5.74 RWF Lectures #1 & #2

Point of View

Isolated (gas phase) molecules: no coherences (intra- or inter-molecular).
At $t = 0$ sudden perturbation:

"photon pluck" $\boldsymbol{\rho}(0)$ [need matrix elements of $\mu(\mathbf{Q})$]

visualization of dynamics $\boldsymbol{\rho}(t)$ [need $\mathbf{H}$ for evolution]

$\mathbf{H} = \mathbf{H}^{(0)} + \mathbf{H}^{(1)}$

$\mathbf{H}^{(1)}$: intramolecular coupling terms (not t-dependent)

$\mathbf{H}^{(0)}$: initially localized, nonstationary state

What do we need?

pre-pluck initial state: simple, localized in both physical and state space
nature of pluck: usually very simple
single orbital
single oscillator
single conformer (even if excitation is to energy above the isomerization barrier)

post-pluck dynamics
nature of pluck determines best choice of $\mathbf{H}^{(0)}$

need $\mathbf{H} = \mathbf{H}^{(0)} + \mathbf{H}^{(1)}$ to describe dynamics

* Reduce $\mathbf{H}$ to $\mathbf{H}^{\text{eff}}$ good for a "short" time
* transformations between basis sets
* evaluate matrix elements of $\mathbf{H}^{\text{eff}}$ and $\boldsymbol{\mu}(\mathbf{Q})$

Visualize dynamics in reduced dimensionality

* $\psi(\mathbf{Q})^*\psi(\mathbf{Q})$ contains too much information
* develop tools to look at individual parts of system — in coordinate and state space

Detection?

* how to describe various detection schemes?
* devise optimal detection schemes

1st essential tool is Angular Momentum Algebra

define basis sets for coupled sub-systems

electronic ψ — symmetry in molecular frame, orbitals

rotational ψ — relationship between molecular and lab frame

alternative choices of complete sets of commuting operators

eg. $J^2L^2S^2J_z$ (coupled) vs. $L^2L_zS^2S_z$ (uncoupled)

reasons for choices of basis set
- nature of pluck
- hierarchy of terms in **H**

transformations between basis sets
- needed to evaluate matrix elements of different operators

effects of coordinate rotation on basis functions and operators
- *spherical tensor* operators

Wigner-Eckart Theorem

Let's begin with a fast review of Angular Momentum

Angular Momentum

$|JM\rangle \qquad 2J+1\ M$ values for each J

$\mathbf{J}^2, \mathbf{J}_z, \mathbf{J}_\pm = \mathbf{J}_x \pm i\mathbf{J}_y$

$$\mathbf{J}_x = \frac{1}{2}\left(\mathbf{J}_+ + \mathbf{J}_-\right) \text{ real}$$

$$\mathbf{J}_y = -\frac{i}{2}\left(\mathbf{J}_+ - \mathbf{J}_-\right) \text{ imaginary}$$

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

$$\mathbf{J}_\pm|JM\rangle = \hbar[J(J+1) - \underbrace{M(M\pm 1)}_{\text{product of } M \text{ values}}]^{1/2}|JM\pm 1\rangle$$

If $\left[\mathbf{A},\mathbf{B}\right] = 0$ then $\quad \mathbf{A}\left|a_i b_j\right\rangle = a_i\left|a_i b_j\right\rangle$

$$\mathbf{B}\left|a_i b_j\right\rangle = b_j\left|a_i b_j\right\rangle$$

(if $[\mathbf{A},\mathbf{B}] \neq 0$, then it is impossible to define an $|a_i b_j\rangle$ basis set. e.g. $\mathbf{J}_x,\mathbf{J}_y$)

2 angular momentum sub-systems, e.g. **L** and **S**

J = **L** + **S**

two choices of basis set

$[\mathbf{J}^2, \mathbf{L}^2, \mathbf{S}^2, \mathbf{J}_z]$	$[\mathbf{L}^2, \mathbf{L}_z, \mathbf{S}^2, \mathbf{S}_z]$
$\left\|LSJM_J\right\rangle$	$\left\|LM_L SM_S\right\rangle$
coupled	uncoupled

trade J for M_L ($M_S = M_J - M_L$)

