$H^{SO} + H^{Zeeman}$
Coupled vs. Uncoupled Basis Sets

Last time:

matrices for $\mathbf{J}^2$, $\mathbf{J}_+$, $\mathbf{J}_-$, $\mathbf{J}_z$, $\mathbf{J}_x$, $\mathbf{J}_y$ in $|jm_j\rangle$ basis for J = 0, 1/2, 1
Pauli spin 1/2 matrices
arbitrary 2×2 $\mathbf{M} = a_0\mathbf{I} + \vec{a}_1 \cdot \vec{\boldsymbol{\sigma}}$

When $\mathbf{M}$ is $\boldsymbol{\rho} \rightarrow$ visualization of fictitious vector in fictitious B-field

When $\mathbf{M}$ is a term in $\mathbf{H} \rightarrow$ idea that arbitrary operator can be decomposed as sum of $\mathbf{J}_i$.

types of operators

$$\left.\begin{array}{r} a\mathbf{J} \\ \vec{\mathbf{q}} \\ \mathbf{J}_1 \cdot \mathbf{J}_2 \end{array}\right] \begin{array}{l} \text{e.g. magnetic moment (}a\text{ is a known constant or a function of r)} \\ \text{how to evaluate matrix elements (e.g. Stark Effect)} \\ \text{e.g. Spin - Orbit} \end{array}$$

TODAY:

1. $\mathbf{H}^{SO} + \mathbf{H}^{Zeeman}$ as illustrative
2. Dimension of basis sets $|JLSM_J\rangle$ and $|LM_LSM_S\rangle$ is same
3. matrix elements of $\mathbf{H}^{SO}$ in both basis sets
4. matrix elements of $\mathbf{H}^{Zeeman}$ in both basis sets
5. ladders and orthogonality for transformation between basis sets. Necessary to be able to evaluate matrix elements of $\mathbf{H}^{Zeeman}$ in coupled basis. Why? Because coupled basis set does not explicitly give effects of $\mathbf{L}_z$ or $\mathbf{S}_z$.

Suppose we have 2 kinds of angular momenta, which can be coupled to each other to form a *total* angular momentum.

$$\left.\begin{array}{ll} \vec{\mathbf{L}} & \text{orbital} \\ \vec{\mathbf{S}} & \text{spin} \\ \vec{\mathbf{J}} = \vec{\mathbf{L}} + \vec{\mathbf{S}} & \text{total} \end{array}\right\} \text{operate on different coordinates or in different vector spaces}$$

The components of **L,S,** and **J** each follow the standard angular momentum commutation rule, but

$$\left[\vec{\mathbf{L}},\vec{\mathbf{S}}\right] = 0 \qquad , \qquad \left[\mathbf{J}_i,\mathbf{L}_j\right] = i\hbar\sum_k \varepsilon_{ijk}\mathbf{L}_k$$

$$\left[\mathbf{J}_i,\mathbf{S}_j\right] = i\hbar\sum_k \varepsilon_{ijk}\mathbf{S}_k .$$

These commutation rules specify that **L** and **S** act like vectors wrt **J** but as scalars wrt to each other.

$$\vec{\mathbf{J}} \rightarrow \left|jm_j\right\rangle$$
$$\vec{\mathbf{L}} \rightarrow \left|\ell m_\ell\right\rangle$$
$$\vec{\mathbf{S}} \rightarrow \left|sm_s\right\rangle$$

Coupled $\left|j\ell s m_j\right\rangle$ vs. *uncoupled* $\left|\ell m_\ell\right\rangle\left|sm_s\right\rangle$ representations.

- * matrix elements of certain operators are more convenient in one basis set than the other
- * a unitary transformation between basis sets must exist
- * limiting cases for energy level patterns

1.

$$\mathbf{H}^{SO} = \xi(r)\boldsymbol{\ell}\cdot\mathbf{s} \equiv \frac{\zeta_{n\ell}}{\hbar}\boldsymbol{\ell}\cdot\mathbf{s}$$

[$\boldsymbol{\ell}$ and **s** will each give a factor of $\hbar$]

$$\mathbf{H}^{\text{Zeeman}} = -\gamma B_z\left(\boldsymbol{\ell}_z + 2\mathbf{s}_z\right) \equiv -\left(\omega_0\right)\left(\boldsymbol{\ell}_z + 2\mathbf{s}_z\right)$$

