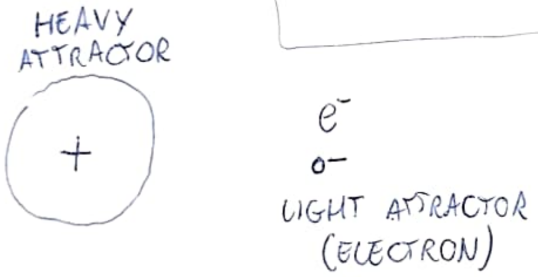
Atoms of Group I FROM HYDROGEN TO ALKALI

↳ THREE LEVELS OF DEPTH (PERTURBATION SPLIT)

	ENERGY	CONTRIBUTIONS
GROSS STRUCTURE	$1 \sim 10$ eV > 200 THz VISIBLE LIGHT RED 400 ~ 800 VIOLET	ELECTROSTATIC INTERACTIONS N-e KINETIC ENERGY
FINE STRUCTURE	$10^{-3} \sim 10^{-2}$ eV ~ 1 THz FAR INFRARED	SPIN-ORBIT (RELATIVISTIC EFF.)
HYPERFINE STRUCTURE	$10^{-6} \sim 10^{-5}$ eV ~ 1 GHz MICROWAVE	NUCLEUS-ELECTRON MAGNETIC INTER.

$$\boxed{1\,\text{eV} \sim 2.4\ 10^{14}\ \text{Hz}}$$

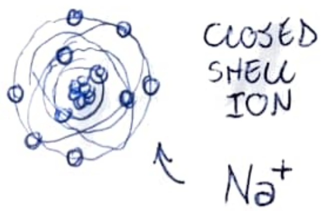
THE PROBLEM



WHAT IS THE H.A.

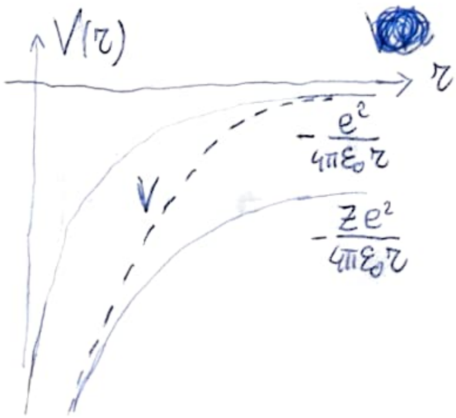
HYDROGEN → ⊕ p^+

ALKALI → (APPROXIMATION)



Effective 2-BODY Dynamics:

$$H = \underbrace{\frac{|\vec{p}_H|^2}{2 m_H}}_{\text{HEAVY KINETIC (NON RELATIVISTIC)}} + \underbrace{\frac{|\vec{p}_e|^2}{2 m_e}}_{\text{ELECTRON KINETIC (SOMEHOW STILL NON RELATIVISTIC)}} + \overbrace{V(|\vec{r}_H - \vec{r}_e|)}^{\text{INTERACTION POTENTIAL}}$$



STEP 1 CHANGE OF COORDINATES

CENTER-OF-MASS COORDINATE AND MOMENTUM	$\vec{R} = \dfrac{\vec{r}_e m_e + \vec{r}_H m_H}{m_e + m_H}$	$\vec{P} = \vec{p}_e + \vec{p}_H$
RELATIVE COORDINATE AND MOMENTUM	$\vec{r} = \vec{r}_e - \vec{r}_H$	$\vec{p} = \dfrac{\dfrac{\vec{p}_e}{m_e} - \dfrac{\vec{p}_H}{m_H}}{\dfrac{1}{m_E} + \dfrac{1}{m_H}}$

$$\begin{aligned} &[r_e, p_e] = i\hbar \\ &[r_H, p_H] = i\hbar \\ &[r_e, p_H] = [r_H, p_e] = 0 \end{aligned} \quad \Longrightarrow \quad \begin{aligned} &[R, P] = [r, p] = i\hbar \\ &[R, p] = [r, P] = 0 \end{aligned}$$

$$H = \underbrace{\frac{|\vec{P}|^2}{2m_+}}_{\substack{\text{FREE PARTICLE} \\ \text{CENTER-OF-MASS} \\ \text{HAMILTONIAN}}} + \underbrace{\frac{|\vec{p}|^2}{2\tilde{m}} + V(|\vec{r}|)}_{\substack{\text{REDUCED RELATIVE} \\ \text{MODEL: PARTICLE IN} \\ \text{CENTRAL POTENTIAL}}}$$

Where $m_+ = m_e + m_H \approx m_H$ TOTAL MASS

$\dfrac{1}{\tilde{m}} = \dfrac{1}{m_e} + \dfrac{1}{m_H} \approx \dfrac{1}{m_e}$ REDUCED MASS

(BUT NOT ALWAYS FREE! RECOIL) ← WE CAN IGNORE THIS PART FOR NOW

$$\frac{|\vec{p}|^2}{2\tilde{m}} = \begin{pmatrix} \text{CARTESIAN} \\ \text{COORDINATES} \\ x, y, z \end{pmatrix} \cdot \frac{-\hbar^2}{2\tilde{m}} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

EASY TO REMEMBER

$$= -\frac{\hbar^2}{2m} \nabla^2 \quad \begin{pmatrix} \text{POLAR} \\ \text{COORDINATES} \\ r, \theta, \varphi \end{pmatrix} \quad -\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \underbrace{\frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \varphi^2}}_{} \right)$$

$$= -\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right) + \frac{1}{2mr^2} \underset{\Uparrow}{L^2}$$

ANGULAR MOMENTUM.
WE NEED A REFRESHER

ORBITAL ANGULAR MOMENTUM

OF A CANONICAL PAIR: COORDINATE $\vec{r}$ + MOMENTUM $\vec{p}$ (THE REDUCED ONES IN THIS CASE)

reads $\vec{L} = \underbrace{\vec{r} \times \vec{p}}_{\text{VECTOR CROSS PRODUCT}}$ CLASSICAL-OR-QUANTUM MECHANICS

$\vec{L}$ IS A (PSEUDO) VECTOR IN PHYSICAL 3D SPACE (NOT IN THE HILBERT SPACE)

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \times \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} y p_z - z p_y \\ z p_x - x p_z \\ x p_y - y p_x \end{pmatrix}$$

