$\mathbf{H}^{SO} + \mathbf{H}^{Zeeman}$ in $|JLSM_J\rangle$ and $|LM_LSM_S\rangle$

Last time:

$$\mathbf{H}^{SO} = \zeta\boldsymbol{\ell}\cdot\mathbf{s} \qquad \rightarrow |JLSM_J\rangle$$
$$\mathbf{H}^{Zeeman} = -\gamma B_z(\mathbf{L}_Z + 2\mathbf{S}_Z) \qquad \rightarrow |LM_L\rangle|SM_S\rangle$$

OK to set up **H** in either basis

problem about $\mathbf{H}^{Zeeman}$ in Coupled Basis → need to work out explicit transformation between basis sets to evaluate matrix elements of $\mathbf{H}^{Zeeman}$ in coupled basis.

Today:

1. Ladders and Orthogonality method for $|JLSM_J\rangle \leftrightarrow |LM_LSM_S\rangle$ (coupled↔uncoupled) transformation, term by term.

2. evaluate $\mathbf{H}^{Zeeman}$ in coupled basis for ^2P state.

3. Correlation Diagram, Noncrossing Rule
   * simple patterns without calculations
   * guidance for "intermediate case"

   War between two limits
   * one term creates $\Delta E_{ij}^{(0)} \neq 0$
   * other term causes $H_{ij}^{(1)} \neq 0$

   The two terms play opposite roles in the two basis sets.

4. Stepwise picture of level structure working out from 2 opposite limits
   * strong spin-orbit, weak Zeeman
   * strong Zeeman, weak spin-orbit

   Distortions from limiting patterns (via 2nd-order nondegenerate perturbation theory) give the "other" (pattern distorting) parameter.

   How does a zero-order picture identify the "picture defining" and the "picture destroying parameters.

$$\mathrm{H}^{\text{Zeeman}} = -\gamma B_z\left(\mathbf{L}_z + 2\mathbf{S}_z\right) = -\gamma B_z\left(\mathbf{J}_z + \mathbf{S}_z\right)$$

$\mathbf{J}_z$: OK; $\mathbf{S}_z$: Not OK — for coupled basis

to evaluate matrix elements of $\mathbf{L}_z$ or $\mathbf{S}_z$ in $\left|JLSM_J\right\rangle$

need to work out $\left|JLSM_J\right\rangle = \sum\limits_{M_L} a_{m_L}\left|LM_L\right\rangle\left|SM_S = M_J - M_L\right\rangle$

ladders and orthogonality $\quad \mathbf{J}_{\pm} = \cdots_{\pm} + \mathbf{S}_{\pm}$

begin with "extreme" $\mathrm{J} = \mathrm{L} + \mathrm{S}\ \ \mathrm{M_J} = \mathrm{J};\ \ \mathrm{M_L} = \mathrm{L},\ \ \mathrm{M_S} = \mathrm{S}$
basis states where there is a 1:1 correspondence

$$\left|JLSM_J = J\right\rangle = \left|LM_L = L\right\rangle\left|SM_S = S\right\rangle \qquad (J = \mathrm{L} + \mathrm{S})$$

$$\mathbf{J}_-\left|L+S\ \ L\ \ S\ \ L+S\right\rangle = \left(\mathbf{L}_- + \mathbf{S}_-\right)\left|LL\right\rangle\left|SS\right\rangle$$

$$\left[(L+S)(L+S+1) - (L+S)(L+S-1)\right]^{1/2}\left|L+S\ \ L\ \ S\ \ L+S-1\right\rangle =$$
$$\left[L(L+1) - L(L-1)\right]^{1/2}\left|LL-1\right\rangle\left|SS\right\rangle + \left[S(S+1) - S(S-1)\right]^{1/2}\left|LL\right\rangle\left|SS-1\right\rangle$$

$$\left|L+S\ \ L\ \ S\ \ L+S-1\right\rangle = \frac{\left[2L\right]^{1/2}\left|LL-1\right\rangle\left|SS\right\rangle + \left[2S\right]^{1/2}\left|LL\right\rangle\left|SS-1\right\rangle}{\left[2(L+S)\right]^{1/2}}$$

