Notes on Westerfit

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1 Symmetry

Initial version of the code will be restricted to $\mathbf{G}_6$ symmetry.

	E	(123)	(23)*	
$\mathbf{G}_6$	1E	2C$_3(z)$	3σ_v	
A$_1$:	1	1	1	J_y, $\cos 3\alpha$
A$_2$:	1	1	-1	J_z, J_x, P_α, $\sin 3\alpha$
E:	2	-1	0	

Table 1: Character Table for the $\mathbf{G}_6$

In development is a $\mathbf{G}_{12}$ version.

	E	(123)	(23)*	(45)	(123)(45)	(23)(45)*	
$\mathbf{G}_{12}$	1	2	3	1	2	3	
Equip. Rot.	R^0	R^0	R_c^π	R_a^π	R_a^π	R_b^π	
A_1 :	1	1	1	1	1	1	$\cos 6\alpha$
A_2 :	1	1	-1	1	1	-1	J_z, P_α, $\sin 6\alpha$
B_1 :	1	1	1	-1	-1	-1	J_y, $\cos 3\alpha$
B_2 :	1	1	-1	-1	-1	1	J_x, $\sin 3\alpha$
E_1 :	2	-1	0	2	-1	0	$e^{\pm\iota\alpha}$
E_2 :	2	-1	0	-2	1	0	$e^{\pm 2\iota\alpha}$

Table 2: Character Table for the $\mathbf{G}_6$

Here are the operators sorted by irreducible representation. Only A1 can appear in the Hamiltonian.

$\hat{O}_{lmo}^{(n)}$	A1	A2
1100	N_y	N_z, N_x
1010	-	P_α
1001	S_y	S_z, S_x
2200	N_z^2, N_y^2, N_x^2, $\{N_z, N_x\}$	$\{N_z, N_y\}$, $\{N_x, N_y\}$
2020	P_α^2, $\cos 3\alpha$	$\sin 3\alpha$
2110	$P_\alpha N_z$, $P_\alpha N_x$	$P_\alpha N_y$
2101	$N_z S_z$, $N_x S_x$, $N_y S_y$, $\{N_z, S_x\}$, $\{N_x, S_z\}$	$\{N_z, S_y\}$, $\{N_y, S_z\}$, $\{N_x, S_y\}$, $\{N_y, S_x\}$
2011	$P_\alpha S_z$, $P_\alpha S_x$	$P_\alpha S_y$

Table 3: Operators & their Symmetries for the SpiTorRot problem

l is rotational order, m is torsional order, o is spin order, and $n = l + m + o$ All terms with even orders of momentum are symmetric with respect to time reversal. $o = 2$ terms are neglected due to lack of relevance

2 Wavefunction

Okay, we want to look at molecular rotations $|NK\rangle$, torsions $|Kv_t\sigma\rangle$, spin-rotation $|JSNK\rangle$, and, later, hyperfine $|FIJK\rangle$.

$$|FIJSNKv_t\sigma\rangle = mess \tag{1}$$

$$|NKM\rangle = (-1)^{M-K}\left(\frac{2N+1}{8\pi^2}\right)^{1/2}\mathscr{D}^N_{-M,-K}(\phi,\theta,\chi) \tag{2}$$

3 Example Matrix Structures

Pure rotation $N = 2$:

$$\begin{pmatrix} \langle -2|-2\rangle & \langle -1|-2\rangle & \langle\ 0|-2\rangle & \langle\ 1|-2\rangle & \langle\ 2|-2\rangle \\ \langle -2|-1\rangle & \langle -1|-1\rangle & \langle\ 0|-1\rangle & \langle\ 1|-1\rangle & \langle\ 2|-1\rangle \\ \langle -2|\ 0\rangle & \langle -1|\ 0\rangle & \langle\ 0|\ 0\rangle & \langle\ 1|\ 0\rangle & \langle\ 2|\ 0\rangle \\ \langle -2|\ 1\rangle & \langle -1|\ 1\rangle & \langle\ 0|\ 1\rangle & \langle\ 1|\ 1\rangle & \langle\ 2|\ 1\rangle \\ \langle -2|\ 2\rangle & \langle -1|\ 2\rangle & \langle\ 0|\ 2\rangle & \langle\ 1|\ 2\rangle & \langle\ 2|\ 2\rangle \end{pmatrix}$$