COMMUTE THUS ALSO $\vec{L} = -\vec{p} \times \vec{r}$

CLASSICAL-OR-QUANTUM

QUANTUM

$\vec{r}$ AND $\vec{p}$ ARE VECTORS OF OPERATORS, THUS $\vec{L}$ AS WELL

$$L_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \text{ etc...}$$

HERMITIANS $L_j^+ = L_j$

$\vec{r}$ AND $\vec{p}$ DO NOT COMMUTE $\triangleright$ L_x, L_y, L_z DO NOT COMMUTE AS WELL

$$[L_x, L_y] = -\hbar^2 \left(\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right) - \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) \right)$$

$$= -\hbar^2 \left(y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial z \partial x} - z^2 \frac{\partial^2}{\partial x \partial y} - xy\frac{\partial^2}{\partial z^2} + xz\frac{\partial^2}{\partial y \partial z} \right) +$$

$$+ \hbar^2 \left(yz\frac{\partial^2}{\partial x \partial z} + x\frac{\partial}{\partial y} - xy\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial x \partial y} + xz\frac{\partial^2}{\partial z \partial y} \right) =$$

$$= \hbar^2 \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) = i\hbar\,(x p_y - y p_x) = i\hbar L_z$$

AND BY EXTENSION

$$[L_i, L_j] = i\hbar \underbrace{\varepsilon_{ijk}}_{\text{COMPLETELY ANTISYMMETRIC TENSOR}} L_k$$

$\triangleleft$ CLOSED LIE ALGEBRA OF HERMITIAN OPS.

$\Downarrow$

THEY GENERATE CONTINUOUS GROUPS (OF ROTATIONS)

$$R(\theta, \varphi, \chi) = e^{i\frac{L_z}{\hbar}\chi} e^{i\frac{L_x}{\hbar}\theta} e^{i\frac{L_z}{\hbar}\varphi}$$

TOTAL ANGULAR MOMENTUM $L^2 = L_x^2 + L_y^2 + L_z^2$

$\downarrow$

COMMUTES $[L^2, L_j] = 0$ QUADRATIC CASIMIR OP. OF THE ALGEBRA

EXAMPLE $[L^2, L_z] = [L_x^2, L_z] + [L_y^2, L_z] =$

$$L_x^2 L_z - L_z L_x^2 + L_y^2 L_z - L_z L_y^2 =$$

$$L_x \cancel{L_z} L_x + L_x[L_x L_z] - L_x \cancel{L_z} L_x - [L_z L_x] L_x + \ldots\ldots =$$

$$L_x(-iL_y) - (iL_y)L_x + L_y(+iL_x) - (-iL_x)L_y = 0$$

TRICKS

RAISING AND LOWERING OPERATORS

$L_\pm = L_x \pm iL_y$ ← NOT HERMITIAN $(L_+)^+ = L_x^+ + (i)^* L_y^+ = L_-$

$$[L_+, L_-] = i[L_y, L_x] - i[L_x, L_y] = 2\hbar L_z$$

[redacted] $[L_z, L_\pm] = [L_z, L_x] \pm i[L_z, L_y] =$

$$= i\hbar L_y \pm \hbar L_x = \pm\hbar(L_x \pm iL_y) = \pm\hbar L_\pm$$

$$L^2 = L_x^2 + L_y^2 + L_z^2$$
$$= L_- L_+ + L_z^2 + \hbar L_z$$
$$= L_+ L_- + L_z^2 - \hbar L_z$$

ALTERNATIVE WAYS OF WRITING L^2

$[L^2, L_z] = 0$ ⇝ SIMULTANEOUS EIGENSTATE WAVEFUNCTION $\psi(\ell, m)$

MEANING OF LABELS

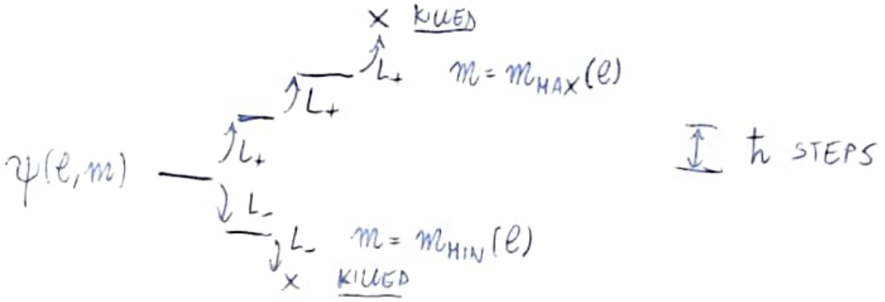
$$\begin{cases} L_z \psi(\ell, m) = \hbar m \psi \\ L^2 \psi(\ell, m) = f(\ell)\psi \end{cases}$$

ACTION OF THE RAISING/LOWERING OPERATOR ? $L_\pm \psi(\ell, m)$

$$L^2(L_\pm \psi(\ell,m)) = f(\ell)(L_\pm \psi(\ell,m))$$
$$L_z(L_\pm \psi(\ell,m)) =$$
$$L_\pm L_z \psi + [L_z, L_\pm]\psi =$$
$$\hbar m(L_\pm \psi) \pm \hbar(L_\pm \psi) = \hbar(m \pm 1)\psi$$

TWO OPTIONS

① $L_+ \psi(\ell, m) \propto \psi'(\ell, m+1)$ ② $L_+ \psi(\ell, m) = 0$ SAME WITH L_-



(ALSO SEE LATER ABOUT NORMALIZATION)

$L_+ \psi(\ell, m_{MAX}(\ell)) = 0$ BUT

$L^2 \psi(\ell, m_{MAX}) = (L_- L_+ + L_z^2 + \hbar L_z)\psi$

$$f(\ell)\,\psi(\ell, m_{MAX}) = \cancel{L_- L_+ \psi} + L_z^2 \psi(\ell, m_{MAX}) + \hbar L_z \psi(\ell, m_{MAX})$$

$$= (\hbar^2 m_{MAX}^2 + \hbar^2 m_{MAX})\psi$$

$$f(\ell) = \hbar^2 m_{MAX}(\ell)\,(1 + m_{MAX}(\ell)) \quad \checkmark$$

SIMILARLY

$L_- \psi(\ell, m_{MIN}) = 0$

$$f(\ell)\,\psi(\ell, m_{MIN}(\ell)) = L^2 \psi = \cancel{L_+ L_- \psi}(\ell, m_{MIN}) + L_z^2 \psi - \hbar L_z = \hbar^2 (m_{MIN} - 1) m_{MIN} \psi$$

$$f(\ell) = \hbar^2 m_{MIN}(m_{MIN} - 1)$$

SYSTEM

$$\begin{cases} m_{MAX}(m_{MAX} + 1) = m_{MIN}(m_{MIN} - 1) \\ m_{MAX} - m_{MIN} = \end{cases}$$ [redacted] $\hbar \underbrace{\mathbb{N}}_{\text{POSITIVE INT.}}$

SOLUTION

$m_{MAX} =$ POSITIVE INTEGER -OR- POS. HALF INTEGER

$m_{MIN} = - m_{MAX}$

FROM NOW ON, WE LABEL $\ell = m_{MAX}$

$$f(\ell) = \hbar^2 \ell(\ell + 1)$$

$$L^2 \psi(\ell, m) = \hbar^2 \ell(\ell+1)\, \psi(\ell, m)$$

$$L_z \psi(\ell, m) = \hbar m \, \psi(\ell, m) \quad *$$

WHERE $\ell \in \frac{\mathbb{N}}{2}$ AND $m \in \{-\ell, \dots, +\ell\}$

* ALSO (L_+, L_-)

⇑

HOWEVER, THESE RULES SIMPLY FOLLOW FROM THE LIE ALGEBRA STRUCTURE

$$[A_i, A_j] = i\hbar \varepsilon_{ijk} A_k$$

AND USE NO OTHER INFORMATION. EVEN THE "INTERNAL MAGNETIC DIPOLE MOMENT" (AKA SPIN) OBEYS THESE RULES.

