COURSE FORMAT:

HOMEWORK (50%): 5-6 Assignments, due every ~2 weeks

MIDTERM (20%): Tentatively Wed, March 23

FINAL PROJECT (30%): Paper (4 pages) + Presentation (10-15 minutes)

- Timeline in syllabus
- Any topic related to atomic physics

General suggestions

- a connection to your area of research
- any modern or historical research topic
- a fundamental topic not covered deeply in class

COURSE OVERVIEW:

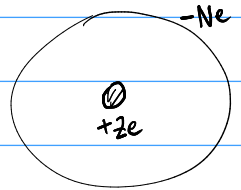
1. ATOMIC STRUCTURE
   - Energy levels of atoms/ions
2. ATOM-LIGHT INTERACTIONS
   - Absorption, emission, coherence

} Midterm

3. ATOMIC ENSEMBLES & SPECIAL TOPICS
   - spectroscopy, laser cooling

Overview of Atomic Structure

- Review: Atoms / Ions



Nucleus: Z protons + $(A-Z)$ neutrons = A nucleons

- A = Mass number
- Z = Atomic number

Electrons: N electrons

Net charge: $(Z-N)e$

- Neutral atom: $N = Z$
- Positive ion: $N < Z$
- Negative ion: $N = Z+1$ ~ why only one? Coulomb > Dipole
  - exist for 90% of atoms - weakly bound

Quick Example:

Iron ion: Fe^{3+} (Fe IV in Spectroscopic notation)

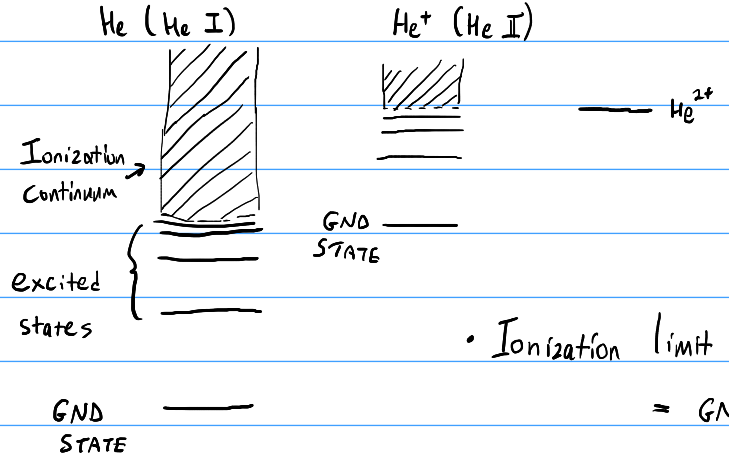
Find the number of

a) Protons (Z) 26

b) Electrons (N) 23

ENERGY SPECTRA

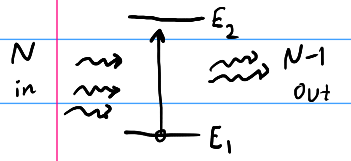
- Discrete bound states + continuum



- Ionization limit: lowest E at which one electron is unbound
  = GND. energy of ion with 1 fewer electron

ATOM-PHOTON INTERACTIONS

ABSORPTION



- ENERGY CONSERVATION:

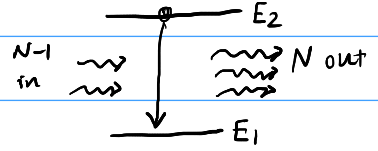
$N h\nu + E_1 = (N-1)h\nu + E_2$

$E_2 - E_1 = h\nu$

ν = FREQ.

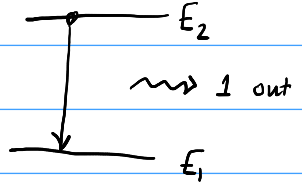
h = Planck's Const

STIMULATED EMISSION



- TIME REVERSE OF ABSORPTION

SPONTANEOUS EMISSION (LET N=1)



- ATOM EMITS WITHOUT APPLIED FIELD
- QUANTUM FIELD THEORY:
  - THE VACUUM FLUCTUATIONS PERTURB THE ATOM

UNITS OF ENERGY

$\Delta E = h\nu$

$= hc/\lambda$

CONVERSIONS

$1\,eV \approx 1.602\times10^{-19}\,J$

$h \approx 4.136\times10^{-15}\,eV\cdot s$

$hc \approx 1.240\times10^{-6}\,eV\cdot m$

$(= 1240\,eV\cdot nm$

$= 1.24\times10^{-4}\,eV\cdot cm)$

EXAMPLES: FIND ΔE in eV associated with

a) $10\ GHz = \nu$

$= (4.136\times10^{-15}\,eV\cdot s)(10^{10}\,s^{-1}) = 4.136\times10^{-5}\,eV$

b) $620\ nm = \lambda$

$\Delta E = (1240\,eV\cdot nm)/(620\,nm) = 2\,eV$

c) $16000\ cm^{-1} = 1/\lambda$

$\Delta E = (1.24\times10^{-4}\,eV\cdot cm)(16000\,cm^{-1}) = 1.984\,eV$

ATOMIC SPECTRA DATABASE

https://www.nist.gov/pml/atomic-spectra-database

→ LEVELS → "Na I"

Configuration	Term	J	Level (cm^{-1})	Uncertainty (cm^{-1})
$2p^6 3s$	^2S	$^1/_2$	0.00000	
$2p^6 3p$	$^2P°$	$^1/_2$	*16 956.17025*	*0.00004*
		$^3/_2$	*16 973.36619*	*0.00005*
$2p^6 4s$	^2S	$^1/_2$	25 739.999	0.003
$2p^6 3d$	^2D	$^5/_2$	29 172.837	0.002
		$^3/_2$	29 172.887	0.002
$2p^6 4p$	$^2P°$	$^1/_2$	*30 266.99*	*0.02*
		$^3/_2$	*30 272.58*	*0.02*

GROSS FINE

HIERARCHY OF ENERGIES

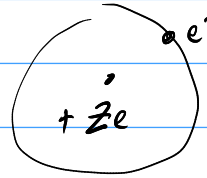
- GROSS STRUCTURE (1-10 eV)
  - electron kinetic energy
    + Coulomb interactions (e-e and e-nucleus)
- FINE STRUCTURE (10^{-3}-10^{-2} eV)
  - Relativistic corrections (esp. spin-orbit coupling)
- HYPERFINE STRUCTURE (10^{-6}-10^{-5} eV)
  - Nuclear magnetism and other nuclear effects

Reading: Foot 1.2, 2.1

HW1: due Wed, Feb. 9

Today: Non-relativistic hydrogen-like atoms

- One electron + nucleus of charge Ze (Li^{2+}, $Z=3$)



$$H = \frac{\vec{p}^2}{2\mu} + V(r) \quad ; \quad \mu = \text{reduced mass} = \frac{m_e m_N}{m_e + m_N} \approx m_e << m_N$$

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

$Zx = x'$

SCHRODINGER EQUATION

$\vec{p} = -i\hbar\vec{\nabla}$

$\vec{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$

$H\psi = E\psi \longrightarrow -\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$

$\frac{\partial^2}{\partial x^2}\frac{1}{Z^2} = \frac{\partial^2}{\partial(Zx)^2} = \frac{\partial^2}{\partial(x')^2}$

Z scaling: divide by Z^2

$$-\frac{\hbar^2}{2\mu}\frac{\nabla^2}{Z^2}\psi - \frac{e^2}{4\pi\varepsilon_0(Zr)}\psi = \left(\frac{E}{Z^2}\right)\psi$$

Could eliminate Z by rescaling: $\vec{r}' = Z\vec{r}$, $E' = E/Z^2$; $(\nabla')^2 = \nabla^2/Z^2$

$\vec{r} = \vec{r}'/Z$; $E = E'Z^2$

distances $\propto \frac{1}{Z}$; Energies $\propto Z^2$

$$[x, p] = i\hbar$$

$$\Rightarrow \Delta x \, \Delta p \geq \hbar/2$$

SEPARATION of UARIABLES

Let $\vec{L} = \vec{r} \times \vec{p}$ (Angular momentum)

Rotational symmetry: $[H, L_i] = 0$; $[H, \vec{L}^2] = 0$; $[H, L_z] = 0$; Also: $[\vec{L}^2, L_z] = 0$

→ Simultaneous eigenstate of H, L^2, L_z

$$\Rightarrow \quad \psi(r, \theta, \phi) = R(r)\, Y_{\ell m}(\theta, \phi)$$

$Y_{\ell m}(\theta, \phi)$ = Spherical harmonics (Foot, table 2.1)

$$\vec{L}^2 Y_{\ell m} = \hbar^2 \ell(\ell+1)\, Y_{\ell m}, \quad \ell = 0, 1, 2, \ldots$$

$$L_z Y_{\ell m} = \hbar m \, Y_{\ell m}, \quad m = -\ell, \ldots, \ell \text{ (integer)}$$

ex. $\ell = 2$

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

Normalization: $$1 = \int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi \; |Y_{\ell m}(\theta, \phi)|^2$$

RADIAL EQUATION

$$H\psi = E\psi \Rightarrow \left[-\frac{\hbar^2\nabla^2}{2\mu} + V(r)\right] R(r) Y_{lm}(\theta,\phi) = E\, R(r) Y_{lm}$$

Spherical coordinates: $\nabla^2\psi = \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) - \frac{1}{r^2}\left(\frac{\vec{L}^2}{\hbar^2}\right)\psi$

- Factor of $\vec{L}^2/\hbar^2$ becomes $\ell(\ell+1)$

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}(rR)Y + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2} RY + V(r) RY = E\, RY$$

Multiply by r:

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}(rR) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}(rR) + V(r)(rR) = E\,(rR)$$

Let $P(r) = rR(r)$

RADIAL EQUATION FOR $P(r)$

$$-\frac{\hbar^2}{2\mu}\frac{d^2P}{dr^2} + \left[\frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}\right] P(r) = E\,P(r)$$

Non-dimensionalize:

Define a new length scale 'a': $E = \frac{-\hbar^2}{2\mu a^2} < 0 \Rightarrow a^2 = \frac{-\hbar^2}{2\mu E} = \frac{\hbar^2}{2\mu|E|}$

Let $\rho = r/a$; $r = a\rho$

$$\frac{-\hbar^2}{2\mu a^2}\frac{d^2P}{d\rho^2} + \left[\frac{\hbar^2 l(l+1)}{2\mu a^2\rho^2} - \frac{Ze^2}{4\pi\epsilon_0 a\rho}\right] P(\rho) = E\,P(\rho)$$

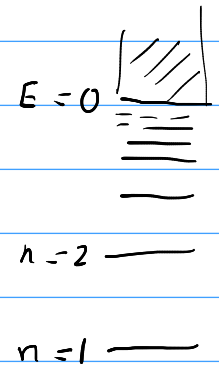
Divide by $E = -|E|$

$$\frac{d^2P}{d\rho^2} + \left[\frac{-l(l+1)}{\rho^2} + \underbrace{\left(\frac{Ze^2\sqrt{2\mu|E|}}{4\pi\epsilon_0|E|\hbar}\right)}_{\lambda}\frac{1}{\rho}\right] P(\rho) = P(\rho)$$

DIMENSIONLESS RADIAL EQN

$$\frac{d^2P}{d\rho^2} + \left[\frac{-\ell(\ell+1)}{\rho^2} + \frac{\lambda}{\rho} \right] P(\rho) = P(\rho)$$

$$\lambda = \frac{Ze^2}{4\pi\varepsilon_0 \hbar} \sqrt{\frac{2\mu}{|E|}}$$



Boundary conditions: $P(0) = 0$, $P(\infty) = 0$

Solution exists $\lambda = 2n$, n = integer $> \ell$

$\Rightarrow$ Quantized energy: $E = \frac{-1}{2n^2} \frac{\mu}{\hbar^2} \left(\frac{Ze^2}{4\pi\varepsilon_0} \right)^2$

