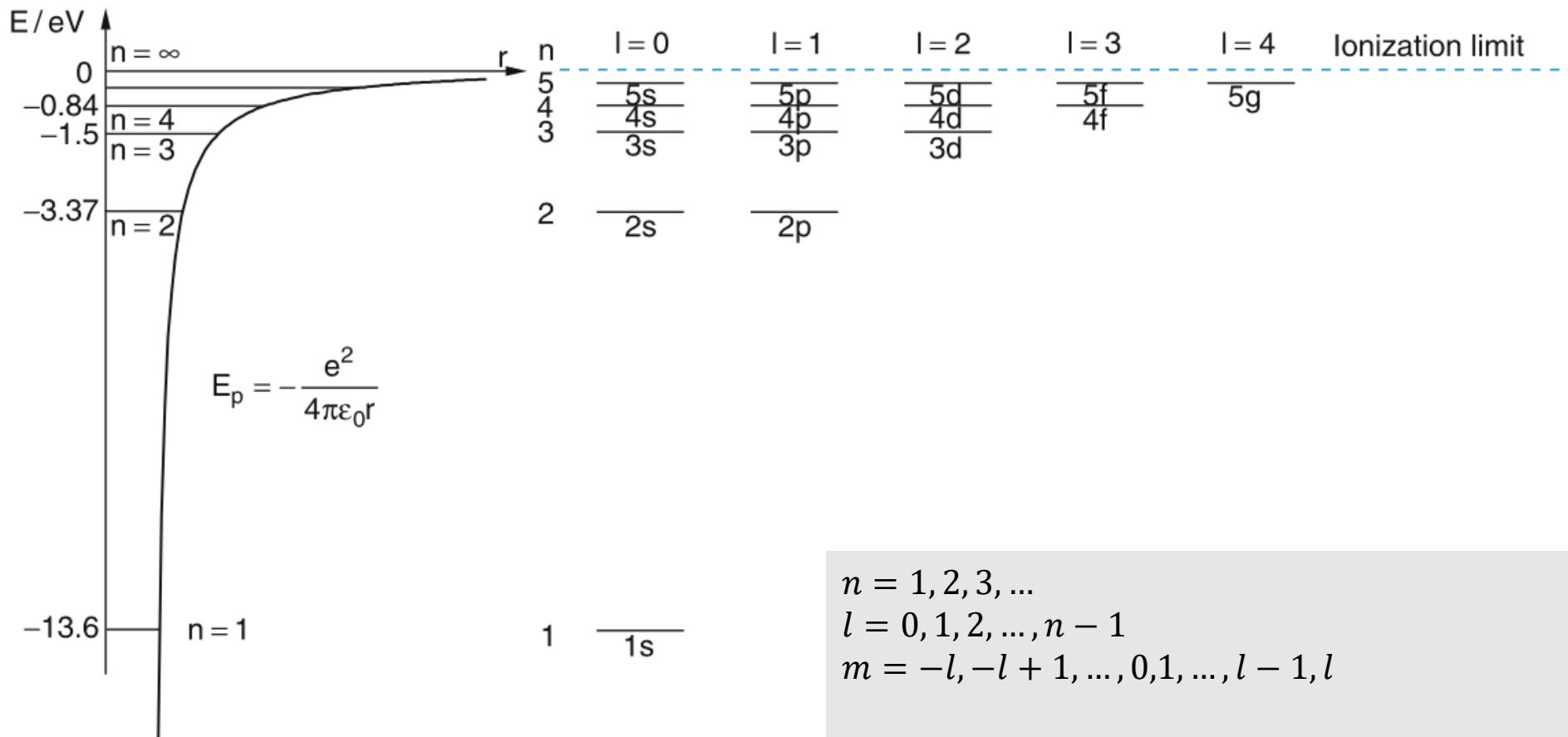
*any time that the wavefunction has a single combination of  $l$  and  $m$*

- What does  $|Y_l^m|^2$  mean physically?

*Related to electric charge distribution*

$$\rho = |\psi(r, \theta, \phi)|^2 dV = |R_{nl}(r)|^2 |Y_l^m(\theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi$$
$$\int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} r^2 |R_{nl}(r)|^2 \sin \theta |Y_l^m(\theta, \phi)|^2 dr d\theta d\phi = 1$$

# Energies of the hydrogen atom ( $Z = 1$ )



$n = 1, 2, 3, \dots$   
 $l = 0, 1, 2, \dots, n - 1$   
 $m = -l, -l + 1, \dots, 0, 1, \dots, l - 1, l$

Number of states with the same energy =  $\sum_0^{n-1} (2l + 1) = n^2$

(based purely on the Schrödinger equation; other effects may lift the degeneracies)

References: Demtröder, Chapters 4 and 5

# Connection of spherical harmonic wave functions to the angular momentum of the particle

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- Classical definition of the angular momentum for a particle with mass  $m$  and velocity  $v$  relative to  $\vec{r} = 0$

$$\vec{L} = \vec{r} \times \vec{p}$$

- $\hat{p} = -i\hbar\nabla$ :  $\hat{L} = -i\hbar(\vec{r} \times \nabla)$

$$\hat{L}_x = -i\hbar(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y})$$

$$\hat{L}_y = -i\hbar(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z})$$

$$\hat{L}_z = -i\hbar(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})$$

Transformation to  
spherical  
coordinates

$$\hat{L}_x = i\hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \cotan \theta \cos \phi \frac{\partial}{\partial \phi} \right)$$

$$\hat{L}_y = i\hbar \left( -\cos \phi \frac{\partial}{\partial \theta} + \cotan \theta \sin \phi \frac{\partial}{\partial \phi} \right)$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$\hat{L}^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$  only depends on azimuthal component + m number

Free particle

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi = E \Psi$$

$$E = \frac{p^2}{2m} \rightarrow \hat{P} = i\hbar \nabla$$

Recall Schrodinger equation in spherical coordinates

$$\frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi_r}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi_r}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi_r}{\partial \phi^2} + \frac{2\mu r^2}{\hbar^2} (E - V) \psi_r = 0$$

$\hat{L}^2$  is proportional to the angular part of the operator

$$\hat{L}^2 Y_l^m = \hbar^2 l(l+1) Y_l^m$$

$$|\hat{L}| = \hbar \sqrt{l(l+1)}$$

$l$  is the orbital angular momentum quantum number

Total angular momentum  
is known if  $l$  is  
known!

Note deviation from Bohr's model ( $L = n\hbar$ )

References: Demtroder, Chapters 4.3.2 and 5.1.2

## Magnetic quantum number

$$\hat{L}_z Y_l^m = -i\hbar \frac{\partial}{\partial \phi} \Theta(\theta) e^{im\phi} = m\hbar Y_l^m$$

- $m$  is an integer that determines the  $z$  component of  $L$

- Example for  $l = 2$   $L = \sqrt{l(l+1)}\hbar = \sqrt{6}\hbar$

$$m = -2, -1, 0, 1, 2$$

$$L_z = -2\hbar, -\hbar, 0, \hbar, 2\hbar$$

- $Y_l^m$  is not an eigenfunction for  $\hat{L}_x$  or  $\hat{L}_y$

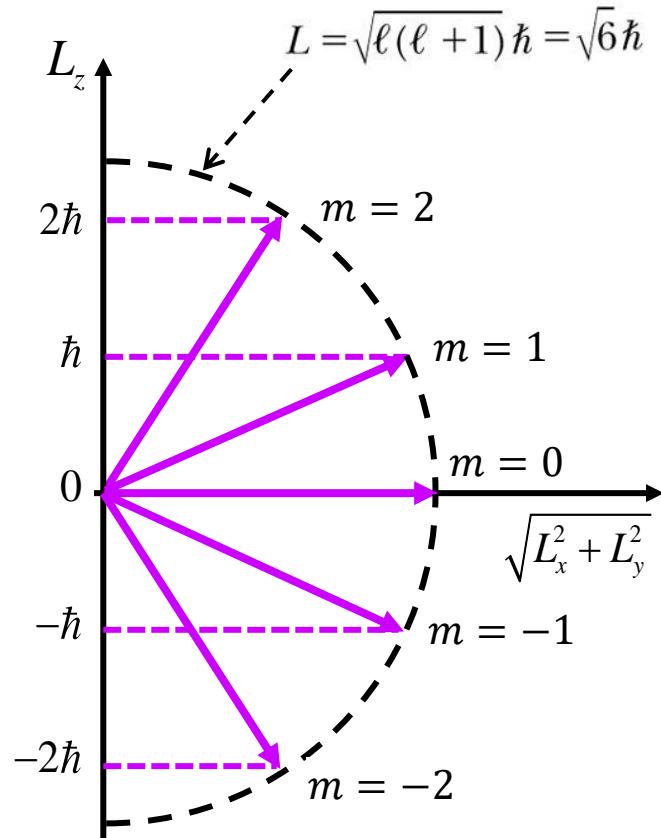
$$(\hat{L}_x^2 + \hat{L}_y^2) = (\hat{L}^2 - \hat{L}_z^2)$$

$$(\hat{L}_x^2 + \hat{L}_y^2) Y_l^m = (l(l+1) - m^2) Y_l^m$$

- Cannot simultaneously measure  $L_x$  and  $L_y$  with  $\hat{L}^2$  and  $\hat{L}_z$

$$\begin{aligned}\hat{L}_x &= i\hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \cotan \theta \cos \phi \frac{\partial}{\partial \phi} \right) \\ \hat{L}_y &= i\hbar \left( -\cos \phi \frac{\partial}{\partial \theta} + \cotan \theta \sin \phi \frac{\partial}{\partial \phi} \right) \\ \hat{L}_z &= -i\hbar \frac{\partial}{\partial \phi}\end{aligned}$$

