My goal for 5.73

Matrix Elements for any kind of $H$

energies and eigenvectors

downward arrow

energy level patterns

transition intensity patterns

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

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

$$\langle A \rangle_i = \text{Trace}(A \rho)$$

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

Dynamics.
Previous Lecture

\[ H^{SO} = \zeta(r) \mathbf{L} \cdot \mathbf{s} \quad \text{product of 2 angular momenta} \]
\[ H^{Zeeman} = -\hbar B_z \gamma (L_z + 2S_z) \quad \text{sum of 2 angular momenta} \]

2 incompatible \( H \)'s

Natural basis sets
- \(|nJLSM\rangle\) for \(H^{SO}\)
- \(|nLMS\rangle\) for \(H^{Zeeman}\)

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\(\leftrightarrow\)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 \([J_\pm = L_\pm + S_\pm]\) 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 $|JLSM\rangle_c \leftrightarrow |LMSM\rangle_u$ $c =$ coupled, $u =$ uncoupled

2. $H^{\text{Zeeman}}$ 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 $M_J$.

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

   War between 2 limiting cases.

   One term gives $\Delta E^{(0)}_{ij} \neq 0$ which tries to preserve one coupling case
   and one term gives $H^{(1)}_{ij} \neq 0$ 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 $H^{(0)}$]? 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 $H^{SO}$, right side is $H^{\text{Zeeman}}$.

   Typically, there is a center-of-gravity rule for each limit.
$B_z \to 0, |\zeta_{np}| \gg 0$
coupled

non-crossing $M_J$
because $[H, J_z] = 0$
$|B_z| \gg 0, \zeta_{np} \to 0$
uncoupled

$\Delta M_J = 0$
(the only interaction terms)

\[
\left(4\left(\frac{1}{2} \zeta_{np}\right) - 2\zeta_{np}\right) = 0
\]
Transformation Uncoupled ↔ Coupled for $H_{\text{Zeeman}}$

$$H^{SO} + H_{\text{Zeeman}} = \frac{\zeta_{nl}}{\hbar} \ell \cdot s - \gamma B_z (L_z + 2S_z)$$

In coupled basis set

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

$H_{\text{Zeeman}}$ need to use coupled → uncoupled transformation

$$|JLSM_j\rangle_c \quad |LM_sSM_{S}\rangle_u$$

$$\begin{align*}
|3\frac{1}{2}1 3\rangle_c &= \frac{1}{2} \left[ \frac{11}{2} \frac{1}{2}\right]_u \\
|3\frac{1}{2}1 1\rangle_c &= \left( \frac{2}{3} \right)^{1/2} \left[ \frac{10}{2} \frac{1}{2}\right]_u + \left( \frac{1}{3} \right)^{1/2} \left[ \frac{11}{2} \frac{1}{2}\right]_u \\
|1\frac{1}{2}2 2\rangle_c &= -\left( \frac{1}{3} \right)^{1/2} \left[ \frac{10}{2} \frac{1}{2}\right]_u + \left( \frac{2}{3} \right) \left[ \frac{11}{2} \frac{1}{2}\right]_u \\
|3\frac{1}{2}1 -\frac{1}{2}\rangle_c &= \left( \frac{2}{3} \right)^{1/2} \left[ \frac{10}{2} -\frac{1}{2}\right]_u + \left( \frac{1}{3} \right)^{1/2} \left[ \frac{11}{2} -\frac{1}{2}\right]_u \\
|1\frac{1}{2}2 -\frac{1}{2}\rangle_c &= -\left( \frac{1}{3} \right)^{1/2} \left[ \frac{10}{2} -\frac{1}{2}\right]_u + \left( \frac{2}{3} \right)^{1/2} \left[ \frac{11}{2} -\frac{1}{2}\right]_u \\
|3\frac{1}{2}1 -\frac{3}{2}\rangle_c &= \left[ \frac{11}{2} -\frac{3}{2}\right]_u
\end{align*}$$
5.73 Lecture #26

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

diagonal
\[
\langle \frac{3}{2}, \frac{1}{2} | \frac{3}{2}, \frac{1}{2} | H^{\text{Zeeman}} | \frac{3}{2}, \frac{1}{2} \rangle_c = -\gamma B_z u \left\langle \frac{1}{2}, \frac{1}{2} | L_z + 2S_z | \frac{1}{2}, \frac{1}{2} \right\rangle_u
\]
\[
= -h\gamma B_z (1+1) = -2h\gamma B_z
\]
\[
\langle \frac{3}{2}, \frac{1}{2} | \frac{3}{2}, \frac{1}{2} | H^{\text{Zeeman}} | \frac{3}{2}, \frac{1}{2} \rangle_c = -\gamma B_z u \left\langle \frac{1}{2}, \frac{1}{2} | L_z + 2S_z | \frac{1}{2}, \frac{1}{2} \right\rangle_u
\]
\[
= -h\gamma B_z (-1+1) = 2h\gamma B_z
\]
\[
\langle \frac{3}{2}, \frac{1}{2} | \frac{3}{2}, \frac{1}{2} | H^{\text{Zeeman}} | \frac{3}{2}, \frac{1}{2} \rangle_c = -\gamma B_z \left[ \frac{2}{3} \left( \frac{1}{2}, \frac{1}{2} | L_z + 2S_z | \frac{1}{2}, \frac{1}{2} \right) + \frac{2}{3} \left( \frac{1}{2}, \frac{1}{2} | L_z + 2S_z | \frac{1}{2}, \frac{1}{2} \right) \right]
\]
\[
= -\gamma B_z \left[ \frac{2}{3} (0+1) + \frac{2}{3} (1-1) \right]
\]
\[
= -\frac{2}{3} h\gamma B_z
\]
\[
\langle \frac{3}{2}, \frac{1}{2} | \frac{3}{2}, \frac{1}{2} | H^{\text{Zeeman}} | \frac{3}{2}, \frac{1}{2} \rangle_c = -\gamma B_z \left[ \frac{2}{3} \left( \frac{1}{2}, \frac{1}{2} | L_z + 2S_z | \frac{1}{2}, \frac{1}{2} \right) + \frac{2}{3} \left( \frac{1}{2}, \frac{1}{2} | L_z + 2S_z | \frac{1}{2}, \frac{1}{2} \right) \right]
\]
\[
= -\gamma B_z \left[ \frac{1}{3} (0+1) + \frac{2}{3} (1-1) \right]
\]
\[
= -\frac{1}{3} h\gamma B_z
\]