- independent of ℓ

LENGTH SCALE

$$\frac{-\hbar^2}{2\mu a^2} = E = \frac{-1}{2n^2}\frac{\mu}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2$$

$$\Rightarrow \quad a = \frac{\hbar^2 n}{\mu}\frac{4\pi\varepsilon_0}{Ze^2} = \frac{n}{Z}\frac{\hbar^2}{\mu}\left(\frac{4\pi\varepsilon_0}{e^2}\right) = \frac{n}{Z}a_0^*$$

When $\mu = m_e$, $a_0^* = \frac{\hbar^2}{m_e}\frac{4\pi\varepsilon_0}{e^2} = a_0$ Bohr radius

$$P(\rho) = P\left(\frac{r}{a}\right) = P\left(\frac{Zr}{na_0^*}\right)$$

$P(\rho) \propto \rho^{l+1} e^{-\rho} H(\rho)$ ~ Polynomial degree $n-l-1$; $\boxed{n-l-1 \text{ zeros}}$ "Radial nodes"

Today:

- Spectroscopic notation for hydrogenic atoms
- Spin-orbit coupling
- Angular momentum addition

Reading: Foot 2.3–2.3.2

WARM-UP:

Calculate $\langle \frac{1}{r^3} \rangle$ for a hydrogen atom in $n=2$, $\ell=1$

GIVEN:

$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{2}{\sqrt{3}} \rho e^{-\rho}$$

$$\psi(r,\theta,\phi) = R_{21}(r) Y_{1m}(\theta,\phi)$$

$$\left\langle \frac{1}{r^3} \right\rangle = \int \frac{1}{r^3} |\psi|^2 d^3r = \int_0^\infty dr\, r^2 \int d\Omega \, \frac{1}{r^3} |R_{21}(r) Y_{1m}(\theta,\phi)|^2 = \left(\int_0^\infty dr \, \frac{1}{r} R_{21}(r)^2\right)\underbrace{\left(\int d\Omega \, |Y_{1m}|^2\right)}$$

$$= \int_0^\infty dr \, \frac{1}{r} \left(\frac{Z}{2a_0}\right)^3 \left(\frac{4}{3}\right) \rho^2 e^{-2\rho}$$

$\rho = Zr/2a_0$

$d\rho = Z\,dr/2a_0 \rightarrow \frac{2a_0}{Z} d\rho = dr$

$$= \int_0^\infty d\rho \, \frac{1}{\rho} \left(\frac{Z}{2a_0}\right)^3 \left(\frac{4}{3}\right) \rho^2 e^{-2\rho}$$

$$= \left(\frac{Z}{2a_0}\right)^3 \left(\frac{4}{3}\right) \left(\int_0^\infty d\rho \, \rho e^{-2\rho}\right)$$

$$\int_0^\infty d\rho \, \rho e^{-2\rho} = -\int_0^\infty d\rho \left(-\tfrac{1}{2}\right) e^{-2\rho} + \rho\left(-\tfrac{1}{2}\right) e^{-2\rho} \Big|_0^\infty$$

$$= \frac{1}{2} \int_0^\infty d\rho \, e^{-2\rho}$$

$$= \frac{1}{2} \left(-\frac{1}{2} e^{-2\rho}\right)_0^\infty = -\frac{1}{4}(0-1) = 1/4$$

$$= \boxed{\frac{1}{3}\left(\frac{Z}{2a_0}\right)^3}$$

NR Hydrogen quantum numbers: n, ℓ, m

Principle quant. #: $n = 1, 2, 3, \ldots$

Ang. Mom. q. #: $\ell = 0, 1, \ldots n-1$

Magnetic/Azimuthal q #: $m_\ell = -\ell, \ldots, \ell$

SPECTROSCOPIC NOTATION

ℓ	LETTER
0	s
1	p
2	d
3	f

EXAMPLES: give spectroscopic notation in the form

$n[\ell]$

↑ letter

1. H ground state

$n=1, \ell=0, m=0$

1s

2. $n=3, \ell=1$ 3p

3. $n=3, \ell=2$ 3d

Electron Spin

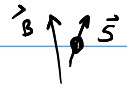
- Electron has $s = 1/2$

$m_s = -s, \ldots, s = -\frac{1}{2}, \frac{1}{2}$

Total: $n\ \ell\ m_\ell\ m_s$

SPIN-ORBIT COUPLING

Recall: Spin in $\vec{B}$ field



• Note: foot $\vec{s} = \frac{\vec{S}}{\hbar}$

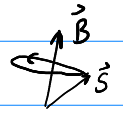
$\vec{l} = \vec{L}/\hbar$

$$U = -\vec{\mu}\cdot\vec{B} = -\left(-g_s \mu_B \frac{\vec{S}}{\hbar}\right)\cdot\vec{B}$$

- electron: $g_s = 2.002318$

μ_B = Bohr magneton = $\frac{e\hbar}{2m_e}$

- causes precession:



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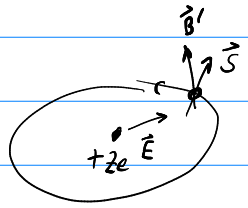
RELATIVISTIC B FIELD

Nuclear charge Produces $\vec{E}$

Electron has velocity $\vec{v}$

Electron frame:

$$\vec{B}' = \frac{1}{c^2}\vec{E}\times\vec{v}$$



Non-inertial frame, acceleration $\vec{a}$

Energy:

$$U' = -\vec{\mu}\cdot\vec{B}' - \vec{S}\cdot\frac{1}{2c^2}\vec{v}\times\vec{a}$$

Thomas's correction (relativity), $v \ll c$ limit

$$= \frac{g_s\mu_B}{\hbar c^2}\vec{S}\cdot(\vec{E}\times\vec{v}) - \frac{1}{2c^2}\vec{S}\cdot\left[\vec{v}\times\left(\frac{-e\vec{E}}{m_e}\right)\right]$$

• Note: Lorentz force $-e\vec{v}\times\vec{B}$ is $\perp$

$$= \frac{g_s e}{2m_e c^2}\vec{S}\cdot(\vec{E}\times\vec{v}) - \frac{e}{2m_e c^2}\vec{S}\cdot(\vec{E}\times\vec{v})$$

• $-e\vec{E} = -\vec{\nabla}V = -\frac{dV}{dr}\hat{r}$

• $\vec{L} = \vec{r}\times\vec{p}$

$$= \frac{(g_s-1)e}{2m_e c^2}\vec{S}\cdot\left(\frac{1}{e}\frac{dV}{dr}\frac{\vec{r}}{r}\times\frac{\vec{P}}{m_e}\right)$$

$$= \frac{(g_s-1)}{2m_e^2 c^2}\left(\frac{1}{r}\frac{dV}{dr}\right)\vec{S}\cdot\vec{L}$$

For Hydrogenic atom: $V(r) = \frac{-Ze^2}{4\pi\varepsilon_0 r}$, $\frac{dV}{dr} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$

Energy

$$U' = \frac{(g_s - 1)}{2m_e^2 c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\frac{1}{r^3}\vec{S}\cdot\vec{L}$$

Calculating $\vec{S}\cdot\vec{L}$:

Define $\vec{J} = \vec{L} + \vec{S}$ (Total electron angular momentum)

Note:

$$\vec{J}^2 = (\vec{L}+\vec{S})\cdot(\vec{L}+\vec{S}) = \vec{L}^2 + \vec{S}^2 + 2\vec{L}\cdot\vec{S}$$

$$\Rightarrow \vec{S}\cdot\vec{L} = \frac{1}{2}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right)$$

Eigenvalues

- "UNCOUPLED" BASIS: $|n\ell s\, m_\ell\, m_s\rangle$

$$\vec{L}^2|n\ell s\, m_\ell m_s\rangle = \hbar^2\ell(\ell+1)\,|n\ell s\, m_\ell m_s\rangle$$

$$\vec{S}^2|n\ell s\, m_\ell m_s\rangle = \hbar^2 s(s+1)\,|n\ell s\, m_\ell m_s\rangle$$

$$L_z|m_\ell m_s\rangle = \hbar m_\ell |m_\ell m_s\rangle$$

$$S_z|m_\ell m_s\rangle = \hbar m_s |m_\ell m_s\rangle$$

} Don't need!

construct eigenstates of $\vec{J}^2$

$$\vec{J}^2|j m_j\rangle = \hbar^2 j(j+1)|j m_j\rangle$$

$$J_z|j m_j\rangle = \hbar m_j |j m_j\rangle$$

$$j = |\ell - s|, \ldots, \ell + s$$

$$m_j = -j, \ldots, j$$

$$|j m_j\rangle = \sum_{m_\ell m_s} |m_\ell m_s\rangle\underbrace{\langle m_\ell m_s | j m_j\rangle}_{\text{CG coeff}}$$

EXAMPLE: Hydrogen 2p state

a) Find allowed j

b) Find $E_{\text{spin-orbit}}$ for each j

a) $n=2,\ l=1,\ S=1/2$

$j = |l-S|, \ldots, l+S = 1-1/2,\ 1+1/2 = \boxed{\frac{1}{2},\ \frac{3}{2}}$

b) $H_{SO} = \frac{(g_s-1)}{2m_e^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\left(\frac{1}{r^3}\right)\left(\frac{1}{2}\right)\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right)$

Degenerate perturbation theory:

$|2p\ m_s\ m_l\rangle$ all degenerate ("degenerate subspace")

First order energy shift:

$E_{SO} = \langle H_{SO}\rangle$

in basis where H_{SO} is diagonal

in this case: $|n\,l\,s\,j\,m_j\rangle$ basis

$$E_{SO} = \langle n\,l\,s\,j\,m_j | H_{SO} | n\,l\,s\,j\,m_j\rangle$$

$$= \frac{(g_s-1)}{4m_e^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\underbrace{\left\langle\frac{1}{r^3}\right\rangle}_{\frac{1}{3}\left(\frac{Z}{2a_0}\right)^3}\hbar^2\Big(j(j+1) - \underbrace{l(l+1)}_{2,\ 8/4} - \underbrace{s(s+1)}_{\frac{1}{2}\frac{3}{2}=3/4}\Big)$$

$= 11/4$

$$= \boxed{\frac{(g_s-1)}{12\,m_e^2c^2}\,\frac{Z^4e^2\hbar^2}{4\pi\varepsilon_0}\left(\frac{1}{2a_0}\right)^3\left(j(j+1) - \frac{11}{4}\right)}$$

$j=1/2$: $j(j+1) = \frac{1}{2}\left(\frac{1}{2}+\frac{2}{2}\right) = 3/4$

$j=3/2$: $j(j+1) = \frac{3}{2}\left(\frac{3}{2}+\frac{2}{2}\right) = 15/4$

Diff: $15/4 - 3/4 = 12/4 = 3$

extra

$$\Delta E_{SO} = E_{SO}(j=3/2) - E_{SO}(j=1/2) = \frac{(g_s-1)\,\hbar^2}{4\cdot 3\,m_e^2c^2}\,\frac{Z^4e^2}{4\pi\varepsilon_0}\left(\frac{1}{2a_0}\right)^3(3)$$

$$= \frac{(g_s-1)}{4m_e^2c^2}\,\frac{\hbar^2Z^4e^2}{4\pi\varepsilon_0}\left(\frac{1}{2a_0}\right)^3$$

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c}$$

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$$

$$\Delta E_{30} = \frac{(g_s-1)\hbar^2 Z^4 e^2}{4 m_e^2 c^2 (4\pi\epsilon_0)} \left(\frac{1}{8}\right)\left(\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2}\right)^3$$

$$= \boxed{\frac{(g_s-1)}{2^5} \frac{Z^4 e^8}{c^2} \frac{m_e}{\hbar^4 (4\pi\epsilon_0)^4}}$$

$$E_2 = \frac{-1}{2(2)^2} \frac{m_e}{\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2$$

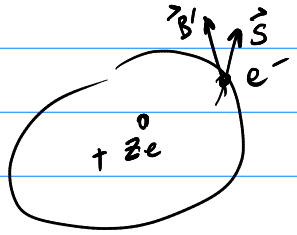
$$\frac{\Delta E_{30}}{E_2} = -\frac{(g_s-1) Z^2 e^4}{2^2 c^2 \hbar^2 (4\pi\epsilon_0)^2} = -\frac{(g_s-1) Z^2}{4}\left(\frac{e^2}{4\pi\epsilon_0 \hbar c}\right)^2$$

$$= -\frac{(g_s-1) Z^2}{4} \alpha^2 \qquad \checkmark$$

TODAY: FINE STRUCTURE OF HYDROGEN

READING: FOOT 2.3.3-4

REVIEW: SPIN-ORBIT COUPLING



$$H_{so} = \left(\frac{Ze^2}{4\pi\epsilon_0}\right)\left(\frac{g_s - 1}{2m_e^2c^2}\right)\frac{1}{r^3}\vec{L}\cdot\vec{S}$$

Define: $\vec{J} = \vec{L} + \vec{S}$

Then, $\vec{L}\cdot\vec{S} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$

WARM-UP: HYDROGENIC $n=2$

LIST THE ALLOWED LEVELS $n[l]_j$: $l = 0, 1$ (s, p) ; $j = l \pm \frac{1}{2}$

$2S_{1/2}$, $2P_{1/2}$, $2P_{3/2}$

ENERGY SPLITTING? $n=2$ → $2P_{3/2}$? $2P_{1/2}$? $2S_{1/2}$? ↕ ΔE?

