$\mathbf{H}^{SO} + \mathbf{H}^{Zeeman}$: Two Incompatible Terms

My goal for 5.73

Matrix Elements for any kind of **H**

$\Downarrow$

energies and eigenvectors

$\downarrow$ $\downarrow$

energy level patterns | transition intensity patterns

Non-degenerate Perturbation Theory
Quasi-degenerate Perturbation Theory
Exact diagonalization

$$\rho(t) = \sum_k p_k \left|\psi_k(t)\right\rangle \left\langle\psi_k(t)\right|$$

$$\langle \mathbf{A} \rangle_t = \text{Trace}\left(\text{A}\rho\right)$$

$$i\hbar\frac{\partial\rho}{\partial t} = \left[\mathbf{H},\rho\right]$$

Dynamics.

Previous Lecture

$\mathbf{H}^{SO} = \xi(r)\boldsymbol{\ell}\cdot\mathbf{s}$ product of 2 angular momenta

$\mathbf{H}^{Zeeman} = -\hbar B_z \gamma\left(\mathbf{L}_z + 2\mathbf{S}_z\right)$ sum of 2 angular momenta

2 incompatible **H**'s

Natural basis sets $|nJLSM_J\rangle$ for $\mathbf{H}^{SO}$

$|nLM_L\rangle|SM_S\rangle$ for $\mathbf{H}^{Zeeman}$

Two types of building blocks:

* uncoupled: each angular momentum reports directly to lab frame

* coupled; each angular momentum couples in body frame to a sum-angular momentum which reports to lab frame

There are many angular momenta: decide on most convenient sequences of couplings and uncouplings. 6-j coefficients give transformation between coupling schemes.

For coupled↔uncoupled transformation, need to know that the dimensions of the two basis sets are the same. Unitary transformation must exist because operators are Hermitian.

Use ladders [$\mathbf{J}_\pm = \mathbf{L}_\pm + \mathbf{S}_\pm$] plus orthogonality to work out the transformation, one pair of basis states at a time.

More compact and generally applicable methods will exploit 3-j and 6-j coefficients for transformations between basis states.

Today:

A note before starting: atoms are spherical, space is isotropic, and distortions from angular symmetry and spatial isotropy are treated as small perturbations.

1. Results from $|\mathrm{JLSM_J}\rangle_c \leftrightarrow |\mathrm{LM_LSM_S}\rangle_u$ c = coupled, u = uncoupled

2. $\mathbf{H}^{\mathrm{Zeeman}}$ in coupled basis set.

3. Ways to deal with 2 incompatible terms.

   Easiest way is by Correlation Diagram (guided by non-crossing rule): states of same rigorous symmetry cannot cross. For coupled and uncoupled representations, the rigorous (conserved) symmetry is $\mathrm{M_J}$.

   We get a pattern without calculations. Gives guidance for what to expect in an intermediate case.

   War between 2 limiting cases.

   One term gives $\Delta E_{ij}^{(0)} \neq 0$ which tries to preserve one coupling case and one term gives $H_{ij}^{(1)} \neq 0$ which tries to destroy that limiting case.

4. Stepwise treatment
   A. Correlation Diagram
   B. Non-degenerate Perturbation Theory: $E^{(0)}$, $E^{(1)}$, $E^{(2)}$ using either basis set as framework [which term is $\mathbf{H}^{(0)}$]? The other term contributes to $E^{(1)}$ and $E^{(2)}$.