BUT THE [redacted] ORBITAL ANGULAR MOMENTUM HAS MORE STRUCTURE

$\vec{L} = \vec{r} \times \vec{p}$ WHICH IMPOSES FURTHER RESTRICTIONS

↗ ↖

TRICK

$$L_z = r_x p_y - r_y p_x$$

CHANGE OF CANONICAL COORDINATES

$$r_1 = \frac{r_x + p_y}{\sqrt{2}} \qquad r_2 = \frac{r_x - p_y}{\sqrt{2}}$$

$$p_1 = \frac{p_x - r_y}{\sqrt{2}} \qquad p_2 = \frac{p_x + r_y}{\sqrt{2}}$$

$$r_1^2 - r_2^2 = 2 r_x p_y$$

$$p_1^2 - p_2^2 = -2 r_y p_x$$

THUS

$[r_1, p_1] = [r_2, p_2] = i\hbar$ (REST ZERO)

$[r_1, r_2] = [r_1, p_2] = \dots = 0$

$$L_z = \underbrace{\frac{1}{2}(r_1^2 + p_1^2)}_{\substack{\text{QUANTUM HARMONIC OSCILLATOR} \\ H_1}} - \underbrace{\frac{1}{2}(r_2^2 + p_2^2)}_{\substack{\text{ANOTHER ONE} \\ H_2}} \rightarrow \text{ENERGY LEVELS } \hbar\left(n + \frac{1}{2}\right)$$

$$[L_z, H_1] = [L_z, H_2] = 0$$

$$[H_1, H_2] = 0$$

SIMULTANEOUS DIAGONALIZATION

$\psi(m, n_1, n_2)$ BUT

$$L_z = H_1 - H_2 \qquad \hbar m \psi = L_z \psi = \hbar\left(\left(n_1 + \frac{1}{2}\right) - \left(n_2 - \frac{1}{2}\right)\right)\psi$$

$$\left.\begin{array}{c} m = n_1 - n_2 \\ \;\;\downarrow \qquad \downarrow \\ \in \mathbb{Z} \quad \in \mathbb{Z} \end{array}\right\} m \in \mathbb{Z} \rightarrow \ell \text{ INTEGER!}$$

BUT ONLY WHEN $\vec{L} = \vec{r} \times \vec{p}$ IS ORBITAL

Why Is This Important?

AS WE SAID ↪ $$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right) = \frac{|\vec{L}|^2}{2mr^2}$$

$$H = \underbrace{-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right) + V_{core}(r)}_{\text{ONLY RADIAL}} + \frac{|L^2|}{2mr^2}$$

$$[r, L^2] = \left[\frac{\partial}{\partial r}, L^2\right] = 0$$

$$\Downarrow$$

$$[H, L^2] = 0$$

$$H\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi)$$

ONE BASIS OF EIGENSOLUTIONS MUST BE OF THE FORM

$$\psi(r,\theta,\varphi) = R(r)\underbrace{Y(\theta,\varphi)}_{\text{EIGENSTATES OF } L^2}$$

Angular Momentum in Polar Coordinates

$$(\hat{x}, \hat{y}, \hat{z}) \longrightarrow (\hat{r}, \hat{\theta}, \hat{\varphi}) \qquad \hat{r} = \begin{pmatrix} \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \\ \cos\theta \end{pmatrix} \quad \hat{\theta} = \begin{pmatrix} \cos\theta\cos\varphi \\ \cos\theta\sin\varphi \\ -\sin\theta \end{pmatrix} \quad \hat{\varphi} = \begin{pmatrix} -\sin\varphi \\ \cos\varphi \\ 0 \end{pmatrix}$$

$\hat{r}$ POINTS OUTWARD

$\hat{\varphi}$ POINTS EASTWARD

$\hat{\theta}$ POINTS SOUTHWARD

GRADIENT

$$\vec{\nabla} = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\,\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\varphi}\,\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}$$

ANGULAR MOMENTUM

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

$$= -i\hbar\left(\cancel{\hat{r}\times\hat{r}}\; r\frac{\partial}{\partial r} + \hat{r}\times\hat{\theta}\; r\,\frac{1}{r}\,\frac{\partial}{\partial\theta} + \hat{r}\times\hat{\varphi}\;\frac{r}{r\sin\theta}\frac{\partial}{\partial\varphi}\right)$$

$$\boxed{\vec{L} = -i\hbar\left(\hat{\varphi}\frac{\partial}{\partial\theta} - \hat{\theta}\,\frac{1}{\sin\theta}\,\frac{\partial}{\partial\varphi}\right)}$$

⇐ r HAS DISAPPEARED ! ANGULAR MOMENTUM ONLY ACTS ON ANGLES, LOL

EXAMPLE

$$L_z = \hat{z}\cdot\vec{L} = -i\hbar\left(\cancel{\hat{z}\cdot\hat{\varphi}}\,\frac{\partial}{\partial\theta} - \hat{z}\cdot\hat{\theta}\,\frac{1}{\sin\theta}\,\frac{\partial}{\partial\varphi}\right) = +i\hbar\,\frac{(-\sin\theta)}{\sin\theta}\,\frac{\partial}{\partial\varphi}$$

$$\boxed{L_z = -i\hbar\frac{\partial}{\partial\varphi}}$$

$\varphi \rightarrow$ ANGLE AROUND THE z-AXIS

$L_z \rightarrow$ DERIVATIVE W/RESPECT TO φ

NOTICE →

STATES WITH $m=0$: $\quad Y(\theta,\varphi) = Y(\theta) \rightarrow \frac{\partial}{\partial\varphi}Y(\theta) = 0$!

