Lifting ENERGY-LEVEL degeneracies in Hydrogen-like atoms

NON RELATIVISTIC PROBLEM $\triangleright$ $$H = \frac{\vec{p}^{\,2}}{2m} + V_{eff}(|\vec{r}|)$$

$m \approx m_e$ REDUCED MASS

$[r_i, p_j] = i\hbar\,\delta_{ij}$ REDUCED COORD-MOM.

TRUE HYDROGEN	ALKALI NEUTRAL ATOMS	ALKALINE-EARTH IONS
$V(r) = -\frac{(Z=1)e^2}{4\pi\varepsilon_0}\frac{1}{r}$	$V(r) = -\frac{(Z=1)e^2}{4\pi\varepsilon_0}\left(\frac{1}{r} + \mathcal{C}(r)\right)$	$V(r) = -\frac{(Z=2)e^2}{4\pi\varepsilon_0}\left(\frac{1}{r} + \mathcal{C}(r)\right)$

RESIDUAL CHARGE (ATOMIC NUMBER) AT THE OUTER SHELL

CORRECTION AT SHORT RADII

ENERGY LEVELS

$$E_{n(\ell)} = -\frac{m_e e^4 Z_R^2}{2(4\pi\varepsilon_0)^2\hbar^2}\left(\frac{1}{n^2} + \tilde{\zeta}_{n,\ell}\right)$$

COMPARING THIS EXPRESSION TO THE ELECTRON REST ENERGY

CORRECTION FOR LOWER ℓ

$$E_{n(\ell)} = -\frac{mc^2}{2} Z_R^2 \underbrace{\left(\frac{e^2}{4\pi\varepsilon_0\hbar c}\right)^2}_{\text{FINE STRUCTURE } \alpha \approx 1/137}\left(\frac{1}{n^2} + \tilde{\zeta}_{n,\ell}\right) = -\frac{mc^2}{2}(Z_R\alpha)^2\left(\dots\right)$$

$$mc^2 \approx m_e c^2 = 511\ \text{KeV} \longrightarrow E^{HYDRO}_{n=1} = -\frac{511\ \text{KeV}}{2(137)^2} = -13.6\ \text{eV}$$

$$E^{\text{HYDRO-LIKE}}_{n(\ell)} = -\frac{m_e c^2}{2}(Z_R\,\alpha)^2\left(\frac{1}{n^2} + \tilde{\mathcal{C}}_{n\ell}\right)$$

NEUTRAL ALKALI $Z_R = 1$

ALKALINE-EARTH IONS $Z_R = 2$

STATES OF THE OUTER SHELL ELECTRON

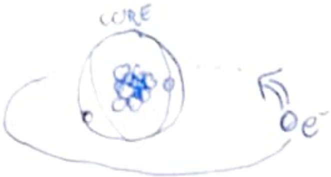
$$|n, \ell, m, s, s_z\rangle \quad s = 1/2$$

DEGENERACY ON m, s_z

Lifting the Degeneracy

1. FINE STRUCTURE A.K.A. SPIN-ORBIT COUPLING [NATIVE PERTURBATION]
2. ZEEMAN SPLITTING [EXTERNAL $\vec{B}$ STATIC, CAN BE PERTURBATIVE]

FINE STRUCTURE (A QUICK OVERVIEW) — LOWEST ORDER OF $\vec{B}$ FIELDS



NO MAGNETIC FIELD IN LAB FRAME

↓

YES EFFECTIVE MAGNETIC FIELD IN e^- REST FRAME

$$\underset{\substack{\uparrow\\ \text{FELT BY THE ELECTRON}\\ \text{IN ITS REST FRAME}}}{\vec{B}} = -\frac{1}{c^2}\,\underset{\substack{\uparrow\\ \text{ELECTRON VELOCITY}\\ \text{IN LAB FRAME}}}{\vec{v}} \times \vec{E} \longleftarrow \text{CORE ELECTRIC FIELD IN LAB FRAME}$$

} THIS COMES FROM RELATIVITY + MAXWELL EQS.