Possible total angular momentum directions when  $\ell = 2$



References: Demtroder, Chapters 4.3.2 and 5.1.2

# Wave functions of the one-electron atom: a summary

- Center-of-mass motion of the atom

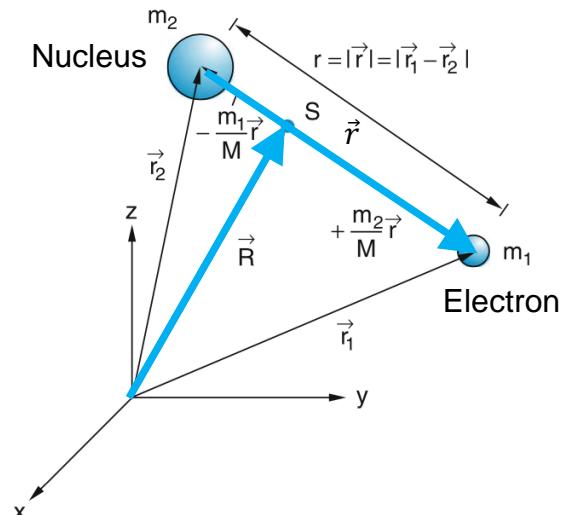
$$g(R) = A e^{ikR}$$

- Stationary wave functions for the electron with three quantum numbers:

$$\psi(r, \theta, \phi) = R_{n,l}(r)Y_l^m(\theta, \phi)$$

- $n$ : Principal quantum number;  $n > 0$
- $l$ : Orbital angular momentum quantum number;  $l \leq n - 1$
- $m$ : Magnetic (azimuthal) quantum number  $|m| < l$
- Energy levels are  $E_n = -\frac{\mu Z^2 e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$ 
  - Energy is independent of  $l$  and  $m_l$  (degeneracy)

References: Demtröder, Chapters 4 and 5



**Table 5.2** Normalized total wave functions of an electron in the Coulomb potential  $E_{\text{pot}} = -Ze^2/(4\pi\epsilon_0 r)$

$n$	$l$	$m$	Eigenfunction $\psi_{n,l,m}(r, \vartheta, \varphi)$
1	0	0	$\frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$
2	0	0	$\frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$
2	1	0	$\frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \cos \vartheta$
2	1	$\pm 1$	$\frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \sin \vartheta e^{\pm i\varphi}$
3	0	0	$\frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2 r^2}{a_0^2}\right) e^{-\frac{Zr}{3a_0}}$
3	1	0	$\frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-\frac{Zr}{3a_0}} \cos \vartheta$
3	1	$\pm 1$	$\frac{1}{81} \cdot \sqrt{\frac{2}{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-\frac{Zr}{3a_0}} \sin \vartheta e^{\pm i\varphi}$
3	2	0	$\frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{Z^2 r^2}{a_0^2} e^{-\frac{Zr}{3a_0}} (3\cos^2 \vartheta - 1)$
3	2	$\pm 1$	$\frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{Z^2 r^2}{a_0^2} e^{-\frac{Zr}{3a_0}} \sin \vartheta \cos \vartheta e^{\pm i\varphi}$
3	2	$\pm 2$	$\frac{1}{162\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{Z^2 r^2}{a_0^2} e^{-\frac{Zr}{3a_0}} \sin^2 \vartheta e^{\pm 2i\varphi}$

# Spatial distributions

- The radial wave function  $R(r)$  can give us the radial probability distribution of the electron but by itself does not represent the probability.
- The probability of finding the electron in a differential volume element  $dx dy dz$  is:

$$dP = |\psi(r, \theta, \phi)|^2 dx dy dz$$

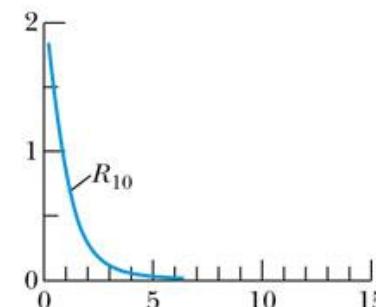
$$dx dy dz = r^2 \sin \theta dr d\theta d\phi$$

$$P(r) dr = r^2 R_{nl}^*(r) R_{nl}(r) dr \int_0^\pi |\Theta(\theta)|^2 \sin \theta d\theta \int_0^{2\pi} |\Phi(\phi)|^2 d\phi$$

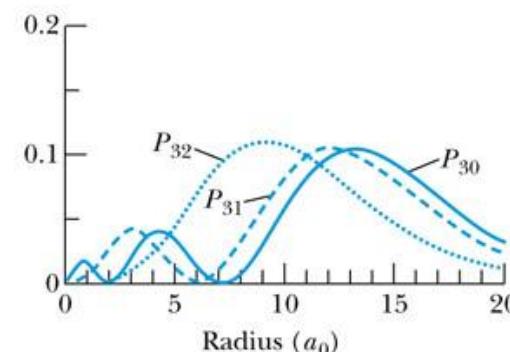
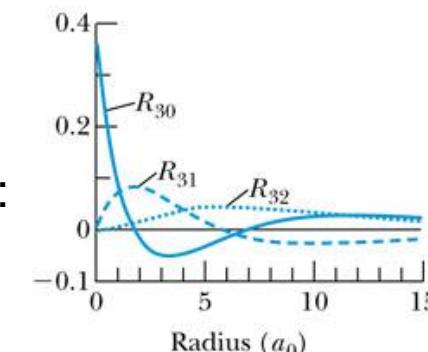
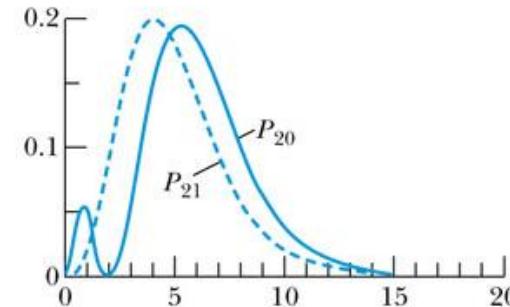
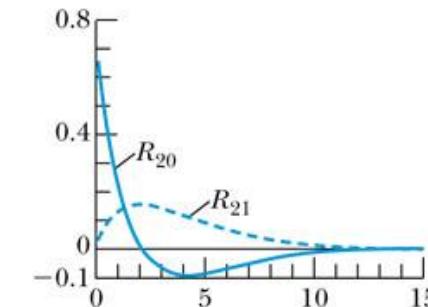
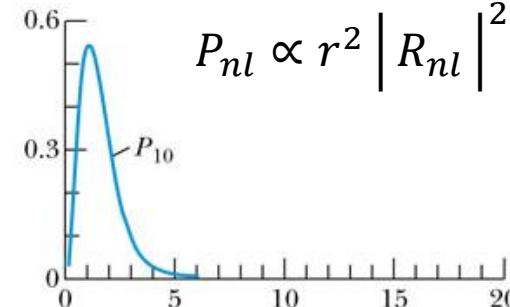
- The  $\theta$  and  $\phi$  integrals are just constants, so the radial probability density is  $P(r) \propto r^2 |R_{nl}(r)|^2$ , depending on only  $n$  and  $l$
- The probability of finding the electron over all space should equal 1:

$$\int_0^\infty r^2 |R_{n,l}(r)|^2 dr = 1$$

Radial wave functions ( $R_{nl}$ )