Pure rotation $N = 1$:

$$\begin{pmatrix} \langle -1|-1\rangle & \langle\ 0|-1\rangle & \langle\ 1|-1\rangle \\ \langle -1|\ 0\rangle & \langle\ 0|\ 0\rangle & \langle\ 1|\ 0\rangle \\ \langle -1|\ 1\rangle & \langle\ 0|\ 1\rangle & \langle\ 1|\ 1\rangle \end{pmatrix}$$

The above matrices are Hermetian so we can invoke Julia's Hermitian(A) command to fill in the bottom triangle. These are the stripped down matrices using $\langle K+n|K\rangle = \langle K+n|H|K\rangle$ notation. The H is dropped for compactness. Based on the below, we can see the off-diagonal arrays start at $K = -N$ and end at $K = N - m$ where m is how many steps off-diagonal the array is.

$$\begin{pmatrix} \langle K+0|-2\rangle & \langle K+1|-2\rangle & \langle K+2|-2\rangle & & & \\ & \langle K+0|-1\rangle & \langle K+1|-1\rangle & \langle K+2|-1\rangle & & \\ & & \langle K+0|\ 0\rangle & \langle K+1|\ 0\rangle & \langle K+2|\ 0\rangle & \\ & & & \langle K+0|\ 1\rangle & \langle K+1|\ 1\rangle & \\ & & & & \langle K+0|\ 2\rangle \end{pmatrix}$$

$$\begin{pmatrix} \langle K+0|-1\rangle & \langle K+1|-1\rangle & \langle K+2|-1\rangle \\ & \langle K+0|\ 0\rangle & \langle K+1|\ 0\rangle \\ & & \langle K+0|\ 1\rangle \end{pmatrix}$$

Stripped down matrix using $\langle K|H|K+n\rangle$ notation

$$\begin{pmatrix} \langle -1|K+0\rangle & \langle\ 0|K-1\rangle & \langle\ 1|K-2\rangle \\ & \langle\ 0|K+0\rangle & \langle\ 1|K-1\rangle \\ & & \langle\ 1|K+0\rangle \end{pmatrix}$$

Spin-rotation for $J = 3/2, S = 1/2$:

$$\left(\begin{array}{ccc|ccccc} \langle 1-1|1-1\rangle & \langle 1\ \ 0|1-1\rangle & \langle 1\ \ 1|1-1\rangle & \langle 2-2|1-1\rangle & \langle 2-1|1-1\rangle & \langle 2\ \ 0|1-1\rangle & \langle 2\ \ 1|1-1\rangle & \langle 2\ \ 2|1-1\rangle \\ \langle 1-1|1\ \ 0\rangle & \langle 1\ \ 0|1\ \ 0\rangle & \langle 1\ \ 1|1\ \ 0\rangle & \langle 2-2|1\ \ 0\rangle & \langle 2-1|1\ \ 0\rangle & \langle 2\ \ 0|1\ \ 0\rangle & \langle 2\ \ 1|1\ \ 0\rangle & \langle 2\ \ 2|1\ \ 0\rangle \\ \langle 1-1|1\ \ 1\rangle & \langle 1\ \ 0|1\ \ 1\rangle & \langle 1\ \ 1|1\ \ 1\rangle & \langle 2-2|1\ \ 1\rangle & \langle 2-1|1\ \ 1\rangle & \langle 2\ \ 0|1\ \ 1\rangle & \langle 2\ \ 1|1\ \ 1\rangle & \langle 2\ \ 2|1\ \ 1\rangle \\ \hline \langle 1-1|2-2\rangle & \langle 1\ \ 0|2-2\rangle & \langle 1\ \ 1|2-2\rangle & \langle 2-2|2-2\rangle & \langle 2-1|2-2\rangle & \langle 2\ \ 0|2-2\rangle & \langle 2\ \ 1|2-2\rangle & \langle 2\ \ 2|2-2\rangle \\ \langle 1-1|2-1\rangle & \langle 1\ \ 0|2-1\rangle & \langle 1\ \ 1|2-1\rangle & \langle 2-2|2-1\rangle & \langle 2-1|2-1\rangle & \langle 2\ \ 0|2-1\rangle & \langle 2\ \ 1|2-1\rangle & \langle 2\ \ 2|2-1\rangle \\ \langle 1-1|2\ \ 0\rangle & \langle 1\ \ 0|2\ \ 0\rangle & \langle 1\ \ 1|2\ \ 0\rangle & \langle 2-2|2\ \ 0\rangle & \langle 2-1|2\ \ 0\rangle & \langle 2\ \ 0|2\ \ 0\rangle & \langle 2\ \ 1|2\ \ 0\rangle & \langle 2\ \ 2|2\ \ 0\rangle \\ \langle 1-1|2\ \ 1\rangle & \langle 1\ \ 0|2\ \ 1\rangle & \langle 1\ \ 1|2\ \ 1\rangle & \langle 2-2|2\ \ 1\rangle & \langle 2-1|2\ \ 1\rangle & \langle 2\ \ 0|2\ \ 1\rangle & \langle 2\ \ 1|2\ \ 1\rangle & \langle 2\ \ 2|2\ \ 1\rangle \\ \langle 1-1|2\ \ 2\rangle & \langle 1\ \ 0|2\ \ 2\rangle & \langle 1\ \ 1|2\ \ 2\rangle & \langle 2-2|2\ \ 2\rangle & \langle 2-1|2\ \ 2\rangle & \langle 2\ \ 0|2\ \ 2\rangle & \langle 2\ \ 1|2\ \ 2\rangle & \langle 2\ \ 2|2\ \ 2\rangle \end{array}\right)$$

We can also remove Stripped down matrix

$$\left(\begin{array}{ccc|ccccc} \langle 1-1|1-1\rangle & \langle 1\ \ 0|1-1\rangle & \langle 1\ \ 1|1-1\rangle & \langle 2-2|1-1\rangle & \langle 2-1|1-1\rangle & \langle 2\ \ 0|1-1\rangle & \langle 2\ \ 1|1-1\rangle & \\ & \langle 1\ \ 0|1\ \ 0\rangle & \langle 1\ \ 1|1\ \ 0\rangle & \langle 2-2|1\ \ 0\rangle & \langle 2-1|1\ \ 0\rangle & \langle 2\ \ 0|1\ \ 0\rangle & \langle 2\ \ 1|1\ \ 0\rangle & \langle 2\ \ 2|1\ \ 0\rangle \\ & & \langle 1\ \ 1|1\ \ 1\rangle & & \langle 2-1|1\ \ 1\rangle & \langle 2\ \ 0|1\ \ 1\rangle & \langle 2\ \ 1|1\ \ 1\rangle & \langle 2\ \ 2|1\ \ 1\rangle \\ \hline & & & \langle 2-2|2-2\rangle & \langle 2-1|2-2\rangle & \langle 2\ \ 0|2-2\rangle & \langle 2\ \ 1|2-2\rangle & \langle 2\ \ 2|2-2\rangle \\ & & & & \langle 2-1|2-1\rangle & \langle 2\ \ 0|2-1\rangle & \langle 2\ \ 1|2-1\rangle & \langle 2\ \ 2|2-1\rangle \\ & & & & & \langle 2\ \ 0|2\ \ 0\rangle & \langle 2\ \ 1|2\ \ 0\rangle & \langle 2\ \ 2|2\ \ 0\rangle \\ & & & & & & \langle 2\ \ 1|2\ \ 1\rangle & \langle 2\ \ 2|2\ \ 1\rangle \\ & & & & & & & \langle 2\ \ 2|2\ \ 2\rangle \end{array}\right)$$