ENERGIES

NON-RELATIVISTIC: $E_n = -\frac{Z^2}{2n^2}\frac{m_e}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2$ (Bohr)

FINE-STRUCTURE CONSTANT: $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$

$$E_n = -\frac{Z^2}{2n^2}\alpha^2 m_e c^2$$

S.O.C. ENERGY

$$H_{so} = \left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\left(\frac{g_s - 1}{2m_e^2c^2}\right)\frac{1}{r^3}\vec{L}\cdot\vec{S} \qquad , \; g_s \approx 2$$

$$= \frac{1}{2} Z \alpha^4 m_e c^2 \left(\frac{a_0}{r}\right)^3 \frac{\vec{L}\cdot\vec{S}}{\hbar^2}$$

FIRST-ORDER ENERGY SHIFT:

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{\ell\,(\ell+\tfrac{1}{2})(\ell+1)} \left(\frac{Z}{n a_0}\right)^3 \qquad \text{for } \ell \neq 0$$

FOR $\ell \neq 0$:

$$E_{so}^{(1)} = \langle n\ell s j m_j | H_{so} | n\ell s j m_j \rangle$$

$$= \frac{1}{2} Z \alpha^4 m_e c^2 \left\langle \frac{a_0^3}{r^3} \right\rangle \left\langle \frac{\vec{L}\cdot\vec{S}}{\hbar^2} \right\rangle$$

$$= \frac{1}{4} Z^4 \alpha^4 m_e c^2 \frac{j(j+1) - \ell(\ell+1) - s(s+1)}{n^3 \ell(\ell+\tfrac{1}{2})(\ell+1)} \qquad (s = \tfrac{1}{2})$$

$$E_{so}^{(1)}(\ell = 0) = 0$$

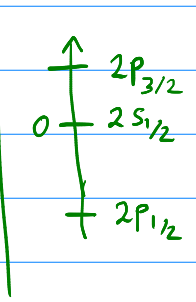
→ E depends on n, j, ℓ

EXERCISE: CALC. E_{so} for $n=2$ STATES

$2p_{1/2}$: $E_{so} \propto \dfrac{\frac{1}{2}(\frac{1}{2}+1) - 2 - \frac{3}{4}}{3/2 \cdot 2} = -\frac{2}{3}$

$2p_{3/2}$: $E_{so} \propto \dfrac{\frac{3}{2}(\frac{3}{2}+1) - 2 - \frac{3}{4}}{3/2 \cdot 2} = \frac{1}{3}$

$2s_{1/2}$: $E_{so} = 0$



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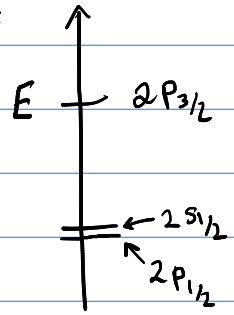


- $E(2S_{1/2}) \approx E(2P_{1/2})$!

$E \sim$ independent of l

MORE RELATIVISTIC CORRECTIONS

KINETIC ENERGY

Relativistic energy: $E = \sqrt{(mc^2)^2 + (pc)^2}$

$$= mc^2\sqrt{1+\left(\frac{p}{mc}\right)^2}$$

$$\approx mc^2\left[1 + \frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 + \cdots\right]$$

$$= \underbrace{mc^2}_{\text{CONST (IGNORE)}} + \underbrace{\frac{p^2}{2m}}_{\text{NON-RELATIVISTIC}} - \underbrace{\frac{p^4}{8m^3c^2}}_{\text{FIRST CORRECTION}} + \cdots$$

$$H_{rel} = -\frac{p^4}{8m_e^3c^2}$$

$$E_{rel}^{(1)} = \langle nl | H_{rel} | nl \rangle = \langle H_{rel} \rangle_{nl} = -\frac{1}{8m_e^3c^2}\langle p^4 \rangle_{nl}$$

SHORTCUT: $H_0 = \frac{p^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0 r}$

$$\Rightarrow \quad p^2 = 2m_e\left(H_0 + \frac{2e^2}{4\pi\varepsilon_0 r}\right)$$

$$\langle p^4 \rangle = \left\langle 4m_e^2 \left(H_0 + \frac{Ze^2}{4\pi\epsilon_0 r}\right)\left(H_0 + \frac{Ze^2}{4\pi\epsilon_0 r}\right)\right\rangle_{n\ell}$$

($H_0 \to E_n$ on both factors)

$$= 4m_e^2 \left(E_n^2 + 2\frac{Ze^2}{4\pi\epsilon_0} E_n \left\langle \frac{1}{r} \right\rangle_{n\ell} + \left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \left\langle \frac{1}{r^2} \right\rangle_{n\ell} \right)$$

$$\left\langle \frac{1}{r} \right\rangle_{n\ell} = \int_0^\infty \frac{1}{r} R_{n\ell}^2(r) r^2 dr = \frac{Z}{n^2 a_0} \qquad \text{(HW 1 \#6)}$$

$$\left\langle \frac{1}{r^2} \right\rangle_{n\ell} = \int_0^\infty \frac{1}{r^2} R_{n\ell}^2(r) r^2 dr = \frac{Z^2}{(\ell+\frac{1}{2}) n^3 a_0^2}$$

Putting it together:

$$E_{rel}^{(1)} = -\frac{1}{2} Z^4 \alpha^4 m_e c^2 \left[\frac{1}{n^3(\ell+\frac{1}{2})} - \frac{3}{4n^4} \right]$$

TOTAL ($\ell \neq 0$):

$$E_{rel}^{(1)} + E_{so}^{(1)} = -\frac{1}{2} Z^4 \alpha^4 m_e c^2 \frac{1}{n^4} \left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right]$$

- Independent of ℓ, for $\ell \neq 0$

what about $\ell = 0$? is it different?

- Short answer: no, the final result is also correct for $\ell = 0$
- To see why, we need the Dirac Eqn.

FULLY RELATIVISTIC THEORY: DIRAC EQN

NON-RELATIVISTIC LIMIT GIVES 3 CORRECTIONS AT ORDER α^4:

$$H_{Dirac} \approx \underbrace{\frac{p^2}{2m_e}}_{} - \underbrace{\frac{p^4}{8m_e^3c^2}}_{} + V(r) - \underbrace{\frac{\hbar^2}{8m_e^2c^2}\nabla^2 V}_{} + H_{SO}$$

DARWIN TERM (H_D)

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\nabla^2\left(\frac{1}{r}\right) = -4\pi\,\delta(\vec{r})$$

$$H_D = \frac{\hbar^2}{8m_e^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)4\pi\,\delta(\vec{r})$$

"Zitterbewegung"
= jittery motion
Due to interference of (+) and (-) frequency solutions in Dirac Eqn
Physically: Interaction with e^+e^- pairs (QED)

$$\langle\delta(\vec{r})\rangle = \int |\psi(\vec{r})|^2\,\delta(\vec{r})\,d^3\vec{r} = |\psi(0)|^2$$

Note: $\psi = R_{nl}Y_{lm}$; $R_{nl} \propto r^l$

$\Rightarrow \psi(0) = 0$ for $l \neq 0$

FOR $l=0$: $\psi(0) = \frac{2}{\sqrt{4\pi}}\left(\frac{Z}{na_0}\right)^{3/2}$

$$\Rightarrow E_D^{(1)} = \langle H_D\rangle = \frac{\hbar^2}{8m_e^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)4\pi\,\frac{4}{4\pi}\left(\frac{Z}{na_0}\right)^3$$

use $a_0 = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{\alpha^2 mc^2}$

$$E_D^{(1)} = \frac{\hbar^2}{2m_e^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\left(\frac{Z}{n}\right)^3\left(\frac{4\pi\varepsilon_0\,\alpha^2 mc^2}{e^2}\right)^3$$

$$= \frac{1}{2}m_e c^2\frac{Z^4}{n^3}\left(\frac{4\pi\varepsilon_0\hbar c}{e^2}\right)^2\alpha^6 \qquad \left(\frac{4\pi\varepsilon_0\hbar c}{e^2} = \alpha^{-1}\right)$$

$$= \boxed{\frac{1}{2}Z^4\alpha^4 m_e c^2\left(\frac{1}{n^3}\right)} \qquad (l=0)$$

Final result:

$$E_{fs}^{(1)} = E_{rel}^{(1)} + E_{so}^{(1)} + E_{D}^{(1)}$$

$$= -\frac{1}{2} Z^4 \alpha^4 \, m_e c^2 \, \frac{1}{n^4} \left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right]$$

Now valid for <u>all</u> ℓ

- Still indep. of ℓ!

TODAY: MULTI-ELECTRON ATOMS

READING: FOOT 4.1 - 4.3

HW1 due Wed, Feb 9

WARM-UP: Hydrogen $2p_{1/2}$ level

WRITE $|2p_{1/2}; m_j = 1/2\rangle$ as a linear combination of states in the uncoupled basis $|2p; m_\ell m_s\rangle$

$$|2p_{1/2}\ m_j = \tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\ |m_\ell = 1, m_s = -\tfrac{1}{2}\rangle - \sqrt{\tfrac{1}{3}}\ |m_\ell = 0, m_s = \tfrac{1}{2}\rangle$$

SPIN WAVEFUNCTIONS

HOW TO WRITE $|n\ell m_\ell m_s\rangle$ AS A FUNCTION?

$$\Psi(\vec{r}, m_s') = R_{n\ell}(r)\, Y_{\ell m}(\theta,\phi)\, \delta_{m_s' m_s}$$

Shorthand:

SPIN UP: $\alpha(m_s') = \delta_{m_s', \frac{1}{2}} = \begin{cases} 1, & m_s' = 1/2 \\ 0, & m_s' = -1/2 \end{cases}$

SPIN DOWN: $\beta(m_s') = \delta_{m_s', -\frac{1}{2}} = \begin{cases} 0, & m_s' = 1/2 \\ 1, & m_s' = -1/2 \end{cases}$

EXAMPLES - WRITE AS A FUNCTION

a) $|2p, m_\ell = 1, m_s = -1/2\rangle = \Psi(\vec{r}, m_s') = R_{21}(r)\, Y_{11}(\theta,\phi)\, \beta(m_s')$

b) $|2p_{1/2}, m_j = 1/2\rangle = \sqrt{\tfrac{2}{3}}\, R_{21}(r)\, Y_{11}(\theta,\phi)\, \beta(m_s')$

$$-\sqrt{\tfrac{1}{3}}\, R_{21}(r)\, Y_{10}(\theta,\phi)\, \alpha(m_s')$$

MULTI-ELECTRON ATOMS

HAMILTONIAN of N-ELECTRON ATOM (NON-RELATIVISTIC)

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}$$

KE — ATTRACTION TO NUCLEUS — e-e REPULSION

- SOLVE: $H\Psi = E\Psi$

– WHAT ARE THE BOUND-STATES ($E<0$)?