CONSTANT IN φ

STATES WITH $m\neq 0$: $\quad Y(\theta,\varphi) = \breve{Y}(\theta)\,e^{im\varphi} \rightarrow -i\hbar\frac{\partial}{\partial\varphi}Y(\theta,\varphi) = \hbar m\,Y$

SIMILARLY

$$L_x = -i\hbar\left(\overbrace{\hat{x}\cdot\hat{\varphi}}^{-\sin\varphi}\,\frac{\partial}{\partial\theta} - \overbrace{\hat{x}\cdot\hat{\theta}}^{\cos\theta\cos\varphi}\,\frac{1}{\sin\theta}\,\frac{\partial}{\partial\varphi}\right) =$$

$$= i\hbar\left(\sin\varphi\,\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\,\frac{\partial}{\partial\varphi}\right)$$

$$L_y = i\hbar\left(-\cos\varphi\,\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\,\frac{\partial}{\partial\varphi}\right)$$

AND THUS

$$L_+ = L_x + iL_y = i\hbar\left(\cot\theta\,(\cos\varphi + i\sin\varphi)\frac{\partial}{\partial\varphi} + (\sin\varphi - i\cos\varphi)\frac{\partial}{\partial\theta}\right)$$

$$= i\hbar\left(\cot\theta\, e^{i\varphi}\frac{\partial}{\partial\varphi} + (-i)\, e^{i\varphi}\frac{\partial}{\partial\theta}\right)$$

AND SIMILARLY FOR L_-

$$\boxed{L_\pm = i\hbar e^{\pm i\varphi}\left(\cot\theta\frac{\partial}{\partial\varphi} \pm (-i)\frac{\partial}{\partial\theta}\right)}$$

$$L_-L_+ = -\hbar^2 e^{-i\varphi}\left(\cot\theta\frac{\partial}{\partial\varphi} + i\frac{\partial}{\partial\theta}\right)e^{i\varphi}\left(\cot\theta\frac{\partial}{\partial\varphi} - i\frac{\partial}{\partial\theta}\right) =$$

USING $\left(\!\!\left(\ \frac{\partial}{\partial\varphi}e^{i\varphi} = e^{i\varphi}\left(i + \frac{\partial}{\partial\varphi}\right)\ \right)\!\!\right)$

$$= -\hbar^2 \cancel{e^{-i\varphi}e^{i\varphi}}\left(\cot\theta\left(i + \frac{\partial}{\partial\varphi}\right) + i\frac{\partial}{\partial\theta}\right)\left(\cot\theta\frac{\partial}{\partial\varphi} - i\frac{\partial}{\partial\theta}\right) =$$

$$= -\hbar^2\left[\cot^2\theta\left(i\frac{\partial}{\partial\varphi} + \frac{\partial^2}{\partial\varphi^2}\right) + \cot\theta\frac{\partial}{\partial\theta} \cancel{- i\cot\theta\frac{\partial^2}{\partial\theta\partial\varphi}} \cancel{+ i\cot\theta\frac{\partial^2}{\partial\theta\partial\varphi}} + \frac{\partial^2}{\partial\theta^2} - \frac{i}{\sin^2}\frac{\partial}{\partial\varphi}\right]$$

USING $\gg$ $\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) = \cot\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2}$

$$L_-L_+ = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - i\frac{\partial}{\partial\varphi} + \cot^2\theta\frac{\partial^2}{\partial\varphi^2}\right]$$

$$|\vec{L}|^2 = L_-L_+ + L_z^2 + \hbar L_z = (\ \downarrow\ ) - \hbar^2\frac{\partial^2}{\partial\varphi^2} - i\hbar^2\frac{\partial}{\partial\varphi}$$

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$ ☺

$L_+|\ell,m\rangle = \alpha|\ell,m+1\rangle$ **BUT** $\beta = \langle\ell,m|L_-|\ell,m+1\rangle = \langle\ell,m+1|L_+|\ell,m\rangle^* = \alpha^*$

$L_-|\ell,m+1\rangle = \beta|\ell,m\rangle$

$$L_-L_+|\ell,m\rangle = |\alpha|^2|\ell,m\rangle = (L^2 - L_z^2 - \hbar L_z)|\ell,m\rangle = (\ell(\ell+1) - m^2 - m)\hbar^2|\ell,m\rangle$$

$\alpha = \hbar\sqrt{\ell(\ell+1) - m(m+1)}\ e^{i\phi}$ ⤷ THIS PHASE CAN BE SET TO ZERO

$$L_\pm|\ell,m\rangle = |\ell,m\pm1\rangle\hbar\sqrt{\ell(\ell+1) - m(m\pm1)}$$

$\underset{\text{INITIAL } m}{\overset{\uparrow}{m}}(\underset{\text{FINAL } m}{\overset{\uparrow}{m\pm1}})$

$[L^2, L_z]=0$ COMMON EIGENBASIS BUT L_z ACTS ONLY ON φ

$$L_z \psi(\theta,\varphi) = -i\hbar \frac{\partial}{\partial\varphi}\psi(\theta,\varphi) \rightsquigarrow Y_{\ell,m}(\theta,\varphi) = \tilde{Y}_{\ell m}(\theta)\, e^{im\varphi} \qquad m\in\left(\begin{matrix}\ell\\ \vdots\\ -\ell\end{matrix}\right.$$

$$\underline{\psi_{\ell,m=\ell}(\theta,\varphi) = \tilde{Y}_{\ell,\ell}(\theta)\, e^{i\ell\varphi}} \qquad \overset{\text{MAX } m}{\underbrace{m=\ell}}$$

$$L_+\psi_{\ell,\ell}=0 \,! \qquad \hbar e^{i\varphi}\left(\frac{\partial}{\partial\theta}+i\cot\theta\frac{\partial}{\partial\varphi}\right)\tilde{Y}_{\ell\ell}(\theta)\, e^{i\ell\varphi}=0$$

$$\left(\frac{\partial}{\partial\theta}+i\cot\theta\left(\frac{\partial}{\partial\varphi}e^{i\ell\varphi}\right)\right)\tilde{Y}_{\ell\ell}(\theta)=0$$

∃! SOLUTION $\forall\ell$!

