ChemE 2200 – Applied Quantum Chemistry Lecture 2

Today:

The Interaction of Electromagnetic Radiation and Matter
The Hydrogen Spectrum
Multi-Electron Atoms

Defining Question:

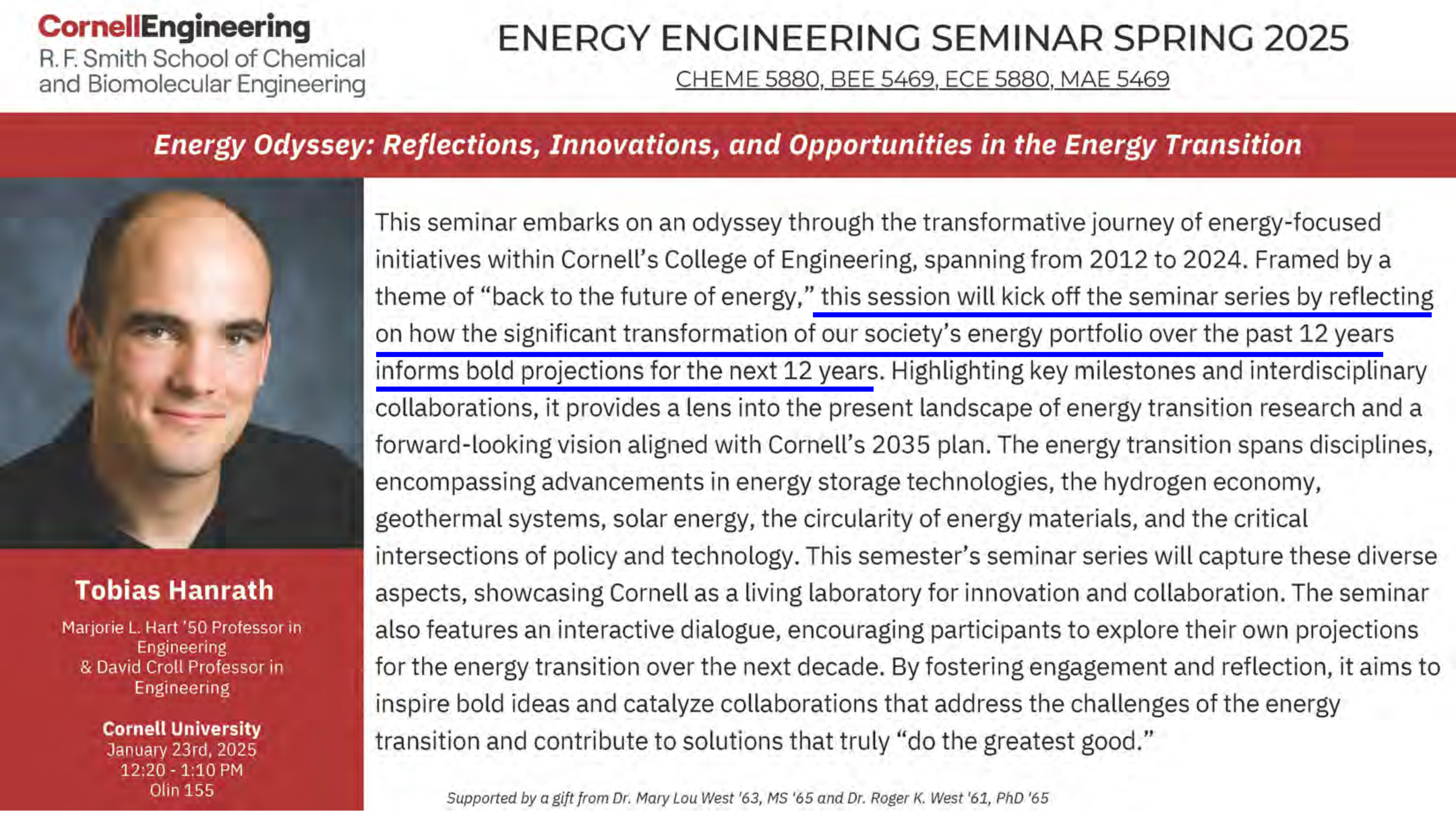
What is a Grotrian Diagram?

Reading for Today's Lecture:

McQuarrie & Simon – Multielectron Atoms
8.1, 8.5, 8.6, 8.9, 8.10, and 8.11

Reading for Quantum Lecture 3:

McQuarrie & Simon – The Chemical Bond: Diatomic Molecules –
9.1-9.3, 9.5-9.13



CornellEngineering
R. F. Smith School of Chemical
and Biomolecular Engineering

ENERGY ENGINEERING SEMINAR SPRING 2025

CHEME 5880, BEE 5469, ECE 5880, MAE 5469

Energy Odyssey: Reflections, Innovations, and Opportunities in the Energy Transition

This seminar embarks on an odyssey through the transformative journey of energy-focused initiatives within Cornell's College of Engineering, spanning from 2012 to 2024. Framed by a theme of "back to the future of energy," this session will kick off the seminar series by reflecting on how the significant transformation of our society's energy portfolio over the past 12 years informs bold projections for the next 12 years. Highlighting key milestones and interdisciplinary collaborations, it provides a lens into the present landscape of energy transition research and a forward-looking vision aligned with Cornell's 2035 plan. The energy transition spans disciplines, encompassing advancements in energy storage technologies, the hydrogen economy, geothermal systems, solar energy, the circularity of energy materials, and the critical intersections of policy and technology. This semester's seminar series will capture these diverse aspects, showcasing Cornell as a living laboratory for innovation and collaboration. The seminar also features an interactive dialogue, encouraging participants to explore their own projections for the energy transition over the next decade. By fostering engagement and reflection, it aims to inspire bold ideas and catalyze collaborations that address the challenges of the energy transition and contribute to solutions that truly "do the greatest good."

Tobias Hanrath

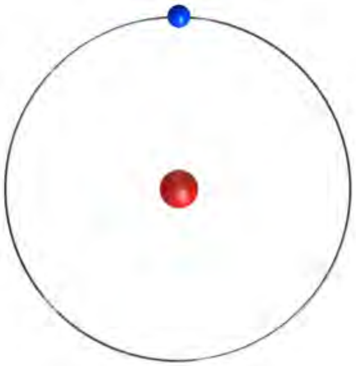
Marjorie L. Hart '50 Professor in Engineering
& David Croll Professor in Engineering

Cornell University
January 23rd, 2025
12:20 - 1:10 PM
Olin 155

Supported by a gift from Dr. Mary Lou West '63, MS '65 and Dr. Roger K. West '61, PhD '65

Tomorrow, 12:20-1:10 p.m. in 155 Olin Hall.

Quantum Mechanics of Closed and Open Systems



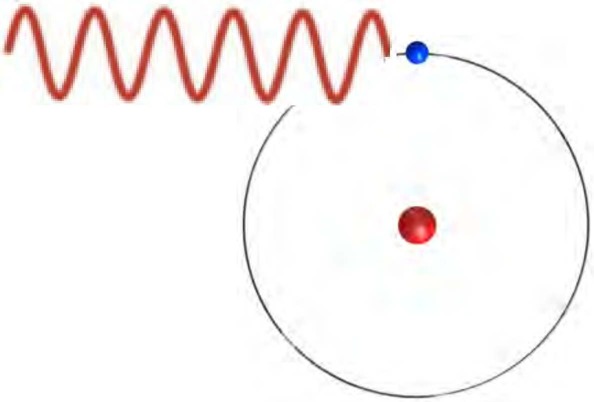
A closed system:
no mass or energy in or out

A hydrogen atom: a proton and an electron

Apply the time-independent Schrödinger equation.

$$\hat{H}\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

$$\hat{H} = \frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r}\right)$$



An open system:
energy enters

A hydrogen atom and a photon

Apply the time-*dependent* Schrödinger equation.

travelling in
the y direction

velocity = c

$$\hat{H}(t)\Psi(r,\theta,\phi,t) = i\hbar\frac{\partial}{\partial t}\Psi(r,\theta,\phi,t)$$

electron-photon potential

$$\hat{H} = \frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r}\right) - \boxed{eE_z z\cos\frac{2\pi}{\lambda}(y+vt)}$$

elementary charge
1.62×10^{-19} coulomb

electric field
strength, esu

polarized along z

Solving the Time–Dependent Schrödinger Equation

$$\hat{H}(t)\Psi(r,\theta,\phi,t) = i\hbar\frac{\partial}{\partial t}\Psi(r,\theta,\phi,t)$$

Assume Ψ is separable. $\Psi(r,\theta,\phi,t) = f(t)\psi(\theta,\phi,t)$

Synopsis of the derivation.

