$H^{SO} + H^{Zeeman}$
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, ½, 1
Pauli spin ½ matrices
arbitrary 2 × 2 matrix $M = a_0 I + \vec{a}_1 \cdot \vec{\boldsymbol{\sigma}}$ decomposed as scalar plus vector.

When **M** is $\boldsymbol{\rho}$ → visualization via fictitious vector in fictitious B-field.

When **M** is a term in **H** → idea that arbitrary operator can be decomposed as a sum of the terms that behave like components of J = 0, J = 1, J = 2… This leads to *spherical tensor algebra*.

types of operators

aJ — e.g. magnetic moment (a is a known constant or a function of r)
$\vec{q}$ — how to evaluate matrix elements (e.g. Stark Effect)
$J_1 \cdot J_2$ — e.g. Spin-Orbit

Special simplification of Trace (**AH**)

For example

$$\mathbf{A} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \mathbf{H} = \begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{pmatrix}$$

$$\mathbf{AH} = \begin{pmatrix} H_{21} & H_{22} & H_{23} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$ simpler

$$\mathrm{Trace}(\mathbf{AH}) = H_{21}$$ extreme simplification!

$\mathbf{A}_{12}$ picks out only $\mathbf{H}_{21}$, $\mathbf{A}_{21}$ picks out only $\mathbf{H}_{12}$.

Extreme labor saving trick!

TODAY:

1. $\mathbf{H}^{SO} + \mathbf{H}^{Zeeman}$ as illustrative
2. Dimension of two basis sets, $|\,JLSM_J\rangle$ and $|\,LM_LSM_S\rangle$, is the same
3. matrix elements of $\mathbf{H}^{SO}$ in both basis sets
4. matrix elements of $\mathbf{H}^{Zeeman}$ in both basis sets
5. ladder operators 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 reveal the effects of $\mathbf{L}_z$ or $\mathbf{S}_z$.

Nos. 3, 4 and 5 will be repeated in Lecture #26.

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

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

$$\vec{J}=\vec{L}+\vec{S} \quad \text{total}$$

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

$$\left[\vec{L},\vec{S}\right]=0 \qquad , \qquad \left[J_i,L_j\right]=i\hbar\sum_k \varepsilon_{ijk}L_k$$

$$\left[J_i,S_j\right]=i\hbar\sum_k \varepsilon_{ijk}S_k.$$

These commutation rules specify that **L** and **S** act like vectors with respect to **J** but as scalars with respect 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 $|j\ell sm_j\rangle$ vs. uncoupled $|\ell m_\ell\rangle|sm_s\rangle$ 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 (and Zeeman tuning rates and intensities for transitions into eigenstates)

assignment

determination of key parameters, structure, and dynamics matrix elements of ℓ and $\mathbf{s}$ will each give a factor of $\hbar$

1.
$$\mathrm{H}^{SO} = \xi(r)\boldsymbol{\ell}\cdot\mathrm{s} \equiv \frac{\zeta_{n\ell}}{\hbar}\boldsymbol{\ell}\cdot\mathrm{s}$$

each will give a factor of $\hbar$

anomalous g - value of e^-

$$\mathrm{H}^{Zeeman} = -\gamma B_z\left(\ell_z + \boxed{2}\mathrm{s}_z\right) \equiv -\left(\omega_0\right)\left(\ell_z + 2\mathrm{s}_z\right)$$

($\zeta_{n\ell}$ and ω_0 are in units of rad/s)

* evaluate matrix elements in both basis sets
* look at energy levels and their Zeeman tuning rate in *high field* $\left|\gamma B_z\right| \gg \zeta_{n\ell}$ limit
* and in *low field* $\left|\gamma B_z\right| \ll \zeta_{n\ell}$ 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)	$\mathrm{H}^{\mathrm{elect}}, \mathrm{J}^2, \mathrm{J}_z, \mathrm{L}^2, \mathrm{S}^2$	coupled basis	recall tensor product states and "entanglement"
	$\left\|nJLSM_J\right\rangle$	(can't be factored)	
b)	$\mathrm{H}^{\mathrm{elect}}, \mathrm{L}^2, \mathrm{L}_z, \mathrm{S}^2, \mathrm{S}_z$	uncoupled basis	
	$\left\|nLM_L\right\rangle\left\|SM_S\right\rangle$	(*explicitly* factored)	

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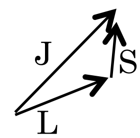
2. Coupled and Uncoupled Basis Sets have the same dimension

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

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



every term in this sum has 2L + 1 and there are 2S + 1 of them. The second term shows that the S,S–1,…–S terms in sum all cancel.