Unfortunately the off-diagonal block isn't square nor symmetric so I can't strip it down much at all. Now for the matrix using $\langle N+m, K+n|NK\rangle$ notation. Much trickier to figure out the patterns cleanly. Purple spans $K = -N+1...N$, green $K = -N...N$, black $K = -N...N$, red $K = -N...N$, blue $K = -N...N-1$.

$$\begin{pmatrix} \langle N+1, K-1|1-1\rangle & \langle N+1, K+0|1-1\rangle & \langle N+1, K+1|1-1\rangle & \langle N+1, K+2|1-1\rangle & & \\ \langle N+1, K-2|1\ 0\rangle & \langle N+1, K-1|1\ 0\rangle & \langle N+1, K+0|1\ 0\rangle & \langle N+1, K+1|1\ 0\rangle & \langle N+1, K+2|1\ 0\rangle \\ & \langle N+1, K-2|1\ 1\rangle & \langle N+1, K-1|1\ 1\rangle & \langle N+1, K+0|1\ 1\rangle & \langle N+1, K+1|1\ 1\rangle \end{pmatrix}$$

With the diagm() function, we can make this a sum of 3 matrices, might not be the fastest though:

$$\begin{pmatrix} \langle N+1, K-1|1-1\rangle & 0 & 0 & 0 & 0 \\ \langle N+1, K-2|1\ 0\rangle & \langle N+1, K-1|1\ 0\rangle & 0 & 0 & 0 \\ 0 & \langle N+1, K-2|1\ 1\rangle & \langle N+1, K-1|1\ 1\rangle & 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} 0 & \langle N+1, K+0|1-1\rangle & 0 & 0 & 0 \\ 0 & 0 & \langle N+1, K+0|1\ 0\rangle & 0 & 0 \\ 0 & 0 & 0 & \langle N+1, K+0|1\ 1\rangle & 0 \end{pmatrix}$$

$$\begin{pmatrix} 0 & 0 & \langle N+1, K+1|1-1\rangle & \langle N+1, K+2|1-1\rangle & 0 \\ 0 & 0 & 0 & \langle N+1, K+1|1\ 0\rangle & \langle N+1, K+2|1\ 0\rangle \\ 0 & 0 & 0 & 0 & \langle N+1, K+1|1\ 1\rangle \end{pmatrix}$$

Now for some real fun, $[N'm'|Nm]$ is going to represent a torsional-rotational block. It is $2N'+1$ by $2N+1$ and contains all appropriate K values. While m spans $-8, -7, ..., 7, 8$, we are truncating to ± 1. Same J as before

$$\begin{pmatrix} [1,-1|1,-1] & [1,+0|1,-1] & [1,+1|1,-1] & [2,-1|1,-1] & [2,+0|1,0] & [2,+1|1,+0] \\ [1,-1|1,+0] & [1,+0|1,+0] & [1,+1|1,+0] & [2,-1|1,+0] & [2,+0|1,+0] & [2,+1|1,+0] \\ [1,-1|1,+1] & [1,+0|1,+1] & [1,+1|1,+1] & [2,-1|1,+1] & [2,+0|1,+1] & [2,+1|1,+1] \\ \hline [1,0|2,-1] & [1,+0|2,-1] & [1,+1|2,-1] & [2,-1|2,-1] & [2,+0|2,-1] & [2,+1|2,-1] \\ [1,-1|2,+0] & [1,+0|2,+0] & [1,+1|2,+0] & [2,-1|2,+0] & [2,+0|2,+0] & [2,+1|2,+0] \\ [1,-1|2,+1] & [1,+0|2,+1] & [1,+1|2,+1] & [2,-1|2,+1] & [2,+0|2,+1] & [2,+1|2,+1] \end{pmatrix}$$