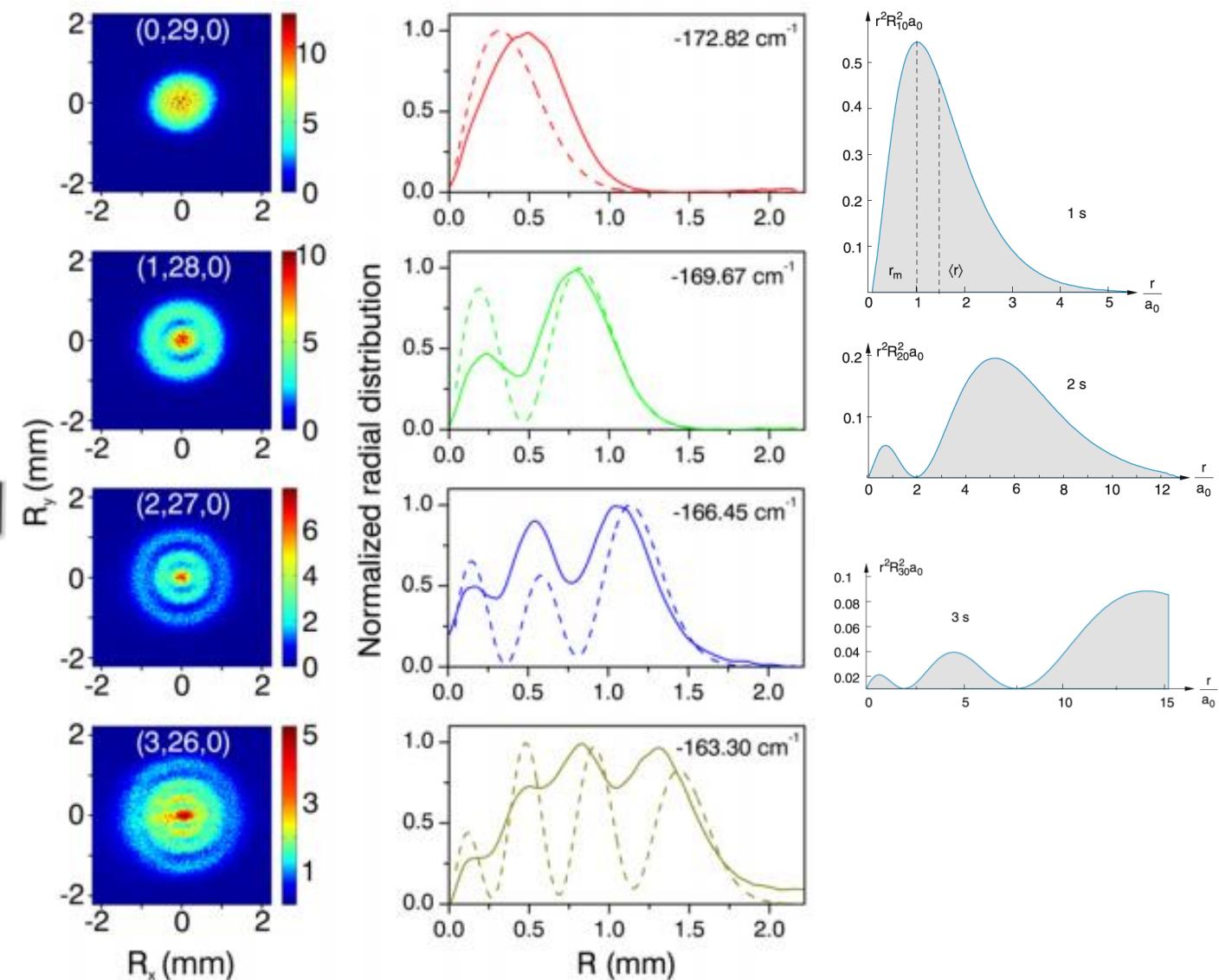
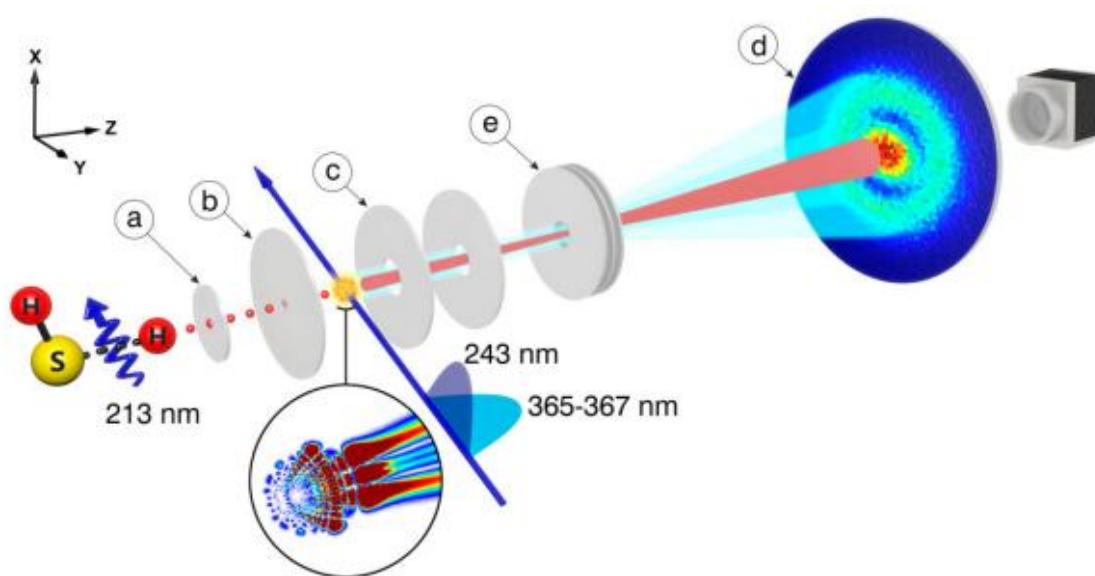
Radial probability distribution ( $P_{nl}$ )



References: Demtröder, Chapters 4 and 5; R. Trebino's lecture notes on Modern Physics

# Example: Photo-dissociation of H<sub>2</sub>S to image the hydrogen wave function

- Photo-dissociation of H<sub>2</sub>S with 213-nm laser
- Further ionization of hydrogen with UV lasers

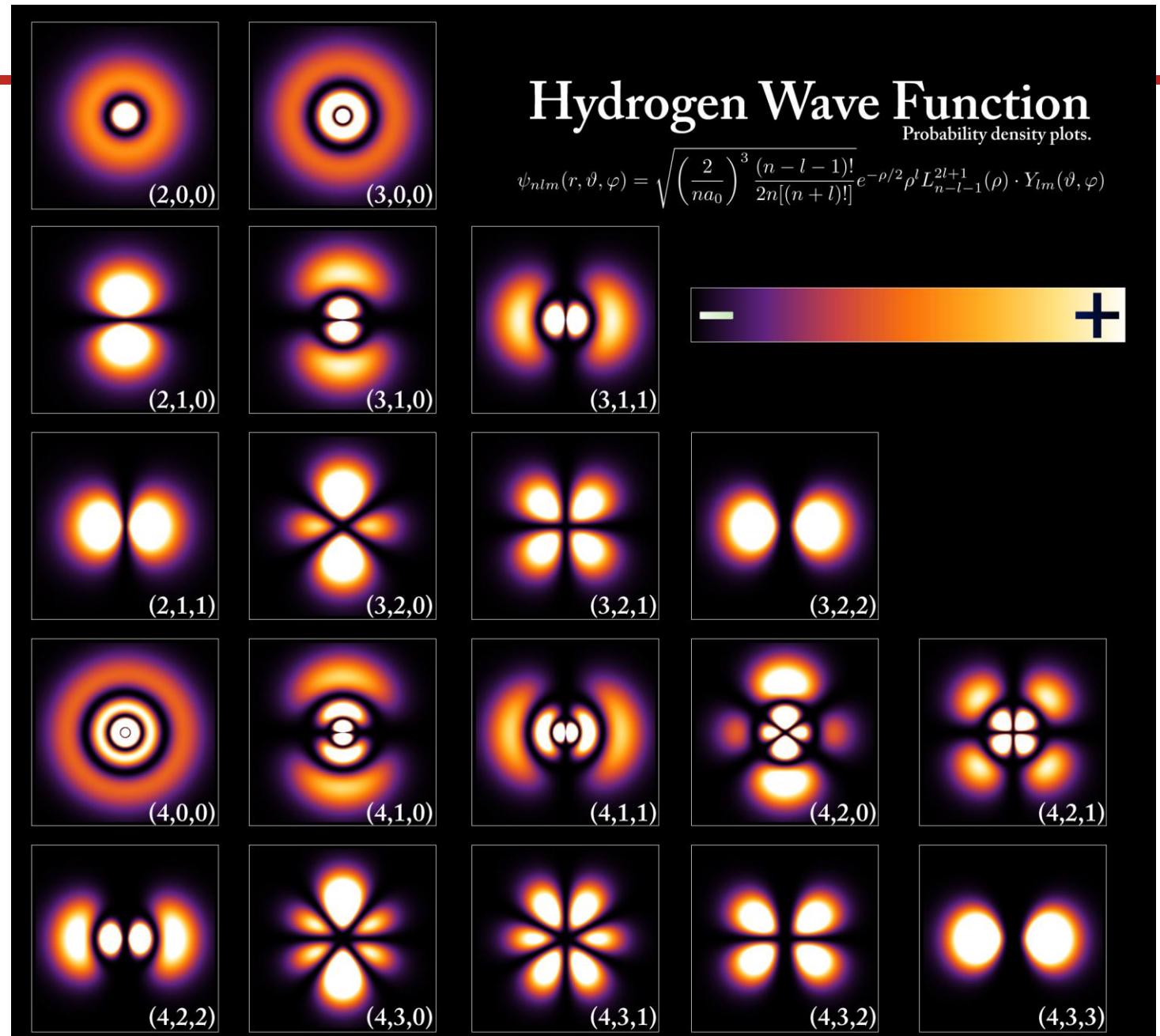


Stodolna et al, PRL (2013) <https://journals.aps.org/prl/pdf/10.1103/PhysRevLett.110.213001>