[anomalous g - value of e^- → the 2 in $2\mathbf{s}_z$; will give a factor of $\hbar$ → $\boldsymbol{\ell}_z$ and $\mathbf{s}_z$]

$$\left(\zeta_{n\ell} \text{ and } \omega_0 \text{ are in rad/s}\right)$$

* evaluate matrix elements in both basis sets

* look at energy levels in high field $\left|\gamma B_z\right| >> \zeta_{n\ell}$ limit

* look at energy levels in low field $\left|\gamma B_z\right| << \zeta_{n\ell}$ limit

Notation: $\begin{cases}\text{lower case for } 1e^- \text{ atom angular momenta}\\ \text{upper case for many-}e^- \text{ angular momenta}\end{cases}$

<u>two different CSCOs</u>

a) $\mathbf{H}^{\text{elect}},\ \mathbf{J}^2, \mathbf{J}_z, \cdots^2, \mathbf{S}^2$ — coupled basis

$|\text{nJLSM}_J\rangle$ — (can't be factored)

b) $\mathbf{H}^{\text{elect}},\ \cdots^2, \cdots_z, \mathbf{S}^2, \mathbf{S}_z$ — uncoupled basis

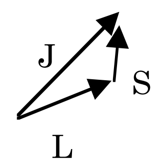
$|\text{nLM}_L\rangle|\text{SM}_S\rangle$ — (explicitly factored)

} recall tensor product states and "entanglement"

2. Coupled and Uncoupled Basis Sets Have Same Dimension

COUPLED $\quad \vec{J} = \vec{L} + \vec{S} \qquad |L - S| \le J \le L + S$

each J has $2J+1$ M_J's



$J = L + S$	$2(L+S)+1$	every J contributes 2L + 1 to sum
$L + S - 1$	$2(L+S-1)+1$	
$L + S - 2$	$2(L+S-2)+1$	
	$\cdots \cdots \cdots \cdots$	If $L > S$, there are $2S+1$ terms in sum
	$\underline{2(\lvert L-S\rvert)+1}$	

$$(2S+1)(2L+1) + \underbrace{2[S + (S-1) + \cdots (-S)]}_{=0} = \underbrace{(2S+1)(2L+1)}$$

$\Uparrow$ total dimension of basis set for specified L,S

UNCOUPLED $\quad \underbrace{LM_L}_{2L+1}\underbrace{SM_S}_{2S+1}$ $\quad$ total dimension $(2L+1)(2S+1)$ again

term for term correspondence between 2 basis sets
$\therefore$ a transformation must exist:

Coupled basis state in terms of uncoupled basis states:

$$|\text{JLSM}_J\rangle = \sum_{M_L} a_{M_L} |\text{LM}_L\rangle \underbrace{|\text{SM}_S = \text{M}_J - \text{M}_L\rangle}_{\text{constraint}}$$

Trade J, M_J for M_L, M_S, but $M_J = M_L + M_S$.

Uncoupled basis state in terms of coupled basis states:

$$\text{OR} \quad \left|LM_J\right\rangle\left|SM_S\right\rangle = \sum_{J=|L-S|}^{L+S} b_J \left|JLS\underbrace{M_J = M_L + M_S}_{\text{constraint}}\right\rangle$$

3. Matrix elements of $\mathbf{H}^{SO} = \frac{\zeta_{n\ell}}{\hbar}\boldsymbol{\ell}\cdot\mathbf{s}$

A. Coupled Representation

$$\vec{\mathbf{J}} = \vec{\mathbf{L}} + \vec{\mathbf{S}} \qquad \mathbf{J}^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L}\cdot\mathbf{S}$$

$$\mathbf{L}\cdot\mathbf{S} = \frac{\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2}{2} \qquad \textbf{(useful trick!)}$$

$$\left\langle J'L'S'M'_J\right|\mathbf{L}\cdot\mathbf{S}\left|JLSM_J\right\rangle = (\hbar^2/2)\left[J(J+1) - L(L+1) - S(S+1)\right]\delta_{J'J}\delta_{L'L}\delta_{S'S}\delta_{M'_JM_J}$$

a purely diagonal matrix.