θ,φ

UNIQUE!! NO DEGENERACY

$$\cancel{e^{i\ell\varphi}}\left(\frac{\partial}{\partial\theta}-\ell\cot\theta\right)\tilde{Y}_{\ell\ell}(\theta)=0 \xrightarrow[\text{SOLUTION}]{\theta\in[0,\pi]\ \text{DIFFERENTIAL EQUATION}} \tilde{Y}_{\ell\ell}(\theta)\propto\sin^\ell(\theta)$$

NORMALIZATION $\Rightarrow$

$$\int e^{-i\ell\varphi}\sin^\ell\theta\; e^{+i\ell\varphi}\sin^\ell\theta\,(d\varphi\,\sin\theta\, d\theta) = 2\pi\int_0^\pi \sin^{2\ell+1}(\theta)\, d\theta$$

$$= 2\pi\int_{-1}^{1}(1-\mu)^\ell\, d\mu = \left(\begin{matrix}\text{TRY IT AT}\\ \text{HOME}\end{matrix}\right) = \frac{4\pi\, 2^{2\ell}(\ell!)^2}{(2\ell+1)!}$$

$$Y_{\ell\ell}(\theta,\varphi) = \underset{\text{CHOOSE A PHASE}}{\boxed{(-1)^\ell}}\left(\frac{(2\ell+1)!}{4\pi}\right)^{1/2}\frac{1}{2^\ell\,\ell!}\,\sin^\ell(\theta)\, e^{i\ell\varphi}$$

FIND THE OTHER $Y_{\ell,m}$

$$L_-|\ell,m\rangle = \sqrt{\ell(\ell+1)-m(m-1)}\;|\ell,m-1\rangle$$

$$Y_{\ell,m-1} = \frac{-\hbar e^{-i\phi}}{\sqrt{\ell(\ell+1)-m(m-1)}}\left(\frac{\partial}{\partial\theta}-i\cot\theta\frac{\partial}{\partial\varphi}\right)Y_{\ell,m}(\theta,\varphi)$$

↑ NORMALIZATION

Spherical Harmonics

TABLE OF AFEW S.H.

NORMALIZE $\int |Y_{em}(\theta,\varphi)|^2 \sin\theta \, d\theta \, d\varphi = 1$

$$Y_{0,0}(\theta,\varphi) = \sqrt{\frac{1}{4\pi}}$$

S ORBITAL "SHARP" NO FINE STRUCTURE

$$Y_{11}(\theta,\varphi) = \sqrt{\frac{3}{8\pi}} \sin\theta \, e^{i\varphi}$$

$$Y_{10}(\theta,\varphi) = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$Y_{1,-1}(\theta,\varphi) = \sqrt{\frac{3}{8\pi}} \sin\theta \, e^{-i\varphi}$$

P ORBITAL "PRINCIPAL" BRIGHTEST LINES IN ATOMIC SPECTRA OF ALKALI

$$Y_{22}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}} \sin^2\theta \, e^{2i\varphi}$$

$$Y_{21}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{15}{2\pi}} \sin\theta \cos\theta \, e^{i\varphi}$$

$$Y_{20}(\theta,\varphi) = \frac{1}{4}\sqrt{\frac{5}{\pi}} \left(3\cos^2\theta - 1\right)$$

$$Y_{2-1} = \ldots \; -\sin\theta \cos\theta \, e^{-i\varphi}$$

$$Y_{2-2} = \ldots \; \sin^2\theta \, e^{-2i\varphi}$$

D ORBITAL "DIFFUSE" WIDE FINE STRUCTURE

$Y_{3m} \rightarrow$ F ORBITAL

FEW CRAZY EXPERIMENTALISTS GO BEYOND $\ell = 3$ FOR SANITY REASONS.

"FOURTH" OR "FUNDAMENTAL"

The radial part

$$\psi(r,\theta,\varphi) = R(r) \, Y_{em}(\theta,\varphi) \qquad H\psi = E\psi$$

$$\left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \left[V_{CORE}(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}\right]\right)R(r) = E\,R(r)$$

$$R(r) = \frac{P(r)}{r} \quad \rhd \quad \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\frac{P(r)}{r} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\left(\frac{1}{r}\frac{\partial P}{\partial r} - \frac{P}{r^2}\right)\right) =$$

$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r\frac{\partial P}{\partial r} - P\right) = \frac{1}{r^2}\left(\frac{\partial P}{\partial r} + r\frac{\partial^2 P}{\partial r^2} - \frac{\partial P}{\partial r}\right) = \frac{1}{r}\frac{\partial^2}{\partial r^2}P \quad \ldots$$

$H\psi = E\psi \Leftrightarrow$

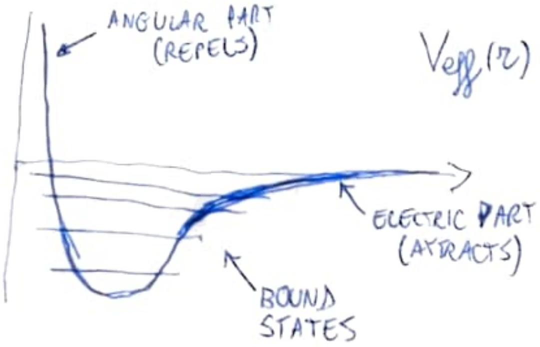
RADIAL KINETIC

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + V_{eff}\right) P(r) = E\,P(r)$$

where $V_{eff} = + \frac{\hbar\, l(l+1)}{2mr^2} - \frac{(Z_{eff})\, e^2}{4\pi\varepsilon_0 r}$

ANGULAR KINETIC $\frac{L^2}{2I}$, $I = mr^2$

SOLUTIONS CAN DEPEND ON l BUT NOT m

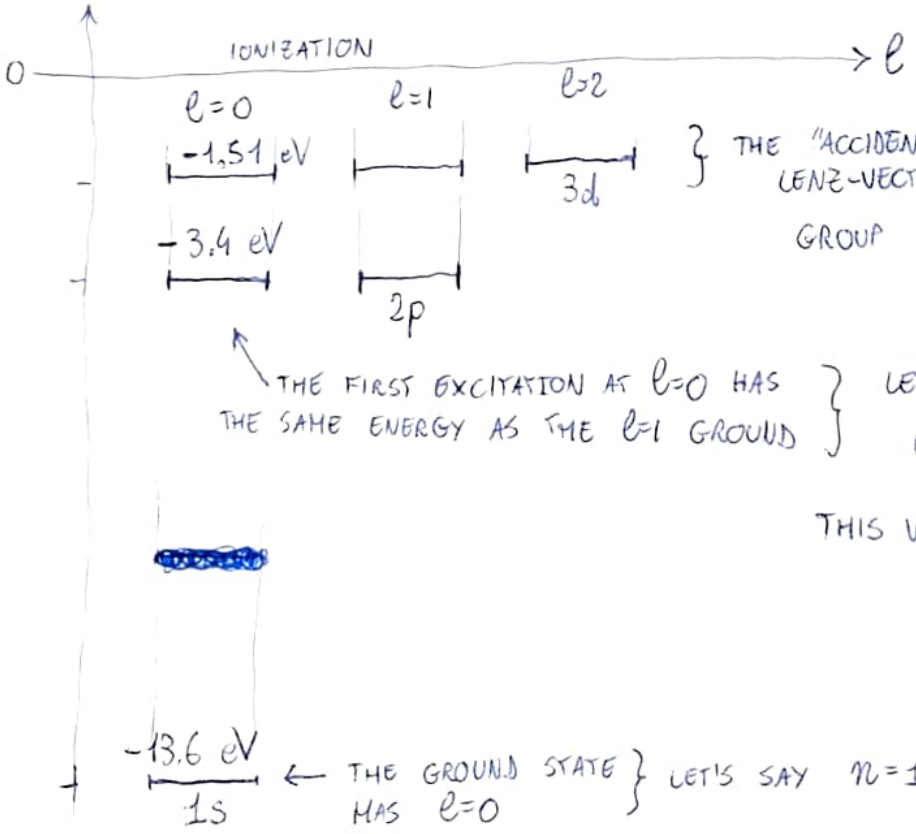


$$\Psi_{l m n} = R_{nl}(r)\, Y_{lm}(\theta, \varphi)$$

ANOTHER LABEL FOR THE RADIAL (BOUND) SOLUTIONS
HISTORICALLY: PRINCIPAL QUANTUM NUMBER

ACTUALLY → IT'S A QUANTUM NUMBER ONLY FOR HYDROGEN

HYDROGEN



} THE "ACCIDENTAL" DEGENERACY COMES FROM LENZ-VECTOR CONSERVATION. SYMMETRY GROUP SO(4) LARGER THAN SO(3)