Stripped down based on 2nd order operators:

$$\begin{pmatrix} [1,-1|1,-1] & [1,+0|1,-1] & & [2,-1|1,-1] & [2,+0|1,-1] & \\ & [1,+0|1,+0] & [1,+1|1,+0] & [2,-1|1,+0] & [2,+0|1,+0] & [2,+1|1,+0] \\ & & [1,+1|1,+1] & & [2,+0|1,+1] & [2,+1|1,+1] \\ \hline & & & [2,-1|2,-1] & [2,+0|2,-1] & \\ & & & & [2,+0|2,+0] & [2,+1|2,+0] \\ & & & & & [2,+1|2,+1] \end{pmatrix}$$

As another example matrix, here's $J = 3/2$, $S = 1/2$ with 2 torsional sates. Since we have $N = 1$ and 2, there are 16 possible states. Each element corresponds to $\langle N'K'v'_t| H |NKv_t\rangle$ and lists the relevant elements used in matrix construction. Equations 10-12 are pure rotation, 29-31 are the $N' = N$ spin-rotation, 32-36 are the $N' = N+1$ spin-rotation, and 45 & 46 are spin-torsion. The notation $23(\#)$ & $24(\#)$ indicate multiplication by the torsional overlap integrals off diagonal in K by 1 and 2, respectively.

$\langle 1,-1,0|$	$\langle 1,0,0|$	$\langle 1,1,0|$	$\langle 1,-1,1|$	$\langle 1,0,1|$	$\langle 1,1,1|$	$\langle 2,-2,0|$	$\langle 2,-1,0|$	$\langle 2,0,0|$	$\langle 2,1,0|$	$\langle 2,2,0|$	$\langle 2,-2,1|$	$\langle 2,-1,1|$	$\langle 2,0,1|$	$\langle 2,1,1|$	$\langle 2,2,1|$
10,29,45	11,30	12,31	45	23(11,30)	24(12,31)	33	34,46	35	36		21(33)	46	24(35)	24(36)	
	10,29,45	11,30		45	23(11,30)	32	33	34,46	35	36	20(32)	21(33)	46	23(35)	24(36)
		10,29,45			45		32	33	34,46	35		20(32)	21(33)	46	23(35)
			10,29,45	11,30	12,31	21(33)	46	23(35)	24(36)		33	34,46	35	36	
				10,29,45	11,30	20(32)	21(33)	46	23(35)	24(36)	32	33	34,46	35	36
					10,29,45		20(32)	21(33)	46	23(35)		32	33	34,46	35
						10,29,45	11,30	12,31			45	23(11,30)	24(12,31)		
							10,29,45	11,30	12,31			45	23(11,30)	24(12,31)	
								10,29,45	11,30	12,31			45	23(11,30)	24(12,31)
									10,29,45	11,30				45	23(11,30)
										10,29,45					45
											10,29,45	11,30	12,31		
												10,29,45	11,30	12,31	
													10,29,45	11,30	12,31
														10,29,45	11,30
															10,29,45

4 Symmetries in Single Diagonalization Approach

For J=3/2, m=-3,0,3:

$$\left[\begin{array}{ccc|ccc|ccc|cccccc|ccc|ccc}
D_{11}+F_3+\rho_{13} & -D_{01} & D_{-11} & -V & \cdot & \cdot & \cdot & \cdot & \cdot & S_{12} & -S_{11}-\eta_{13} & S_{01} & -S_{-11} & \cdot & -S_{02} & & & & & & \\
-D_{01} & D_{00}+F_3 & D_{01} & \cdot & -V & \cdot & \cdot & \cdot & \cdot & S_{02} & S_{10} & \cdot & S_{-11} & S_{01} & S_{11}-\eta_{13} & S_{12} & & & & & \\
D_{-11} & D_{01} & D_{11}+F_3-\rho_{13} & \cdot & \cdot & -V & \cdot & \cdot & \cdot & & & & & & & & & & & & \\ \hline
-V & \cdot & \cdot & D_{11}+F_0 & -D_{01} & D_{-11} & -V & \cdot & \cdot & & & & & & & & S_{12} & -S_{11} & S_{01} & -S_{-11} & \cdot & -S_{02} \\
\cdot & -V & \cdot & -D_{01} & D_{00}+F_0 & D_{01} & \cdot & -V & \cdot & & & & & & & & S_{02} & S_{10} & \cdot & S_{-11} & S_{01} & S_{11} & S_{12} \\
\cdot & \cdot & -V & D_{-11} & D_{01} & D_{11}+F_0 & \cdot & \cdot & -V & & & & & & & & & & & & \\ \hline
\cdot & \cdot & \cdot & -V & \cdot & \cdot & D_{11}+F_3-\rho_{13} & -D_{01} & D_{-11} & & & & & & & & S_{12} & \eta_{13}-S_{11} & S_{01} & -S_{-11} & S_{10} & -S_{02} \\
\cdot & \cdot & \cdot & \cdot & -V & \cdot & -D_{01} & D_{00}+F_3 & D_{01} & & & & & & & & S_{02} & S_{10} & \cdot & S_{-11} & S_{01} & S_{11}+\eta_{13} & S_{12} \\
\cdot & \cdot & \cdot & \cdot & \cdot & -V & D_{-11} & D_{01} & D_{11}+F_3+\rho_{13} & & & & & & & & & & & & \\ \hline
S_{12} & S_{02} & \cdots & & & & & & & E_{22}+F_3+\rho_{23} & -E_{12} & E_{02} & & & & & -V & & & & \\
-S_{11}-\eta_{13} & S_{10} & S_{-11} & & & & & & & -E_{12} & E_{11}+F_3+\rho_{13} & -E_{01} & -E_{11} & E_{01} & E_{02} & & \cdot & -V & & & \\
S_{01} & S_{01} & \cdots & & & & & & & E_{02} & -E_{01} & E_{00}+F_3 & E_{01} & E_{11}+F_3-\rho_{13} & E_{12} & & & & -V & & \\
-S_{-11} & S_{10} & S_{11}-\eta_{13} & & & & & & & & E_{-11} & E_{01} & & & & & & & & \\
\cdot & -S_{02} & S_{12} & & & & & & & E_{02} & E_{12} & E_{22}+F_3-\rho_{23} & & & & & & & & \\ \hline
& & & S_{12} & S_{02} & \cdots & & & & -V & \cdot & \cdot & & & & & E_{22}+F_0 & -E_{12} & E_{02} & -V & \\
& & & -S_{11} & S_{10} & S_{-11} & & & & \cdot & -V & \cdot & & & & & -E_{12} & E_{11}+F_0 & -E_{01} & \cdot & -V \\
& & & S_{01} & S_{01} & \cdots & & & & \cdot & \cdot & -V & & & & & E_{02} & -E_{01} & E_{00}+F_0 & \cdots \\ \hline
& & & & & & S_{12} & S_{02} & & & & & & & & -V & & & & E_{22}+F_3-\rho_{23} & -E_{12} & E_{02} \\
& & & & & & \eta_{13}-S_{11} & S_{10} & S_{-11} & & & & & & & \cdot & -V & & & -E_{12} & E_{11}+F_3-\rho_{13} & -E_{01} \\
& & & & & & S_{01} & S_{01} & \cdots & & & & & & & & & -V & & E_{02} & E_{-11} & E_{00}+F_3 & E_{22}+F_3+\rho_{23}
\end{array}\right]$$