$\vec{E}$ IS RADIAL SO $\vec{E} = -\frac{\vec{\nabla} V}{-e} = +\frac{\vec{r}}{e|\vec{r}|}\,\partial_r V_{eff}(r)$ WHILE $\underbrace{\vec{v} = \frac{\vec{p}}{m\cancel{\gamma}}}_{\substack{\text{NON-RELATIVISTIC}\\ \text{APPROXIMATION}\\ \gamma \approx 1}}$

$$\vec{B}_{FELT} = -\frac{1}{c^2}\left(\frac{\vec{p}}{m} \times \vec{r}\right)\left(+\frac{1}{er}\frac{\partial V_{eff}}{\partial r}\right)$$

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

EVEN IN QUANTUM MECHANICS

$$\vec{B}_{FELT} = \left(+\frac{1}{emc^2 r}\frac{\partial V}{\partial r}\right)\vec{L}$$

$\vec{L}$ ← ANGULAR MOMENTUM IN THE LAB FRAME

NOW THE e^- SPIN HAS A MAGNETIC DIPOLE MOMENT ASSOCIATED TO IT

$$\vec{\mu} = -\frac{e}{2m}\,g_s\,\vec{S} \longleftarrow \text{SPIN ANGULAR MOMENTUM}$$

$$= -\underset{\substack{\uparrow\\ \text{BOHR}\\ \text{MAGNETON}}}{\mu_B}\,\underset{\substack{\uparrow\\ \text{electron}\\ \text{g-FACTOR}}}{g_s}\,\frac{\vec{S}}{\hbar} \qquad \boxed{\mu_B = \frac{e\hbar}{2m_e}}$$

A RIGID SYSTEM OF (SPHERICALLY-DISTRIBUTED) MASSIVE CHARGES HAS

$$\vec{\mu} = \frac{q}{2m}\vec{L}$$

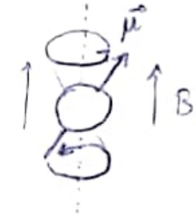
THIS MODEL FAILS FOR THE ELECTRON BY A FACTOR g_s ← SPIN HAS NO CLASSICAL EXPLANATION

$g_s = 2$ FROM DIRAC FREE THEORY, VALID FOR ANY FERMION $s = 1/2$ } CORRECTIONS ?

$g_s = 2.00231930436 22(15)$ FROM QED → DIGITS TESTED EXTENSIVELY IN EXPERIMENTS ☺

COUPLING $\vec{B}$ TO $\vec{\mu}$

$$H = -\vec{\mu}\cdot\vec{B}$$ ← SO SIMPLE } PRECESSION HAMILTONIAN



$$H\begin{pmatrix}\text{ELECTRON}\\ \text{REST}\\ \text{FRAME}\end{pmatrix} = -\left(-\frac{\mu_B g_s}{\hbar}\right)\vec{S}\cdot\left(\frac{1}{emc^2 r}\frac{\partial V}{\partial r}\right)\vec{L} =$$

$$= +\frac{\mu_B g_s}{emc^2\hbar}\left(\frac{1}{r}\frac{\partial V_{eff}}{\partial r}\right)\vec{S}\cdot\vec{L}$$

HOWEVER, WE NEED TO MOVE BACK TO THE LAB FRAME

NET EFFECT → $g_s \xrightarrow[\text{LAB}]{\text{TO}} g_s - 1$

$$H\begin{pmatrix}\text{LAB}\\ \text{FRAME}\end{pmatrix} = \frac{\mu_B(g_s-1)}{emc^2\hbar}\left(\frac{1}{r}\frac{\partial V_{eff}}{\partial r}\right)\vec{S}\cdot\vec{L}$$

PLUGGING HYDRO-LIKE POTENTIAL

$$V(r) = -\frac{Z_R e^2}{4\pi\varepsilon_0}\left(\frac{1}{r} + C(r)\right)$$

$$H_{\text{SPIN ORBIT}} = \underbrace{\overbrace{\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\frac{\mu_B(g_s-1)}{emc^2\hbar}}^{\text{CONSTANTS}}\underline{\left(\frac{1}{r^3} - \frac{\dot{C}(r)}{r}\right)}}_{\text{THIS IS ONLY RADIAL}}\ \underbrace{\vec{S}\cdot\vec{L}}_{\text{OPERATOR ACTING ON SPIN \& ORBITAL ANGULAR MOMENTA}}$$

$|s, s_z\rangle \quad |\ell, m\rangle$

$$\vec{S}\cdot\vec{L} = S^z L^z + \underbrace{S^x L^x + S^y L^y}$$

$|\ell, m, s_z\rangle$ IS NOT EIGENSTATE OF THIS PART. <u>CHANGE OF BASIS</u>

$$\boxed{\vec{J}\begin{pmatrix}\text{TOTAL}\\ \text{ANGULAR}\\ \text{MOMENTUM}\end{pmatrix} = \vec{L} + \vec{S}}$$