# Probability density $|\psi_{nlm}|^2$

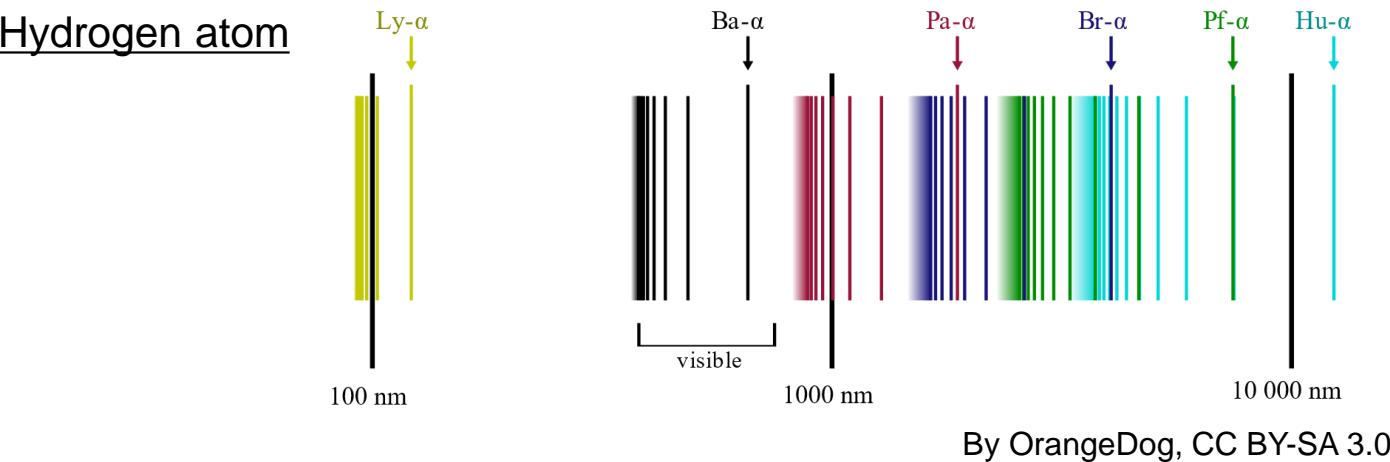
Plot your own at

<https://www.falstad.com/qmatom/>

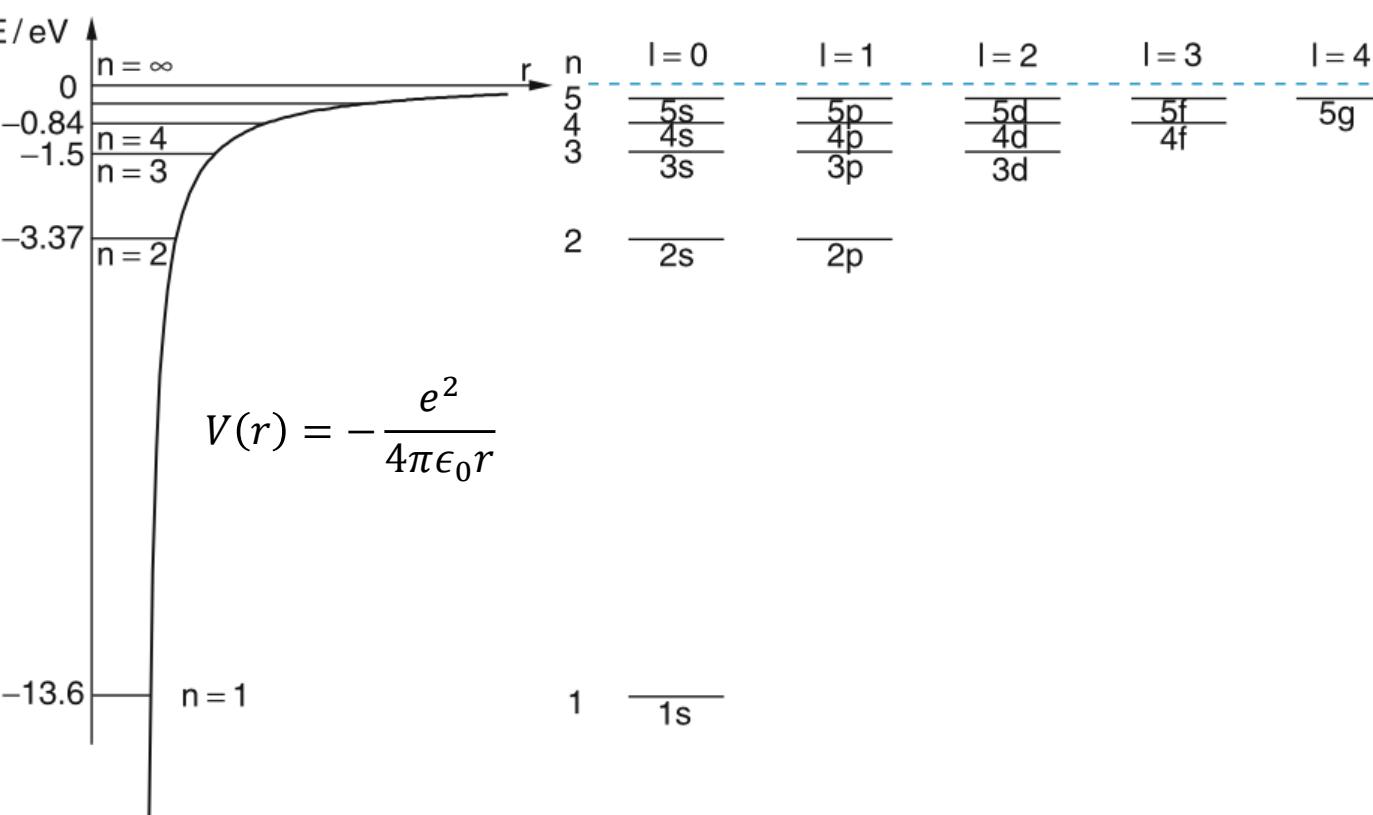


## What do transitions between different angular momentum numbers look like?

- Electron wavefunction solutions are standing waves, with electronic charge distribution
  - Transitions between different  $n$  correspond to changing electronic charge distribution.
- We can figure out what are allowable transitions by calculating the electric dipole moment associated with each transition. If we do this (out of the scope for this course), we get the selection rules:
  - $\Delta n$  can be anything
  - $\Delta l = \pm 1$  and  $\Delta m_l = 0, \pm 1$
- Let's gain some intuitions on what the EM fields look like by visualizing the transitions between different spherical harmonics.
  - Code: SphHarm\_transitions.m
    - Initial state:  $(L, M)$
    - Final state:  $(L_2, M_2)$



By OrangeDog, CC BY-SA 3.0



# Polarizations of absorbing and emitted EM fields

- Due to selection rules, the allowed transitions involve changes in  $l$  and  $m$  of  $\Delta l = \pm 1$  and  $\Delta m = 0, \pm 1$
- Use the code SphHarm\_transitions to visualize what is happening when an atom is oscillating between the following  $(l, m)$  states:

$$(0,0) \leftrightarrow (1,0)$$

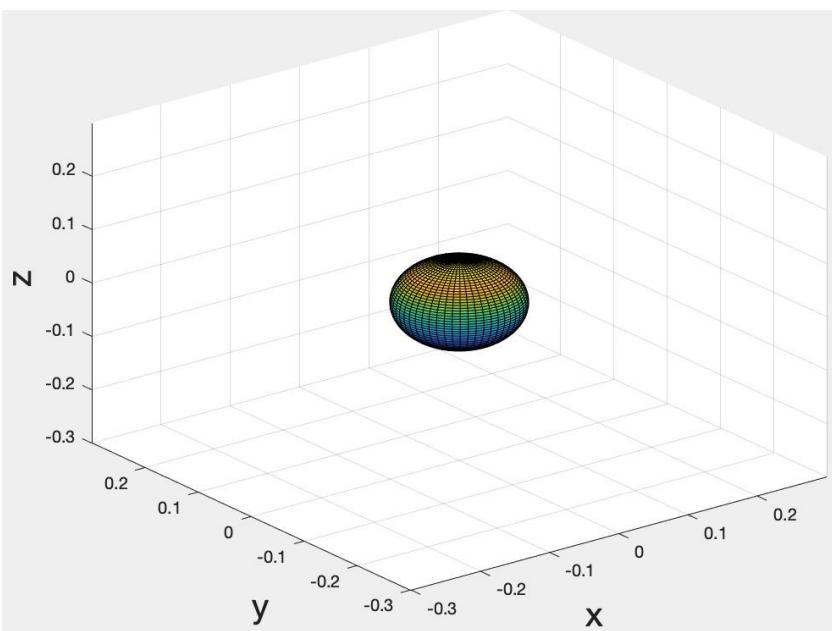
$$(0,0) \leftrightarrow (1,1)$$

$$(0,0) \leftrightarrow (1,-1)$$

- Which polarizations are associated with these transitions?