After unitary transformations:

$$\left[\begin{array}{ccc|ccc|ccc|ccc|ccc|ccc}
D_{11}-D_{-11}+F_3 & \sqrt{2}D_{01} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \rho_{13} & S_{12} & \cdot & S_{11}+S_{-11} & \cdot & \cdot & \cdot & \eta_{13} & \cdot & \cdot \\
\sqrt{2}D_{01} & D_{00}+F_3 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & -\sqrt{2}S_{02} & \cdot & \sqrt{2}S_{10} & \cdot & \cdot & \cdot & \cdot & \eta_{03} & \cdot \\
\cdot & \cdot & D_{11}+D_{-11}+F_3 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & S_{11}-S_{-11} & \sqrt{2}S_{01} & S_{12} & \cdot & \cdot & \cdot & \cdot & \cdot & \eta_{13} \\ \hline
\cdot & \cdot & \cdot & D_{11}-D_{-11}+F_0 & \sqrt{2}D_{01} & \cdot & \rho_{13} & \cdot & \cdot & \cdot & \cdot & \cdot & S_{12} & \cdot & S_{11}+S_{-11} & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \sqrt{2}D_{01} & D_{00}+F_0 & \cdot & -\sqrt{2}V & \cdot & -\sqrt{2}V & \cdot & \cdot & \cdot & -\sqrt{2}S_{02} & \cdot & \sqrt{2}S_{10} & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & D_{11}+D_{-11}+F_0 & \cdot & -\sqrt{2}V & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \hline
\rho_{13} & \cdot & \cdot & -\sqrt{2}V & \cdot & \cdot & D_{11}-D_{-11}+F_3 & \sqrt{2}D_{01} & \cdot & \eta_{13} & \cdot & \cdot & \cdot & \cdot & \cdot & S_{12} & \cdot & S_{11}+S_{-11} \\
\cdot & \cdot & \rho_{13} & \cdot & -\sqrt{2}V & \cdot & \sqrt{2}D_{01} & D_{00}+F_3 & \cdot & \cdot & \eta_{13} & \cdot & \cdot & \cdot & \cdot & -\sqrt{2}S_{02} & \cdot & \sqrt{2}S_{10} \\
S_{12} & -\sqrt{2}S_{02} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & E_{22}+F_3 & \eta_{13} & \cdot & E_{12} & \cdot & \cdot & \cdot & \cdot & \cdot & \rho_{23} \\ \hline
S_{11}-S_{-11} & \cdot & \cdot & & & & \eta_{13} & & & E_{11}-E_{-11}+F_3 & \sqrt{2}E_{01} & E_{12} & & & & \rho_{13} & & \\
\sqrt{2}S_{01} & & & & & & & & \eta_{13} & \sqrt{2}E_{01} & E_{00}+F_3 & \sqrt{2}E_{02} & & & & & & \\
S_{11}+S_{-11} & \sqrt{2}S_{10} & & & & & & & E_{12} & E_{12} & \sqrt{2}E_{02} & E_{22}+F_3 & & & & & & \\ \hline
& & & S_{12} & -\sqrt{2}S_{02} & & & & & & & & E_{22}+F_0 & E_{12} & & -\sqrt{2}V & & \\
& & & S_{11}+S_{-11} & \sqrt{2}S_{10} & & & & & & & & E_{12} & E_{11}-E_{-11}+F_0 & & & -\sqrt{2}V & \\
& & & & & & & & & & & & E_{12} & & E_{22}+F_0 & & & -\sqrt{2}V \\ \hline
\eta_{13} & \cdot & & & & & S_{12} & -\sqrt{2}S_{02} & & & & \rho_{23} & -\sqrt{2}V & & & E_{22}+F_3 & E_{12} & \\
\cdot & \eta_{03} & & & & & S_{11}+S_{-11} & \sqrt{2}S_{10} & \rho_{13} & & & & & -\sqrt{2}V & & \sqrt{2}E_{01} & E_{00}+F_3 & \sqrt{2}E_{02} \\
\cdot & \eta_{13} & & & & & & & & & & & & & -\sqrt{2}V & E_{12} & \sqrt{2}E_{02} & E_{22}+F_3
\end{array}\right]$$