B. Uncoupled Representation

$$\mathbf{L}\cdot\mathbf{S} = \underbrace{\mathbf{L}_z\mathbf{S}_z}_{\text{diagonal}} + \frac{1}{2}\underbrace{\left(\mathbf{L}_+\mathbf{S}_- + \mathbf{L}_-\mathbf{S}_+\right)}_{\text{off-diagonal}}$$

$$\left\langle L'M'_LS'M'_S\right|\mathbf{L}\cdot\mathbf{S}\left|LM_LSM_S\right\rangle = \hbar^2\delta_{L'L}\delta_{S'S}\times$$

(L: can't change L; S: can't change S)

$$\left\{\left[M_LM_S\delta_{M'_LM_L}\delta_{M'_SM_S}\right] + \frac{1}{2}\left[L(L+1) - M'_LM_L\right]^{1/2}\times\right.$$

$$\left.\left[S(S+1) - M'_SM_S\right]^{1/2}\delta_{M'_LM_L\pm1}\times\delta_{M'_SM_S\mp1}\right\} \qquad \Delta M_L = -\Delta M_S = 0, \pm1$$

Nonlecture notes for evaluated matrices

$S = 1/2, \qquad L = 0,1,2 \qquad$ ^2S, ^2P, ^2D states

$^{2S+1}L_J$ — <u>NONLECTURE</u> for $\mathbf{H}^{SO}$: **COUPLED** BASIS

$^2S_{1/2}$ $\qquad \mathbf{H}^{SO}_{COUPLED} = \frac{\hbar}{2}\zeta_{ns}(0)$

^2P $\qquad \mathbf{H}^{SO}_{COUPLED} = \frac{\hbar}{2}\zeta_{np}$

$$\left(\begin{array}{cc|cccc} -2 & 0 & 0 & 0 & 0 & 0 \\ 0 & -2 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{array}\right) \begin{array}{l} J = 1/2 \\ \\ J = 3/2 \end{array}$$

	L	J	J(J+1) – L(L+1) – S(S+1) =			
$(^2S_{1/2})$	0	1/2	3/4	0	3/4	0
$(^2P_{1/2})$	1	1/2	3/4	2	3/4	–2
$(^2P_{3/2})$	1	3/2	15/4	2	3/4	+1
$(^2D_{3/2})$	2	3/2	15/4	6	3/4	–3
$(^2D_{5/2})$	2	5/2	35/4	6	3/4	+2

^2D $\qquad \mathbf{H}^{SO}_{COUPLED} = \frac{\hbar}{2}\zeta_{nd}$

$$\overbrace{}^{J=3/2}\left(\begin{array}{cccc|cccccc} -3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -3 & 0 & 0 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 \end{array}\right)_{J=5/2}$$

center of gravity rule: trace of matrix = 0
(obeyed for all *scalar* terms in **H**)

^{2S+1}L NONLECTURE for H^{SO} : **UNCOUPLED** BASIS

^{2}S $\quad \mathbf{H}^{SO}_{UNCOUPLED} = \hbar\zeta_{ns}(1/2 \cdot 0) = (0)$

^{2}P $\quad \mathbf{H}^{SO}_{UNCOUPLED} = \hbar\zeta_{np} \times$

$$
\begin{array}{cc}
M_L & M_S \\
1 & 1/2 \\
1 & -1/2 \\
0 & 1/2 \\
0 & -1/2 \\
-1 & 1/2 \\
-1 & -1/2
\end{array}
\begin{pmatrix}
1/2 & 0 & 0 & 0 & 0 & 0 \\
0 & -1/2 & 2^{-1/2} & 0 & 0 & 0 \\
0 & 2^{-1/2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 2^{-1/2} & 0 \\
0 & 0 & 0 & 2^{-1/2} & -1/2 & 0 \\
0 & 0 & 0 & 0 & 0 & 1/2
\end{pmatrix}
$$

Each box is for one value of $M_J = M_L + M_S$.

^{2}D $\quad \mathbf{H}^{SO}_{UNCOUPLED} = \hbar\zeta_{nd} \times$

$$
\begin{array}{cc}
M_L & M_S \\
2 & 1/2 \\
2 & -1/2 \\
1 & 1/2 \\
1 & -1/2 \\
0 & 1/2 \\
0 & -1/2 \\
-1 & 1/2 \\
-1 & -1/2 \\
-2 & 1/2 \\
-2 & -1/2
\end{array}
\begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 1/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1/2 & (3/2)^{1/2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & (3/2)^{1/2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & (3/2)^{1/2} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & (3/2)^{1/2} & -1/2 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/2 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}
$$