operators $\mathbf{L}_z$, $\mathbf{L}_\pm$, $\mathbf{S}_z$, $\mathbf{S}_\pm$ destroy J quantum number (coupled basis destroyed)
(not commute with $\mathbf{J}^2$)

operators $\mathbf{L}_\pm$, $\mathbf{S}_\pm$, $\mathbf{J}_\pm$ destroy M_L, M_S, M_J (both bases destroyed)

example of incompatible terms in **H**

$$\mathbf{H}^{\mathrm{SO}} = \sum_{\mathrm{i}} \xi(r_i)\boldsymbol{\ell}_i \cdot \mathbf{s}_i \to \zeta(NLS)\mathbf{L}\cdot\mathbf{S}$$

$$\mathbf{H}^{\mathrm{Zeeman}} = B_z \underbrace{\mu_0}_{\boxed{1.4\ \mathrm{MHz/Gauss}}} (\mathbf{L}_z + 2\mathbf{S}_z)$$

(special case valid only for $\Delta L = \Delta S = 0$ matrix elements)

note that $\mathbf{H}^{\mathrm{SO}}$ and $\mathbf{H}^{\mathrm{Zeeman}}$ are incompatible because

$$[\mathbf{L}_z, \mathbf{L}\cdot\mathbf{S}] = \frac{\hbar}{2}(\mathbf{L}_+\mathbf{S}_- - \mathbf{L}_-\mathbf{S}_+)$$

$$[\mathbf{S}_z, \mathbf{L}\cdot\mathbf{S}] = \frac{\hbar}{2}(\mathbf{L}_-\mathbf{S}_+ - \mathbf{L}_+\mathbf{S}_-)$$

(note that if $\mathbf{H}^z$ were $\propto$ ($\mathbf{L}_z + \mathbf{S}_z$), the $\mathbf{H}^{\mathrm{SO}}$ and $\mathbf{H}^{\mathrm{Zeeman}}$ simplified operators would commute and both would be diagonal in $|LSJM_J\rangle$.)

So we have to choose between coupled and uncoupled basis sets.

Which do we choose? The one that gives a better representation of the spectrum and dynamics **without** considering off-diagonal matrix elements! (You are free to choose either basis, but one is always more convenient for specific experiment.)

$\mathbf{H}^{\mathrm{SO}}$ lifts degeneracy of J's in L–S state

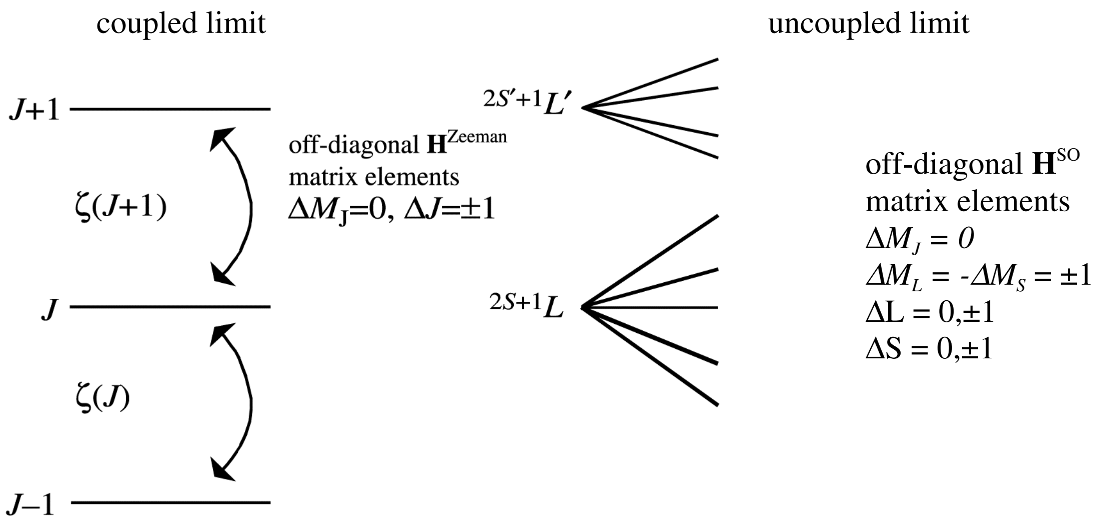
$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

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

$$\mathbf{L}\cdot\mathbf{S} = \tfrac{1}{2}\hbar[\mathbf{J}(\mathbf{J}+1) - \mathbf{L}(\mathbf{L}+1) - \mathbf{S}(\mathbf{S}+1)]$$

$\mathbf{H}^{\mathrm{Zeeman}}$ lifts degeneracy of M_J's within J.

$$E_{M_J} = g_J \mu_0 B_z M_J \qquad g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$



$\mathbf{H}^{(0)} = \mathbf{H}^{\mathrm{SO}}$
$\mathbf{H}^{(1)} = \mathbf{H}^{\mathrm{Zeeman}}$
Landé interval rule.