THE FIRST EXCITATION AT $l=0$ HAS THE SAME ENERGY AS THE $l=1$ GROUND } LET'S SAY $l=0$ $n=2$ AND $l=1$ $n=2$ (NOT 1)

THIS WAY $E_{nl} = E_{n\cancel{l}} = -\frac{mZ^2e^4}{8\varepsilon_0 h}\frac{1}{n^2}$

← THE GROUND STATE HAS $l=0$ } LET'S SAY $n=1$

→ IN THIS NOTATION l GOES FROM 0 TO $n-1$; BUT IT'S RATHER n GOES FROM $l+1$ TO ∞, AND THE ENERGY DEPENDS ONLY ON n

OTHER ALKALI DO NOT HAVE THE EXTRA SYMMETRY SO THE DEGENERACY IS REMOVED E_{nl}, BUT WE USE THE SAME LABELING CONVENTIONS

Other ALKALI - example: Sodium

$$H=\sum_{j}^{elec.}\left(-\frac{\hbar^2}{2m}\nabla_j^2-\frac{Ze^2}{4\pi\varepsilon_0 r_j}\right)+\sum\frac{e^2}{4\pi\varepsilon_0|\vec{r}_j-\vec{r}_{j'}|}$$

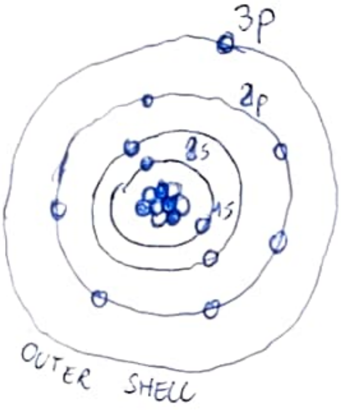
NOT SOLVABLE

GOOD APPROXIMATION
HARTREE - FOCK

NO CORRELATIONS/ENTANGLEMENT
→ ELECTRONS OCCUPY ORTHOGONAL ORBITALS
→ MINIMIZE ENERGY FUNCTIONAL OVER ORBITALS

HARSH APPROXIMATION
SHELL MODEL
(KINDA STILL WORKS)

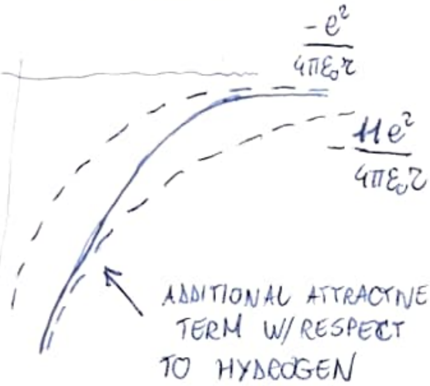
→ FIRST, ELECTRONS FILL AN ATOMIC SHELL $(2(\ell+1)$ ELECTRONS IN AN ℓ-ORBITAL$)$
→ THEN, THEY SCREEN THE NUCLEAR POTENTIAL
→ REPEAT UNTIL NO MORE ELECTRONS



OUTER SHELL EXPERIENCES

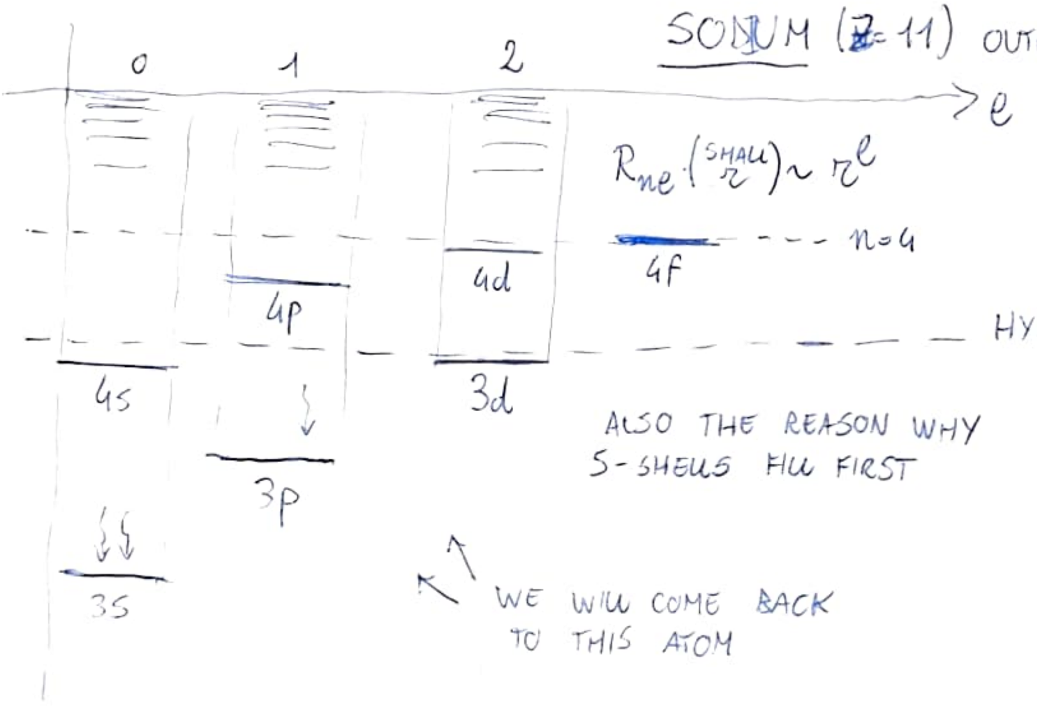
~ HYDROGEN BUT MORE ATTRACTIVE CLOSE TO THE CORE