SUM OF TWO ANGULAR MOMENTUM OPERATOR ALGEBRAS (OR <u>FUSION</u>)

$$[J_j, J_k] = [L_j, L_k] + \cancel{[L_j, S_k]} + \cancel{[S_k, L_j]} + [S_j, S_k] =$$

$$i\varepsilon_{jk\ell}L_\ell + i\varepsilon_{jk\ell}S_\ell = i\varepsilon_{jk\ell}(L+S)_\ell = i\varepsilon_{jk\ell}J_\ell$$

ALSO AN ANGULAR MOMENTUM

PRODUCT BASIS

$|\ell, m; s, s_z\rangle$

↳ BASE UPON L^2, L_z, S^2, S_z ALL COMMUTING

$$\begin{pmatrix} L^2 \\ L_z \\ S^2 \\ S_z \end{pmatrix} |\ell, m; s, s_z\rangle = |\cdot\rangle \begin{pmatrix} \hbar^2 \ell(\ell+1) \\ \hbar m \\ \hbar^2 s(s+1) \\ \hbar s_z \end{pmatrix}$$

FUSION BASIS

$|\ell, s; J, J_z\rangle$

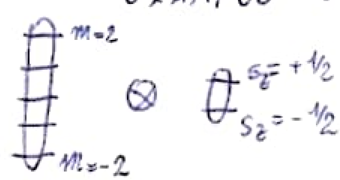
↳ BASED UPON L^2, S^2, J^2, J_z ALL COMMUTING

$$\begin{pmatrix} L^2 \\ S^2 \\ J^2 \\ J_z \end{pmatrix} |\cdot\rangle = |\cdot\rangle \begin{pmatrix} \hbar^2 \ell(\ell+1) \\ \hbar^2 s(s+1) \\ \hbar^2 J(J+1) \\ \hbar J_z \end{pmatrix}$$

SPACE OF FIXED ℓ, s

↳ DIMENSION $(2\ell+1)(2s+1) = 2(2\ell+1)$

EXAMPLE $\ell = 2$

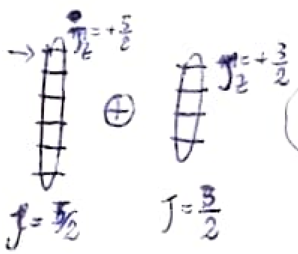


DIM $5 \times 2 = 10$

⇓ FUSES INTO $\underline{\oplus \; J\text{-SPACES}}$ FROM $|\ell - s|$ TO $\ell + s$

THEREFORE $\ell + \frac{1}{2}, \ell - \frac{1}{2}$

(CONSEQUENCE OF WIGNER ECKART)



DIM $6 + 4 = 10$

CLEBSCH-GORDAN

$$\overset{\text{FIXED}}{|\ell, s}; J, J_z\rangle = \sum |\ell, m; s, s^z\rangle \, C^{J, J_z}_{\ell m, s_z}$$

$$|J, J_z\rangle = \sum_{m, s^z = J_z - m} |m, s^z\rangle \, C^{J \, J_z}_{m \, s_z}$$

IT IS EASY TO FIND $|J_{MAX}, J_{MAX}\rangle = |\ell+s, \ell+s\rangle$

BECAUSE $|J = \ell+s, J = \ell+s\rangle = \underbrace{+1}_{\text{CHOICE}} \; |m = \ell, s_z = +s\rangle$

↳ FIND THE REST OF THE J-SELL BY APPLYING $J_- = J_x - i J_y$

$J_z = J$
$J_z = J - 1$
⋮

THEN ↳ FIND THE OTHER J-SHELL(S) BY ORTHOGONALIZING

$|J = \ell+s-1, J_z = \ell+s-1\rangle$ IS ORTHOGONAL TO $|J = \ell+s, J_z = \ell+s-1\rangle$