Time–Dependent portion: Requires energy is conserved.

$$E_{\text{photon}} = E_{\text{final state}} - E_{\text{initial state}}$$

Seems appropriate because time and energy
are complementary quantum variables: $(\Delta E)(\Delta t) \geq \frac{\hbar}{2}$

Spatial portion: Requires angular momentum is conserved.

$$\int \psi^*_{\text{final}}\hat{T}\psi_{\text{initial}}d\tau = 0\,?$$ Transition is forbidden.

$$\neq 0\,?$$ Transition is allowed.

$$\hat{T} = e(E_x x + E_y y + E_z z)$$

Yields two selection rules for the hydrogen atom: $\Delta\ell = \pm 1$ and $\Delta m_\ell = 0, \pm 1$

Hint: to check if a transition is allowed, you need only check if
$\int \psi^*_{\text{final}}\hat{T}\psi_{\text{initial}}d\tau = 0$ or $\neq 0$. *No need to evaluate the integral.*

Photon-Induced Transition Probabilty

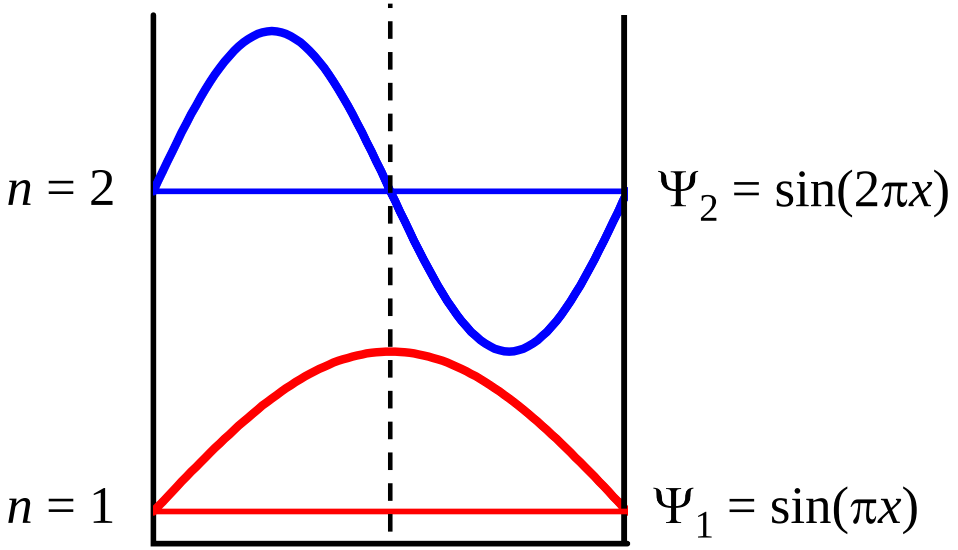
What does the integral $\int \psi^*_{\text{final}} \hat{T} \psi_{\text{initial}} d\tau$ represent?

The integral calculates the overlap between the state created by the photon absorption, $\hat{T}\psi_{\text{initial}}$, and the proposed final state, Ψ_{final}.

That is, does the transition operator T transform Ψ_{initial} into a state function that overlaps with Ψ_{final}?

Recall, eigenfunctions of a system are orthogonal: $\int \psi^*_{\text{final}} \psi_{\text{initial}} d\tau = 0$

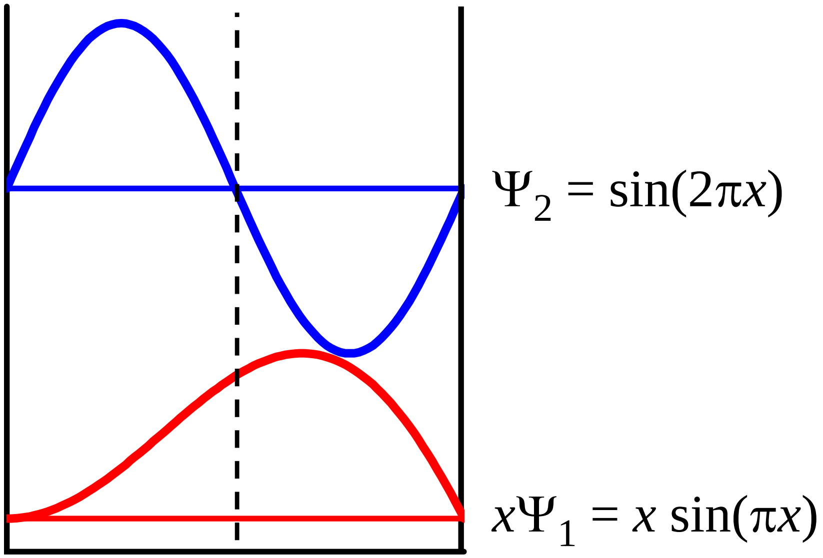
Particle in a Box.



$$\int \psi^*_2 \psi_1 d\tau = \int \sin(\pi x)\sin(2\pi x)dx = 0$$

Ψ_1 and Ψ_2 are orthogonal.

irradiate Ψ_1 with x-polarized photons

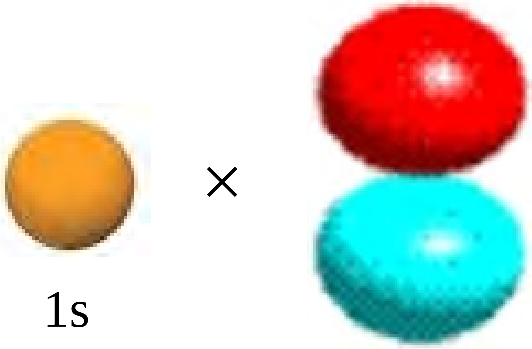


$$\int \psi^*_2 \hat{T} \psi_1 d\tau = \int \sin(\pi x)\, x \sin(2\pi x)dx \neq 0$$

Photon-induced transition is allowed.

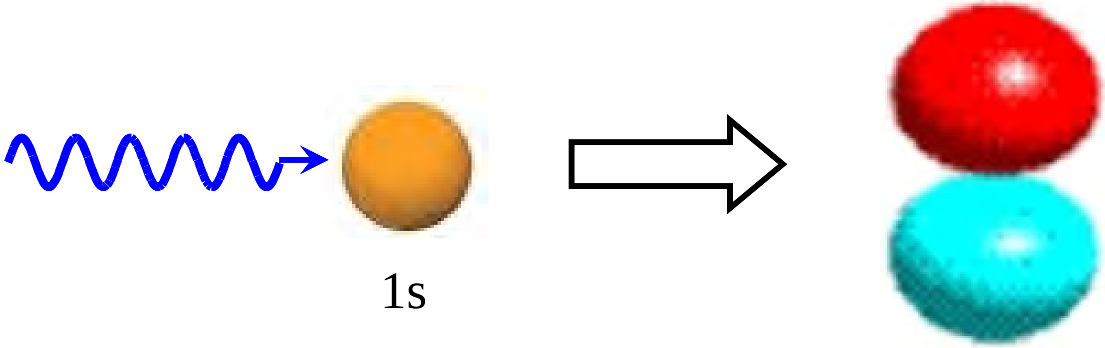
The Hydrogen Atom and Electromagnetic Radiation

The hydrogen atom electron orbitals are orthogonal. $\int \psi_{2p}^{*} \psi_{1s} d\tau \ = \ 0$



1s × 2p$_z$ = 0

The hydrogen atom can absorb a photon with energy $E_{\text{photon}} = E_{2p} - E_{1s}$



1s

$$\hat{T}\psi_{1s} \ = \ (eE_z z)\psi_{1s} \ \rightarrow \ \psi_{2p_z}$$

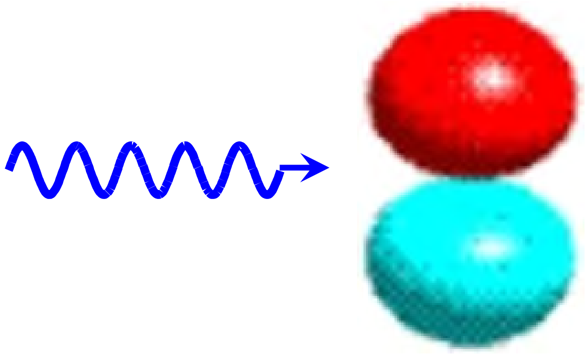
$$\int \psi_{2p}^{*} \hat{T} \psi_{1s} d\tau \ \propto \ \int \psi_{2p}^{*} (eE_z z) \psi_{1s} d\tau \ \propto \ \int \psi_{2p}^{*} \psi_{2p} d\tau \ \neq \ 0$$

Photon-induced transition from 1s to 2p$_z$ is allowed.