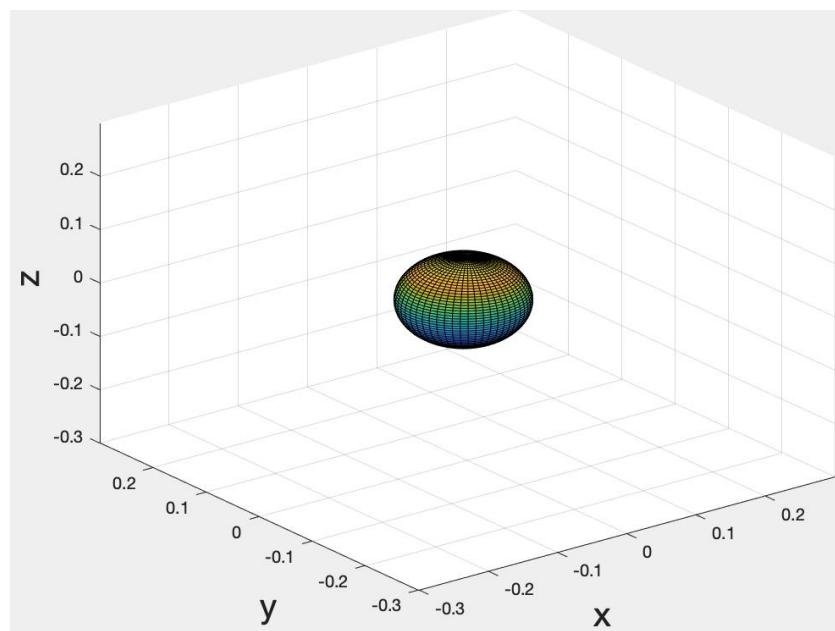
Linearly polarized in  $\hat{z}$   
prop  $xy$  plane

$$A: (0,0) \leftrightarrow (1,0)$$



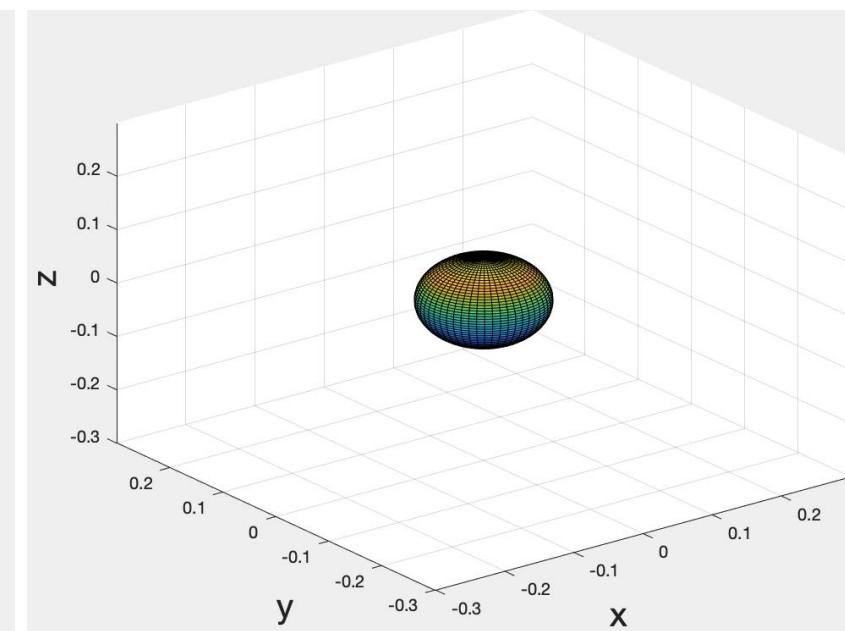
circ. polarized in  $xy$  plane  
when viewed along  $\hat{z}$

$$B: (0,0) \leftrightarrow (1,1)$$

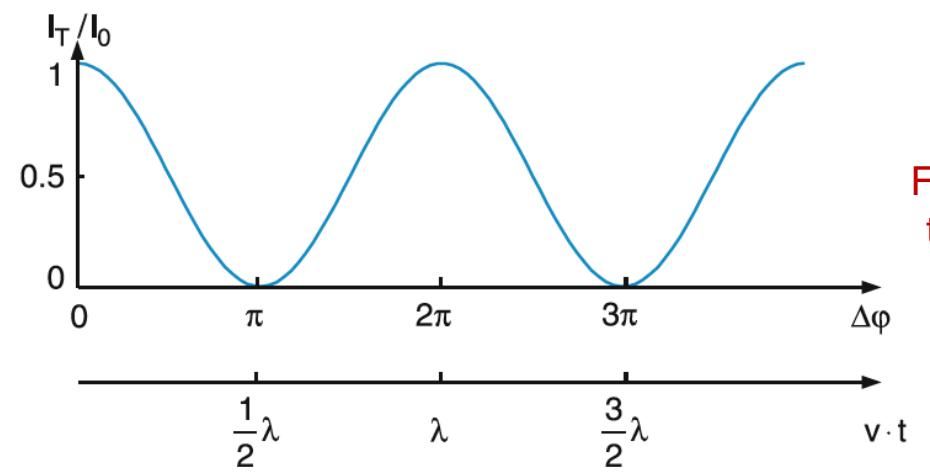
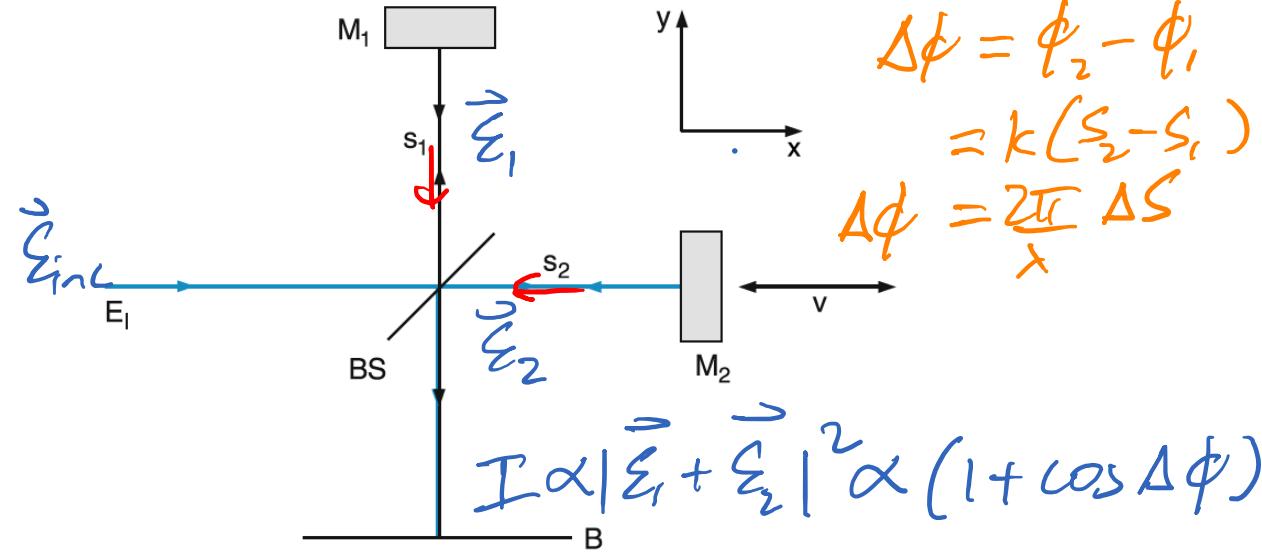