~ HIGHER ℓ PUSH e^- AWAY FROM THE CORE → LESS SHIFT



THUS, THE 11th-electron OF SODIUM SEES THE CORE AS "ALMOST" A HYDROGEN, BUT NOT QUITE

SODIUM ($Z=11$) OUTER SHELL e^-



$R_{n\ell}(\overset{\text{SMALL}}{r})\sim r^{\ell}$

HYDROGEN $n=3$
$\left(\frac{1}{3}\right)^2\cdot 13.6$ eV

ALSO THE REASON WHY S-SHELLS FILL FIRST

WE WILL COME BACK TO THIS ATOM

Dipole Transitions

$$H_{TOTAL} = \underset{\text{DONE ✓}}{H_{ATOM}} + \underset{\text{IGNORE THIS FOR NOW}}{\begin{pmatrix}\text{LAMB?}\\\text{SHIFT}\end{pmatrix}} + \underset{\text{DONE ✓}}{H_{LIGHT}} + H_{\substack{\text{ATOM}\\\text{LIGHT}\\\text{INTERACTION}}}$$

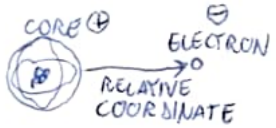
$$\rightarrow \sim \underline{\underline{-\vec{d}\cdot\vec{E}}} + \mathcal{O}(\text{MULTIPOLES}$$

$$H_{ALI} = \boxed{-\underset{\text{ATOM OPERATOR}}{\vec{d}}\cdot\underset{\text{LIGHT OPERATOR}}{\vec{E}}}$$

(ELECTRIC) DIPOLE COUPLING

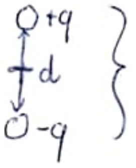
FOR AN ALKALI ATOM

$$\vec{d} = q\vec{r} \qquad \underset{\substack{\uparrow\\\text{CHARGE OF THE ELECTRON}}}{q = -e}$$

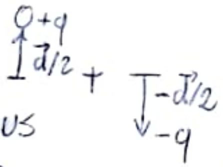


$$H_{ALI} = +e\underset{\substack{\downarrow\\\text{VECTOR IN THE DIRECTION}\\\text{OF POLARIZATION } \vec{\epsilon}_{k\lambda}}}{\vec{E}}\cdot\vec{r}_{\substack{\text{OUTER SHELL}\\\text{ELECTRON}\\\text{(RELATIVE) COORDINATE}}}$$

REFRESHER → CLASSICAL DIPOLE



} IS A DIPOLE



THUS

$$\Uparrow |q\vec{d}| \text{ IN DIRECTION } +\hat{d}$$

WE MUST UNDERSTAND HOW $\vec{r}$ ACTS AS AN OPERATOR ON ATOMIC LEVELS $|n, \ell, m, \cancel{s}\rangle$ (electron spin HAS NO EL. DIPOLE)

FACT 1 NO DIAGONAL COMPONENT

$$\langle n, \ell, m|\hat{\vec{r}}|n, \ell, m\rangle = 0$$

(PROOF) $\breve{R}$ PARITY TRANSFORMATION

$$\breve{R}\,\psi(x, y, z) = \psi(-x, -y, -z)$$

$$\breve{R}\,\psi(r, \theta, \varphi) = \psi(r, \pi-\theta, \varphi+\pi)$$

$$\breve{R}\hat{\vec{r}}\breve{R}^{\dagger} = -r$$

$$\Updownarrow$$

$$\{\hat{\vec{r}}, \breve{R}\} = 0$$

WHY?

$$\breve{R}\left(R_{n\ell}(r)\,Y_{\ell m}(\theta, \varphi)\right) = (-1)^{\ell}\,R_{n\ell}\,Y_{\ell m}$$

$$Y_{\ell\ell} = \sin^{\ell}(\theta)\,e^{i\ell\varphi}$$

$$\breve{R}\,Y_{\ell\ell} = \sin^{\ell}(\pi-\theta)\,e^{i\ell(\varphi+\pi)} = e^{i\ell\pi}e^{i\ell\varphi}\sin^{\ell}(\theta)$$

$$= e^{i\ell\pi}\,Y_{\ell\ell} = (-1)^{\ell}\,Y_{\ell\ell}$$

BUT ALSO $[\tilde{R}, L_\pm] = 0 \qquad [\tilde{R}, \vec{L}] = 0 \iff$ $\vec{L}$ IS A PSEUDOVECTOR !

$$\vec{L} = \vec{r} \times \vec{p} \rightsquigarrow [\tilde{R}, \vec{r} \times \vec{p}] = \tilde{R}\,\vec{r} \times \vec{p} - \vec{r} \times \vec{p}\,\tilde{R}$$

$$= (-\vec{r}\tilde{R}) \times \vec{p} - \vec{r} \times (-\tilde{R}\vec{p}) = 0$$

THEREFORE $\quad \tilde{R}\, Y_{\ell\, \ell-1}(\theta, \varphi) = \dfrac{1}{\sqrt{\ell(\ell+1) - \ell(\ell-1)}}\, \tilde{R}\, L_-\, Y_{\ell\ell}(\theta, \varphi) =$

$$= \frac{1}{\sqrt{\dots}} L_- \tilde{R}\, Y_{\ell\ell} = \frac{(-1)^\ell}{\sqrt{\dots}} L_- Y_{\ell\ell}(\theta,\varphi) = (-1)^\ell\, Y_{\ell,\ell-1}(\theta,\varphi)$$

AND BY RECURSION IT WORKS FOR ANY m

BUT NOW CONSIDER

$$\langle n,\ell,m|\,\vec{r}\,|n,\ell,m\rangle = \langle n,\ell,m|\underbrace{R^\dagger R}_{\text{IDENTITY}}\,\vec{r}\,|n,\ell,m\rangle =$$

$$= \underset{\substack{\uparrow \\ \text{MINUS}}}{-} \langle n,\ell,m|R^\dagger\, \vec{r}\, R|n,\ell,m\rangle = -(-1)^\ell \langle n,\ell, m|\vec{r}|n\,\ell\,m\rangle (-1)^\ell =$$

$$= -\cancel{(-1)^{2\ell}}\langle n\ell m|\vec{r}|n\ell m\rangle = 0 \;!$$

VALID ALSO FOR $\langle n'\ell m|\vec{r}|n\ell m\rangle$

FACT 2, selection Rule on $\boxed{\ell}$

WE START FROM A (NOT PROVEN) EQUATION

$$\boxed{[L^2, [L^2, \vec{r}\,]] = 2\hbar^2 \{\vec{r}, L^2\}}$$

$$\downarrow \qquad \swarrow$$

$$\langle n'\ell'\, m'| \qquad\qquad |n\,\ell\, m\rangle$$

THIS CAN BE DEMONSTRATED USING ONLY

$$\vec{L} = \vec{r} \times \vec{p} \qquad L^2 = L_x^2 + L_y^2 + L_z^2 = \vec{L}\cdot\vec{L}$$