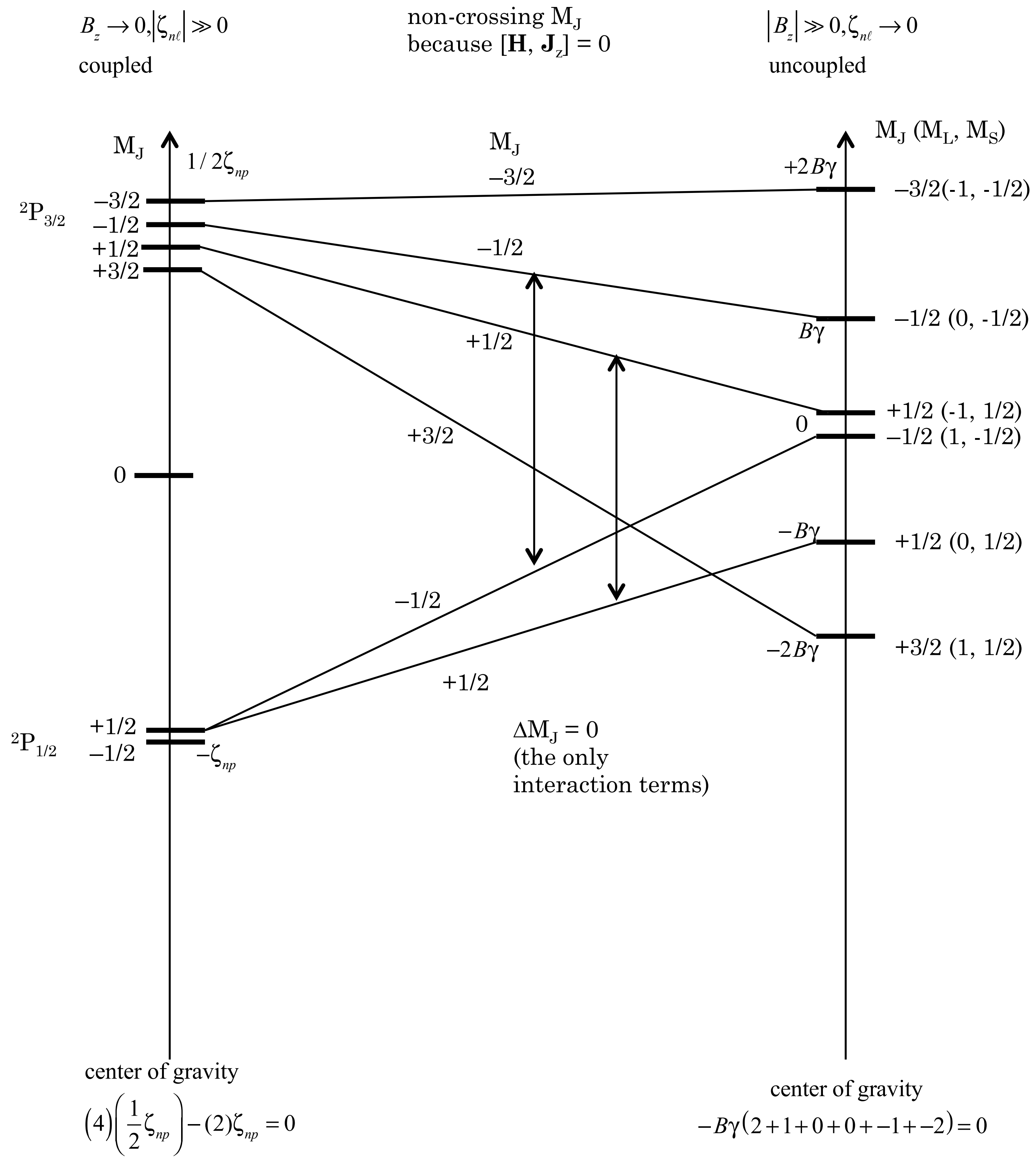
5. Limiting patterns and types of distortion from the simple pattern

   * energy levels
   * transition intensities

   Correlation diagram: left side is $\mathbf{H}^{\mathrm{SO}}$, right side is $\mathbf{H}^{\mathrm{Zeeman}}$.

Typically, there is a center-of-gravity rule for each limit.