What if the photon is *x* polarized? Allowed? Final state?

The Hydrogen Atom and Electromagnetic Radiation

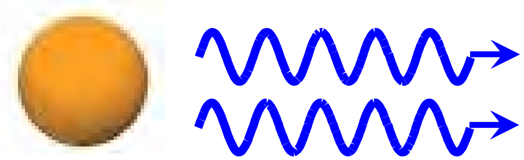
Photon-stimulated emission



initial
state

$$\int \psi_{1s}^{*}\hat{T}\psi_{2p}\,d\tau \;\propto\; \int \psi_{1s}^{*}(eE_z z)\psi_{2p}\,d\tau \;\propto\; \int \psi_{1s}^{*}\psi_{1s}\,d\tau \;\neq\; 0$$

Photon-induced transition from $2p_z$ to 1s is allowed.



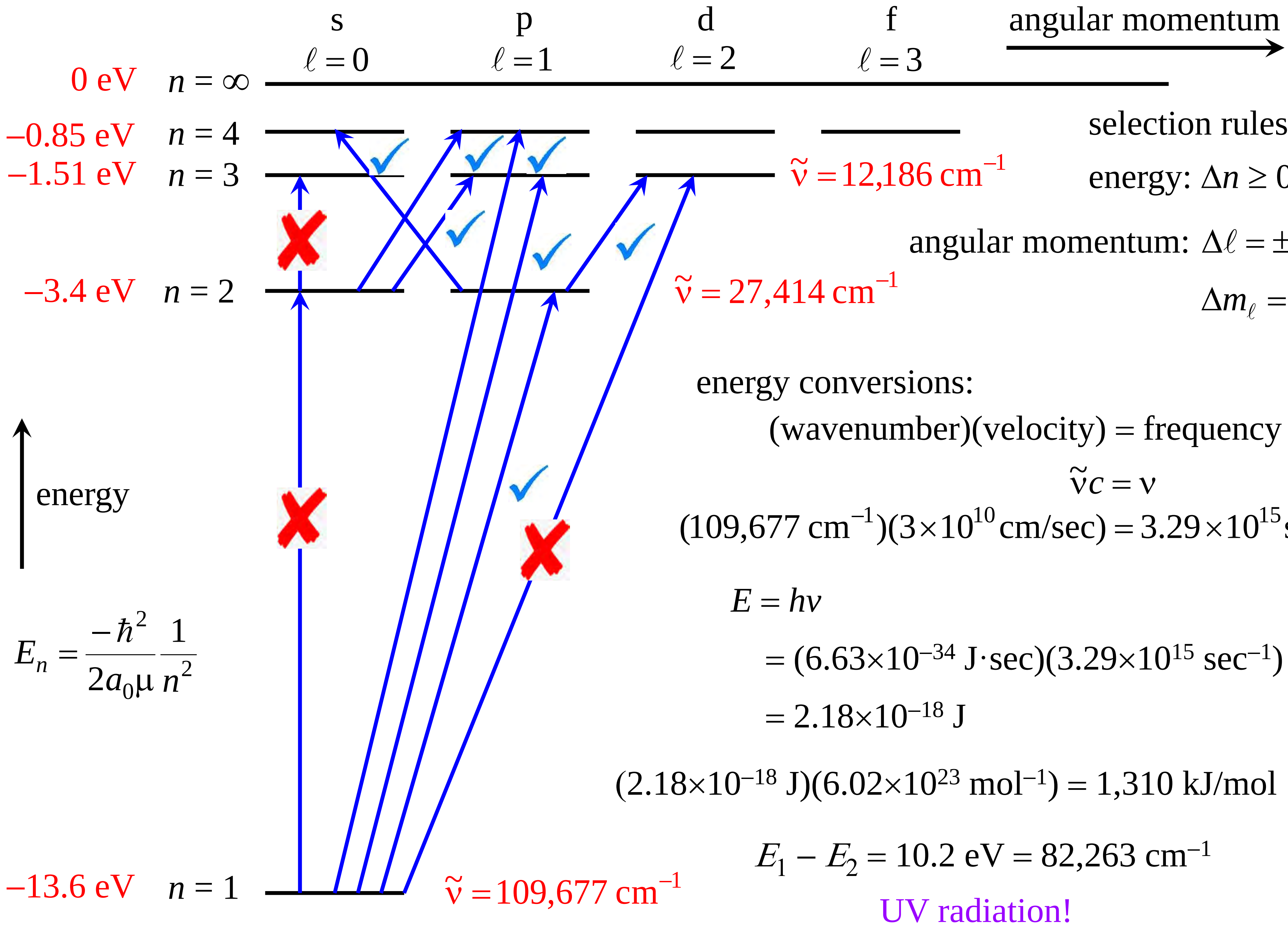
final
state

Two photons with exactly the same energy,
exactly the same phase,
and exactly the same direction.

a “LASER”

Light Amplification by Stimulated Emission of Radiation

The Hydrogen Atom Energy Levels



$$E_n = \frac{-\hbar^2}{2a_0\mu}\frac{1}{n^2}$$

selection rules:

energy: $\Delta n \geq 0$

angular momentum: $\Delta\ell = \pm 1$

$\Delta m_\ell = 0, \pm 1$

energy conversions:

(wavenumber)(velocity) = frequency

$$\tilde{\nu}c = \nu$$

$$(109{,}677\ \text{cm}^{-1})(3\times10^{10}\ \text{cm/sec}) = 3.29\times10^{15}\ \text{sec}^{-1}$$

$$E = h\nu$$

$$= (6.63\times10^{-34}\ \text{J}\cdot\text{sec})(3.29\times10^{15}\ \text{sec}^{-1})$$

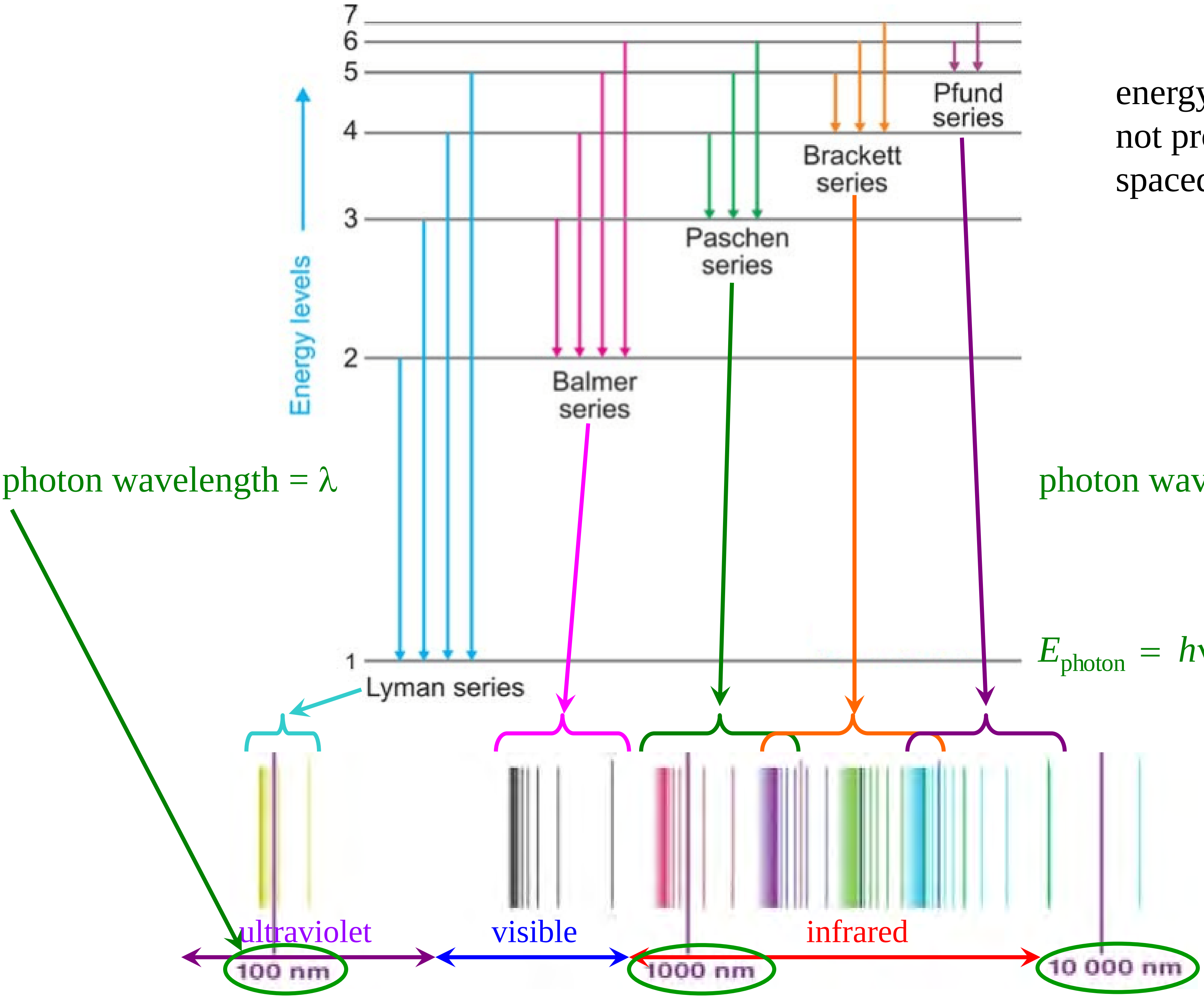
$$= 2.18\times10^{-18}\ \text{J}$$

$$(2.18\times10^{-18}\ \text{J})(6.02\times10^{23}\ \text{mol}^{-1}) = 1{,}310\ \text{kJ/mol}$$