INSIDE THE SPACE $\{|m = \ell, s_z = s-1\rangle, |m = \ell-1, s_z = s\rangle\}$

↳ EVENTUALLY REPEAT (NOT NEEDED FOR $s = 1/2$)

$$H_{\substack{\text{SPIN}\\\text{ORBIT}}} = \left(\text{STUFF}(r)\right) \vec{S}\cdot\vec{L} \quad \text{AND}$$

$$(\vec{S}+\vec{L})^2 = J^2 = S^2 + L^2 + \underbrace{\vec{S}\cdot\vec{L} + L\cdot\vec{S}}_{2\vec{S}\cdot\vec{L}} \qquad \vec{S}\cdot\vec{L} = \frac{1}{2}\left(J^2 - L^2 - S^2\right)$$

FIRST ORDER PERTURBATION } $H^{(1)} = \Pi_{n\ell}\, H_{\substack{\text{SPIN}\\\text{ORBIT}}}\, \Pi_{n\ell}$ PRECISELY (DIAGONAL IN $\ell S J J_z$)

$$\Delta E_{\substack{\text{SPIN}\\\text{ORBIT}}} = \langle n\,\ell\,J\,J_z | H_{\substack{\text{SPIN}\\\text{ORBIT}}} | n\,\ell\,J\,J_z\rangle$$

$$= \frac{\mu_B (g_S - 1)\hbar}{2mc^2 e} \langle n,\ell | \underbrace{\left(\frac{1}{r}\frac{\partial V_{eff}}{\partial r}\right)}_{\text{POSITIVE}} | n,\ell\rangle \Big(\underbrace{J(J+1)}_{\text{SPLIT!}} - \underbrace{\ell(\ell+1) - \overset{s(s+1)}{\tfrac{3}{4}}}_{\text{SHIFT}} \Big)$$

STILL DEGENERATE IN J_z

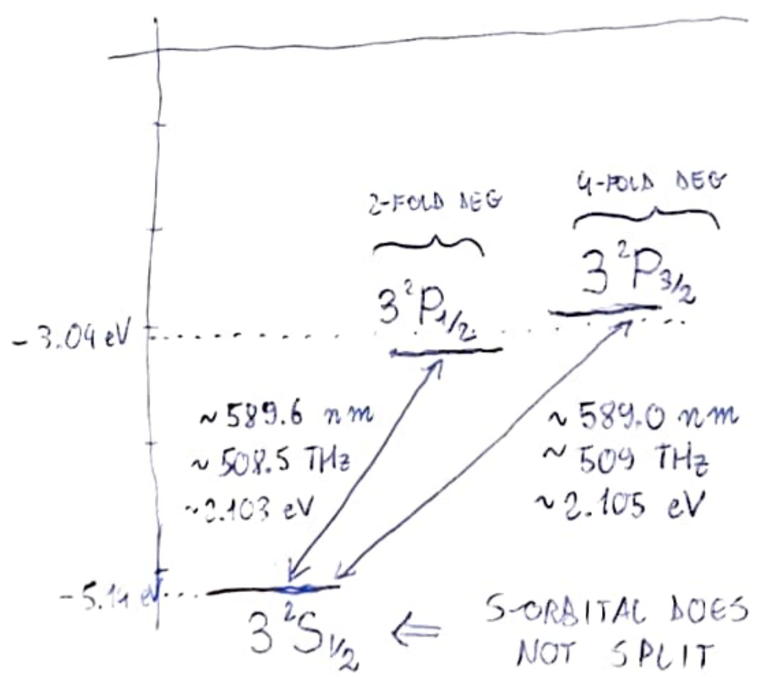
ℓ — $J = \ell + 1/2$ GOES UP IN ENERGY; $J = \ell - 1/2$ GOES DOWN IN ENERGY

$\boxed{\text{LABELING LEVELS}}$

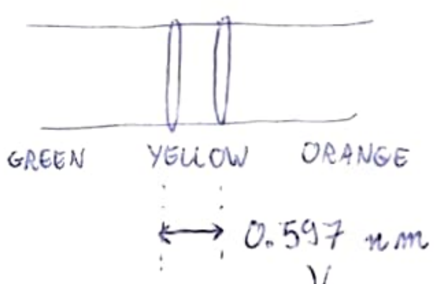
$$n\,{}^{2S+1}L_J$$

FOR HYDRO-LIKE $2S+1$ IS ALWAYS 2

$\boxed{{}^{11}\mathrm{Na}^{\sim 23}}$ Sodium ... AGAIN



EMISSION/ABSORPTION SPECTRUM



⇓

SHARP 10^{-3} OF THE WAVELENGHT

AT THIS ENERGYSCALE THERE ARE ALSO RELATIVISTIC EFFECTS THAT SHIFT $|n\ell\rangle$ RIGIDLY. BORING.