$$\left|L+S\ \ L\ \ S\ \ L+S-1\right\rangle = \left(\frac{L}{L+S}\right)^{1/2}\left|LL-1\right\rangle\left|SS\right\rangle + \left(\frac{S}{L+S}\right)^{1/2}\left|LL\right\rangle\left|SS-1\right\rangle$$

for ^{2}P $L = 1$, $S = 1/2$

$$\boxed{\left|3/2\ \ 1\ \ 1/2\ \ 1/2\right\rangle_{\mathrm{c}} = \left(\frac{2}{3}\right)^{1/2}\left|1\ \ 0\right\rangle\left|\frac{1}{2}\ \ \frac{1}{2}\right\rangle_{\mathrm{u}} + \left(\frac{1}{3}\right)^{1/2}\left|11\right\rangle\left|\frac{1}{2} - \frac{1}{2}\right\rangle_{\mathrm{u}}}$$

orthogonality: there are only 2 $\mathrm{M_J} = 1/2$ possibilities, J = 3/2 and J = 1/2 for specified L,S

$$\left|\frac{1}{2}1\frac{1}{2}\frac{1}{2}\right\rangle = -\left(\frac{1}{3}\right)^{1/2}|10\rangle\left|\frac{1}{2}\frac{1}{2}\right\rangle + \left(\frac{2}{3}\right)^{1/2}|11\rangle|1/2-1/2\rangle$$

(I always choose – sign in front of smaller coefficient - arbitrary phase choice)

Nonlecture: Summary for ^{2}P (coupled → uncoupled)

$$\left|\frac{3}{2}1\frac{1}{2}\frac{3}{2}\right\rangle = \left|11\frac{1}{2}\frac{1}{2}\right\rangle$$

$$\left|\frac{3}{2}1\frac{1}{2}\frac{1}{2}\right\rangle = \left(\frac{2}{3}\right)^{1/2}\left|10\frac{1}{2}\frac{1}{2}\right\rangle + \left(\frac{1}{3}\right)^{1/2}\left|11\frac{1}{2}-\frac{1}{2}\right\rangle = \begin{pmatrix}(2/3)^{1/2}\\(1/3)^{1/2}\end{pmatrix}_u$$

$$\left|\frac{1}{2}1\frac{1}{2}\frac{1}{2}\right\rangle = -\left(\frac{1}{3}\right)^{1/2}\left|10\frac{1}{2}\frac{1}{2}\right\rangle + \left(\frac{2}{3}\right)^{1/2}\left|11\frac{1}{2}-\frac{1}{2}\right\rangle = \begin{pmatrix}-(1/3)^{1/2}\\(2/3)^{1/2}\end{pmatrix}_u$$

continue down to $M_J = -1/2$, $M_J = -3/2$ (or start at $M_J = -3/2$ and ladder up.

Now work in Coupled Representation for $\mathbf{H}^{SO} + \mathbf{H}^{Zeeman}$

$$\mathbf{H}^{SO} + \mathbf{H}^{Zeeman} = \underbrace{\frac{\zeta_{n\ell}}{\hbar}\boldsymbol{\ell}\cdot\mathbf{s} - \gamma B_z \mathbf{J}_z}_{\text{diagonal, easy}} - \underbrace{\gamma B_z \mathbf{S}_z}_{}$$

off diagonal in J (can't be off diagonal in L,S,M_J - WHY?)

recall $\left[\begin{array}{l}\boldsymbol{\ell}\cdot\mathbf{s} = \frac{\hbar^2}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]\\ \mathbf{J}_z = \hbar M_J\end{array}\right.$

For ^{2}P, there are 2 2 × 2 $M_J = 1/2$ and $M_J = -1/2$ blocks.

$$\begin{array}{lllll} & J & L & S & M_J \end{array}$$

Evaluate $\langle 3/2 \quad 1 \quad 1/2 \quad 1/2|\mathbf{S}_z|3/2 \quad 1 \quad 1/2 \quad 1/2\rangle$

by inserting the above transformation into the uncoupled basis set.