^{2}P State Correlation Diagram



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Transformation Uncoupled↔Coupled for $\mathbf{H}^{\text{Zeeman}}$

$$\mathbf{H}^{\text{SO}} + \mathbf{H}^{\text{Zeeman}} = \frac{\zeta_{n\ell}}{\hbar}\,\ell\cdot\mathbf{s} - \gamma B_z\left(\mathbf{L}_z + 2\mathbf{S}_z\right)$$

In coupled basis set

$$\mathbf{H}^{\text{SO}} = \frac{\hbar\zeta_{n\ell}}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

$\mathbf{H}^{\text{Zeeman}}$ need to use coupled→uncoupled transformation

$$
\begin{array}{lcl}
|JLSM_J\rangle_c & & |LM_LSM_S\rangle_u \\
\left|\frac{3}{2}1\frac{1}{2}\frac{3}{2}\right\rangle_c & = & \left|11\frac{1}{2}\frac{1}{2}\right\rangle_u \\
\left|\frac{3}{2}1\frac{1}{2}\frac{1}{2}\right\rangle_c & = & \left(\frac{2}{3}\right)^{1/2}\left|10\frac{1}{2}\frac{1}{2}\right\rangle_u + \left(\frac{1}{3}\right)^{1/2}\left|11\frac{1}{2}-\frac{1}{2}\right\rangle_u \\
\left|\frac{1}{2}1\frac{1}{2}\frac{1}{2}\right\rangle_c & = & -\left(\frac{1}{3}\right)^{1/2}\left|10\frac{1}{2}\frac{1}{2}\right\rangle_u + \left(\frac{2}{3}\right)^{1/2}\left|11\frac{1}{2}-\frac{1}{2}\right\rangle_u \\
\left|\frac{3}{2}1\frac{1}{2}-\frac{1}{2}\right\rangle_c & = & \left(\frac{2}{3}\right)^{1/2}\left|10\frac{1}{2}-\frac{1}{2}\right\rangle_u + \left(\frac{1}{3}\right)^{1/2}\left|1-1\frac{1}{2}\frac{1}{2}\right\rangle_u \\
\left|\frac{1}{2}1\frac{1}{2}-\frac{1}{2}\right\rangle_c & = & -\left(\frac{1}{3}\right)^{1/2}\left|10\frac{1}{2}-\frac{1}{2}\right\rangle_u + \left(\frac{2}{3}\right)^{1/2}\left|1-1\frac{1}{2}\frac{1}{2}\right\rangle_u \\
\left|\frac{3}{2}1\frac{1}{2}-\frac{3}{2}\right\rangle_c & = & \left|1-1\frac{1}{2}-\frac{1}{2}\right\rangle_u
\end{array}
$$

Matrix Elements of $\mathbf{H}^{\text{Zeeman}}$ in Coupled Basis

diagonal $${}_c\left\langle \frac{3}{2}1\frac{1}{2}\frac{3}{2}\middle|\mathbf{H}^{\text{Zeeman}}\middle|\frac{3}{2}1\frac{1}{2}\frac{3}{2}\right\rangle_c = -\gamma B_z\ {}_u\left\langle 11\frac{1}{2}\frac{1}{2}\middle|\mathbf{L}_z+2\mathbf{S}_z\middle|11\frac{1}{2}\frac{1}{2}\right\rangle_u$$
$$= -\hbar\gamma B_z(1+1) = -2\hbar\gamma B_z$$

$${}_c\left\langle \frac{3}{2}1\frac{1}{2}-\frac{3}{2}\middle|\mathbf{H}^{\text{Zeeman}}\middle|\frac{3}{2}1\frac{1}{2}-\frac{3}{2}\right\rangle_c = -\gamma B_z\ {}_u\left\langle 1-1\frac{1}{2}-\frac{1}{2}\middle|\mathbf{L}_z+2\mathbf{S}_z\middle|1-1\frac{1}{2}-\frac{1}{2}\right\rangle_u$$
$$= -\hbar\gamma B_z(-1+-1) = 2\hbar\gamma B_z$$