– WHAT ARE THEIR ENERGIES?

MULTI-ELECTRON WAVEFUNCTIONS:

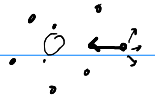
$$\Psi = \Psi(\underbrace{\vec{r}_1, m_{s1}}_{\text{"1"}}; \underbrace{\vec{r}_2, m_{s2}}_{\text{"2"}}; \cdots; \underbrace{\vec{r}_N, m_{sN}}_{\text{"N"}})$$

$$= \Psi(1, 2, \cdots, N)$$

CENTRAL FIELD APPROXIMATION

~ NET e-e REPULSIVE FORCE ≈ CENTRAL:

FORCES ON ELECTRON 1:



SUM: ↩0

$$\vec{F}_{NET} \approx f(r)\,\hat{r}$$

POTENTIAL: $V_{CF}(r)$

CENTRAL FIELD HAMILTONIAN

$$H_0 = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V_{CF}(r_i) = \sum_i h_i$$

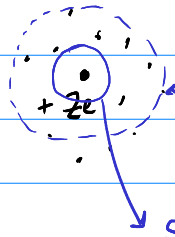
PERTURBATION THEORY: $H_1 = H - H_0$ "Residual non-central potential"

– THE PERTURBATION IS IMPORTANT, THOUGH

CHARGE SCREENING

- COMPARE $V_{CF}(r)$ TO $V(r)$
- RECALL GAUSS'S LAW: $\int E \cdot dA = \frac{Q_{enc}}{\varepsilon_0}$

POTENTIAL SEEN BY i-th ELECTRON:

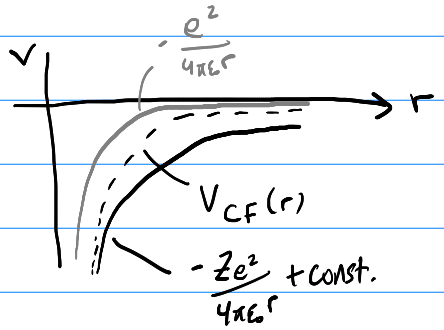


LARGE r: $Q_{enc} \approx e$ (FOR $N = Z$)

OR $(Z-(N-1))e$ IN GENERAL

SMALL r: $Q_{enc} \approx Ze$

PLOT:



ASIDE: WHY "+ const" ?

$$\vec{F} = -e\vec{E} = -\nabla V$$

$$e\vec{E} = \nabla V$$

$r \to \infty$: $\frac{dV_{CF}}{dr} = eE_r = \frac{e^2}{4\pi\varepsilon_0 r^2}$

$$V_{CF}(r) = \int \frac{e^2}{4\pi\varepsilon_0 r^2} dr = -\frac{e^2}{4\pi\varepsilon_0 r} + \text{const}$$

$V_{CF}(r \to \infty) = 0 \rightarrow \text{const} = 0$

$r \to 0$: $\frac{dV_{CF}}{dr} = eE_r = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$

$$V_{CF} = \int \frac{Ze^2}{4\pi\varepsilon_0 r^2} dr = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \text{const}$$

EIGEN STATES of H_0 (CENTRAL FIELD)

PRODUCT STATES:

Let $\Psi(1, 2, \cdots N) = \psi_1(1)\,\psi_2(2)\,..\,\psi_N(N)$

WHERE: $h_i \psi_i = E_i \psi_i$

THEN:

$$H_0 \Psi = \left(\sum_i h_i \right) \psi_1(1)\,..\,\psi_N(N)$$

$$= \left(\sum_i E_i \right) \psi_1(1)\,..\,\psi_N(N) = \left(\sum_i E_i \right) \Psi$$

$$= E \Psi$$

where $E = E_1 + E_2 + \cdots + E_N$

TODAY: PAULI PRINCIPLE

WARM-UP:

FOR $n=3$ IN HYDROGEN

HOW MANY $(n l m_l m_s)$ STATES

for each l?

$l = 0, 1, 2$

$N_l = 2 \times (2l+1)$

$N_0 = 2(2\times0+1) = 2 \rightarrow s^2$

$N_1 = 2(2\times1+1) = 6 \rightarrow p^6$

$N_2 = 2(2\times2+1) = 10 \rightarrow d^{10}$

(ELECTRON CONFIGURATIONS)

CENTRAL FIELD APPROX (CONTINUED):

MANY-ELECTRON WAVEFUNCTION

$$\Psi(1,2,3,\ldots N) = \psi_1(1)\,\psi_2(2)\cdots\psi_N(N)$$

EACH ψ_i SATISFIES A SINGLE-PARTICLE SCHRÖDINGER EQN

$$h_i \psi_i = E_i \psi_i$$

OR $$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{CF}(r)\right)\psi_i = E_i \psi_i$$

$$\Rightarrow \psi_i(r, m_s) = R_{n_i l_i}(r)\, Y_{l_i m_{l_i}}(\theta,\phi)\, \chi_{m_{s_i}}(m_s)$$

NOT HYDROGENIC! — USUAL SPHERICAL HARMONIC — SPIN: $\chi_\uparrow = \alpha$, $\chi_\downarrow = \beta$

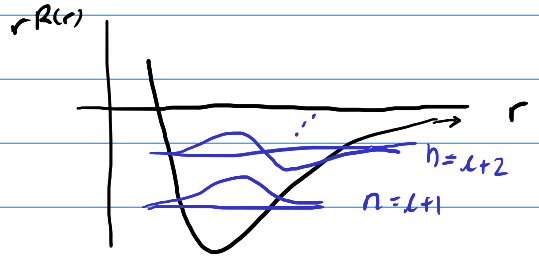
TOTAL $E = E_1 + E_2 + \cdots + E_N$

PRINCIPLE QUANTUM NUMBER n:

- Hydrogen: $R_{nl}(r)$ HAS $n-l-1$ NODES FOR $r>0$

→ LET $n = l+1+$ (RADIAL NODES)

$$V_{eff}(r) = V_{CF}(r) + \frac{\hbar^2 l(l+1)}{2mr^2}$$



IDENTICAL PARTICLES

- ELECTRONS ARE FERMIONS:

$N=2$:

$$\Psi(1,2) = -\Psi(2,1) \qquad \text{(ANTISYMMETRIC)}$$

N ELECTRONS:

$$\Psi(1,2,\ldots i,\ldots j\ldots N) = -\Psi(1,2,\ldots,j,\ldots i,\ldots N)$$

ANTISYMMETRIC STATES

TWO ELECTRONS:

GIVEN $\psi_1(r,m_s)$ AND $\psi_2(r,m_s)$

$$E = E_1 + E_2$$

TWO DEGENERATE STATES:

$$\Psi(1,2) = \psi_1(1)\psi_2(2)$$

$$\Psi'(1,2) = \psi_2(1)\psi_1(2)$$

ANTISYMMETRIC LINEAR COMBINATION:

$$\Psi_A(1,2) = \frac{1}{\sqrt{2}}\left[\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)\right] = -\Psi_A(2,1) \quad \checkmark$$

SUPPOSE $\psi_1 = \psi_2$: $\Psi_A(1,2) = \frac{1}{\sqrt{2}}\left(\psi_1(1)\psi_1(2) - \psi_1(1)\psi_1(2)\right)$

$= 0$

– CAN'T ANTISYMMETRIZE!

→ "PAULI EXCLUSION PRINCIPLE"

NO TWO ELECTRONS CAN BE IN THE SAME QUANTUM STATE $(n\ \ell\ m_\ell\ m_s)$

SLATER DETERMINANTS

$$\Psi_A(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1) & \psi_2(1) \\ \psi_1(2) & \psi_2(2) \end{vmatrix}$$

N ELECTRONS

$$\Psi_A(1,2,\cdots N) = \frac{1}{\sqrt{N!}} \sum_\sigma \epsilon_{\sigma_1\sigma_2\cdots\sigma_N} \psi_{\sigma_1}(1)\psi_{\sigma_2}(2)\cdots\psi_{\sigma_N}(N)$$

↳ ANTISYM. SYMBOL (LEVI-CIVITA): $\epsilon_\sigma = \begin{cases} 1, & \sigma \text{ even perm.} \\ -1, & \sigma \text{ odd perm.} \\ 0, & \text{not a perm.} \end{cases}$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \cdots & \psi_N(1) \\ \psi_1(2) & \ddots & \psi_N(2) \\ \vdots & \ddots & \vdots \\ \psi_1(N) & \cdots & \psi_N(N) \end{vmatrix}$$

EXAMPLE: He GND STATE $1s^2$

BOTH ELECTRONS HAVE $n=1,\ \ell=0,\ m_\ell=0$

SINGLE-PARTICLE STATES:

$\psi_1(r, m_s) = u_{100}(\vec{r})\,\alpha(m_s)$ SPIN UP

$\psi_2(r, m_s) = u_{100}(\vec{r})\,\beta(m_s)$ SPIN DOWN

SLATER DETERMINANT:

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\left(\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)\right)$$

$$= \frac{1}{\sqrt{2}}\left(u_{100}(1)\,\alpha(1)\,u_{100}(2)\beta(2) - u_{100}(2)\,\alpha(2)\,u_{100}(1)\,\beta(1)\right)$$

$$= \frac{1}{\sqrt{2}}\,u_{100}(1)\,u_{100}(2)\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)$$

NOTE: THIS IS AN EIGENSTATE OF TOTAL SPIN

$$\vec{S} = \vec{S}_1 + \vec{S}_2$$

$$|S=0, M_S=0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

MANY LOW-Z ATOMS ARE IN $\vec{S}^2$ EIGENSTATES LIKE THIS (NEXT WEEK)

CFA → SHELL MODEL

- EACH ELECTRON HAS UNIQUE $n\ \ell\ m_\ell\ m_s$
- ENERGIES DEPEND ON n, ℓ

n : "SHELL"

$n\ell$: "SUB-SHELL"

ELECTRON CONFIGURATION : LIST $n\ell$ VALUES

	ℓ	# STATES $= 2(2\ell+1)$
s	0	2
p	1	6
d	2	10
f	3	14

EXAMPLE :

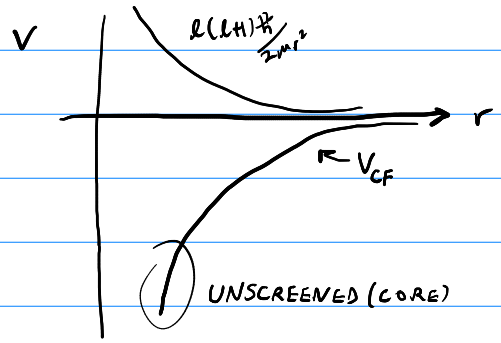
He GND STATE: $1s\ 1s = 1s^2$

Li GND STATE: $1s\ 1s\ 2s = 1s^2\ 2s$

B GND STATE: $1s^2\ 2s^2\ 2p$

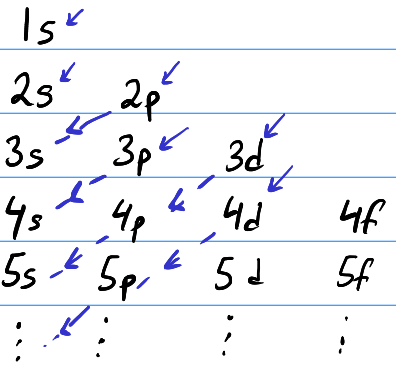
- NOTICE THAT 2s FILLS BEFORE 2p

REASON: CHARGE SCREENING + CENTRIFUGAL BARRIER



SMALL ℓ → ELECTRON REACHES SMALL r (LARGER Z_{eff})

APPROXIMATE FILLING ORDER (GND STATES):



EXAMPLE: Si ($Z = 14$)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

TODAY: LS COUPLING

WARM-UP: PREDICT GND STATE ELECTRON CONFIG. OF S: (Z=14)

1s
2s 2p
3s 3p 3d

"Aufbau" principle ("Building-up")

Si: $1s^2\ 2s^2\ 2p^6\ 3s^2 3p^2$

→ NOTE: 4 FILLED SUBSHELLS

1 PARTIALLY FILLED SUBSHELL ($3p^2$)

DEGENERACY OF ELECTRON CONFIG.