$$E_1 - E_2 = 10.2\ \text{eV} = 82{,}263\ \text{cm}^{-1}$$

UV radiation!

The Hydrogen Atom Spectrum



energy levels
not properly
spaced

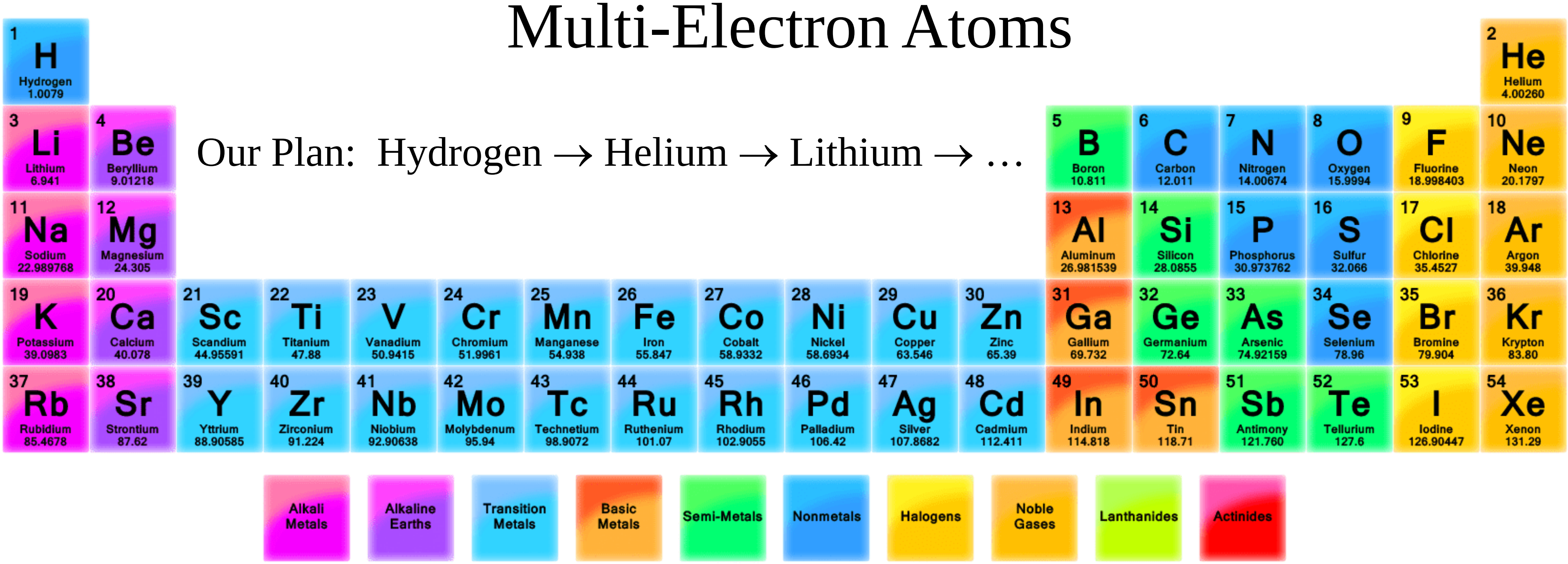
photon wavelength = λ

$$\text{photon wavenumber} = \tilde{\nu} = \frac{1}{\lambda}$$

$$E_{\text{photon}} = h\nu = hc\tilde{\nu} = \frac{hc}{\lambda}$$

Multi-Electron Atoms

Our Plan: Hydrogen → Helium → Lithium → …



1 H Hydrogen 1.0079																	2 He Helium 4.00260
3 Li Lithium 6.941	4 Be Beryllium 9.01218											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
11 Na Sodium 22.989768	12 Mg Magnesium 24.305											13 Al Aluminum 26.981539	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.95591	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium 98.9072	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.90447	54 Xe Xenon 131.29

Alkali Metals	Alkaline Earths	Transition Metals	Basic Metals	Semi-Metals	Nonmetals	Halogens	Noble Gases	Lanthanides	Actinides

Helium: start with the hydrogen Hamiltonian $\hat{H} = \frac{\hbar^2}{2m_e}\nabla^2_{e_1} - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1}\right)$

and add terms. kinetic energy of electron 2: $\frac{\hbar^2}{2m_e}\nabla^2_{e_2}$

nucleus – electron 2 electrostatic attraction: $-\frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_2}\right)$

electron 1 – electron 2 electrostatic repulsion: $+\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}}\right)$

The helium atom is a ‘three-body problem.’ *Insoluble analytically.* What to do?

The Helium Atom

Apply approximation methods and verify with spectroscopy.

Exact solution: $\Psi_{\mathrm{He}}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$

Assume the wavefunction is separable: $\Psi_{\mathrm{He}} = \Psi_{e_1}(r_1, \theta_1, \phi_1)\Psi_{e_2}(r_2, \theta_2, \phi_2)$

Good approximations for the individual electron wavefunctions are the hydrogen atomic orbitals, quantized by *n*, *l*, and *m*.

How are the electrons allocated in the ground state?

Fill the lowest energy orbitals first, with regard to the laws of quantum mechanics.

Rule 1: Because electrons are fermions, every electron must have a unique state, defined by the electron's quantum numbers. *Pauli Exclusion Principle*

principal	n: 1, 2, 3, …
orbital angular momentum	ℓ : $0, 1, 2, \ldots, n-1$
orbital angular momentum *z* projection	m_ℓ : $0, \pm 1, \pm 2, \ldots, \pm \ell$
spin angular momentum	m_s : $\pm ½$

What is spin angular momentum?

Spin

Intrinsic quantized properties of all particles: mass

electric charge

spin angular momentum (aka ‘spin’)

spin quantum number, s	allowed spin states, m_s	particles
0	0	π meson (pion), K meson (kaon)
½	–½, +½	electron, proton, neutron, neutrino
1	–1, 0, +1	photon, gluon
$3/2$	$-3/2, -1/2, +1/2, +3/2$	(none)
2	–2, –1, 0, +1, +2	graviton

integral spins: energy (Bosons)

non-integral spins: matter (Fermions)