$\mathbf{H}^{(0)} = \mathbf{H}^{\mathrm{Zeeman}}$
$\mathbf{H}^{(1)} = \mathbf{H}^{\mathrm{SO}}$

Patterns in both frequency and time domain get destroyed. Assignments are based on recognition of patterns. Selection rules for transitions get bent.
Extra lines, intensity anomalies (borrowing, interference).
We must do extra work to describe both $\rho(0)$ and $\rho(t)$.

<u>Limiting cases are nice</u>

simple patterns (sometimes too simple to determine all coupling constants — restrictive selection rules)
easy to compute matrix elements
dynamics is often simple with periodic grand recurrences

<u>Deviations from limiting cases</u>

terms that can no longer be ignored have matrix elements that are difficult or tedious to evaluate. Large $\mathbf{H}^{\mathrm{eff}}$ matrix must be diagonalized to describe dynamics.

<u>Atoms</u>

couple $n_i \ell_i m_{\ell_i} s_i m_{s_i}$ of each e$^-$ to make many-e$^-$ L–S–J state of atom

electron orbital

$$\langle \theta,\phi | \ell m_\ell \rangle = Y_{\ell m_\ell}(\theta,\phi) \qquad \text{spherical polar coordinates}$$

only one kind of coordinate system: origin at nucleus, z-axis specified in laboratory electronic configuration: $\left(n_1\ell_1\right)^{N_1}\left(n_2\ell_2\right)^{N_2}\ldots$

individual spin-orbitals are coupled to make L–S–J states

- * Slater determinants
- * matrix elements of $\sum\limits_{i\neq j} \frac{1}{r_{ij}}$
- * Gaunt coefficients, Slater-Condon parameters: Coulomb and exchange integrals

one spin-orbital is plucked by photon — generate perfectly known superposition of L–S–J eigenstates at $t = 0$

- * explicit time evolution
- * problem set

LECTURE #1 STOPS HERE

Coupled vs. Uncoupled Representations

$\left|nLSJM_J\right\rangle$ $\qquad\qquad$ $\left|nLM_L\right\rangle\left|SM_S\right\rangle$

2 basis sets have same dimensionality

Uncoupled $(2L+1)(2S+1)$

$$\text{Coupled} \quad \sum_{J=|L-S|}^{L+S}(2J+1)=(2L+1)(2S+1)$$

$$\Uparrow$$

$$\text{triangle rule} \qquad L-S\leq J\leq L+S$$

What is happening here? M_L, M_S being replaced by $J, M_J = M_L + M_S$

actually only one quantum number is being replaced by one quantum number

convenient notation (especially for more complicated cases)

unitary transformation: $U^{LSM_J}_{M_L=M_J-M_{S},J}$ $\quad\leftarrow$ conserved $\quad\leftarrow$ exchanged

This sort of notation is useful for working out series of transformations

$$\left.nLSJM_J\right\rangle=\sum_{M_L=M_J-M_S}\underbrace{\left|nLM_LSM_S\right\rangle\left\langle nLM_LSM_S\right|}_{\text{completeness}}\left.nLSJM_J\right\rangle$$

vector coupling or Clebsch-Gordan coefficient

$$=\sum_{M_L=M_J-M_S}\left.nLM_LSM_S\right\rangle(-1)^{L-S+M_J}(2J+1)^{1/2}\begin{pmatrix}L & S & J\\ M_L & M_S & -M_J\end{pmatrix}$$

$$=\sum_{M_L=M_J-M_S}U^{LSM_J}_{\underbrace{M_L=M_J-M_{S}}_{\text{replaced}},\underbrace{J}_{\text{constructed}}}\left.nLM_LSM_S\right\rangle$$