- DUE TO PARTIALLY FILLED SUBSHELLS
- CONSIDER 1 UNFILLED SUB SHELL $(n\ell)^k$

HOW MANY QUANTUM STATES (SLATER DETERMINANTS) AVAILABLE?

$$|m_{\ell 1} m_{s1}, m_{\ell 2} m_{s2}, \ldots, m_{\ell k} m_{sk}\rangle$$

- # SINGLE-ELECTRON STATES (ORBITALS): $2(2\ell+1) = N_s$
- # WAYS TO CHOOSE k OF THEM TO FILL:

$$g = \binom{N_s}{k} = \frac{N_s!}{(N_s-k)!\,k!}$$

EXAMPLE: np^2 : $\ell = 1$, $k = 2$; $N_s = 2 \cdot 3 = 6$

$$g = \binom{6}{2} = \frac{6 \cdot 5}{2} = \boxed{15}$$

That's a lot of states!

15 Degenerate states

PERTURBATIONS CAN BREAK DEGENERACY

PERTURBATIONS THAT BREAK THIS DEGENERACY

- NON-CENTRAL e-e INTERACTION
  "RESIDUAL ELECTROSTATIC INTERACTION" (H_1)
- SPIN-ORBIT COUPLING (H_2)
- EXTERNAL FIELDS (H')

FOR NOW, ASSUME $H_1 \gg H_2, H'$ (LARGEST PERTURBATION)

RESIDUAL ELECTROSTATIC INTERACTION

NON-RELATIVISTIC:

$$H_{NR} = \sum_i \left(\frac{P_i^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right) + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

CFA: $H_0 = \sum_i \left(\frac{P_i^2}{2m} + V_{cf}(r_i) \right)$

Let $H_1 = H_{NR} - H_0$ so $H_{NR} = H_0 + H_1$

$$H_1 = \sum_i \left(-\frac{Ze^2}{4\pi\varepsilon_0 r_i} - V_{CF}(r_i) \right) + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

1ST-ORDER DEGENERATE PERTURBATION THEORY:

- FIND H_1 AS A MATRIX ON THE DEGEN. SUB SPACE OF SLATER DET. STATES $\{|1\rangle, |2\rangle, \ldots |g\rangle\}$

$$[H_1] = \begin{pmatrix} \langle 1|H_1|1\rangle & \langle 1|H_1|2\rangle & \cdots & \langle 1|H_1|g\rangle \\ \langle 2|H_1|1\rangle & \vdots & & \vdots \\ \vdots & & & \\ \langle g|H_1|1\rangle & \cdots & & \langle g|H_1|g\rangle \end{pmatrix}$$

-- i.e. FOR np^2, IT'S A 15×15 MATRIX

1ST-ORDER ENERGY SHIFTS = EIGVALS OF $[H_1]$

ZERO-TH ORDER WAVEFUNCTIONS = EIG. VECTORS OF $[H_1]$

SUPPOSE $\begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_g \end{pmatrix}$ IS AN EIG. VECTOR OF $[H_1]$:

$$[H_1]\begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_g \end{pmatrix} = E_1 \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_g \end{pmatrix}$$

THEN, $E \approx E_0 + E_1$

E_0: CFA; E_1: CORRECTION DUE TO H_1

$$|\Psi\rangle = c_1|1\rangle + c_2|2\rangle + \cdots + c_g|g\rangle$$

- SUM OF SLATER DETERMINANTS
- SAME CONFIG., DIFFERENT M_{Li}, M_{Si} VALUES

- GENERAL SOLUTION? MOSTLY:

LS COUPLING

- SIMPLIFY USING SYMMETRIES:

$[H_1, \vec{S}] = 0$ (spin-independent)

$[H_1, \vec{L}] = 0$ (ROTATIONAL SYMMETRY)

⇒ CAN FIND SIMULT. EIG. VECTORS OF $[H_1]$, $\vec{L}^2$, $\vec{S}^2$, L_z, S_z

$|\Psi\rangle = |\ldots (n\ell)^k \; L \; S \; L_z \; S_z\rangle$ "LS COUPLING"

(RUSSELL-SAUNDERS COUPLING)

- USUALLY, ONLY 1 STATE PER L, S, L_z, S_z

(BUT NOT ALWAYS, i.e. FOR SOME d CONFIGS LIKE nd^4)

- ALSO, ENERGY IS INDEP. OF L_z, S_z (BY ROTATIONAL SYM. ABOUT x, y)

INSTEAD OF DIAGONALIZING $[H,]$, FIRST CHANGE TO LS BASIS

- USUALLY, $[H,]$ BECOMES DIAGONAL
  → ENERGY = DIAGONAL ELEMENT
- AT LEAST, $[H,]$ IS BLOCK DIAG. WITH SMALLER BLOCKS

TERM SYMBOLS

- SPECTROSCOPIC NOTATION FOR L, S:

$$^{2S+1}L$$

↳ Letter

- EXAMPLE: Si gnd state has $L=1$, $S=1$
  FIND TERM SYMBOL

$2S+1 = 3$: ^3P

ALLOWED TERMS

- ANGULAR MOM. ADDITION, RESTRICTED BY PAULI

EXAMPLE: He $1s^2$

$N_s = 2(2L+1) = 2$

$k = 2$

$$\binom{N_s}{k} = \frac{2!}{2!(2-2)!} = 1$$

ONLY 1 STATE

TODAY: • ALLOWED LS TERMS
• HUND'S RULES

READING: FOOT 5.0 (LS COUPLING)
3.1-3.2 (Helium)

WARM-UP:

1. GIVEN TWO DISTINGUISABLE SPINS $s_1 = \frac{1}{2}$, $s_2 = \frac{1}{2}$, LET $\vec{S} = \vec{s}_1 + \vec{s}_2$
$\vec{S}^2$ HAS EIG. VALS $\hbar^2 S(S+1)$
FIND ALLOWED S
$S = |s_1 - s_2|, \ldots s_1 + s_2 = \boxed{0, 1}$

2. CALCULATE THE DEGENERACY FOR THE GIVEN ELECTRON CONFIG.S:

a) $1s^2$ (He GND)
$N_s = 2(2l+1) = 2$ (SINGLE-ELECTRON STATES)
$k = 2$ (ELECTRONS)
$\binom{N_s}{k} = \frac{2!}{2!(2-2)!} = \boxed{1}$
ONLY 1 STATE:
$|m_{l1}=0, m_{s1}=\uparrow, m_{l2}=0, m_{s2}=\downarrow\rangle = \frac{1}{\sqrt{2}} u_{1s}(1) u_{1s}(2) \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$
$= \frac{1}{\sqrt{2}} u_{1s}(1) u_{1s}(2) \left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)$

NOTES:
• $|\uparrow\uparrow\rangle$ NOT ALLOWED BY PAULI EXCLUSION
• $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) = |S=0, M_S=0\rangle$: SINGLET STATE
• → He GND STATE IS A SINGLET (^1S)

b) $1s2s$
TWO "GROUPS": 1s, 2s → DISTINGUISHABLE
4 STATES: $|1s\uparrow, 2s\uparrow\rangle$, $|1s\uparrow, 2s\downarrow\rangle$
$|1s\downarrow, 2s\uparrow\rangle$, $|1s\downarrow, 2s\downarrow\rangle$
NOTE: CAN FORM S=0 AND S=1
i.e. ^1S AND ^3S

ALLOWED TERMS FOR EQUIVALENT ELECTRONS $n\ell^k$

- ANGULAR MOM. ADDITION, RESTRICTED BY PAULI
- STRATEGY: COUNTING. SAME # STATES IN DECOUPLED AND LS BASES

EXAMPLE: np^2 $\quad N_s = 2(2\ell+1) = 6$

- $g = \binom{6}{2} = 15$

LIST ALL 15:

#	$m_{\ell 1}$	m_{s1}	$m_{\ell 2}$	m_{s2}	$M_L = m_{\ell 1} + m_{\ell 2}$	$M_S = m_{s1} + m_{s2}$	COUNTED AS: L	S
1	1	$\frac{1}{2}$	1	$-\frac{1}{2}$	2	0	2	0
2	"	"	0	$\frac{1}{2}$	1	1	1	1
3			0	$-\frac{1}{2}$	1	0	2	0
4			-1	$\frac{1}{2}$	0	1	1	1
5			-1	$-\frac{1}{2}$	0	0	2	0
6	1	$-\frac{1}{2}$	0	$\frac{1}{2}$	1	0	1	1
7			0	$-\frac{1}{2}$	1	-1	1	1
8			-1	$\frac{1}{2}$	0	0	1	1
9			-1	$-\frac{1}{2}$	0	-1	1	1
10	0	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	0	0	0
11			-1	$\frac{1}{2}$	-1	1	1	1
12			-1	$-\frac{1}{2}$	-1	0	2	0
13	0	$-\frac{1}{2}$	-1	$\frac{1}{2}$	-1	0	1	1
14			-1	$-\frac{1}{2}$	-1	-1	1	1
15	-1	$\frac{1}{2}$	-1	$-\frac{1}{2}$	-2	0	2	0

- $M_L = 2$, $M_S = 0$ → $L = 2$, $S = 0$ b/c only one $M_L = 2$ state so must have $S = 0$

^1D: $L = 2$, $S = 0$

M_L \ M_S	0
2	✓
1	✓
0	✓
-1	✓
-2	✓

M_L \ M_S	-1	0	1
1	✓	✓	✓
0	✓	✓	✓
-1	✓	✓	✓

$L = 1$, $S = 1$

^3P

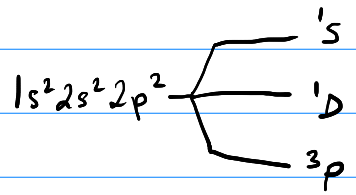
M_L \ M_S	0
0	✓

$L = 0$, $S = 0$

^1S

- SUMMARY: $np^2 \rightarrow {}^1D, {}^3P, {}^1S$ TERMS ALLOWED

EXAMPLE: C (Z=6)



- OTHER CASES TABULATED IN BRANSDEN & JOACHAIN TABLE 7.7
  - EXAMPLE: $np^3 \rightarrow {}^2P, {}^2D, {}^4S$

TODAY: HUND'S RULES

FINE-STRUCTURE IN LS COUPLING

READING: FOOT 5.1

HW2 DUE WED, FEB 23

WARM-UP: FIND ALLOWED TERMS (^{2S+1}L)

1) $1s^2 2s 2p$ (Be^*)

$S = \frac{1}{2} \pm \frac{1}{2} = 0, 1$

$L = 1 \rightarrow P$

2s & 2p NON-EQUIVALENT

$2S+1 = 1, 3$

TERMS: ^3P, ^1P

2) $1s^2 2s^2 2p^4$ (O)

EQUIVALENT np^4 ELECTRONS → ^1S, ^1D, ^3P

3) $1s^2 2s 2p^2$ (B^*)

p^2 ELECTRONS:

TERM	S	L
^1S	0	0
^1D	0	2
^3P	1	1

Add 2s →

TERM	S	L
^2S	$1/2$	0
^2D	$1/2$	2
^2P	$1/2$	1
^4P	$3/2$	1

← Above ionization limit

PREDICTING LS LOWEST-ENERGY STATE

HUND'S RULES (EMPIRICAL)

- FOR CONFIGURATIONS WITH <u>ONE</u> INCOMPLETE SUBSHELL

  LOWEST-ENERGY TERM HAS

  1) LARGEST SPIN (S)
  2) LAGEST L AMONG STATES W/ LARGEST S

EXAMPLE: PREDICT GND STATE LS OF

Ti ($Z=22$)

ELEC. CONFIG. $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,\underline{\underline{3d^2}}$