off-diagonal
\[
\langle \frac{3}{2}, \frac{1}{2} | \frac{3}{2}, \frac{1}{2} | H^{\text{Zeeman}} | \frac{3}{2}, \frac{1}{2} \rangle_c = -h\gamma B_z \left[ \frac{2}{3} (0+1) + \frac{2}{3} (1-1) \right]
\]
\[
= \frac{2}{3} h\gamma B_z
\]
\[
\langle \frac{3}{2}, \frac{1}{2} | \frac{3}{2}, \frac{1}{2} | H^{\text{Zeeman}} | \frac{3}{2}, \frac{1}{2} \rangle_c = -h\gamma B_z \left[ \frac{2}{3} (0+1) + \frac{1}{3} (1-1) \right]
\]
\[
= \frac{2}{3} h\gamma B_z
\]
\[
\langle \frac{1}{2}, \frac{1}{2} | \frac{1}{2}, \frac{1}{2} | H^{\text{Zeeman}} | \frac{1}{2}, \frac{1}{2} \rangle_c = -h\gamma B_z \left[ \frac{1}{3} (0+1) + \frac{2}{3} (1-1) \right]
\]
\[
= \frac{2}{3} h\gamma B_z
\]
\[
\langle \frac{1}{2}, \frac{1}{2} | \frac{1}{2}, \frac{1}{2} | H^{\text{Zeeman}} | \frac{1}{2}, \frac{1}{2} \rangle_c = -h\gamma B_z \left[ \frac{1}{3} (0+1) + \frac{2}{3} (1-1) \right]
\]
\[
= \frac{2}{3} h\gamma B_z
\]
\[
\langle \frac{3}{2}, \frac{1}{2} | \frac{3}{2}, \frac{1}{2} | H^{\text{Zeeman}} | \frac{3}{2}, \frac{1}{2} \rangle_c = +2h\gamma B_z
\]
Now that we have the full $H^{\text{Zeeman}}$ 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

\[
\begin{align*}
    J = 3/2 & \quad \zeta / 2 - 2\gamma B_z \\
    J = 1/2 & \quad \frac{2\sqrt{2}}{3}\gamma B_z
\end{align*}
\]

\[
\begin{align*}
    J = 3/2 & \quad \frac{2\sqrt{2}}{3}\gamma B_z \\
    J = 1/2 & \quad -\zeta + \frac{1}{3}\gamma B_z
\end{align*}
\]

\[
\begin{align*}
    J = 3/2 & \quad \frac{2\gamma B_z}{3} - \frac{2\sqrt{2}}{3}\gamma B_z \\
    J = 1/2 & \quad -\zeta - \frac{1}{3}\gamma B_z
\end{align*}
\]

### Uncoupled H

\[
\begin{align*}
    \zeta / 2 - 2\gamma B_z & \quad m_L = 1, m_S = 1/2 \\
    \zeta / 2 & \quad m_L = 1, m_S = -1/2 \\
    -\zeta / 2 & \quad m_L = 0, m_S = 1/2 \\
    -\sqrt{2}\zeta & \quad m_L = 0, m_S = -1/2 \\
    -\zeta / 2 & \quad m_L = -1, m_S = 1/2 \\
    \zeta / 2 + 2\gamma B_z & \quad m_L = -1, m_S = -1/2
\end{align*}
\]

\[
E_{J,M_J} = E_{3/2,3/2} = \frac{\zeta}{2} - 2\gamma B_z
\]

\[
E_{\pm,1/2} = \left( -\frac{\zeta}{4} - \frac{\gamma B_z}{2} \right) \pm \left[ \frac{9}{16} \zeta^2 + \frac{(\gamma B_z)^2}{4} - \frac{\gamma B_z \zeta}{4} \right]^{1/2}
\]

\[
E_{\pm,-1/2} = \left( -\frac{\zeta}{4} + \frac{\gamma B_z}{2} \right) \pm \left[ \frac{9}{16} \zeta^2 + \frac{(\gamma B_z)^2}{4} - \frac{\gamma B_z \zeta}{4} \right]^{1/2}
\]

\[
E_{3/2,-3/2} = \frac{\zeta}{2} + 2\gamma B_z
\]

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.