Inverse transformation (unitary, so $\mathbf{U}^{-1} = \mathbf{U}^{\dagger}$, but $\mathbf{U}$ is real. $\mathbf{U}^{-1}_{ij} = \mathbf{U}_{ji}$)

$$\left|nLM_L SM_S\right\rangle = \sum_{J=|L-S|}^{L+S} \left|nLSJM_J\right\rangle\left\langle nLSJM_J \middle| nLM_L SM_S\right\rangle$$

$$= \sum_{J=|L-S|}^{L+S} \left|nLSJM_J = M_L + M_S\right\rangle(-1)^{L-S+M_J}(2J+1)^{1/2}\begin{pmatrix} L & S & J \\ M_L & M_S & -M_J \end{pmatrix}$$

$$= \underbrace{\sum_{J=|L-S|}^{L+S}}_{\text{replaced}} U^{LSM_J}_{J,\underbrace{M_L=M_J-M_S}_{\text{constructed}}}\left|nLSJM_J = M_L + M_S\right\rangle$$

<u>General properties of 3-j coefficients</u>

$j_3 = j_1 + j_2$

$$\left\langle j_1 m_1 j_2 m_2 \middle| \underbrace{j_3 m_3}_{\text{special}}\right\rangle \equiv (-1)^{j_1-j_2+m_3}(2j_3+1)^{1/2}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix}$$

This is $-m_3$ so that sum of bottom row = 0

$m_1 + m_2 = m_3$

Be careful writing in opposite direction

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \equiv (-1)^{j_1-j_2-m_3}(2j_3+1)^{-1/2}\left\langle j_1 m_1 j_2 m_2 \middle| j_3 - m_3\right\rangle$$

special properties:

1. even permutation of columns: +1
   odd permutation of columns: $(-1)^{j_1+j_2+j_3}$
2. reverse sign of all 3 arguments in bottom row: $(-1)^{j_1+j_2+j_3}$

Suppose one has $\mathbf{j}_3 = \mathbf{j}_1 - \mathbf{j}_2$ e.g. $\mathbf{S} = \mathbf{J} - \mathbf{L}$
must reverse sign of M_L in 3-j

$$\left\langle nJM_J LM_L \middle| SM_S\right\rangle \equiv (-1)^{J-L+M_S}(2S+1)^{1/2}\begin{pmatrix} J & L & S \\ M_J & -M_L & -M_S \end{pmatrix}$$ [note sum $M_J - M_L - M_S = 0$]

<u>Matrix Elements of **H**</u>

H is a sum of 2 parts, one easily evaluated in coupled basis and another easily evaluated in uncoupled basis

$$\mathbf{H} = \mathbf{H}(1)\text{ (uncoupled)} + \mathbf{H}(2)\text{(coupled)}$$

Must evaluate all of **H** in some basis set. Choose uncoupled.

$$\mathbf{H}(\text{uncoupled}) = \mathbf{H}(1)(\text{uncoupled}) + \mathbf{T}^{\dagger}\mathbf{H}(2)(\text{coupled})\mathbf{T}$$

$$|LM_L SM_S\rangle = \sum_{J=|L-S|}^{L+S} |LSJM_J\rangle \underbrace{\langle LSJM_J | LM_L = M_J - M_S SM_S\rangle}_{T_{J,M_L=M_J-M_S}}$$

Want matrix elements of **H**(2):

$$\left[\mathbf{T}^{\dagger}\mathbf{H}(2)\text{ coupled})\mathbf{T}\right]_{LM_L=M_J-M_S SM_S, L'M'_L=M'_J-M'_S S'M'_S}$$

$$= \sum_{J=|L-S|}^{L+S} \sum_{J'=|L'-S'|}^{L'+S'} \langle LM_L = M_J - M_S SM_S \;\; LSJM_J\rangle$$

$$\times \quad \mathbf{H}(2)_{LSJM_J, L'S'J'M'_J} \langle L'S'J'M'_J \;\; L'M'_L = M'_J - M'_S S'M'_S\rangle$$

$$= \sum_{J=|L-S|}^{L+S} \sum_{J'=|L'-S'|}^{L'+S'} (-1)^{L+L'-S-S'+M_J+M'_J}\left[(2J+1)(2J'+1)\right]^{1/2}$$