4. Matrix Elements of $\mathbf{H}^{\text{Zeeman}} = -\gamma B_z(\mathbf{L}_z + 2\mathbf{S}_z)$

   A. very easy in uncoupled representation

$$\mathbf{H}^{\text{Zeeman}}_{\text{uncoupled}} = -\gamma B_z \langle L'M_L'S'M_S'|\mathbf{L}_z + 2\mathbf{S}_z|LM_LSM_S\rangle$$
$$= -\gamma B_z \hbar (M_L + 2M_S)\delta_{L'L}\delta_{S'S}\delta_{M_L'M_L}\delta_{M_S'M_S}$$

   strictly diagonal

   B. coupled representation

$$\mathbf{L}_z + 2\mathbf{S}_z = \underbrace{\mathbf{J}_z}_{\text{easy}} + \underbrace{\mathbf{S}_z}_{\text{hard — no clue!}}$$

   can't evaluate matrix elements in coupled representation without a new trick

---

5. If we wish to work in *coupled* representation, because it diagonalizes $\mathbf{H}^{\text{SO}}$, need to find transformation

$$|JLSM_J\rangle = \sum_{M_L} a_{M_L} |LM_LSM_S = M_J - M_L\rangle$$

lengthy procedure: $\mathbf{J}_\pm = \mathbf{L}_\pm + \mathbf{S}_\pm$ and orthogonality

Always start with an extreme M_L, M_S basis state, where we are assured of a trivial correspondence between basis sets:

$$M_L = L, \quad M_S = S, \quad M_J = M_L + M_S = L + S, \quad J = L + S$$
$$\underbrace{|J = L + S \;\; LSM_J = L + S\rangle}_{\text{coupled}} = \underbrace{|LM_L = L \;\; SM_S = S\rangle}_{\text{uncoupled}}$$

$$\mathbf{J}_-\,|\overbrace{L+S}^{J}\;\;LS\;\;\overbrace{L+S}^{M_J}\rangle = (\mathbf{L}_- + \mathbf{S}_-)|LM_L = L\;\; SM_S = S\rangle$$

$$\begin{bmatrix}(L+S)(L+S+1)\\ -(L+S)(L+S-1)\end{bmatrix}^{1/2}|L+S\;\;LS\;\;L+S-1\rangle = \left[L(L+1)-L(L-1)\right]^{1/2}|LL-1SS\rangle + \left[S(S+1)-S(S-1)\right]^{1/2}|LLSS-1\rangle$$

Thus we have derived a specific linear combination of 2 uncoupled basis states.

There is only one other orthogonal linear combination belonging to the same value of $M_L + M_S = M_J$: it must belong to the $|\underbrace{L+S-1}_{\text{lower J}}\;\;LS\;\;L+S-1\rangle$ basis state.

NONLECTURE
Work this out for ^2P

$$|JLSM_J\rangle = |\underbrace{3/2\;\;1\;\;1/2\;\;3/2}\rangle = |LM_LSM_S\rangle = |\underbrace{1\;\;1\;\;1/2\;\;1/2}\rangle$$

$$|JLSM_J - 1\rangle = \frac{2^{1/2}|1\;\;0\;\;1/2\;\;1/2\rangle + |1\;\;1\;\;1/2\;\;-1/2\rangle}{3^{1/2}}$$

now use orthogonality:

$$|J-1LSM_J-1\rangle = |1/2\;\;1\;\;1/2\;\;1/2\rangle = \frac{-|1\;\;0\;\;1/2\;\;1/2\rangle + 2^{1/2}|1\;\;1\;\;1/2\;\;-1/2\rangle}{3^{1/2}}.$$

Continue laddering down to get all 4 J = 3/2 and all 2 J = 1/2 basis states.

$$|3/2\;\;1\;\;1/2\;\;-1/2\rangle = \left(\frac{2}{3}\right)^{1/2}|1\;\;0\;\;1/2\;\;-1/2\rangle + \left(\frac{1}{3}\right)^{1/2}|1\;\;-1\;\;1/2\;\;1/2\rangle$$

$$|3/2\;\;1\;\;1/2\;\;-3/2\rangle = |1\;\;-1\;\;1/2\;\;-1/2\rangle$$

$$|1/2\;\;1\;\;1/2\;\;1/2\rangle = -\left(\frac{1}{3}\right)^{1/2}|1\;\;0\;\;1/2\;\;-1/2\rangle + \left(\frac{2}{3}\right)^{1/2}|1\;\;-1\;\;1/2\;\;1/2\rangle$$

You work out the transformation for ^2D!

Next step will be to evaluate $\mathbf{H}^{SO} + \mathbf{H}^{Zeeman}$ in both coupled and uncoupled basis sets and look for limiting behavior.