circ. polarized  
opposite handedness

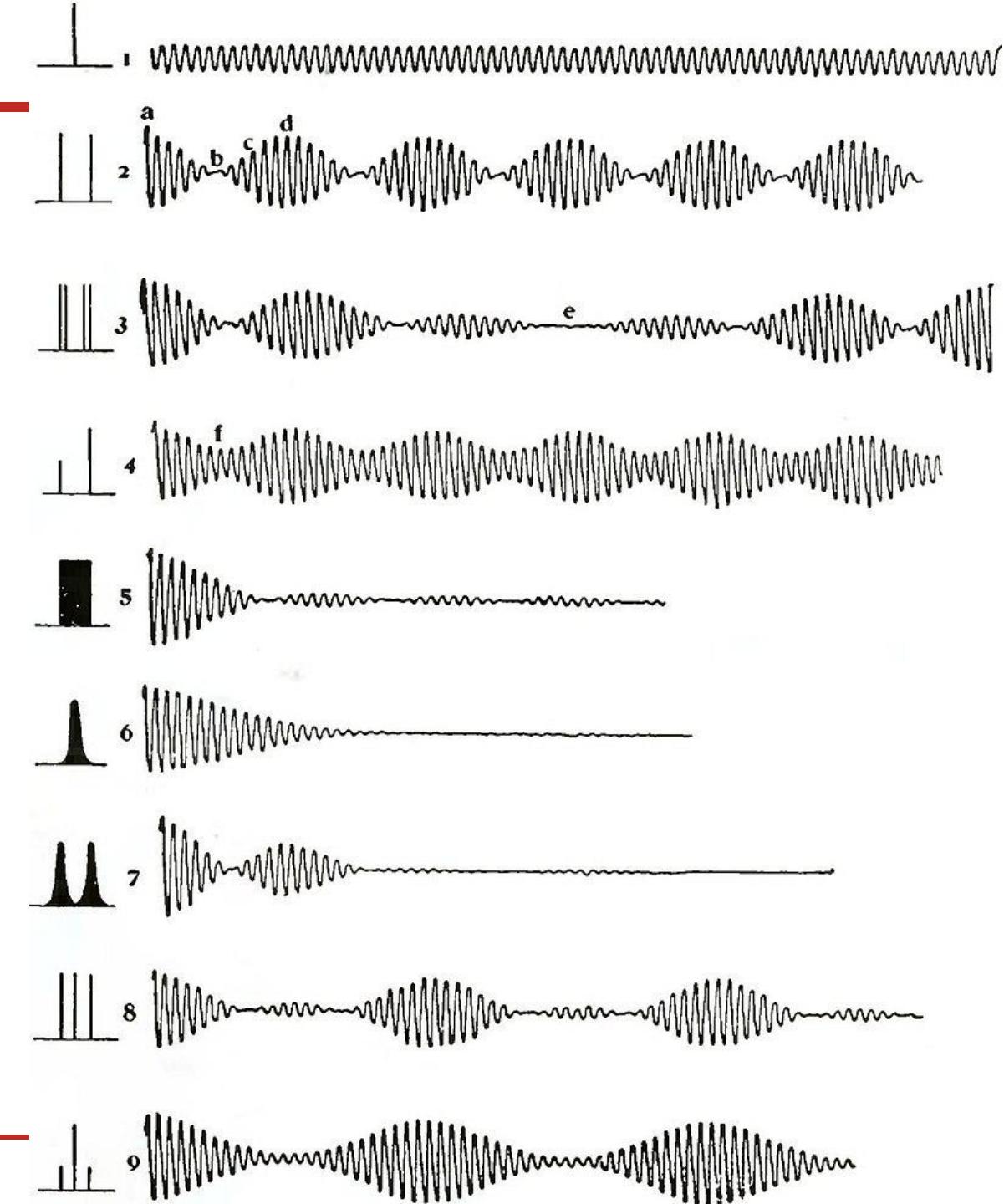
$$C: (0,0) \leftrightarrow (1,-1)$$



# How to measure atomic spectra: Michelson interferometers



Fourier transform  
to get spectrum



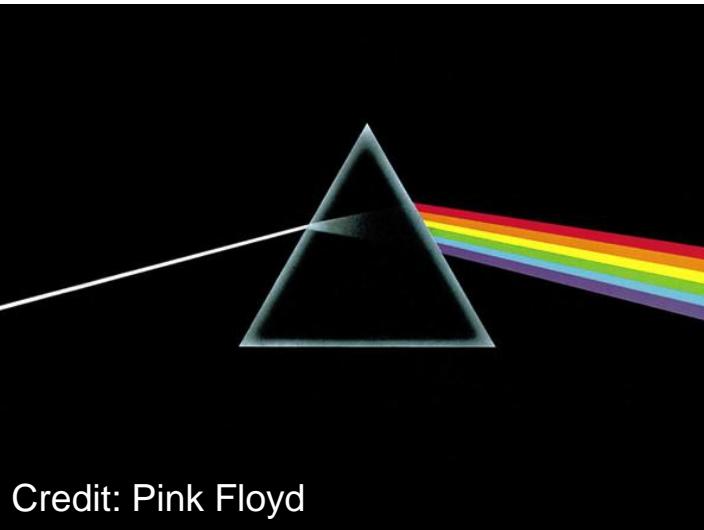
References: Demtroder, Chapter 11.2.2

Michelson, "Light waves and their uses"

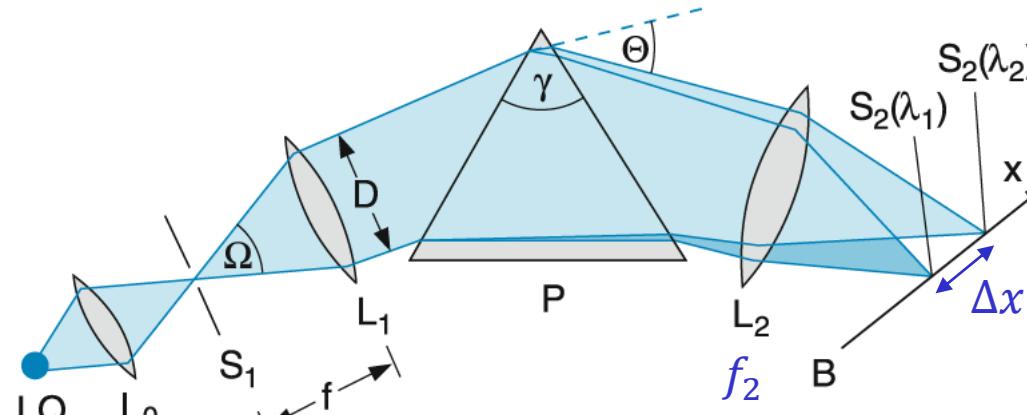
# Another spectroscopic method: use dispersion

Reference: Demtröder, Chapter 11

Need spatial dispersion: different wavelengths need to land on different spots



## Prism spectrograph

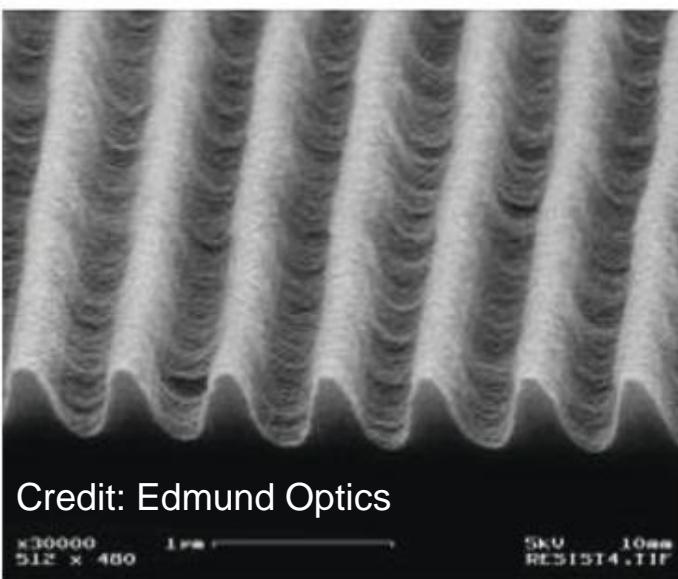


$$\frac{dx}{d\lambda} = f_2 \frac{d\theta}{d\lambda}$$

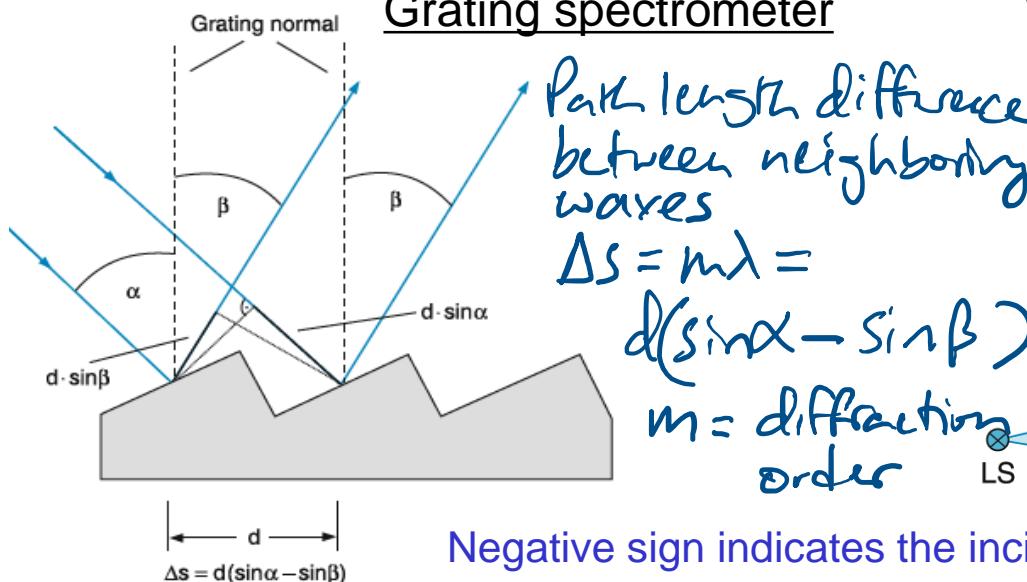
*focal length of imaging lens*

*angular dispersion (function of prism geometry + material)*

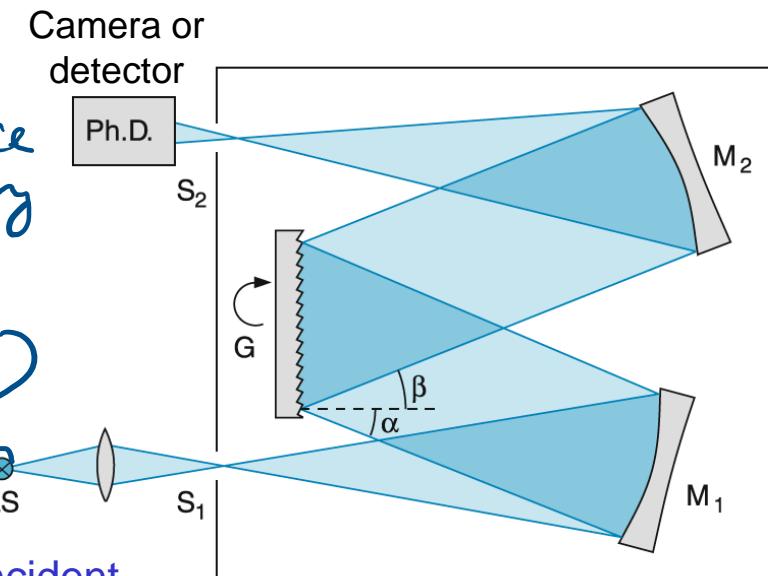
$$= \left( \frac{dx}{d\lambda} \right) \frac{(\lambda_2 - \lambda)}{\Delta\lambda}$$