$$\left[\frac{2}{3}\langle \overset{L}{1} \quad \overset{M_L}{0} \quad \overset{S}{1/2} \quad \overset{M_S}{1/2}|\mathbf{S}_z|1 \quad 0 \quad 1/2 \quad 1/2\rangle + \frac{1}{3}\langle 1 \quad 1 \quad 1/2 \quad -1/2|\mathbf{S}_z|1 \quad 1 \quad 1/2 \quad -1/2\rangle\right] =$$

$$\hbar\left[\left(\frac{2}{3}\right)\left(\frac{1}{2}\right) + \left(\frac{1}{3}\right)\left(-\frac{1}{2}\right)\right] = \hbar\left[\frac{1}{6}\right]$$

THERE ARE NO OFF-DIAGONAL MATRIX ELEMENTS OF H^{Zeeman} IN THE UNCOUPLED BASIS SET.

$$\left\langle 3/2 \quad 1 \quad 1/2 \quad 1/2 \middle| \mathbf{S}_z \middle| 1/2 \quad 1 \quad 1/2 \quad 1/2 \right\rangle = -\frac{2}{3}^{1/2}\left(\frac{1}{2}\right) + \frac{2}{3}^{1/2}\left(-\frac{1}{2}\right) = -\frac{2}{3}^{1/2}$$

etc. for $\mathbf{S}_z$ (^{2}P) Basis State

$$\mathbf{S}_z = \hbar \begin{pmatrix} 1/2 & & & & & \\ & 1/6 & -2^{1/2}/3 & & & \\ & \text{sym} & -1/6 & & & \\ & & & -1/6 & +2^{1/2}/3 & \\ & & & \text{sym} & 1/6 & \\ & & & & & -1/2 \end{pmatrix} \begin{matrix} |3/2 \; 1 \; 1/2 \; 3/2\rangle \\ |3/2 \; 1 \; 1/2 \; 1/2\rangle \\ |1/2 \; 1 \; 1/2 \; 1/2\rangle \\ |3/2 \; 1 \; 1/2 \; -1/2\rangle \\ |1/2 \; 1 \; 1/2 \; -1/2\rangle \\ |3/2 \; 1 \; 1/2 \; -3/2\rangle \end{matrix}$$

(trace $\mathbf{S}_z = 0$)

2 2 × 2's and 2 1 × 1's

[If we had worked in **uncoupled** representation, $\mathbf{H}^{\text{Zeeman}}$ would have been fully diagonal but $\mathbf{H}^{\text{SO}}$ would be 2 2×2's and 2 1×1's. $\mathbf{H}^{\text{Zeeman}}$ produces $\Delta E_{ij}^{(0)} \neq 0$ across which $\mathbf{H}^{\text{SO}}$ has $\text{H}_{ij}^{(1)} \neq 0$.

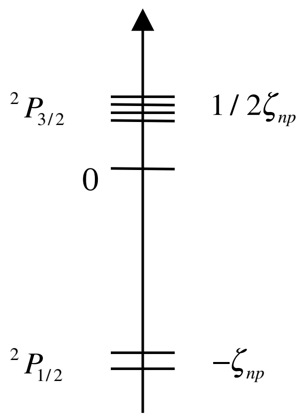
[If we work in coupled representation, $\mathbf{H}^{\text{SO}}$ is diagonal but $\mathbf{H}^{\text{Zeeman}}$ is off - diagonal. $\mathbf{H}^{\text{SO}}$ produces $\Delta E_{ij}^{(0)} \neq 0$ across which $\mathbf{H}^{\text{Zeeman}}$ has $H_{ij}^{(1)} \neq 0$.