$${}_c\left\langle \frac{3}{2}1\frac{1}{2}\frac{1}{2}\middle|\mathbf{H}^{\text{Zeeman}}\middle|\frac{3}{2}1\frac{1}{2}\frac{1}{2}\right\rangle_c = -\gamma B_z\left[\left(\frac{2}{3}\right)_u\left\langle 10\frac{1}{2}\frac{1}{2}\middle|\mathbf{L}_z+2\mathbf{S}_z\middle|10\frac{1}{2}\frac{1}{2}\right\rangle_u + \left(\frac{1}{3}\right)_u\left\langle 11\frac{1}{2}-\frac{1}{2}\middle|\mathbf{L}_z+2\mathbf{S}_z\middle|11\frac{1}{2}-\frac{1}{2}\right\rangle_u\right]$$
$$= -\hbar\gamma B_z\left[\frac{2}{3}(0+1)+\frac{1}{3}(1-1)\right]$$
$$= -\frac{2}{3}\hbar\gamma B_z$$

$${}_c\left\langle \frac{1}{2}1\frac{1}{2}\frac{1}{2}\middle|\mathbf{H}^{\text{Zeeman}}\middle|\frac{1}{2}1\frac{1}{2}\frac{1}{2}\right\rangle_c = -\gamma B_z\left[\left(\frac{1}{3}\right)_u\left\langle 10\frac{1}{2}\frac{1}{2}\middle|\mathbf{L}_z+2\mathbf{S}_z\middle|10\frac{1}{2}\frac{1}{2}\right\rangle_u + \frac{2}{3}\left\langle 11\frac{1}{2}-\frac{1}{2}\middle|\mathbf{L}_z+2\mathbf{S}_z\middle|11\frac{1}{2}-\frac{1}{2}\right\rangle\right]$$
$$= -\hbar\gamma B_z\left[\frac{1}{3}(0+1)+\frac{2}{3}(1-1)\right] = -\frac{1}{3}\hbar\gamma B_z$$

off-diagonal $${}_c\left\langle \frac{3}{2}1\frac{1}{2}\frac{1}{2}\middle|\mathbf{H}^{\text{Zeeman}}\middle|\frac{1}{2}1\frac{1}{2}\frac{1}{2}\right\rangle_c = -\hbar\gamma B_z\left[-\frac{2}{3}^{1/2}(0+1)+\frac{2}{3}^{1/2}(1-1)\right] = +\frac{2}{3}^{1/2}\hbar\gamma B_z$$

$${}_c\left\langle \frac{3}{2}1\frac{1}{2}-\frac{1}{2}\middle|\mathbf{H}^{\text{Zeeman}}\middle|\frac{3}{2}1\frac{1}{2}-\frac{1}{2}\right\rangle_c = -\hbar\gamma B_z\left[\frac{2}{3}(0-1)+\frac{1}{3}(-1+1)\right] = +\frac{2}{3}\hbar\gamma B_z$$