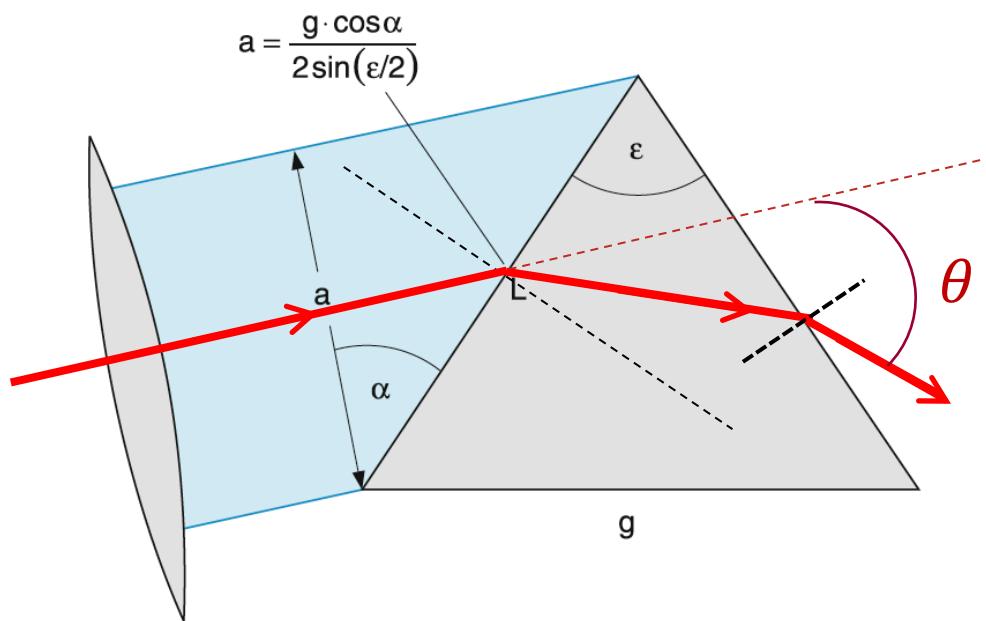
## Grating spectrometer



Negative sign indicates the incident and reflected beams are on opposite side of the grating normal

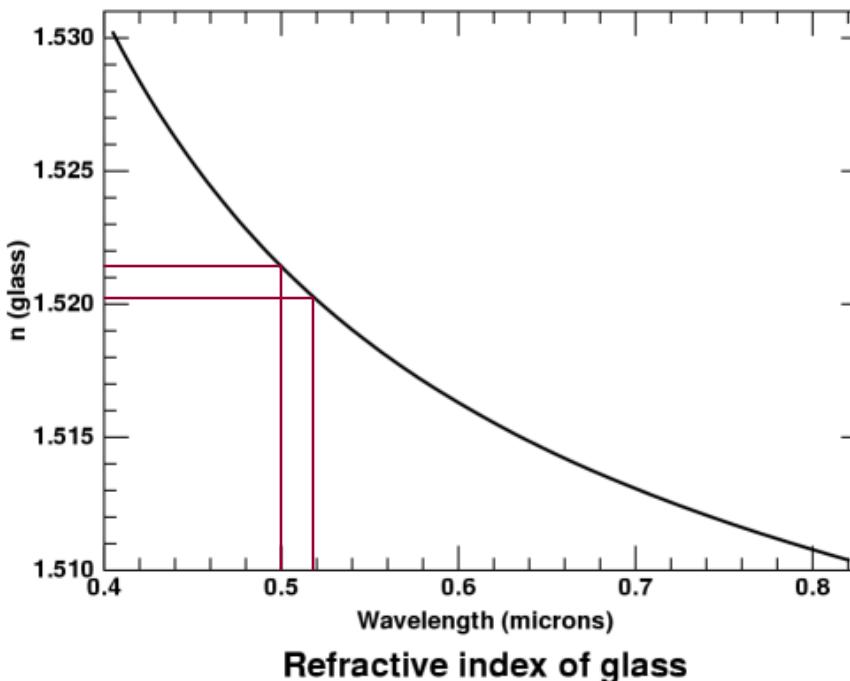


# Resolution limits of spectrometers – prism spectrograph (1)



$$\frac{d\theta}{d\lambda} = \left( \frac{dn}{d\theta} \right)^{-1} \underbrace{\frac{dn}{d\lambda}}_{\text{dispersion of material}}$$

Estimate the minimum resolvable wavelength ( $\Delta\lambda$ ) at  $\lambda = 500$  nm for a glass prism with base width 5 cm.



$$\frac{dn}{d\lambda} \sim 5 \times 10^{-5} \text{ nm}^{-1}$$

at 500 nm

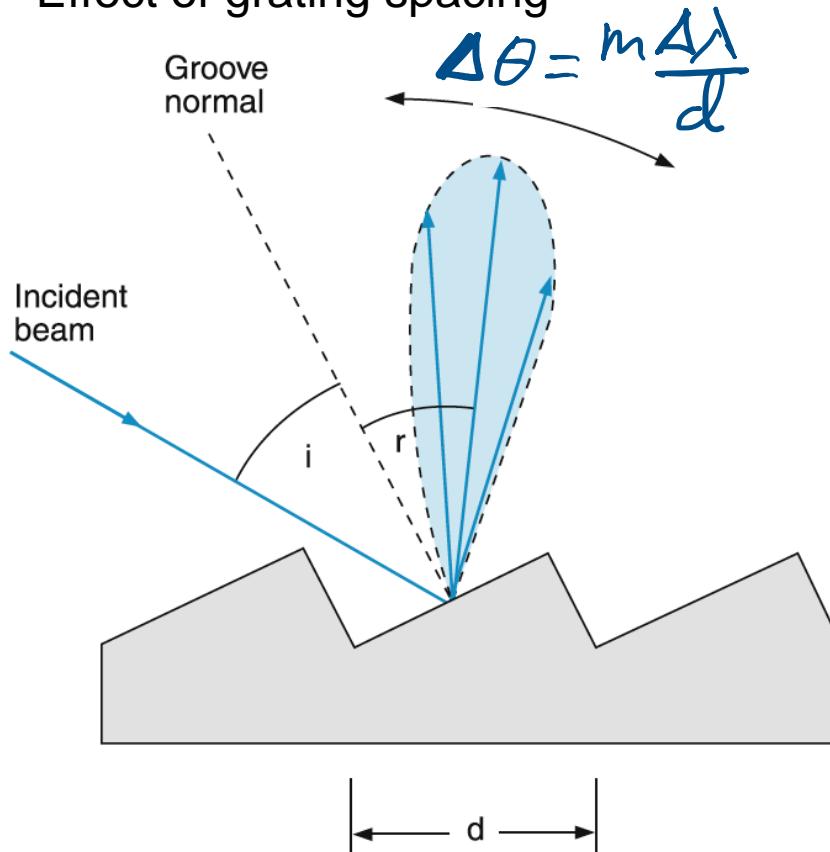
$$\Delta\lambda = \frac{\lambda}{g} \left( \frac{dn}{d\lambda} \right)^{-1}$$

$$\Delta\lambda = 0.2 \text{ nm}$$

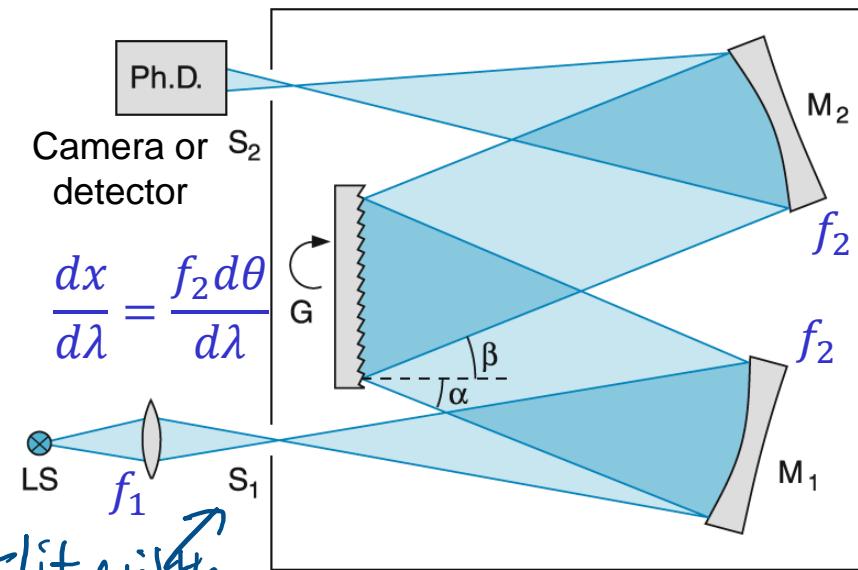
Resolution from finite size of prism:  $\frac{\lambda}{\Delta\lambda} = g \frac{dn}{d\lambda}$

## Resolution limits of spectrometers – grating spectrometer (2)

### Effect of grating spacing



### Effect of entrance slit



$$\frac{dx}{d\lambda} = \frac{f_2 d\theta}{d\lambda}$$

slit width

Unless otherwise noted, for problems in this class assume that  $f_1 = f_2$ .

$$\Delta\lambda_{min} = s \left( \frac{f_2}{f_1} \right) \left( \frac{dx}{d\lambda} \right)^{-1}$$

For  $\lambda = 500 \text{ nm}$  and  $dx/d\lambda = 2 \text{ mm/nm}$ , how small does the entrance slit have to be to resolve lines separated by  $0.025 \text{ nm}$ ?

$$s = (0.025 \text{ nm}) \left( \frac{2 \text{ mm}}{\text{nm}} \right) = 0.05 \text{ mm}$$

## Grating design for hydrogen spectroscopy

---

- We want to observe the first Balmer line of hydrogen at 656.3 nm from a neighboring line at 656 nm using a spectrometer.
- The spectrometer has an arm length of 0.5 meters and the grating is to be used in the first order.
- You can assume that the width of the spectral line is on the same order as the grating period.
- What is the minimum number of lines per millimeter on the grating?