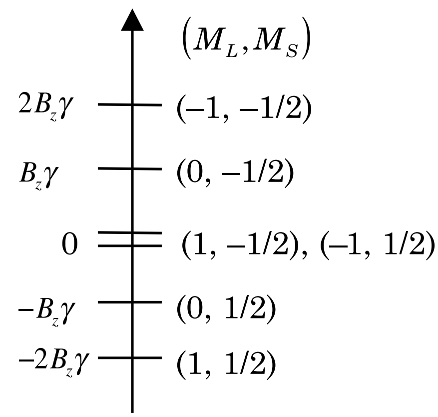
WAR: $\mathbf{H}^{\text{SO}}$ tries to force system to coupled representation
$\mathbf{H}^{\text{Zeeman}}$ tries to force system to uncoupled representation

2 Limiting Cases: weak and strong spin-orbit.

extreme level patterns

$B_z \to 0, \zeta_{n\ell} >> 0$ COUPLED	(connect same — M_J states)	$B_z >> 0, \zeta_{n\ell} \to 0$ UNCOUPLED





correlation diagram: <u>noncrossing rule for M_J</u>: why?
states of same M_J do not cross

In coupled (strong spin-orbit) picture $\mathbf{H}^{\text{Zeeman}}$ is $\mathbf{H}^{(1)}$
In uncoupled picture (strong field) $\mathbf{H}^{\text{SO}}$ is $\mathbf{H}^{(1)}$
^{2}P matrices for $\mathbf{H}^{\text{SO}} + \mathbf{H}^{\text{Zeeman}}$

<u>coupled</u>

$M_J = 3/2 \qquad \zeta/2 - 2\gamma B_z$

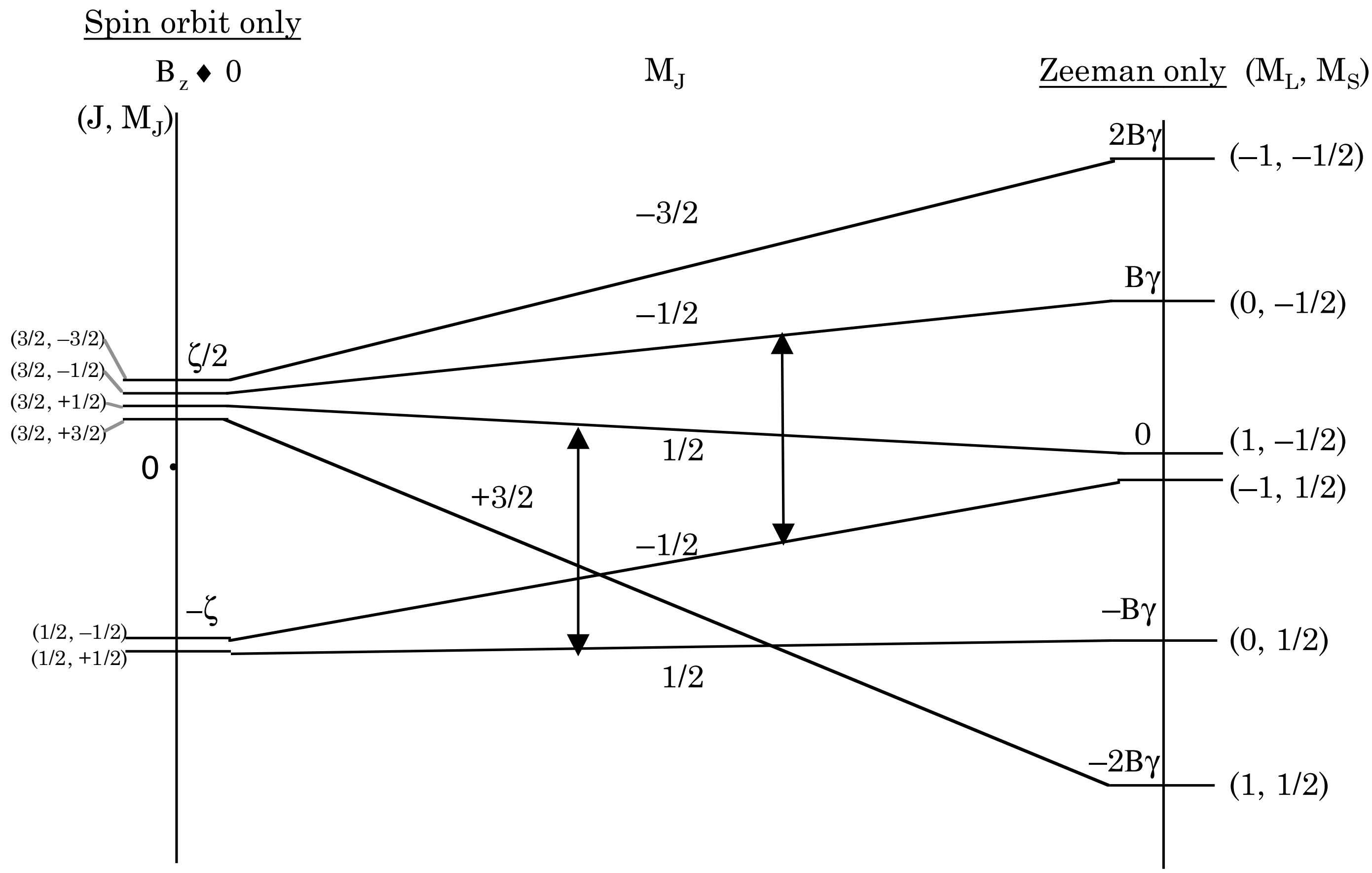
$$M_J = 1/2 \quad \begin{matrix} j = 3/2 \\ j = 1/2 \end{matrix} \begin{pmatrix} \zeta/2 - \frac{2}{3}\gamma B_z & \left(\frac{2}{3}\right)^{1/2}\gamma B_z \\ sym & -\zeta - \frac{1}{3}\gamma B_z \end{pmatrix}$$