Adding Electrons to Orbitals

Add electrons to nuclei: $\mathrm{H}: \psi = \psi_{1s}$

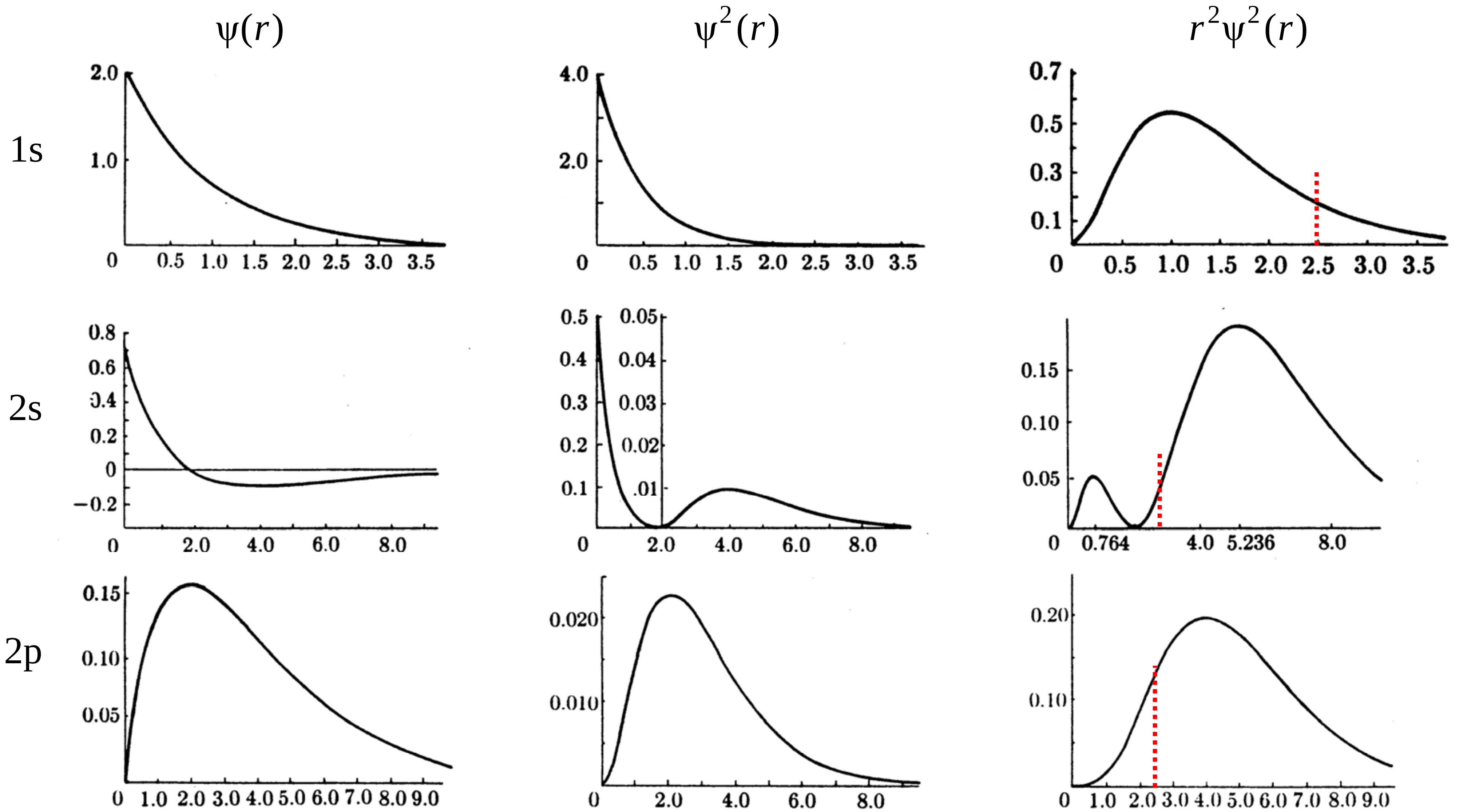
$\mathrm{He}: \psi = \psi_{1s_1}\psi_{1s_2}$

$\mathrm{Li}: \psi = \psi_{1s_1}\psi_{1s_2}\psi_{2s_3}$ or $\psi = \psi_{1s_1}\psi_{1s_2}\psi_{2p_{z3}}$?

Fill the lowest energy orbitals first.

For hydrogen, 2s and $2p_z$ are the same energy. Does this change for lithium?

The Filled 1s Orbital Shields the Nuclear Charge



The 2s orbital penetrates into the 1s electron cloud more than the 2p orbital penetrates into the 1s electron cloud.

from M. Karplus and R. N. Porter, *Atoms and Molecules: An Introduction for Students of Physical Chemistry*, (Benjamin, 1970), pp 130-131.

Adding Electrons to Orbitals, continued

Rule 2: For atoms will filled core orbitals, the *s* orbital is lower energy than the *p* orbital, which is lower energy than the *d* orbital, which is lower energy than the *f* orbital …

H: $1s_1$

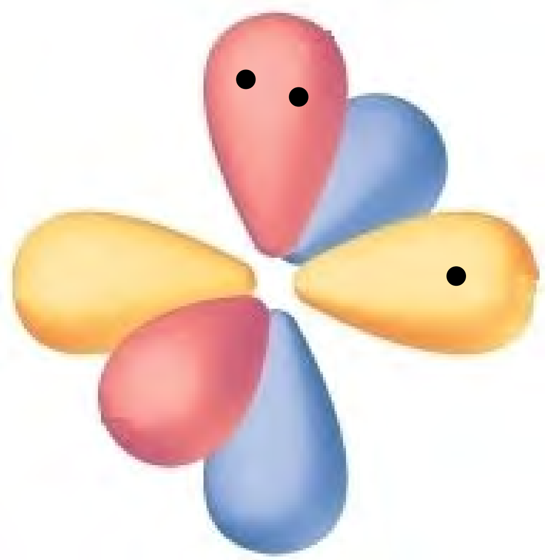
He: $1s_1 1s_2$

Li: $1s_1 1s_2 2s_3$

Be: $1s_1 1s_2 2s_3 2s_4$

B: $1s_1 1s_2 2s_3 2s_4 2p_{z5}$

C: $1s_1 1s_2 2s_3 2s_4 2p_{z5} 2p_{z6}$ or $1s_1 1s_2 2s_3 2s_4 2p_{z5} 2p_{x6}$ or $1s_1 1s_2 2s_3 2s_4 2p_{z5} 2p_{y6}$?



Placing electrons in different orbitals reduces electron-electron repulsion.

Rule 3: For orbitals with equal energy (for example, $2p_x$, $2p_y$, and $2p_z$), place electrons in different orbitals.

Adding Electrons to Orbitals, continued

C: $1s_1 1s_2 2s_3 2s_4 2p_{z5} 2p_{x6}$ Electron spin in $2p_z$ and $2p_x$?

For $1s_2$ and $2s_4$ the electron spin was dictated by the Pauli Exclusion Principle.

If the $2p_z$ electron is spin +½ should the $2p_x$ electron be spin +½ or spin –½?

Does it matter?

Rule 4: A state function for a system of two or more electrons must be *anti-symmetric* with the interchange of the labels of any two electrons.

$$\Psi \xrightarrow{\text{switch labels of any two electrons}} -\Psi \quad \text{anti-symmetric}$$

$$\Psi \longrightarrow +\Psi \quad \text{symmetric}$$

Designate the wavefuntion of an electron with $m_s = +½$ to be α
and the wavefuntion of an electron with $m_s = –½$ to be β.

He: $1s_1\alpha_1 1s_2\beta_2 \;=\; 1s_1 1s_2 \alpha_1 \beta_2$

$$1s_1 1s_2 \alpha_1 \beta_2 \longrightarrow 1s_2 1s_1 \alpha_2 \beta_1$$

neither symmetric nor anti-symmetric.

Anti-symmetric Orbitals

He: $\boxed{1s_1 1s_2}\alpha_1\beta_2$

the orbital portion
is symmetric

Write the spin portion as symmetric and anti-symmetric state functions.

$\alpha_1\beta_2 + \beta_1\alpha_2 \longrightarrow \alpha_2\beta_1 + \beta_2\alpha_1$ symmetric

$\alpha_1\beta_2 - \beta_1\alpha_2 \longrightarrow \alpha_2\beta_1 - \beta_2\alpha_1$ anti-symmetric

The state function for He is $1s_1 1s_2(\alpha_1\beta_2 - \beta_1\alpha_2)$..

C: $1s_1 1s_2 2s_3 2s_4 2p_{z5} 2p_{z6}$

The orbital portion is neither symmetric nor anti-symmetric.

C: $1s_1 1s_2 2s_3 2s_4 (2p_{z5} 2p_{x6} + 2p_{x5} 2p_{z56})$ symmetric

C: $1s_1 1s_2 2s_3 2s_4 (2p_{z5} 2p_{x6} - 2p_{x5} 2p_{z6})$ anti-symmetric

Evaluating $\langle E \rangle = \int \psi^* \hat{H} \psi \, d\tau$ reveals that the anti-symmetric state function is the lower energy.

(Recall the approximate Ψ is not an eigenfunction; cannot use $\hat{H}\psi = E\psi$)

The Ground State of Carbon is a Triplet

C: $1s_1 1s_2 2s_3 2s_4 (2p_{z5} 2p_{x6} - 2p_{x5} 2p_{z6})$

To use the lower-energy anti-symmetric orbital state function, we must append a symmetric spin state function.

$$\left.\begin{array}{ll} \alpha_5\alpha_6 & \text{symmetric} \\ \beta_5\beta_6 & \text{symmetric} \\ \alpha_5\beta_6 + \beta_5\alpha_6 & \text{symmetric} \end{array}\right\} \text{three states – a triplet}$$

$$\alpha_5\beta_6 - \beta_5\alpha_6 \quad \text{anti-symmetric} \quad \text{a singlet}$$

The ground state of carbon has $2p_z$ and $2p_x$ electrons with both spins +½ or both spins –½.