TAB. 7.7: $nd^2 \rightarrow {}^1S,\ {}^1D,\ {}^1G,\ {}^3P,\ ({}^3F)$

$S=1,\ L=3$

FINE STRUCTURE

- RECALL:

$$H = H_0 + H_{RE} + H_{SO}$$

H_0: CFA; H_{RE}: RESIDUAL ELECTROSTATIC; H_{SO}: SPIN-ORBIT INTERACTION

- ASSUMING $H_{RE} >> H_{SO} \rightarrow$ LS COUPLING

- $H_{SO} \rightarrow$ PERTURBATION OF LS TERMS

DEGENERACY of LS: $|LS\ M_L\ M_S\rangle$

SAME $H_0 + H_{RE}$ ENERGY FOR ALL M_L, M_S (GIVEN LS)

H_{SO}: SPLITS DEGENERACY

SPIN-ORBIT INTERACTION

$$H_{so} = f(r_1)\,\vec{l}_1\cdot\vec{s}_1 + f(r_2)\,\vec{l}_2\cdot\vec{s}_2 + \cdots$$

$$= \sum_{i=1}^{N} f(r_i)\,\vec{l}_i\cdot\vec{s}_i \qquad \text{(SUM OVER ELECTRONS)}$$

DEGENERATE PERT. THEORY: FIND EIG. VALUS/VECS OF MATRIX

$$[H_{so}] = [\langle M_L' M_S' | H_{so} | M_L M_S \rangle]$$

EXAMPLE: Si: $[Ne]3s^2 3p^2$ (^3P)

$S=1,\ L=1 \rightarrow$ DEGENERACY $= 3\times 3 = 9$ STATES

$$[H_{so}] = \begin{bmatrix} \langle 11|H_{so}|11\rangle & \langle 11|H_{so}|10\rangle & \cdots \\ \langle 10|H_{so}|11\rangle & \ddots & \\ \vdots & & \ddots \end{bmatrix}$$

EFFECTIVE HAMILTONIAN

- SAME MATRIX ELEMENTS AS A SIMPLER HAMILTONIAN:

$$\langle M_L' M_S' | H_{so} | M_L M_S \rangle = \langle M_L' M_S' | A_{LS}\,\vec{L}\cdot\vec{S} | M_L M_S \rangle$$

  - A_{LS} = CONST, INDEP. OF M_L', M_S', M_L, M_S
- EFFECTIVE HAMILTONIAN:

$$H_{so}^{(LS)} = A_{LS}\,\vec{L}\cdot\vec{S}$$

- VALID IN LS COUPLING FOR 1ST-ORDER PERT. THEORY

TODAY: HW 2 DUE

FINE STRUCTURE (FOOT 5.1)

WARM-UP: PICK AN ATOM WITH GROUND STATE ELECTRON CONFIGURATION HAVING:

a) ONE ALLOWED LS TERM i.e. F: $1s^2 2s^2 2p^5 \rightarrow {}^2P$

b) MORE THAN ONE LS TERM, AND USE HUND'S RULE TO PREDICT LOWEST-ENERGY TERM

ie S_i: [Ne] $3s^2 3p^2 \rightarrow$ ^3P (GND) MAX S

^1D

^1S

FINE STRUCTURE

- RECALL: H_{so} SPLITS LS TERMS INTO FINE STRUCTURE LEVELS

$$H_{so} = \sum_{i=1}^{N} f(r_i)\, \vec{l}_i \cdot \vec{s}_i$$

- EFFECTIVE HAMILTONIAN:

$$H_{so}^{(LS)} = \beta_{LS}\, \vec{L}\cdot\vec{S}/\hbar^2$$

- VALID IN LS COUPLING FOR 1ST-ORDER PERT. THEORY
- DIAGONALIZE:

$\vec{J} = \vec{L} + \vec{S}$ (TOTAL ELECTRONIC ANGULAR MOMENTUM)

$$\vec{J}^2 = (\vec{L}+\vec{S})\cdot(\vec{L}+\vec{S}) = \vec{L}^2 + 2\vec{L}\cdot\vec{S} + \vec{S}^2$$

$$\Rightarrow \vec{L}\cdot\vec{S} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$$

$$H_{SO}^{(LS)} = \frac{1}{2}\beta_{LS}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right)/\hbar^2$$

DIAGONAL IN $|LSJM_J\rangle$ BASIS

QUANTITY	EIGENVAL
$\vec{J}^2$	$\hbar^2 J(J+1)$
$\vec{L}^2$	$\hbar^2 L(L+1)$
$\vec{S}^2$	$\hbar^2 S(S+1)$

$$E_{SO} = \beta_{LS}\ \frac{1}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

NOTATION: ${}^{2S+1}L_J$ ("LEVEL")

- REMAINING DEGENERACY: M_J

INTERVAL RULE

$$E_{SO}^{(J)} - E_{SO}^{(J-1)} = \frac{\beta_{LS}}{2}\left[J(J+1) - (J-1)J\right]$$
$$= \frac{\beta_{LS}}{2}\left[J^2 + J - J^2 + J\right] = \beta_{LS}\,J$$

$$\Rightarrow E_{SO}^{(J+1)} - E_{SO}^{(J)} = \beta_{LS}(J+1)$$

$$\frac{E_{SO}^{(J+1)} - E_{SO}^{(J)}}{E_{SO}^{(J)} - E_{SO}^{(J-1)}} = \frac{J+1}{J}$$

EXAMPLE: Mg^* $3s3p\ (^3P)$

$E - E_{GND}\ (cm^{-1})$	ΔE	J
21,850	-20	0
21,870	0	1
21,911	41	2

a) LIST POSSIBLE J

$L=1, S=1 \rightarrow J = 0, 1, 2$

b) LABEL LEVELS BY J

BASED ON INTERVAL RULE

$$\frac{E_{so}^{(J+1)} - E_{so}^{(J)}}{E_{so}^{(J)} - E_{so}^{(J-1)}} = \frac{J+1}{J}$$

$$\Rightarrow \frac{E_{so}^{(2)} - E_{so}^{(1)}}{E_{so}^{(1)} - E_{so}^{(0)}} = 2$$

DERIVATION of $\vec{L}\cdot\vec{S}$ INTERACTION

- RECALL:

$$H_{so} = \sum_{i=1}^{N} f(r_i)\, \vec{l}_i \cdot \vec{s}_i$$

$$\rightarrow H_{so}^{(LS)} = \left(\frac{\beta_{LS}}{\hbar^2}\right) \vec{L}\cdot\vec{S}$$

1. Radial part factors out:

$$H_{so} \rightarrow \tilde{H}_{so} = \sum_j \beta_j\, \vec{l}_j \cdot \vec{s}_j \qquad \text{(SUM OVER ELECTRONS IN OPEN SHELLS)}$$

- Effective Hamiltonian (same Matrix el. on this subspace)

$$\langle M_L' M_S' | H_{so} | M_L M_S \rangle = \langle M_L' M_S' | \tilde{H}_{so} | M_L M_S \rangle$$

EXAMPLE: Si $3s^2 3p^2$

$$\tilde{H}_{SO} = \beta_{3p}\, \vec{l}_1 \cdot \vec{s}_1 + \beta_{3p}\, \vec{l}_2 \cdot \vec{s}_2$$

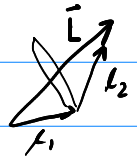
$$\beta_{3p} = \langle f(r) \rangle_{3p} = \int_0^\infty dr \cdot r^2 \, f(r) \, |R_{31}(r)|^2$$

↳ CFA Radial wvfn.

2. KEY STEP: REPLACING $\vec{l}_j \to \vec{L}$, $\vec{s}_j \to \vec{S}$

VECTOR MODEL (CLASSICAL)

- CONSIDER 2 ELECTRONS: $\vec{L} = \vec{l}_1 + \vec{l}_2$
- $\vec{L}$ IS CONSERVED:



- ON AVG, $\langle \vec{l}_1 \rangle = P_{ROJ_{\vec{L}}}(\vec{l}_1) = \left(\frac{\vec{l}_1 \cdot \vec{L}}{|\vec{L}|} \right) \frac{\vec{L}}{|L|} \propto \vec{L}$

QUANTUM: PROJECTION THEOREM

$$\langle M_L' | \vec{l}_j | M_L \rangle = \frac{\langle \vec{l}_j \cdot \vec{L} \rangle}{\hbar^2 L(L+1)} \langle M_L' | \vec{L} | M_L \rangle = C_L^{(j)} \langle M_L' | \vec{L} | M_L \rangle$$

- HERE, $\langle \vec{l}_j \cdot \vec{L} \rangle = \langle M_L | \vec{l}_j \cdot \vec{L} | M_L \rangle = \langle M_L' | \vec{l}_j \cdot \vec{L} | M_L' \rangle$ (INDEP. OF M_L, M_L')
- SIMILAR FOR $\vec{s}_j$
- PUT TOGETHER:

$$\langle M_L' M_S' | \vec{l}_j \cdot \vec{s}_j | M_L M_S \rangle = \underbrace{\langle M_L' | \vec{l}_j | M_L \rangle}_{\text{SPATIAL}} \cdot \underbrace{\langle M_S' | \vec{s}_j | M_S \rangle}_{\text{SPIN ONLY}}$$

$$= C_L^{(j)} C_S^{(j)} \langle M_L' M_S' | \vec{L} \cdot \vec{S} | M_L M_S \rangle$$

FULL MATRIX ELEMENTS

$$\langle M_L' M_S' | H_{SO} | M_L M_S \rangle = \underbrace{\sum_j \beta_j \, C_L^{(j)} C_S^{(j)}}_{\beta_{LS}} \langle M_L' M_S' | \vec{L}\cdot\vec{S} | M_L M_S \rangle$$

$$= \langle M_L' M_S' | \beta_{LS} \, \vec{L}\cdot\vec{S} | M_L M_S \rangle$$

HUND'S RULE FOR J

3) FOR A GIVEN TERM, ASSUMING ONLY ONE PARTIALLY FILLED SUBSHELL, LOWEST LEVEL HAS:

a) LOWEST J IF SUBSHELL < HALF-FILLED

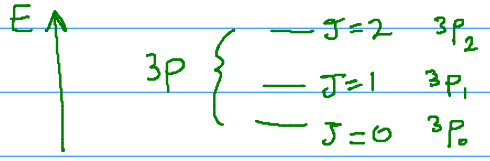
b) HIGHEST J IF SUBSHELL > HALF-FILLED

(c) NO RULE IF HALF-FILLED)

EXERCISE: Si $[Ne]\ 3s^2 3p^2$ (^3P) GND STATE

DRAW ENERGY LEVELS, LABEL THE LEVELS $^{2S+1}L_J$

$S=1,\ L=1 \rightarrow J=0,1,2$



TODAY: HYPERFINE STRUCTURE

READING: FOOT 6.1

PAPER TOPIC PROPOSAL DUE WED, MAR 9

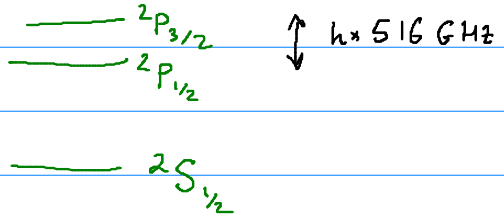
- PARAGRAPH + 1 REFERENCE

WARM-UP: Na (Z=1)

1. FIND ALLOWED L, S, J FOR
   a) GND: [Ne] 3s $L=0, S=\frac{1}{2}$
   b) Exc.: [Ne] 3p $L=1, S=\frac{1}{2}, J=\frac{1}{2}, \frac{3}{2}$
2. DRAW ENERGY LEVEL DIAGRAM

   LABEL $^{2S+1}L_J$

   - HUND'S RULE FOR J: $J=\frac{1}{2}$ LOWEST

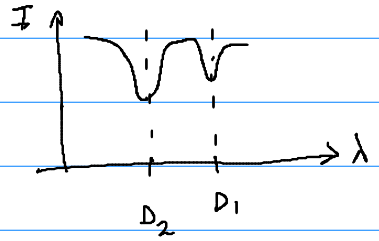


SODIUM DOUBLET

$^2S_{1/2} \rightarrow {}^2P_{1/2}$: $\lambda_{air} = 590$ nm "D1 LINE" (YELLOW)