<u>uncoupled</u>

$$\zeta/2 - 2\gamma B_z$$

$$M_L, M_S = \begin{matrix} (1,-1/2) \\ (0,1/2) \end{matrix} \begin{pmatrix} -\zeta/2 & 2^{-1/2}\zeta \\ sym & -\gamma B_z \end{pmatrix}$$

CONTINUED AT BOTTOM OF PAGE 26-6



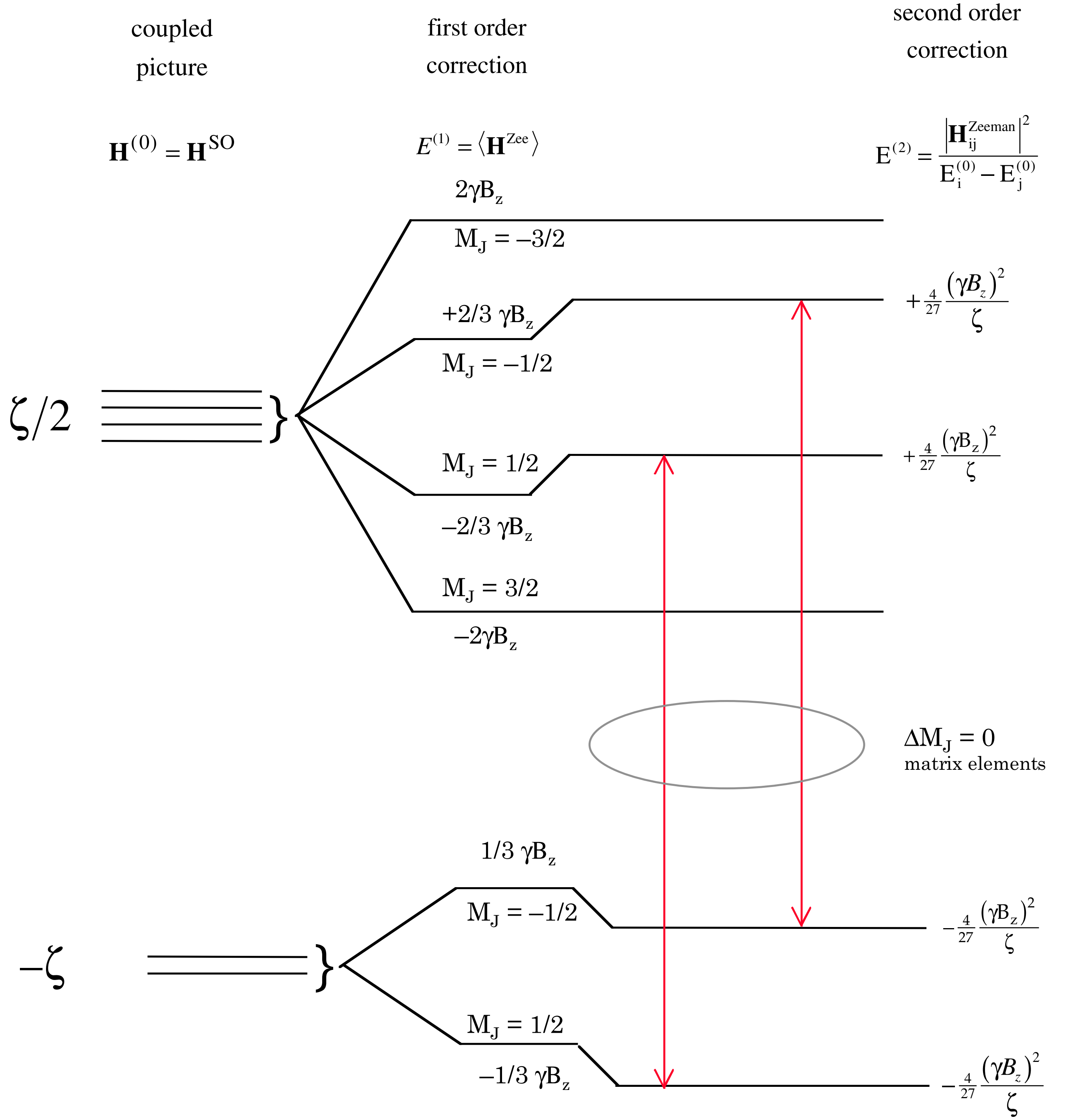
There are only repulsions (shown by vertical arrows) between same-M_J pairs.