Hund’s Rules: Maximize the total electron spin in the open subshell.

Mandates electrons in different orbitals ($2p_x$ and $2p_z$), which minimizes electron-electron repulsion and minimizes nucleus-electron screening.

aka the ‘bus seat rule.’

Maximize the total orbital angular momentum quantum number L.

Not needed until Ti. (will be ignored here.)

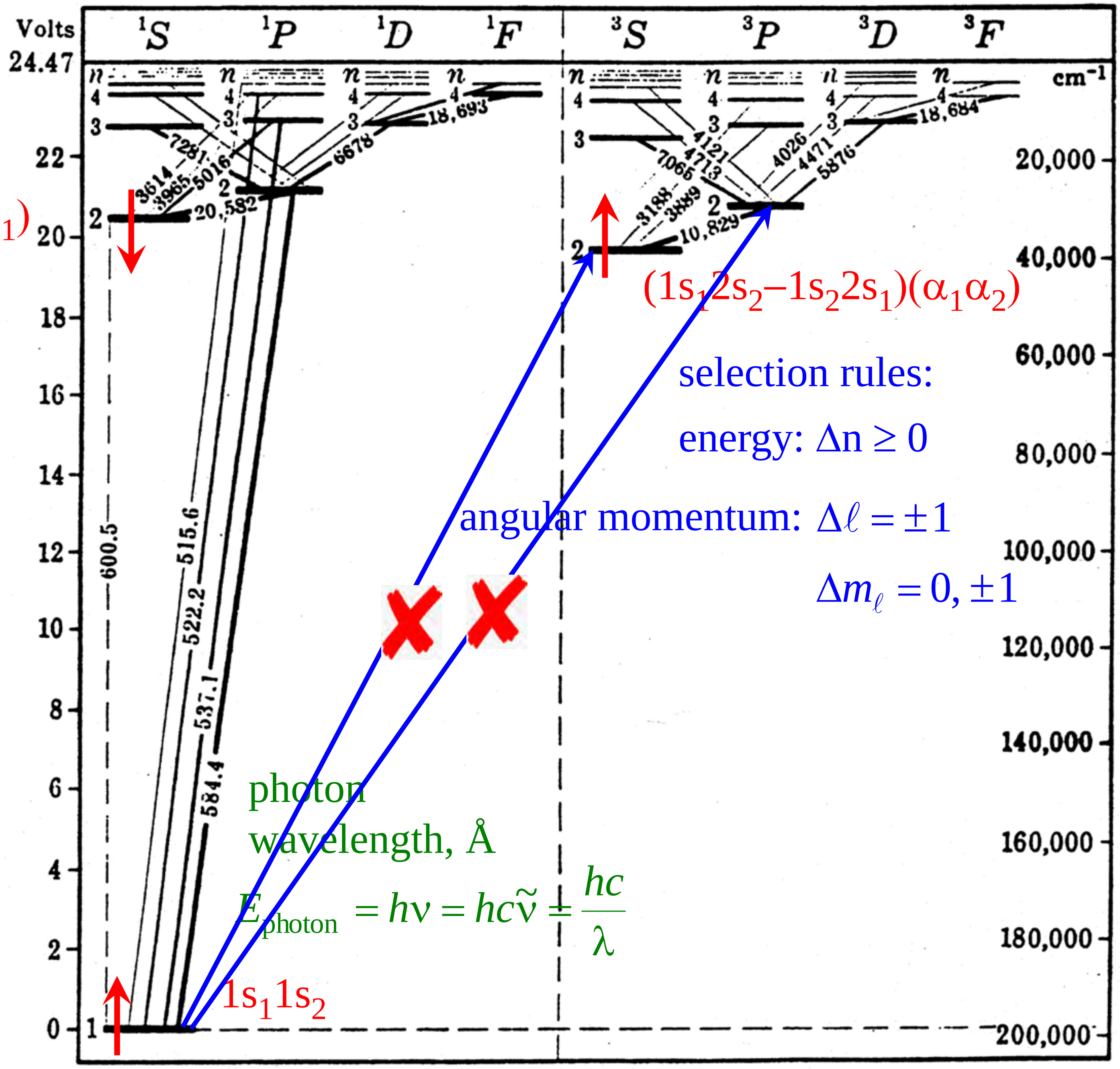
Maximize the total orbital + spin angular momentum, $L + S$.

aka spin-orbit coupling, ~1–10 cm^{-1}. (will be ignored here.)

The Helium Atom Energy Levels

singlet states

triplet states



$(1s_1 2s_2 + 1s_2 2s_1)$
$(\alpha_1\beta_2 - \beta_1\alpha_2)$

$(1s_1 2s_2 - 1s_2 2s_1)(\alpha_1\alpha_2)$

energy in eV

1 eV
$= 8066 \text{ cm}^{-1}$
$= 96 \text{ kJ/mol}$

selection rules:

energy: $\Delta n \geq 0$

angular momentum: $\Delta\ell = \pm 1$

$\Delta m_\ell = 0, \pm 1$

energy in wavenumbers

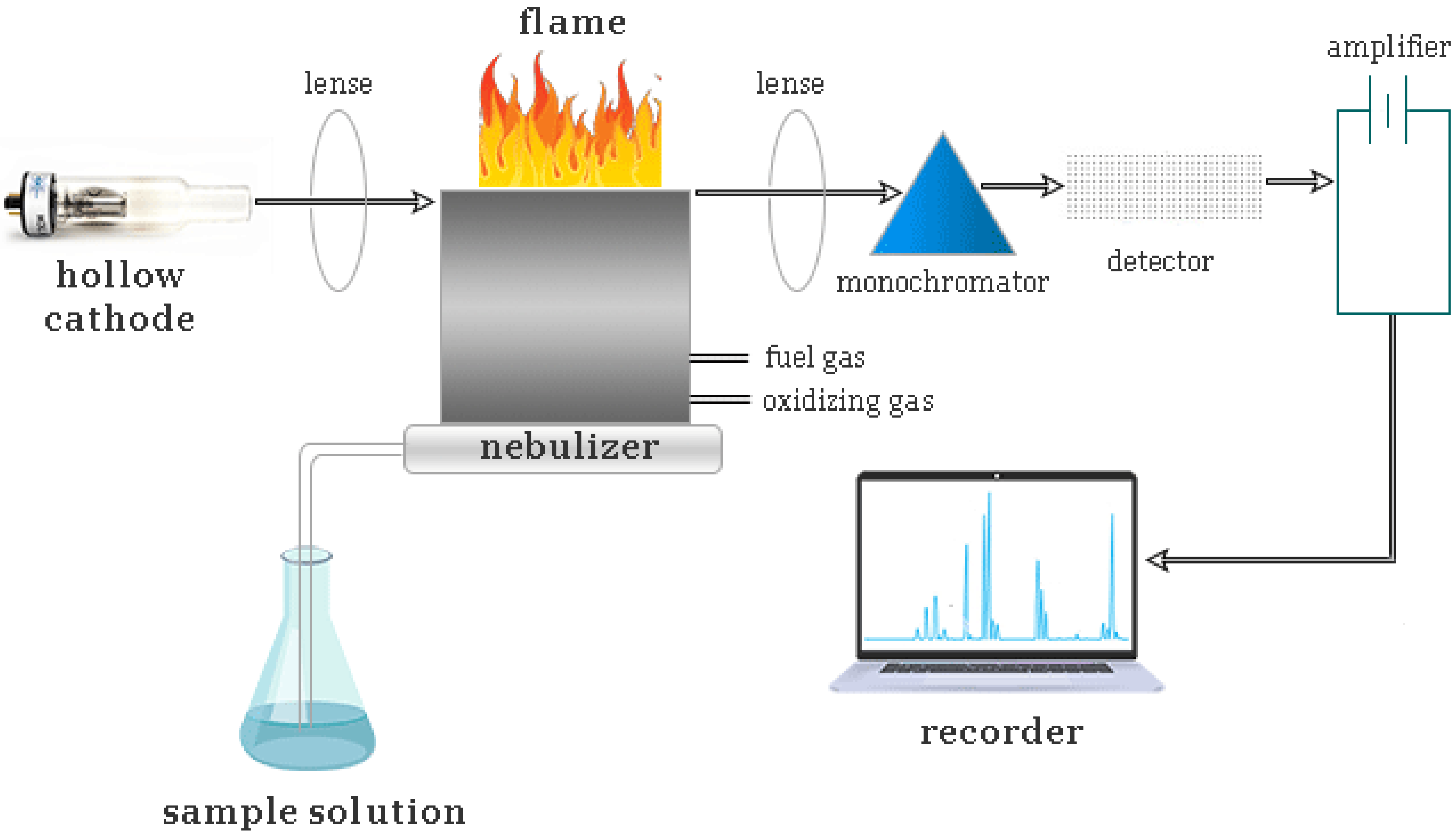
photon wavelength, Å

$$E_{\text{photon}} = h\nu = hc\tilde{\nu} = \frac{hc}{\lambda}$$

$1s_1 1s_2$

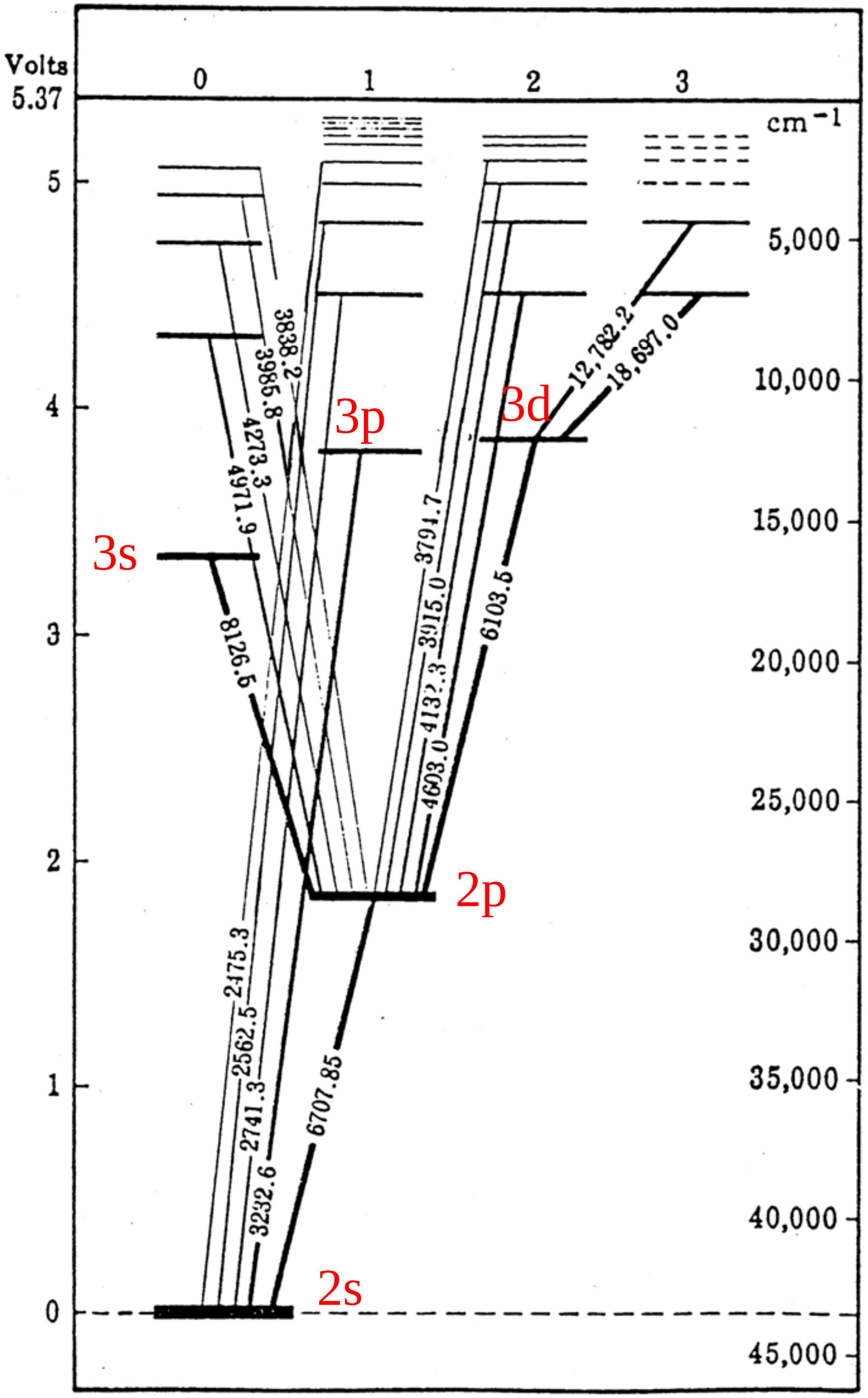
from G. Herzberg, *Atomic Spectra and Atomic Structure*, (Dover, New York, 1944), p. 65

Atomic Absorption Spectroscopy



Useful for elemental analysis

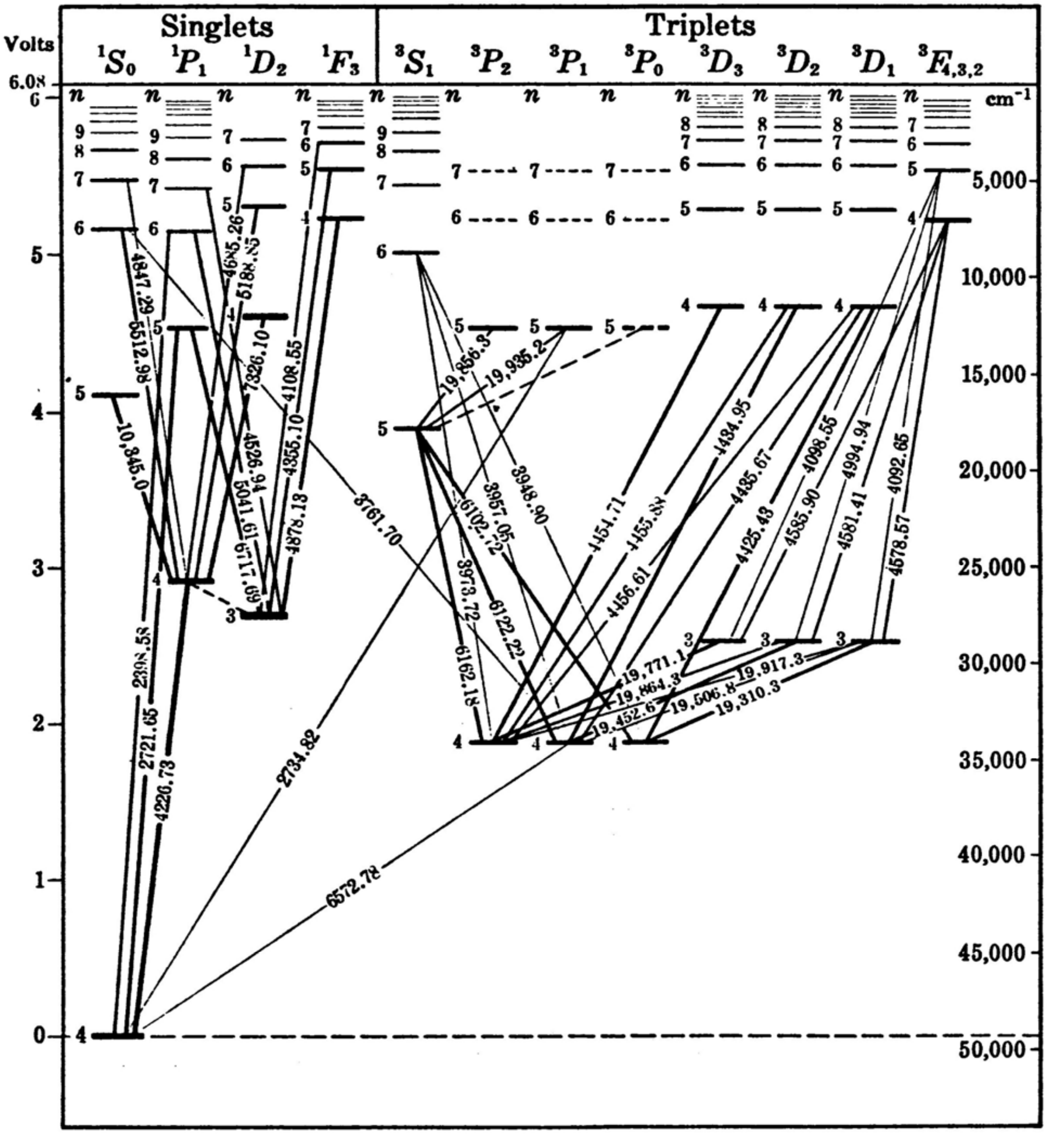
Grotriam Diagram for Lithium



Named for Walter Grotrian, who introduced the diagrams in his 1928 book “Graphische Darstellung der Spektren von Atomen und Ionen mit Ein, Zwei und Drei Valenzelektronen” (“Graphical representation of the spectra of atoms and ions with one, two and three valence electrons”).