EXTERNAL, STATIC MAGNETIC FIELDS

$\vec{B}$ UNIFORM, CONSTANT, "CLASSICAL"

$$H_B = -\underbrace{\vec{\mu}_s}_{\text{SPIN MAGNETIC DIPOLE MOMENT}} \cdot \vec{B} - \underbrace{\mu_L}_{\text{ORBITAL MAGNETIC DIPOLE MOMENT}} \cdot \vec{B} = \frac{\mu_B}{\hbar}\left(g_s \vec{S} + g_L \vec{L}\right)\cdot \vec{B}$$

g-FACTORS
$$\begin{cases} g_s & \text{SPIN g-FACTOR OF ELECTRON} \approx 2{,}0023 \\ g_L & \text{ORBITAL g-FACTOR} = \dfrac{m}{m_e} = \dfrac{1}{1 + m_e/m_{core}} \approx 1 - \varepsilon \end{cases}$$

REDUCED MASS

$$\frac{\text{ROTATE}}{\text{UNTIL } B \text{ IS ALIGNED ALONG } \hat{z}} \qquad H_B = \frac{\mu_B}{\hbar}\left(\sim 2\, S_z + \sim 1\, L_z\right) B_z$$

TWO SCENARIOS

$\boxed{1}$ STRONG FIELDS

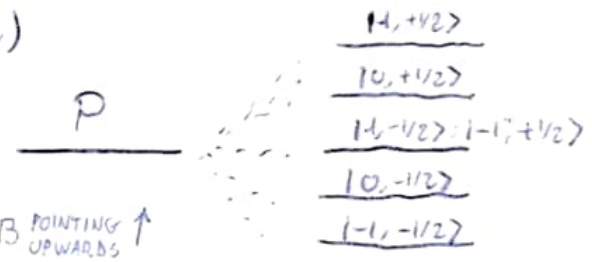
PASCHEN-BACK eff.

$$\underbrace{\Delta E_B}_{} \gg \Delta E_{SPIN\text{-}ORBIT} \qquad \boxed{B \sim 1\ \text{Tesla}}$$

AT THIS ENERGYSCALE, (m, S_z) ARE "GOOD" QUANTUM NUMBERS

$$\Delta E_{n\ell m s_z} = \langle n \ell m s_z | H_B | n \ell m s_z \rangle \cong \frac{\mu_B B}{\hbar}\langle 2 S_z + L_z \rangle$$
$$= \mu_B B\,(2 s_z + m)$$

TRIVIAL
(MORE INTERESTING W/ HYPERFINE)



$\boxed{2}$ WEAK FIELDS

Zeeman
ANOMALOUS

$$\underbrace{\Delta E_B}_{} \lesssim \Delta E_{SPIN\ ORBIT} \qquad |n, \ell, J, J_z\rangle$$

AT THIS ENERGYSCALE, GOOD QUANTUM NUMBERS

$$\Delta E_{n\ell J J_z} = \langle n \ell J J_z | H_B | n \ell J J_z \rangle = \qquad \vec{L} = \vec{J} - \vec{S}$$
$$= \frac{\mu_B B}{\hbar}\langle g_s S_z + g_L L_z \rangle = \frac{\mu_B B}{\hbar}\langle g_L J_z + (g_s - g_L) S_z \rangle$$
$$= \frac{\mu_B B}{\hbar}\left(g_L j_z \hbar + (g_s - g_L)\langle n \ell J J_z | S_z | n \ell J J_z \rangle\right)$$

NOT AN EIGENVECTOR OF S_z

HOW TO CALCULATE $\langle S_z \rangle$ WE USE THE

PROJECTION THEOREM

↳ FIND THE PROOF ON TEXT BOOKS/INTERNET

$$\langle \vec{A} \rangle = \left\langle \left(\frac{(\vec{J}\cdot\vec{A})}{J^2} \right) \vec{J} \right\rangle = \langle (J^2)^{-1} (\vec{J}\cdot\vec{A}) \vec{J} \rangle$$

↑ ANY VECTOR OPERATOR QUANTITY

↑ MORE PRECISE NOTATION

$$\langle n \ell j j_z | S_z | n \ell j j_z \rangle = \langle n \ell j j_z | (J^2)^{-1} (\vec{J}\cdot\vec{S}) J_z | n \ell j j_z \rangle =$$

$$= \frac{J_z}{\hbar j(j+1)} \langle n \ell j j_z | \vec{J}\cdot\vec{S} | n \ell j j_z \rangle$$