$^2S_{1/2} \rightarrow {}^2P_{3/2}$: $\lambda_{air} = 589.6$ nm "D2 LINE"

SPECTRUM OF SUNLIGHT



- ABSORPTION BY Na ATOMS IN SUN'S ATMOSPHERE (PHOTOSPHERE)

REVIEW:

CFA → ELECTRON CONFIG, DEGEN. IN $m_{\ell i}, m_{si}$

RESIDUAL ELECTROSTATIC → LS COUPLING

$|L S M_L M_S\rangle$

SPIN-ORBIT INTERACTION $A\vec{L}\cdot\vec{S}$

→ $\vec{J} = \vec{L} + \vec{S}$

LEVELS $|L S J M_J\rangle$

NOW: NUCLEAR SPIN $\vec{I}$

NUCLEAR MAGNETIC MOMENT $\vec{\mu}_I = g_I \mu_N \vec{I}/\hbar$

NUCLEAR MAGNETON: $\mu_N = \frac{e\hbar}{2m_p} = \frac{m_e}{m_p}\mu_B \approx \frac{\mu_B}{1836}$

(PROTON: $g_p \approx 5.6$)

$\vec{\mu}_I$ INTERACTS WITH MAGNETIC FIELD OF ELECTRONS ($\vec{B}_e$)

- $\vec{\mu}_{si}, \vec{\mu}_{Li}$ → MAGNETIC DIPOLES

$H_{HF} = -\vec{\mu}_I \cdot \vec{B}_e$

- VECTOR MODEL: $\vec{\ell}_i, \vec{s}_i$ PRECESS ABOUT $\vec{J}$

⇒ EFFECTIVE $H_{HF}^{(J)} = A\vec{I}\cdot\vec{J}/\hbar^2$

TOTAL INTERNAL ANGULAR MOMENTUM

$\vec{F} = \vec{I} + \vec{J}$

$\vec{F}^2 = (\vec{I}+\vec{J})\cdot(\vec{I}+\vec{J}) = \vec{I}^2 + 2\vec{I}\cdot\vec{J} + \vec{J}^2$

$\Rightarrow H_{HF}^{(J)} = \frac{A}{2\hbar^2}\left[\vec{F}^2 - \vec{I}^2 - \vec{J}^2\right]$

DECOUPLED I, J: $|LSJ\ I\ M_J M_I\rangle$

COUPLED: $|LSJI\ F\ M_f\rangle$

ALLOWED $F = |I-J|, \ldots, I+J$

EXAMPLE: ^{23}Na, $I = \frac{3}{2}$

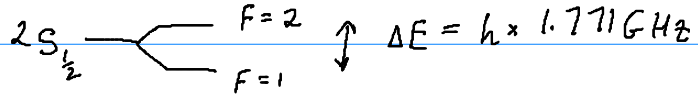
↑ MASS NUMBER (ISOTOPE)

GROUND STATE: $^2S_{1/2}$

- FIND ALLOWED F

$F = 3/2 \pm 1/2 =$ $\boxed{1, 2}$

DIAGRAM:



TODAY: Zeeman effect

READING: Foot 5.5, 6.3

WARM-UP: ELECTRON SPIN IN B FIELD

FIND ENERGY LEVELS vs. B

GIVEN: $H = -\vec{\mu}_s \cdot \vec{B}$

$\vec{\mu}_s = -g_s \mu_B \vec{S}/\hbar$

$g_s \approx 2.0$

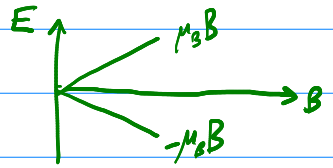
$\vec{B} = B\hat{z}$

SOLUTION:

$H = g_s \mu_B S_z B/\hbar$

EIG. VALUES

$E = \pm g_s \mu_B (\frac{1}{2}) B \approx \boxed{\pm \mu_B B}$



COUPLED SPINS IN $\vec{B}$ FIELD

- Two spins $\vec{S}_1$, $\vec{S}_2$ $\quad \uparrow_{S_1} \ldots \uparrow_{S_2} \quad \Uparrow \vec{B}$
- $H_0 = A\,\vec{S}_1 \cdot \vec{S}_2 / \hbar^2$
- $H' = -\vec{\mu}_1 \cdot \vec{B} - \vec{\mu}_2 \cdot \vec{B} = \frac{\mu_B B}{\hbar}\left(g_1 S_{1z} + g_2 S_{2z}\right)$

FIND ENERGY vs. B

- ASSUME $H' << H_0$
- START WITH H_0 EIG. STATES

$\vec{S} = \vec{S}_1 + \vec{S}_2 \rightarrow S^2, S_z$ EIG. STATES

$H_0 = \frac{A}{2\hbar^2}\left[\vec{S}^2 - \vec{S}_1^2 - \vec{S}_2^2\right]$

DEGENERATE EIG. STATES:

$$H_0 |S M_S\rangle = \frac{A}{2}\left[S(S+1) - S_1(S_1+1) - S_2(S_2+1)\right] |S M_S\rangle$$

EXAMPLE: $S_1 = 1/2$, $S_2 = 1/2$

$S = 0, 1$

E
- $S=1$ ← 3 STATES ($M_S = -1, 0, 1$)
- $S=0$ ← 1 STATE ($M_S = 0$)

H' LIFTS DEGENERACY

$S=1$: $[H']_1 = \begin{pmatrix} \langle 1\,1|H'|1\,1\rangle & \langle 1\,1|H'|1\,0\rangle & \langle 1\,1|H'|1\,-1\rangle \\ \vdots & \vdots & \vdots \end{pmatrix}$ (M_S)

3×3 MATRIX $\Rightarrow$ 3 EIG VALUES

CALCULATING MATRIX ELEMENTS:

$$H' = \frac{\mu_B B}{\hbar}\left(g_1 S_{1z} + g_2 S_{2z}\right)$$

PROJECTION THEOREM (GENERAL)

FOR ANY $\vec{V}$, TOTAL ANG. MOM. $\vec{J}$:

$$\langle J M_J' | \vec{V} | J M_J\rangle = \frac{\langle J|\vec{V}\cdot\vec{J}|J\rangle}{\hbar^2 J(J+1)} \langle J M_J'|\vec{J}|J M_J\rangle$$

$\vec{V} \to \vec{S}_1$, $\vec{J} \to \vec{S}$, z COMPONENT:

$$\langle S M_S'|S_{1z}|S M_S\rangle = \frac{\langle S|\vec{S}_1\cdot\vec{S}|S\rangle}{\hbar^2 S(S+1)} \underbrace{\langle S M_S'|S_z|S M_S\rangle}_{\hbar M_S \delta_{M_S' M_S}}$$

→ DIAG. MATRIX

$\vec{S} = \vec{S}_1 + \vec{S}_2 \to \vec{S}_2 = \vec{S} - \vec{S}_1 \to \vec{S}_2^2 = \vec{S}^2 - 2\vec{S}_1\cdot\vec{S} + \vec{S}_1^2$

$$\vec{S}_1\cdot\vec{S} = \frac{1}{2}\left(\vec{S}^2 + \vec{S}_1^2 - \vec{S}_2^2\right)$$

$$\langle S|\vec{S}_1\cdot\vec{S}|S\rangle = \frac{\hbar^2}{2}\left[S(S+1) + S_1(S_1+1) - S_2(S_2+1)\right]$$

COMBINE:

$$\langle SM_S' | S_{1z} | SM_S \rangle = \underbrace{\frac{S(S+1) + S_1(S_1+1) - S_2(S_2+1)}{2S(S+1)}}_{P_1} \hbar M_S \, \delta_{M_S' M_S}$$

LIKEWISE,

$$\langle SM_S' | S_{2z} | SM_S \rangle = \underbrace{\frac{S(S+1) + S_2(S_2+1) - S_1(S_1+1)}{2S(S+1)}}_{P_2} \hbar M_S \, \delta_{M_S' M_S}$$

ENERGIES:

$$H' = \frac{\mu_B B}{\hbar} \left(g_1 S_{1z} + g_2 S_{2z} \right)$$

EIG. VALS:

$$E(M_S) = \frac{\mu_B B}{\hbar} \underbrace{\left(g_1 P_1 + g_2 P_2 \right)}_{g_{eff}} \hbar M_S = \mu_B B \, g_{eff} \, M_S$$

EFFECTIVE g FACTOR: (WEIGHTED AVG.)

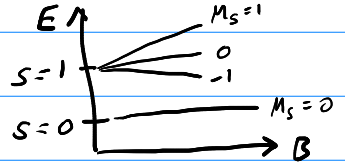
$$g_{eff} = g_1 \frac{S(S+1) + S_1(S_1+1) - S_2(S_2+1)}{2S(S+1)} + g_2 \frac{S(S+1) + S_2(S_2+1) - S_1(S_1+1)}{2S(S+1)}$$

EXAMPLE: $S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$, $S = 0, 1$; $g_1 = g_2 = 2$

$S = 0$: $g_{eff,0} = 0$ (SPINS ANTI-ALIGNED)

$S = 1$: $g_{eff,1} = \frac{2+0}{2} + 1 = 2$ (SPINS ALIGNED)

$$E(S=1, M_S) = 2\mu_B B M_S$$



NOTE: IF $g_1 = g_2$, THEN $g_{eff} = g_1 = g_2$

LS COUPLING

$\vec{L} = \vec{l}_1 + \cdots + \vec{l}_N$	$\vec{S} = \vec{s}_1 + \cdots + \vec{s}_N$
$g_{Li} = 1$	$g_{si} \approx 2.0$
EFFECTIVE: $g_L = 1$	EFFECTIVE: $\rightarrow g_S = 2$

FINE STRUCTURE:

$$\vec{J} = \vec{L} + \vec{S}$$

$$E(M_J) = g_J \mu_B B M_J$$

LANDÉ g FACTOR:

$$g_J = g_L \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} + g_S \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

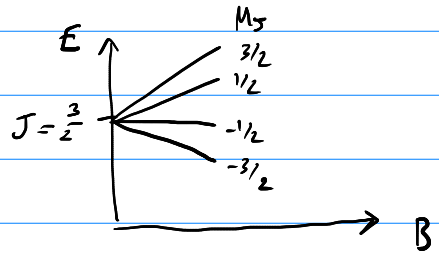
EX: Na $^2P_{3/2}$ EXCITED STATE. FIND g_J AND E vs. B (NEGLECT I)

$L = 1$, $S = 1/2$, $J = 3/2$, $g_L = 1$, $g_S = 2$

$g_J = 4/3$

$\Delta E = \frac{4}{3} \mu_B B M_J$

$M_J = \pm\frac{1}{2}, \pm\frac{3}{2}$



TODAY: WEAK-FIELD (LINEAR) ZEEMAN EFFECT

WARM-UP:

TWO SPINS $\vec{S}_1, \vec{S}_2$; $H_0 = \frac{A}{\hbar^2}\vec{S}_1 \cdot \vec{S}_2$

$S_1 = 1$, $S_2 = 1$, $g_1 = 1$, $g_2 = 2$

FIND ENERGY SHIFT DUE TO MAGNETIC FIELD $\vec{B} = B\hat{z}$ (FIRST ORDER)

FOR $S = 0, 1, 2$ [SOLVE IN GROUPS]

a) $S = 0$

$H' = \mu_B B(g_1 S_{1z} + g_2 S_{2z})/\hbar$

$E' = \langle H' \rangle = \boxed{0}$

WIGNER-ECKART THEOREM:

$\langle S=0, M_S=0 | S_{1z} | S=0, M_S=0 \rangle = 0$

b) $S = 1$

$$g_{eff} = g_1 \frac{S(S+1) + S_1(S_1+1) - S_2(S_2+1)}{2S(S+1)} + g_2 \frac{S(S+1) + S_2(S_2+1) - S_1(S_1+1)}{2S(S+1)}$$