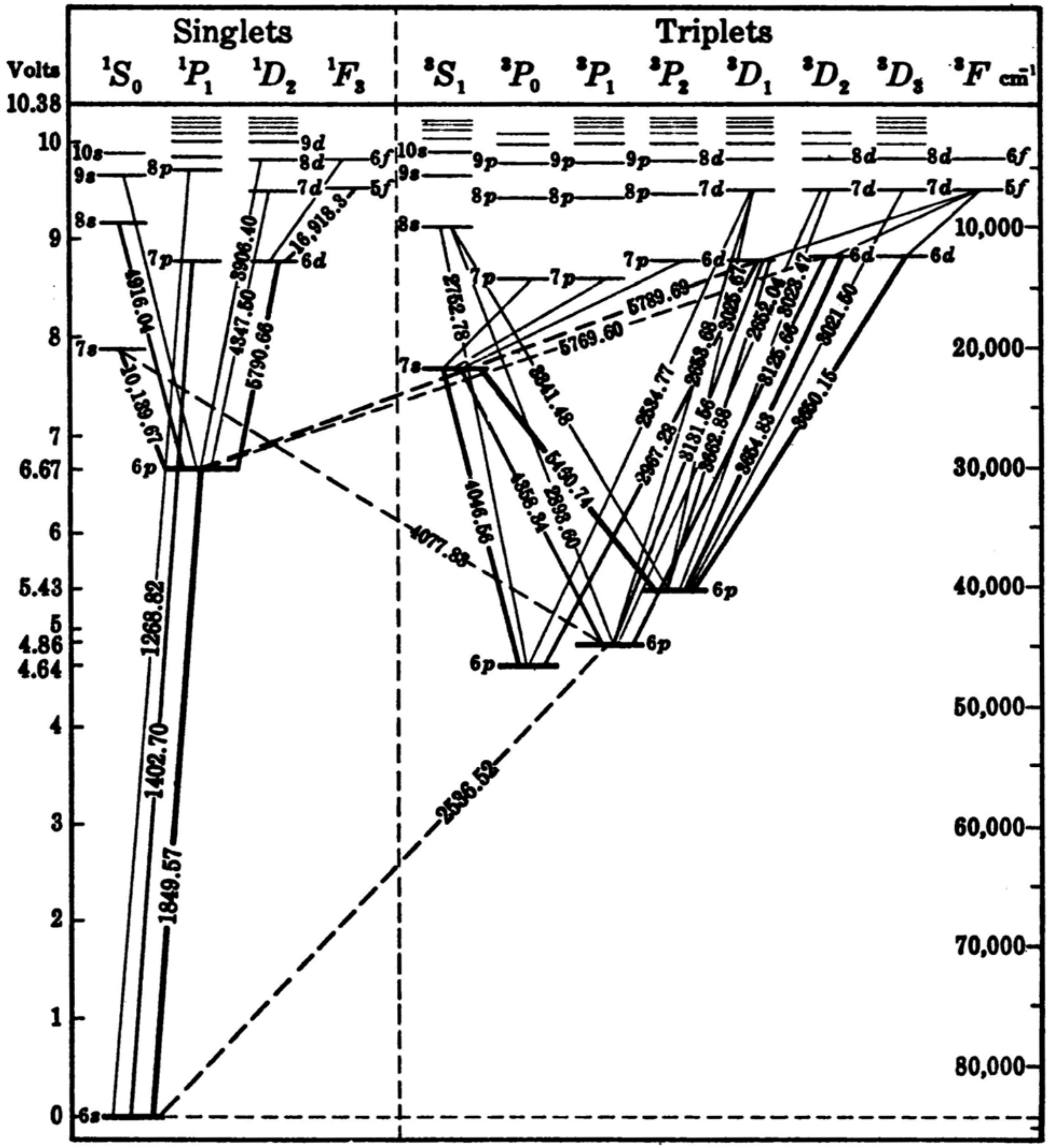
from G. Herzberg, *Atomic Spectra and Atomic Structure*, (Dover, New York, 1944), p. 57.

Grotriam Diagram for Calcium



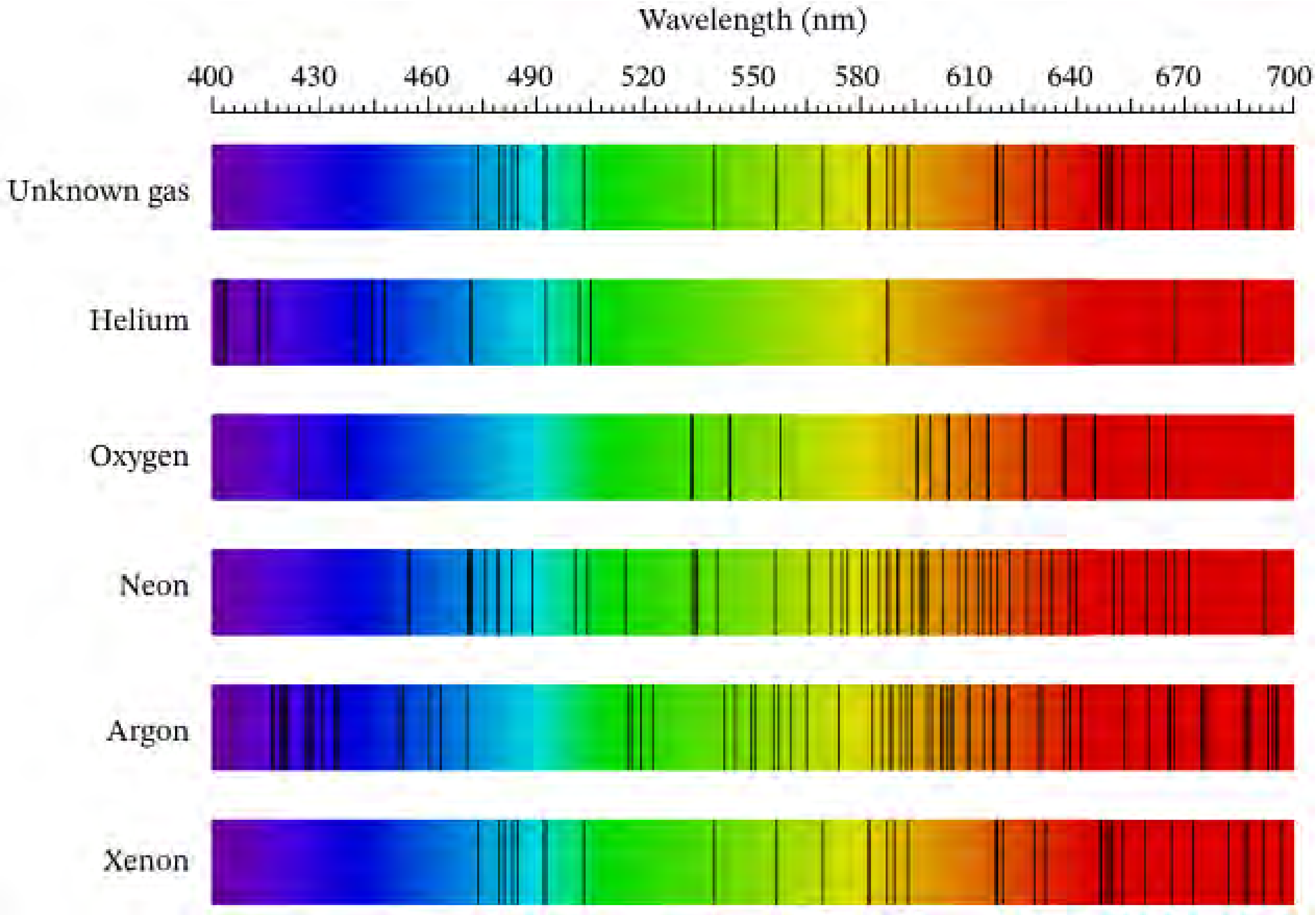
from G. Herzberg, *Atomic Spectra and Atomic Structure*, (Dover, New York, 1944), p. 77

Grotriam Diagram for Mercury



from G. Herzberg, *Atomic Spectra and Atomic Structure*, (Dover, New York, 1944), p. 20

What is the Unknown Gas?



www.nagwa.com/en/explainers/469167813067 - Emisson and Absorption Spectra

Calculation Session 1

Exercises 1 and 4.

ChemE 2200 TAs:
Lara Capellino
Kong Chen
Emily Destito
Vivian Liu
Amy Wu