$$\times \begin{pmatrix} L & S & J \\ M_J - M_S & M_S & -M_J \end{pmatrix}\begin{pmatrix} L' & S' & J' \\ M'_J - M_{S'} & M_{S'} & -M'_J \end{pmatrix}\mathbf{H}(2)_{LSJM_J, L'S'J'M'_J}$$

alternatively, might want **H**(coupled). Need **TH**(1)(uncoupled)$\mathbf{T}^{\dagger}$

$$\left[\mathbf{TH}(1)\text{ uncoupled})\mathbf{T}^{\dagger}\right]_{LSJM_J, L'S'J'M'_J} = \sum_{M_L=M_J-S\geq -L}^{M_J+S\leq L} \sum_{M'_L=M'_J-S'\geq -L'}^{M'_J+S'\leq L'}$$

(or, if $S > L$, for $M_S = M_J - L \geq -S$ to $M_S = M_J + L \leq S$)

$$(-1)^{L+L'-S-S'+M_J+M'_J}\left[(2J+1)\; 2J'+1)\right]^{1/2}$$

$$\times \begin{pmatrix} L & S & J \\ M_J - M_S & M_S & -M_J \end{pmatrix}\begin{pmatrix} L' & S' & J' \\ M'_J - M'_S & M'_S & -M'_J \end{pmatrix}\mathbf{H}(1)_{LM_L SM_S, L'M'_L S'M'_S}$$

Other kinds of useful transformations

3-j are good to go from coupled↔uncoupled: trade J for M_L or M_S

6-j and 9-j are useful to go between different coupled basis set: trade one intermediate angular momentum magnitude for another

Suppose you have 3 nonzero sub-system angular momenta

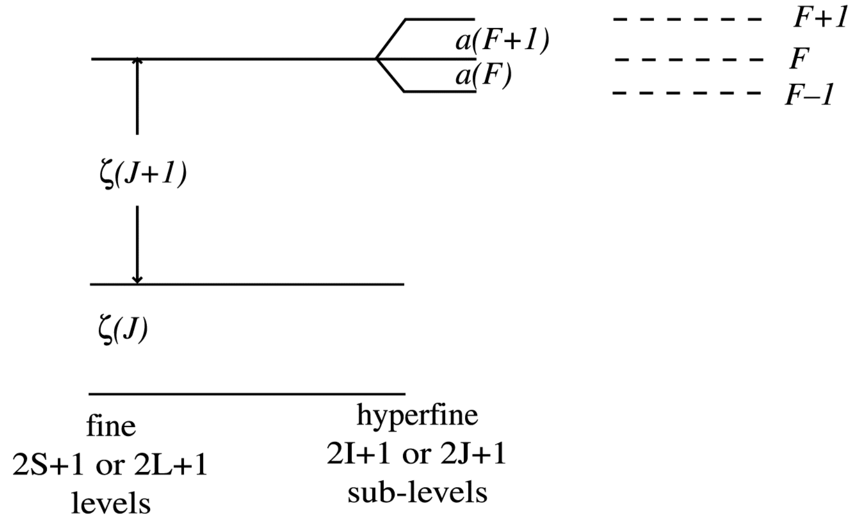
s, $\boldsymbol{\ell}$, and **I** (nuclear spin)

$\mathbf{H} = \mathbf{H}^{SO} + \mathbf{H}^{mhfs}$ $\quad\quad \mathbf{H}^{mhfs} = a\mathbf{I}\cdot\mathbf{j}$

$\boldsymbol{\ell} + \mathbf{s} = \mathbf{j}$ $\quad\quad (\boldsymbol{\ell} + \mathbf{s})^2 = \mathbf{j}^2$ $\quad\quad \boldsymbol{\ell}\cdot\mathbf{s} = \frac{1}{2}[j(j+1) - \ell(\ell+1) - s(s+1)]$

$\mathbf{j} + \mathbf{I} = \mathbf{F}$ $\quad\quad (\mathbf{j} + \mathbf{I})^2 = \mathbf{F}^2$ $\quad\quad \mathbf{j}\cdot\mathbf{I} = \frac{1}{2}[F(F+1) - j(j+1) - I(I+1)]$

patterns



interval rules

assignment

recurrent dynamics

simple patterns when $|\zeta| >> |a|$. Different kind of simple patterns when $|a| >> |\zeta|$.