BUT $\vec{L} = \vec{J} - \vec{S}$ SO

$$L^2 = J^2 + S^2 - 2 \vec{J}\cdot\vec{S} \rightsquigarrow \vec{J}\cdot\vec{S} = \frac{J^2 + S^2 - L^2}{2}$$

$$\langle n \ell j j_z | S_z | n \ell j j_z \rangle = \frac{j(j+1) + s(s+1) - \ell(\ell+1)}{2j(j+1)} J_z \hbar$$

IN CONCLUSION $\boxed{\Delta E_{n\ell j j_z} = + \mu_B J_z g_J(j,\ell) B_z}$ where

$$\underbrace{g_J^{(\ell,j)}}_{\text{LANDÉ } g_J\text{-FACTOR}} = \underbrace{g_L}_{\approx 1} + \underbrace{(g_S - g_L)}_{\approx 1} \frac{j(j+1) - \ell(\ell+1) + \frac{3}{4}}{2j(j+1)}$$

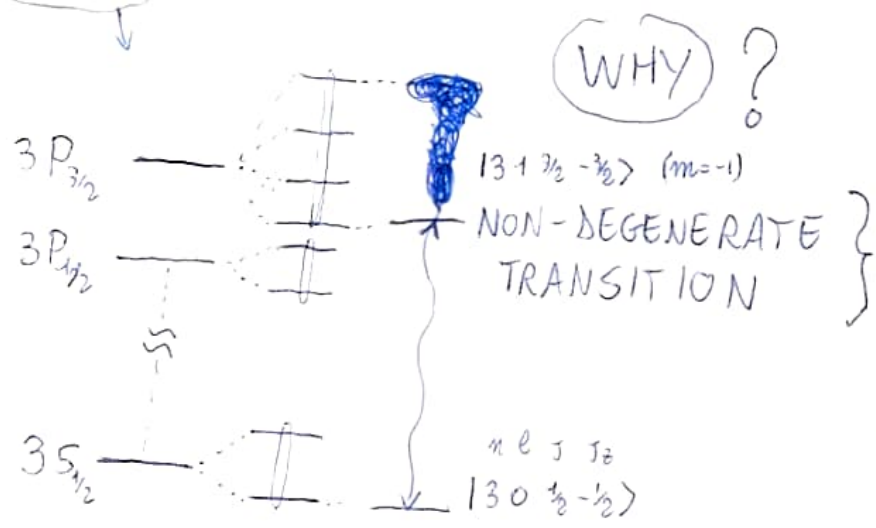
LOW ORBITALS (EXERCISE)

$S_{1/2}$ $g_J \approx 2 \approx g_S$

$P_{1/2}$ $g_J \approx \frac{2}{3}$

$P_{3/2}$ $g_J \approx \frac{4}{3}$

SODIUM LOL



THIS CAN BE AN ATOM QUBIT

↓

DYNAMIC IS CONTROLLED BY LIGHT W/ ELECTRIC DIPOLE TRANSITIONS

... SPEAKING OF ALLOWED TRANSITIONS, IT IS IMPORTANT TO REVIEW THE DIPOLE TRANSITION SELECTION RULES AT THE FINE-STRUCTURE ENERGYSCALE

$|n\, \cancel{\ell\, m}\, s_z\rangle$ BAD QUANTUM NUMBERS

$|n\, \ell\, j\, j_z\rangle$ GOOD QUANTUM NUMBERS

HYDROGEN-LIKE ELECTRIC DIPOLE $\quad -e\langle n\, \ell\, j\, j_z|\vec{r}\,|n'\, \ell'\, j'\, j_z'\rangle$

(✓) $\Delta \ell = \pm 1$

(✗) ~~$\Delta m = 0, \pm 1$~~ NOPE, m IS NOT A GOOD QUANTUM NUMBER

(✓) $\Delta j = 0, \pm 1$ EXCEPT $j = j' = 0$

(✓) $\Delta j_z = 0, \pm 1$ BUT $\Delta j_z \neq 0$ WHEN $j = j'$

THE NEW RULES COME FROM THE WIGNER-ECKART THEOREM, THE PROOF IS TEDIOUS AND LONG.