coupled	uncoupled
$$E^{\pm}_{M_J=1/2} = \left(-\frac{\zeta}{4} - \frac{\gamma B_z}{2}\right) \pm \left[\frac{9}{16}\zeta^2 + \frac{(\gamma B_z)^2}{4} - \frac{\gamma B_z \zeta}{4}\right]^{1/2}$$	$E_{\pm}$ = same as coupled (even though matrices are different)
$$M_J = -1/2 \quad \begin{matrix} j=3/2 \\ j=1/2 \end{matrix} \begin{pmatrix} \zeta/2 + \frac{2\gamma B_z}{3} & -\frac{2^{1/2}}{3}\gamma B_z \\ sym & -\zeta + \frac{1}{3}\gamma B_z \end{pmatrix}$$	$$\begin{pmatrix} \gamma B_z & 2^{-1/2}\zeta \\ sym & -\zeta/2 \end{pmatrix}$$
$$E^{\pm}_{M_J=-1/2} = \left(-\frac{\zeta}{4} + \frac{\gamma B_z}{2}\right) \pm \left[\frac{9}{16}\zeta^2 + \frac{1}{4}(\gamma B_z)^2 - \frac{\gamma B_z \zeta}{4}\right]^{1/2}$$	$E^{\pm}$ = same as coupled
$E_{M_J} = -3/2$ $\quad \zeta/2 + 2\gamma B_z$	$\zeta/2 + 2\gamma B_z$