	$J =$	Dimension
	$L+S$	$2(L+S)+1$
	$L+S-1$	$2(L+S-1)+1$
	$L+S-2$	$2(L+S-2)+1$
	……	…………
	$\lvert L-S\rvert$	$2(\lvert L-S\rvert)+1$

Every allowed value of J contributes $2L$ + 1 to sum. How many allowed values of J are there?

If L > S, there are 2S + 1 terms in sum.

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

total dimension of basis set for specified L and S

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

There is a term by term correspondence between the 2 basis sets $\therefore$ a transformation must exist:

Coupled basis state in terms of uncoupled basis states:

$$\left|JLSM_J\right\rangle = \sum_{M_L} a_{M_L}\left|LM_L\right\rangle\left|S\,\underbrace{M_S = M_J - M_L}_{\text{constraint}}\right\rangle$$

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

Going in the opposite direction: express uncoupled basis state in terms of coupled basis states:

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

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

A. Coupled Representation

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

L and S commute because they operate in different vector spaces

$$\mathbf{L}\cdot\mathbf{S}=\frac{\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2}{2}$$

(useful trick!)

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

an entirely diagonal matrix.

B. Uncoupled Representation: work out all of the matrix elements.

$\mathbf{L}\cdot\mathbf{S}=\underbrace{\mathbf{L}_z\mathbf{S}_z}_{\text{diagonal}}+\underbrace{\tfrac{1}{2}(\mathbf{L}_+\mathbf{S}_-+\mathbf{L}_-\mathbf{S}_+)}_{\text{off-diagonal}}$: because $\mathbf{L}_+\mathbf{S}_-+\mathbf{L}_-\mathbf{S}_+=(\mathbf{L}_x+i\mathbf{L}_y)(\mathbf{S}_x-i\mathbf{S}_y)+(\mathbf{L}_x-i\mathbf{L}_y)(\mathbf{S}_x+i\mathbf{S}_y)=2(\mathbf{L}_x\mathbf{S}_x+\mathbf{L}_y\mathbf{S}_y)$

$$\left\langle L'M_L'S'M_S'\right|\mathrm{L}\cdot\mathrm{S}\left|LM_LSM_S\right\rangle=\hbar^2\delta_{L'L}\delta_{S'S}\times$$

can't change L

can't change S

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

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

Non-Lecture notes for evaluated matrices

$S=1/2, \qquad L=0,1,2 \qquad \boxed{{}^2S,\ {}^2P,\ {}^2D\text{ states}}$

NONLECTURE for $\mathbf{H}^{\mathrm{SO}}$: **COUPLED** BASIS

$^{2S+1}L_J$

$^2S_{1/2}$ $\quad \mathrm{H}^{\mathrm{SO}}_{\mathrm{COUPLED}} = \frac{\hbar}{2}\zeta_{ns}(0) = 0$ a 1 × 1 matrix with matrix element = 0

$^2P_{1/2\ \&\ 3/2}$ $\quad \mathrm{H}^{\mathrm{SO}}_{\mathrm{COUPLED}} = \frac{\hbar}{2}\zeta_{np}$

$$\begin{array}{c}\left(\begin{array}{cc|cccc}-2 & 0 & 0 & 0 & 0 & 0\\ 0 & -2 & 0 & 0 & 0 & 0\\ \hline 0 & 0 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 1 & 0 & 0\\ 0 & 0 & 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 0 & 0 & 1\end{array}\right)\end{array}\begin{array}{l}J = 1/2 \quad (2\times 2)\\ \\ \\ J = 3/2 \quad (4\times 4)\\ \\ \end{array}$$

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

$^2D_{\frac{3}{2}\text{ and }\frac{5}{2}}$ $\quad \mathrm{H}^{\mathrm{SO}}_{\mathrm{COUPLED}} = \frac{\hbar}{2}\zeta_{nd}$

$$\begin{array}{c} J = 3/2 \\ \left(\begin{array}{cccc|cccccc}-3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & -3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & -3 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & -3 & 0 & 0 & 0 & 0 & 0 & 0\\ \hline 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2\end{array}\right) \\ J = 5/2 \end{array}\begin{array}{l}(4\times 4)\\ \\ \\ (6\times 6)\end{array}$$