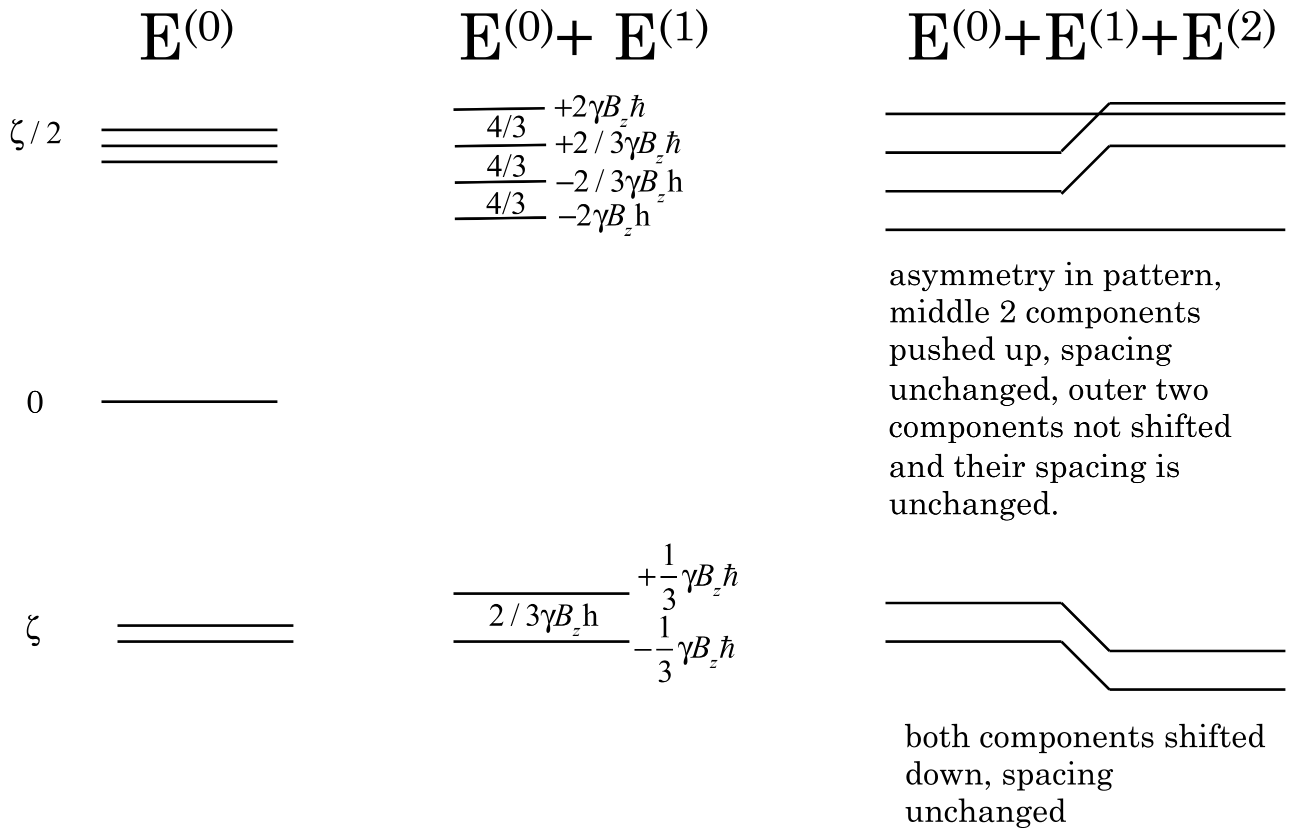
$${}_c\left\langle \frac{1}{2}1\frac{1}{2}-\frac{1}{2}\middle|\mathbf{H}^{\text{Zeeman}}\middle|\frac{1}{2}1\frac{1}{2}-\frac{1}{2}\right\rangle_c = -\hbar\gamma B_z\left[\frac{1}{3}(0-1)+\frac{2}{3}(-1+1)\right] = +\frac{1}{3}\hbar\gamma B_z$$

$${}_c\left\langle \frac{3}{2}1\frac{1}{2}-\frac{1}{2}\middle|\mathbf{H}^{\text{Zeeman}}\middle|\frac{1}{2}1\frac{1}{2}-\frac{1}{2}\right\rangle_c = -\hbar\gamma B_z\left[-\frac{2}{3}(0-1)\right] = -\hbar\gamma B_z\left(\frac{2}{3}^{1/2}\right)$$

$${}_c\left\langle \frac{3}{2}1\frac{1}{2}-\frac{3}{2}\middle|\mathbf{H}^{\text{Zeeman}}\middle|\frac{3}{2}1\frac{1}{2}-\frac{3}{2}\right\rangle_c = +2\hbar\gamma B_z$$