$= 1 \times \frac{1}{2} + 2 \times \frac{1}{2} = 3/2$

$E' = g_{eff}\mu_B B M_S = \frac{3}{2}\mu_B B M_S = \boxed{0, \pm\frac{3}{2}\mu_B B}$

c) $S = 2$

$g_{eff} = \ldots = 3/2$

$E' = \frac{3}{2}\mu_B B M_S = \boxed{0, \pm\frac{3}{2}\mu_B B, \pm 3\mu_B B}$

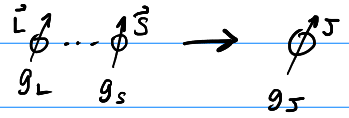
EFFECTIVE g FACTOR IN LS COUPLING (g_J)

- FOOT 5.5
- $\vec{J} = \vec{L} + \vec{S}$

EFFECTIVE SPIN-ORBIT INTERACTION : $H_{SO} = \frac{\beta}{\hbar^2} \vec{L} \cdot \vec{S}$

→ LEVELS $^{2S+1}L_J$

EACH J HAS EFFECTIVE (LANDÉ) g_J:



$$g_J = g_L \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} + g_S \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

($g_L \to 1$, $g_S \to 2$)

$$= \boxed{\frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}}$$

EXAMPLE: Na excited state [Ne]3p $^2P_{1/2}$

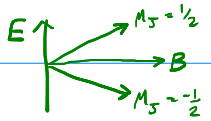
a) FIND g_J

$L = 1, S = \frac{1}{2}, J = \frac{1}{2}$

$$g_J = \frac{3}{2} + \frac{\frac{1}{2}\cdot\frac{3}{2} - 2}{\frac{1}{2} + \frac{2}{2}} = \frac{3}{2} + \frac{\overbrace{\frac{3}{4} - \frac{8}{4}}^{-5/4}}{3/2} = \frac{3}{2} - \frac{5}{6} = \frac{18-10}{12} = \boxed{\frac{2}{3}}$$

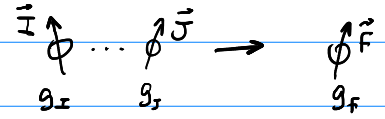
b) PLOT E VS. B IGNORING NUCLEAR SPIN

$E' = g_J \mu_B B M_J = \pm \frac{1}{3} \mu_B B$



HYPERFINE g FACTOR

- FOOT 6.3-1
- HYPERFINE INTERACTION: $H_{hf} = \frac{A}{\hbar^2} \vec{I} \cdot \vec{J}$



For $g_I \approx 0$, $g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)}$

EXAMPLE: ^{23}Na $(I = \frac{3}{2})$, $^2P_{1/2}$ excited state

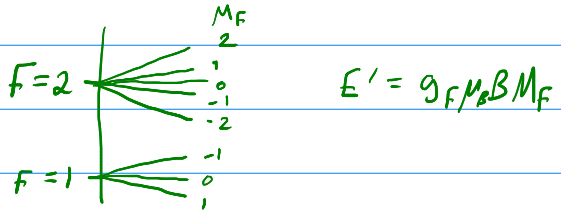
FIND F, g_F (RECALL: $g_J = 2/3$)

a) $F = |I-J|, \ldots I+J = 1, 2$

b) $g_{F=1} = -1/6$

c) $g_{F=2} = 1/6$

d) Sketch E vs. B in weak B field



$E' = g_F \mu_B B M_F$

NOTE: ENERGY OF $F=2$, $M_F = \pm 2$ $= \pm \frac{1}{3} \mu_B B$

- SAME AS WITHOUT NUCLEUS (STRETCHED STATES: FULLY POLARIZED)

TODAY: · HYPERFINE PASCHEN-BACK EFFECT (6.3.2)
· INTERMEDIATE FIELD (6.3.3)

WARM-UP: FOR ^{23}Na $^2P_{1/2}$ excited state, $A_{hf} = h \cdot 94.4\,MHz$

FIND B (in Gauss) such that $\mu_B B = A_{hf}$. $(1G = 10^{-4}\,T)$.

GIVEN $\mu_B/h \approx 1.40\,MHz/G$

SOLUTION: $B = A/\mu_B = \frac{94.4\,MHz}{1.4\,MHz/G} = \boxed{67.4\,G}$

· This roughly where we transition from low- to high- field

HYPERFINE STRUCTURE AT HIGH $\vec{B}$ FIELD

· $H_{hf} = \frac{A}{\hbar^2}\vec{I}\cdot\vec{J}$

· $H_{Zeeman} = \frac{\mu_B B}{\hbar}(g_J J_z + g_I I_z) \approx \frac{\mu_B B}{\hbar} g_J J_z$

· HIGH FIELD: $\mu_B B \gg A$

· DIAGONALIZE $H_{Zeeman} \rightarrow |M_I M_J\rangle$ BASIS

· NON-DEGENERATE PERT. THEORY:

$$E \approx \langle H_{hf} + H_{Zeeman} \rangle = \left\langle M_I M_J \left| \frac{A}{\hbar^2}\vec{I}\cdot\vec{J} + \frac{\mu_B B}{\hbar} g_J J_z \right| M_I M_J \right\rangle$$

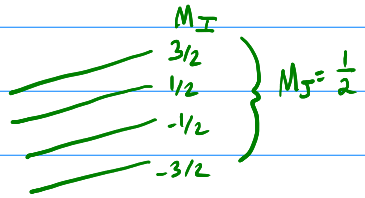
$$= A M_I M_J + \mu_B B g_J M_J$$

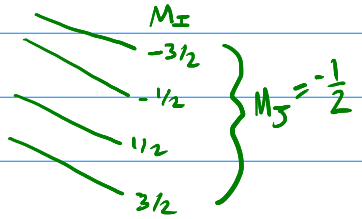
EXAMPLE: ^{23}Na $[Ne]3p\ ^2P_{1/2}$ excited state

GIVEN: $I = 3/2$, $g_J = 2/3$, $\mu_B B \gg A$

a) LIST EIG. STATES $|M_I M_J\rangle$ FROM HIGH TO LOW ENERGY

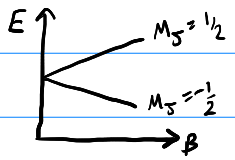
b) SKETCH E vs. B for $\mu_B B \gg A$; LABEL M_I, M_J



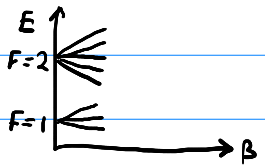


REVIEW: OTHER LIMITS

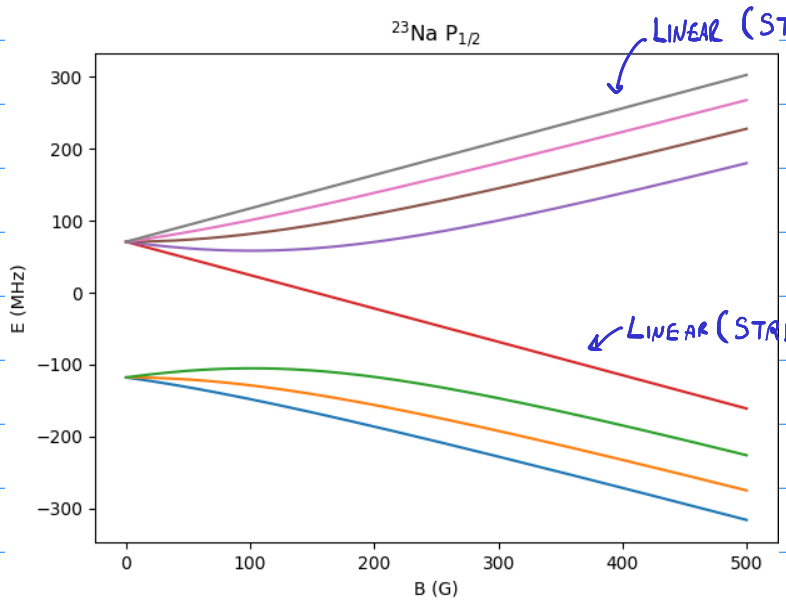
1. NO NUCLEUS:



2. LOW-B HF



EXACT:



EXACT SOLUTION

- $H = \frac{A}{\hbar^2}\vec{I}\cdot\vec{J} + \frac{\mu_B B}{\hbar} g_J J_z$

- $F_z = I_z + J_z$

- $[H, F_z] = 0 \rightarrow$ SIMULTANEOUS EIG. STATES

- USE $|M_I M_J\rangle$ BASIS: $F_z |M_I M_J\rangle = \hbar(M_I + M_J)|M_I M_J\rangle$
- LET $M_F = M_I + M_J$
  $\Rightarrow M_f = -2, -1, 0, 1, 2$

1. STRETCHED STATES

$M_f = 2$:

ONLY $M_I = \frac{3}{2}, M_J = \frac{1}{2} \rightarrow$ MUST BE AN EIG. STATE

EIG. VAL:

$\vec{I}\cdot\vec{J} = \frac{1}{2}(I_+ J_- + I_- J_+) + I_z J_z \quad \left(I_\pm = I_x \pm i I_y,\ J_\pm = J_x \pm i J_y\right)$

$$H\left|\tfrac{3}{2}\tfrac{1}{2}\right\rangle = \left\{\frac{A}{\hbar^2}\left[\frac{1}{2}\left(\cancel{I_+ J_-}^{\,0} + I_- \cancel{J_+}^{\,0}\right) + I_z J_z\right] + \frac{\mu_B B}{\hbar} g_J J_z\right\}\left|M_I = \tfrac{3}{2}, M_J = \tfrac{1}{2}\right\rangle$$

$$= \left(A IJ + \mu_B B g_J J\right)\left|M_I = I, M_J = J\right\rangle$$

$M_f = \pm(I+J)$:

$$\boxed{E_{M_f = \pm(I+J)} = AIJ \pm \mu_B B(g_J J + g_I I)}$$

STRETCHED STATES

FOR OUR EXAMPLE, $I = \frac{3}{2}, J = \frac{1}{2}$

$$\rightarrow E_\pm = \frac{3}{4}A \pm \frac{2}{3}\left(\frac{1}{2}\right)\mu_B B$$

2. OTHER STATES

EXAMPLE: $M_f = 1$

TWO BASIS STATES: $|M_I = \frac{3}{2},\ M_J = \frac{-1}{2}\rangle \equiv |\alpha\rangle$

$|M_I = \frac{1}{2},\ M_J = \frac{1}{2}\rangle \equiv |\beta\rangle$

IN GENERAL,

- FOR $J = \frac{1}{2}$, AT MOST TWO BASIS STATES

EIGENSTATES FOR GIVEN M_f ARE A LINEAR COMBINATION:

$$|\psi\rangle = a|\alpha\rangle + b|\beta\rangle$$

SOLVE: $H|\psi\rangle = E|\psi\rangle$

GIVES A MATRIX EIG.VAL. PROBLEM

$$\begin{pmatrix} \langle\alpha|H|\alpha\rangle & \langle\alpha|H|\beta\rangle \\ \langle\beta|H|\alpha\rangle & \langle\beta|H|\beta\rangle \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = E \begin{pmatrix} a \\ b \end{pmatrix}$$

CAN EVALUATE MATRIX ELEMENTS USING

$$J_\pm |jm\rangle = \hbar \sqrt{j(j+1) - m(m\pm1)}\ |j, m\pm1\rangle$$

EIGVALUES (again restoring g_I):

$$E_\pm(M_F) = -\frac{A}{4} + \mu_B B\, g_I M_F \pm \frac{A}{2}\sqrt{z^2 + 2M_F z + (I+\tfrac{1}{2})^2}$$

where $\quad z = \mu_B B\,(g_J - g_I)/A$

ANOTHER EXAMPLE: H GND STATE: $I = \frac{1}{2}$, $J = \frac{1}{2}$; $A = h \cdot 1420\,\text{MHz}$