^{137}Ba $\quad\quad$ sd ^{1,3}D $\rightarrow s_1, \ell_1 = 0, s_2, \ell_2 = 2, I = 3/2$

4 nonzero sub-system angular momenta! How do we transform between different ways of coupling these angular momenta?

6-j

3 fundamental angular momenta: *a, b, c*

3 possible "intermediate" angular momenta: *e f g*

$a + b = e$
$a + c = f$
$b + c = g$

1 total angular momentum: F (*my notation is different from that in* Brown and Carrington)

e.g.

$\boldsymbol{\ell} + \mathbf{s} = \mathbf{j}$
$\mathbf{j} + \mathbf{I} = \mathbf{F}$
$(\mathbf{H}^{SO} >> \mathbf{H}^{hfs})$
usual except for $L = 0$ states

OR

$\mathbf{s} + \mathbf{I} = \mathbf{G}$
$\mathbf{G} + \boldsymbol{\ell} = \mathbf{F}$
$(\mathbf{H}^{hfs} >> \mathbf{H}^{SO})$
high Rydberg states of many-e^- atoms with one e^- in valence s-orbital

$$\left|((a,b)e,c)FM_F\right\rangle = \sum_g \left|(a,(b,c)g)FM_F\right\rangle[(2e+1)(2g+1)]^{1/2}(1)^{a+b+c+F}\begin{Bmatrix} a & b & e \\ c & F & g \end{Bmatrix}$$

LHS: Couple $a + b$ to make e, couple $e + c$ to make F. RHS: couple $b + c$ to make g, couple $g + a$ to make F.
6-j is independent of M_F. Projection quantum number defined for only total, F. To define a different projection quantum number instead of M_F, must perform coupled → uncoupled transformations followed by uncoupled to coupled transformations.

6-j invariant under interchange of any 2 columns and upper and lower arguments of each of any 2 columns.

6-j can be expressed as product of 4 3-j's.

9-j

4 fundamental angular momenta: *a, b, c, d*
many possible intermediate angular momenta.

$$\left|((a,d)g,(b,c)h)i\right\rangle = \sum [(2e+1)(2f+1)(2g+1)(2h+1)]^{1/2}\begin{Bmatrix} a & b & e \\ d & c & f \\ g & h & i \end{Bmatrix}\left|((a,b)e,(d,c)f)i\right\rangle$$

LHS: $a + d = g,\ b + c = h,\ g + h = i$
RHS: $a + b = e,\ d + c = f,\ e + f = i$

multiply by $(-1)^P$ (P is sum of all 9 arguments)
upon exchange of any 2 rows or columns

9-j unchanged by even permutation (123→231) of rows or columns or reflection about either diagonal

If one argument of 9-j is 0, reduces to a 6-j.

Now go to the diatomic molecules

electronic wavefunction
rotational wavefunction
two coordinate systems! Laboratory-fixed and molecule (body)-fixed.

three angular momentum sub-systems

$|LM_L\rangle|SM_S\rangle|RM_R\rangle$ total orbital, total spin, nuclear rotation

or more if we have Rydberg states. But L is never defined because a molecule is not spherical. We get Λ but not L!

$\mathbf{R}$	nuclear rotation
$\mathbf{N}^+ = \mathbf{R} + \Lambda^+\hat{\mathbf{k}}$	total angular momentum of ion-core exclusive of electron spin
Λ^+ is $\mathbf{L}_z^+$	projection of L^+ on bond axis (z)
$\mathbf{N} = \mathbf{N}^+ + \ell_z$	total angular momentum exclusive of electron spin
ℓ_z	projection of Rydberg e^- orbital angular momentum on z-axis
$\mathbf{J} = \mathbf{N} + \mathbf{S}$	total angular momentum
$\mathbf{R} = \mathbf{J} - \mathbf{L} - \mathbf{S}$	
$\mathbf{S}$	total spin
$\mathbf{S}^+$	spin of ion-core.

Many angular momenta. Many coupling schemes.

Watson's idea: $|(\text{ion - core})(\text{Rydberg } e^-) \text{ totals}\rangle$

Hund's coupling cases: *a, b, c, d, e* or $|(a^+)b\rangle$, for example.

Hierarchy of $\Sigma 1/r_{ij}$, $\mathbf{H}^{SO}$, $\mathbf{H}^{ROT}$.