$$\mathbf{H}^{\text{Zeeman}} = \hbar\gamma B_z \begin{pmatrix} -2 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{2}{3} & -\frac{2}{3}^{1/2} & 0 & 0 & 0 \\ 0 & -\frac{2}{3}^{1/2} & -\frac{1}{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{2}{3} & \frac{2}{3}^{1/2} & 0 \\ 0 & 0 & 0 & \frac{2}{3}^{1/2} & \frac{1}{3} & 0 \\ 0 & 0 & 0 & 0 & 0 & +2 \end{pmatrix}$$

Now that we have the full $\mathbf{H}^{\text{Zeeman}}$ matrix in the coupled basis set, we can analyze it by non-degenerate perturbation theory in the strong spin-orbit limit.



What about eigenvectors? Relative intensities of transitions into shifted components are altered.

You should draw a similar diagram for the strong Zeeman limit.

Coupled **H**

$$
\begin{array}{lll}
m_J = 3/2 & & \boxed{\zeta/2 - 2\gamma B_z} \\[1em]
m_J = 1/2 & \begin{array}{c} J=3/2 \\ J=1/2 \end{array} & \boxed{\begin{array}{cc} \zeta/2 - \frac{2}{3}\gamma B_z & \frac{2^{1/2}}{3}\gamma B_z \\ sym & -\zeta - \frac{1}{3}\gamma B_z \end{array}} \\[1em]
m_J = -1/2 & \begin{array}{c} J=3/2 \\ J=1/2 \end{array} & \boxed{\begin{array}{cc} \zeta/2 + \frac{2\gamma}{3} B_z & -\frac{2^{1/2}}{3}\gamma B_z \\ \text{sym} & -\zeta + \frac{1}{3}\gamma B_z \end{array}} \\[1em]
m_J = -3/2 & & \boxed{\zeta/2 + 2\gamma B_z}
\end{array}
$$

Uncoupled **H**

$$
\begin{array}{ll}
\boxed{\zeta/2 - 2\gamma B_z} & m_L = 1,\ m_S = 1/2 \\[1em]
\boxed{\begin{array}{cc} -\zeta/2 & 2^{-1/2}\zeta \\ \text{sym} & -\gamma B_z \end{array}} & \begin{array}{l} m_L = 1,\ m_S = -1/2 \\ m_L = 0,\ m_S = 1/2 \end{array} \\[1em]
\boxed{\begin{array}{cc} \gamma B_z & 2^{-1/2}\zeta \\ \text{sym} & -\zeta/2 \end{array}} & \begin{array}{l} m_L = 0,\ m_S = -1/2 \\ m_L = \text{-}1,\ m_S = 1/2 \end{array} \\[1em]
\boxed{\zeta/2 + 2\gamma B_z} & m_L = -1,\ m_S = -1/2
\end{array}
$$

$$
\boxed{
\begin{aligned}
E_{J,M_J} &= E_{3/2,3/2} = \zeta/2 - 2\gamma B_z \\
E_{\pm,1/2} &= \left(-\frac{\zeta}{4} - \frac{\gamma B_z}{2}\right) \pm \left[\frac{9}{16}\zeta^2 + \frac{(\gamma B_z)^2}{4} - \frac{\gamma B_z \zeta}{4}\right]^{1/2} \\
E_{\pm,-1/2} &= \left(-\frac{\zeta}{4} + \frac{\gamma B_z}{2}\right) \pm \left[\frac{9}{16}\zeta^2 + \frac{(\gamma B_z)^2}{4} - \frac{\gamma B_z \zeta}{4}\right]^{1/2} \\
E_{3/2,-3/2} &= \zeta/2 + 2\gamma B_z
\end{aligned}
}
$$

Same energy levels as coupled.

Even though each of the matrices are different, when evaluated in the two basis sets, the eigen-energies must be identical.