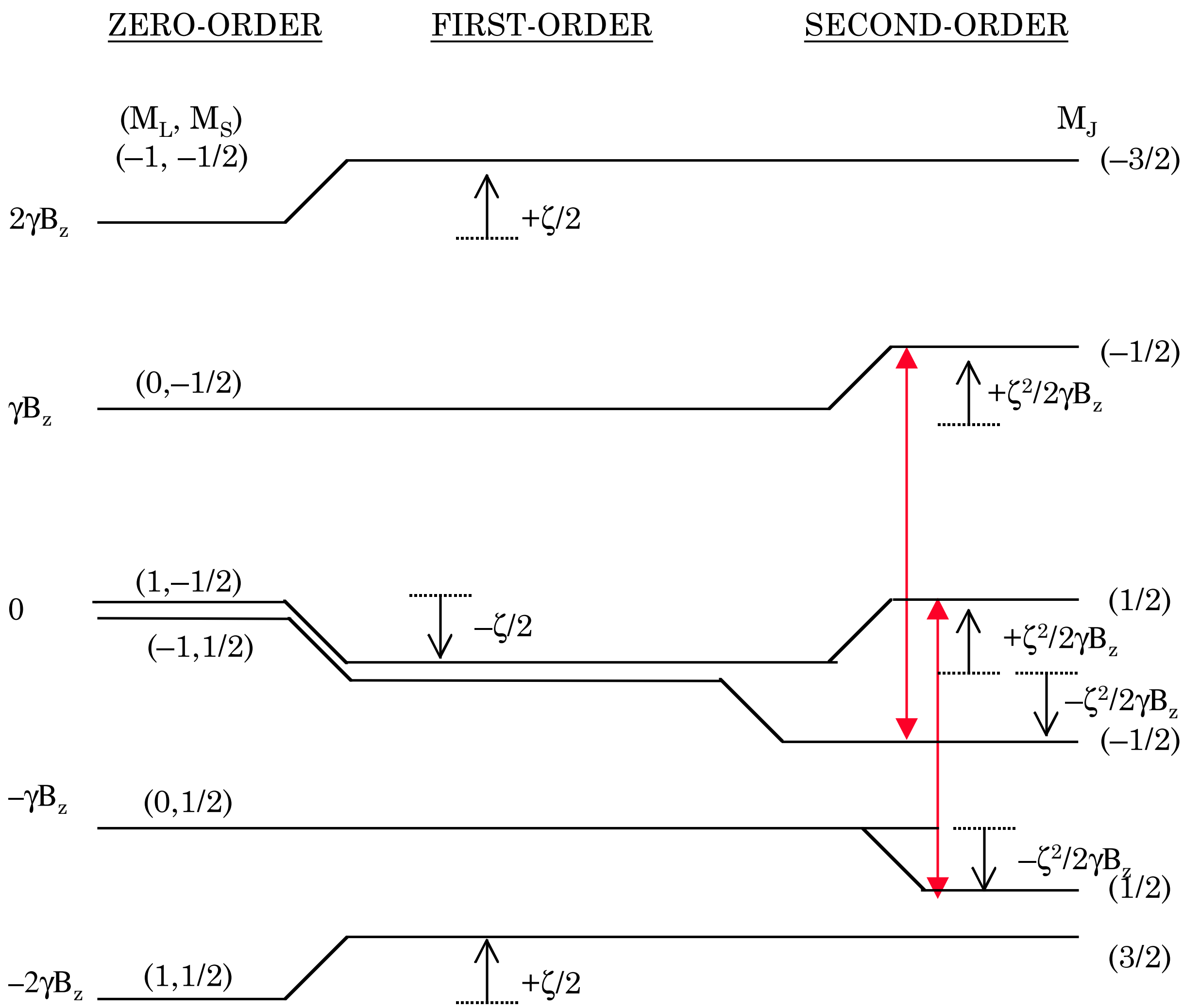
Energy eigenvalues come out to be identical (as they must) in both representations.

Coupled picture is good for 2nd order perturbation theory in the weak field ($|\gamma B| << \zeta_{n\ell}$) limit.

Zeeman splitting (and tuning rates, $\frac{dE}{dB_z}$, as B_z is varied)



Uncoupled picture is good for strong field limit where B_z causes $\vec{L} + \vec{S}$ to uncouple from $\vec{J}$ and into the laboratory (Paschen - Back limit).



Regular Zeeman Pattern.

Small distortions from equal intervals, from which ζ may be determined.

Extra distortions. Repulsions between Same-M_J components

This is a regular Zeeman pattern, but with small distortions (shown as vertical arrors on expanded scale) from equal intervals, from which ζ may be determined.