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

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

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

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

$$
\begin{array}{c|cc|cccccc}
M_J & M_L & M_S & & & & & & \\
3/2 & 1 & 1/2 & 1/2 & 0 & 0 & 0 & 0 & 0 \\
1/2 & 1 & -1/2 & 0 & -1/2 & 2^{-1/2} & 0 & 0 & 0 \\
1/2 & 0 & 1/2 & 0 & 2^{-1/2} & 0 & 0 & 0 & 0 \\
-1/2 & 0 & -1/2 & 0 & 0 & 0 & 0 & 2^{-1/2} & 0 \\
-1/2 & -1 & 1/2 & 0 & 0 & 0 & 2^{-1/2} & -1/2 & 0 \\
-3/2 & -1 & -1/2 & 0 & 0 & 0 & 0 & 0 & 1/2
\end{array}
$$

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

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

$$
\begin{array}{c|cc|cccccccccc}
M_J & M_L & M_S & & & & & & & & & & \\
5/2 & 2 & 1/2 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
3/2 & 2 & -1/2 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
3/2 & 1 & 1/2 & 0 & 1 & 1/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1/2 & 1 & -1/2 & 0 & 0 & 0 & -1/2 & (3/2)^{1/2} & 0 & 0 & 0 & 0 & 0 \\
1/2 & 0 & 1/2 & 0 & 0 & 0 & (3/2)^{1/2} & 0 & 0 & 0 & 0 & 0 & 0 \\
-1/2 & 0 & -1/2 & 0 & 0 & 0 & 0 & 0 & 0 & (3/2)^{1/2} & 0 & 0 & 0 \\
-1/2 & -1 & 1/2 & 0 & 0 & 0 & 0 & 0 & (3/2)^{1/2} & -1/2 & 0 & 0 & 0 \\
-3/2 & -1 & -1/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/2 & 1 & 0 \\
-3/2 & -2 & 1/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 \\
-5/2 & -2 & -1/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{array}
$$

End of Non-Lecture

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

   A. Very easy in uncoupled representation

$$\begin{aligned} \mathrm{H}^{Zeeman}_{\text{uncoupled}} &= -\gamma B_z \left\langle L'M_L'S'M_S' \middle| \mathrm{L}_z + 2\mathrm{S}_z \middle| LM_L SM_S \right\rangle \\ &= -\gamma B_z \hbar \left(M_L + 2M_S\right) \delta_{L'L}\delta_{S'S}\delta_{M_L'M_L}\delta_{M_S'M_S} \end{aligned}$$

   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, discussed in item #5

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5. If we wish to work in *coupled* representation, because it diagonalizes $\mathbf{H}^{\mathrm{SO}}$, we need to find the transformation between coupled and uncoupled representations.

$$\left|\mathrm{JLSM_J}\right\rangle = \sum_{\mathrm{M_L}} \mathrm{a_{M_L}} \left|\mathrm{LM_L SM_S = M_J - M_L}\right\rangle$$

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

Always start with an extreme $\mathrm{M_L}$, $\mathrm{M_S}$ basis state, where we are assured of a trivial 1 to 1 correspondence between basis sets:

$$M_L = L, \quad M_S = S, \quad M_J = M_L + M_S = L + S, \quad J = L + S$$

$$\underbrace{\left|J = L + S \;\; LSM_J = L + S\right\rangle}_{\text{coupled}} = \underbrace{\left|LM_L = L \;\; SM_S = S\right\rangle}_{\text{uncoupled}}$$

Now the fun begins …

Apply $\mathbf{J}_-$ to both sides of the equation:

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

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

Thus we have derived an equality between one coupled basis state and a specific linear combination of two uncoupled basis states.

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

NONLECTURE

Work this out for ^2P using $\mathbf{J}^- = \mathbf{L}^- + \mathbf{S}^-$

$$\left|JLSM_J\right\rangle = \underbrace{\left|3/2\quad 1\quad 1/2\quad 3/2\right\rangle} = \left|LM_LSM_S\right\rangle = \underbrace{\left|1\quad 1\quad 1/2\quad 1/2\right\rangle}$$

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

now use orthogonality:

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

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

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

$$\left|3/2\quad 1\quad 1/2\quad -3/2\right\rangle = \left|1\quad -1\quad 1/2\quad -1/2\right\rangle$$

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

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.

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