$$\{r_j, p_{j'}\} = i\hbar\, \delta_{jj'}$$

BUT IT IS DIFFICULT! MAYBE AN ASSIGNMENT

$$\langle n'\,\ell'\,m'|\,(L^2)^2\vec{r} - 2L^2 r L^2 + \vec{r}(L^2)^2\,|n\,\ell\,m\rangle =$$

$$2\hbar^2 \langle n'\,\ell'\,m'|\,\vec{r}L^2 + L^2 r\,|n\,\ell\,m\rangle =$$

$$\cancel{\hbar^4}\left([\ell'(\ell'+1)]^2 - 2\,\ell'(\ell'+1)\ell(\ell+1) - [\ell(\ell+1)]^2\right)\langle n'\ell' m'|\vec{r}|n\ell m\rangle =$$

$$2\cancel{\hbar^4}\left(\ell'(\ell'+1) + \ell(\ell+1)\right)\langle n'\ell' m'|\vec{r}|n\ell m\rangle$$

$$0 = \left[\left(\ell'(\ell'+1) - \ell(\ell+1)\right)^2 - 2\left(\ell'(\ell'+1) + \ell(\ell+1)\right)\right]\underbrace{\langle n'\ell' m'|\vec{r}|n\ell m\rangle}$$

TO HAVE THIS M.E. NONZERO THE PREFACTOR HAS TO BE ZERO

$$\underset{Ⓐ}{(\ell'-\ell+1)}\underset{Ⓑ}{(\ell'-\ell+1)}\underset{Ⓒ}{(\ell+\ell')}\underbrace{(\ell'+\ell+2)}_{\text{NEVER ZERO}} \qquad \text{WITH } \ell,\ell' \geq 0$$

OPTIONS

A | $\ell' = \ell+1$ ✓ OK
B | $\ell' = \ell-1$ ✓ OK
C | $\ell = \ell' = 0$ HOWEVER $\langle n00|\vec{r}|n'00\rangle$ BECAUSE OF PARITY ARGUMENT

SELECTION RULE ON $\boxed{\ell}$ $\quad \Delta\ell = \pm 1$

FACT 3, LET'S NOW ASSUME $\vec{E}$ IS POLARIZED ALONG Z-AXIS

$L_z \cdot |\ell, m\rangle = \hbar m$ AND $L_z = r_x p_y - r_y p_x$

clearly $[L_z, z] = 0$ CUZ z COMMUTES WITH $r_{xy}\ p_{xy}$

$$0 = \langle n'\ell' m'|[L_z, z]|n\ell m\rangle =$$

$$\langle n'\ell' m'|(L_z z - z L_z)|n\ell m\rangle = \hbar(m'-m)\underbrace{\langle n'\ell' m'|\hat{z}|n\ell m\rangle}$$

TO HAVE THIS MATRIX ELEMENT NONZERO, I NEED $m' = m$

SELECTION RULE ON $\boxed{m}$ Z-POLARIZATION $\quad \Delta m = 0$

FACT 4 NOW $\vec{E}$ POLARIZED ON $\hat{x}$ (OR $\hat{y}$) AXES

$$[L_z, x] = (xp_y - yp_x)x - x(xp_y - yp_x) = y(xp_x - p_x x) = i\hbar y$$

$$[L_z, y] = \dots = -i\hbar x$$

$$\Downarrow$$

$$[L_z, x+iy] = (i\hbar y) + i(-i\hbar x) = \hbar(x+iy)$$

ALSO $[L_z, x-iy] = -\hbar(x-iy)$

$$\langle n'l'm'|[L_z, x+iy]|nlm\rangle = \hbar\langle n'l'm'|(x+iy)|nlm\rangle$$

$$\hbar(m'-m-1)\langle n'l'm'|x+iy|nlm\rangle = 0$$

AND

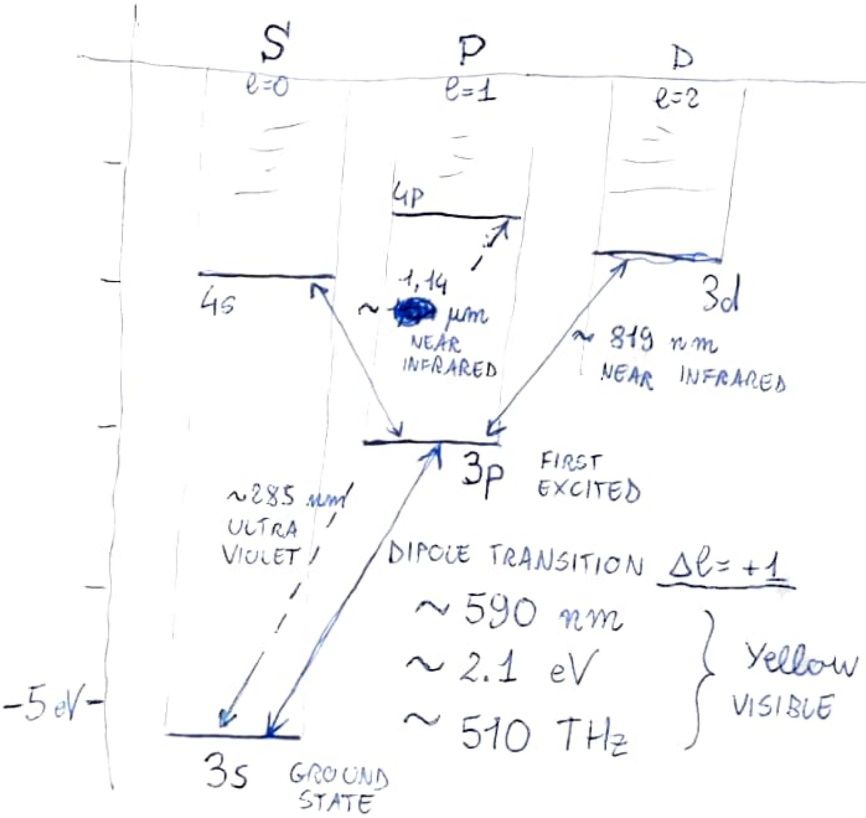
$$\hbar(m'-m+1)\langle n'l'm'|x-iy|nlm\rangle = 0$$

TO HAVE $\langle\cdot'|x|\cdot\rangle \neq 0$ AT LEAST ONE $\langle\cdot'|x\pm iy|\cdot\rangle$ MUST BE NONZERO → BUT THEN $m'=m+1$ OR $m'=m-1$

SELECTION RULE ON m
xy-PLANE POLARIZATION

$$\Delta m = \pm 1$$

SODIUM (AGAIN)



SODIUM D-LINE
CHECK: SODIUM LAMP ON GOOGLE

WE WILL COME BACK TO THIS TRANSITION