$$\Delta\theta = \frac{m \Delta\lambda}{d} \approx \frac{\Delta x}{L} \quad \text{width of the spectral line}$$

$$\Delta x \approx \frac{m \Delta\lambda L}{d} ; m=1$$

Set  $\Delta x = d$ : the width of the spectral line on the order of the grating period

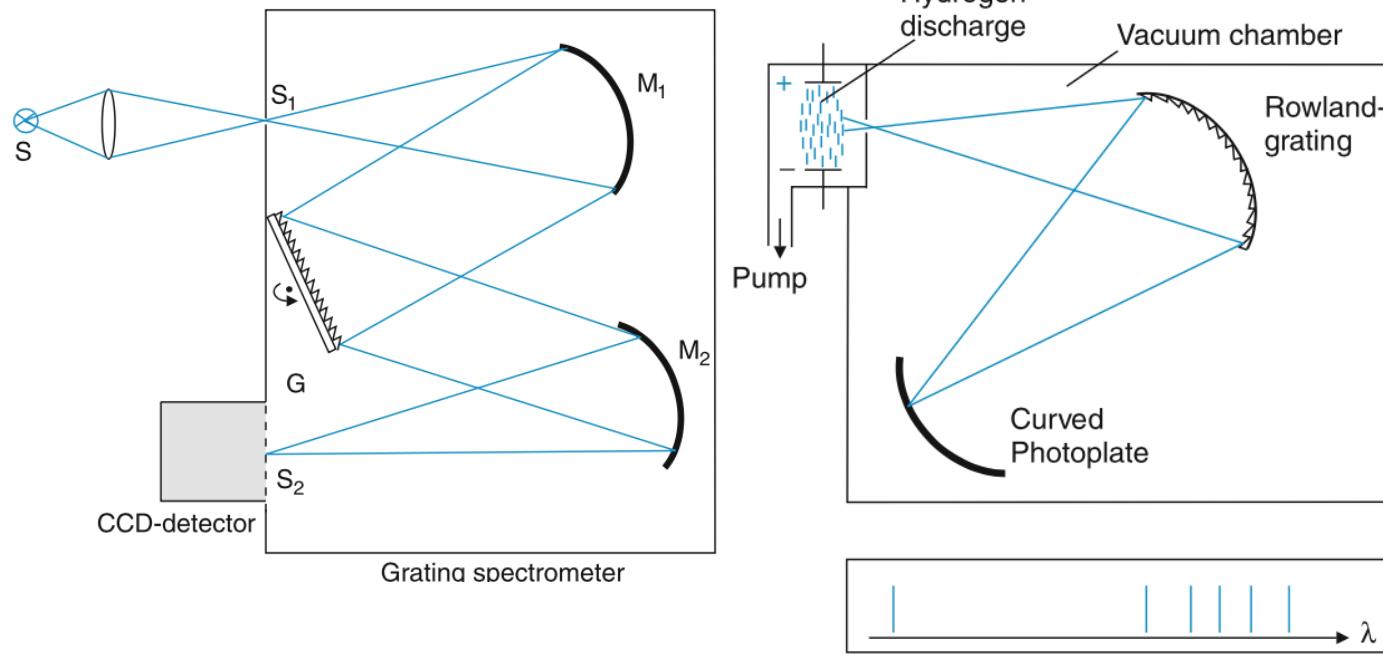
$$d^2 = \Delta\lambda L$$

$$d = 1.22 \times 10^{-5} m = 0.0122 \text{ mm}$$

$$d^{-1} = 81 \text{ grooves/mm}$$

# Connecting solutions of the Schrödinger equation for hydrogen to experimental observations

- Transitions of the Lyman series are in the vacuum ultra-violet (VUV) range, which means that the excitation as well as emission light will get absorbed by the atmosphere → need to do some measurements in vacuum



Intensity	Vacuum Wavelength (Å)	Spectrum	Reference
15	926.2256	H I	MK00a
20	930.7482	H I	MK00a
30	937.8034	H I	MK00a
50 P	949.7430	H I	MK00a
100 P	972.5367	H I	MK00a
300 P	1025.7222	H I	MK00a
1000 P	1215.66824	H I	MK00a
500 P	1215.67364	H I	MK00a

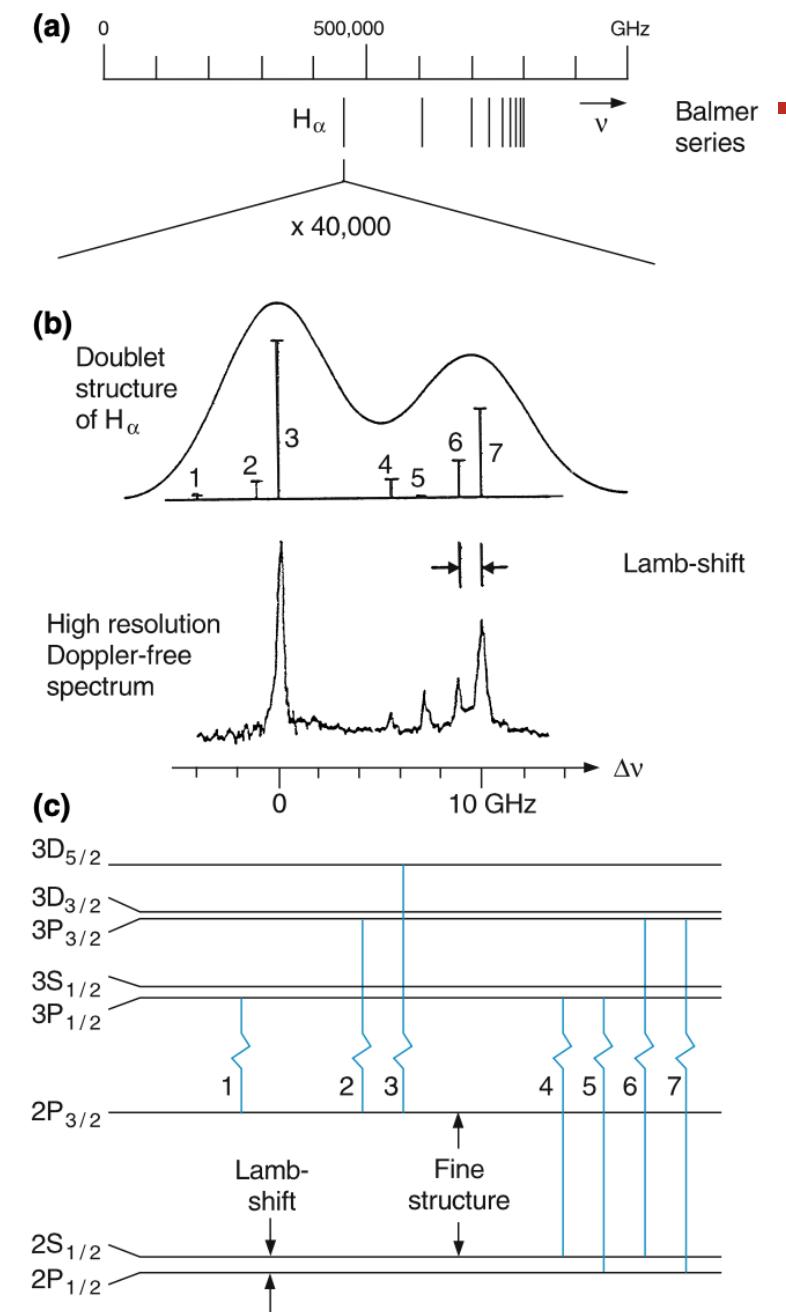
	$n$	$\lambda_{\text{air}}/\text{\AA}$	$\nu_{\text{vac}}/\text{cm}^{-1}$	$\nu_{Ry}/\text{cm}^{-1}$
$H_\alpha$	3	6,562.79	15,233.21	15,233.00
$H_\beta$	4	4,861.33	20,564.77	20,564.55
$H_\gamma$	5	4,340.46	23,032.54	23,032.29
$H_\delta$	6	4,101.73	24,373.07	24,372.80
$H_\varepsilon$	7	3,970.07	25,181.33	25,181.08
$H_\zeta$	8	3,889.06	25,705.84	25,705.68
$H_\eta$	9	3,835.40	26,065.53	26,065.35
$H_\vartheta$	10	3,797.91	26,322.80	26,322.62
$H_\iota$	11	3,770.63	26,513.21	26,512.97
$H_\kappa$	12	3,750.15	26,658.01	26,657.75
$H_\lambda$	13	3,734.37	26,770.65	26,770.42
$H_\mu$	14	3,721.95	26,860.01	26,859.82
$H_\nu$	15	3,711.98	26,932.14	26,931.94

References: Demtröder, Chapters 5 and 11

<https://pmi.nist.gov/PhysRefData/Handbook/Tables/hydrogentable2.htm>

# What the Schrödinger equation solutions do not tell us

- High spectral resolution results show deviations between measured lines and predicted results from Schrödinger theory:
  - Deviations in the absolute wave numbers by up to  $0.2 \text{ cm}^{-1}$
  - Doublets for all spectral lines with  $l = 0$ ; further splitting for levels with  $l > 0$  (Fine structure)
  - Ground state ( $n = 1, l = 0$ ) shows splitting into two components known as the hyperfine structure
- Need further corrections for
  - Electron spin
  - Special relativity (Fine structure)
  - Effect of vacuum fluctuations (Lamb shift)
  - Effect of the structure of the nucleus (Hyperfine structure)



References: Demtröder, Chapter 5