A_1 matrix:

$$\left[\begin{array}{ccc|ccc|ccc|ccc}
D_{11}-D_{-11}+F_3 & \sqrt{2}D_{01} & \cdot & \rho_{13} & S_{12} & S_{11}+S_{-11} & \cdot & \cdot & \cdot & \eta_{13} & \cdot & \cdot \\
\sqrt{2}D_{01} & D_{00}+F_3 & \cdot & \cdot & -\sqrt{2}S_{02} & \sqrt{2}S_{10} & \cdot & \cdot & \cdot & \cdot & \eta_{03} & \cdot \\
\cdot & \cdot & D_{11}+D_{-11}+F_0 & -\sqrt{2}V & \cdot & \cdot & S_{11}-S_{-11} & \sqrt{2}S_{01} & S_{12} & \cdot & \cdot & \cdot \\ \hline
\rho_{13} & \cdot & -\sqrt{2}V & D_{11}+D_{-11}+F_3 & \cdot & \eta_{13} & \cdot & \cdot & \cdot & S_{11}-S_{-11} & \sqrt{2}S_{01} & S_{12} \\
S_{12} & -\sqrt{2}S_{02} & \cdot & \cdot & E_{22}+F_3 & E_{12} & \cdot & \cdot & \cdot & \cdot & \cdot & \rho_{23} \\
S_{11}+S_{-11} & \sqrt{2}S_{10} & \cdot & \eta_{13} & E_{12} & E_{11}+E_{-11}+F_3 & \cdot & \cdot & \cdot & \rho_{13} & \cdot & \cdot \\ \hline
\cdot & \cdot & S_{11}-S_{-11} & \cdot & \cdot & \cdot & E_{11}-E_{-11}+F_0 & \sqrt{2}E_{01} & E_{12} & -\sqrt{2}V & \cdot & \cdot \\
\cdot & \cdot & \sqrt{2}S_{01} & \cdot & \cdot & \cdot & \sqrt{2}E_{01} & E_{00}+F_0 & \sqrt{2}E_{02} & \cdot & -\sqrt{2}V & \cdot \\
\cdot & \cdot & S_{12} & \cdot & \cdot & \cdot & E_{12} & \sqrt{2}E_{02} & E_{22}+F_0 & \cdot & \cdot & -\sqrt{2}V \\ \hline
\eta_{13} & \cdot & \cdot & S_{11}-S_{-11} & \cdot & \rho_{13} & -\sqrt{2}V & \cdot & \cdot & E_{11}-E_{-11}+F_3 & \sqrt{2}E_{01} & E_{12} \\
\cdot & \eta_{03} & \cdot & \sqrt{2}S_{01} & \cdot & \cdot & \cdot & -\sqrt{2}V & \cdot & \sqrt{2}E_{01} & E_{00}+F_3 & \sqrt{2}E_{02} \\
\cdot & \cdot & \cdot & S_{12} & \rho_{23} & \cdot & \cdot & \cdot & -\sqrt{2}V & E_{12} & \sqrt{2}E_{02} & E_{22}+F_3
\end{array}\right]$$

A_2 matrix:

$$\left[\begin{array}{c|cc|cc|ccc|cc|cc}
D_{11}+D_{-11}+F_3 & \cdot & \cdot & \rho_{13} & \cdot & S_{11}-S_{-11} & \sqrt{2}S_{01} & S_{12} & \cdot & \cdot & \cdot & \eta_{13} \\ \hline
\cdot & D_{11}-D_{-11}+F_0 & \sqrt{2}D_{01} & -\sqrt{2}V & \cdot & \cdot & \cdot & \cdot & S_{12} & S_{11}+S_{-11} & \cdot & \cdot \\
\cdot & \sqrt{2}D_{01} & D_{00}+F_0 & \cdot & -\sqrt{2}V & \cdot & \cdot & \cdot & -\sqrt{2}S_{02} & \sqrt{2}S_{10} & \cdot & \cdot \\ \hline
\rho_{13} & -\sqrt{2}V & \cdot & D_{11}-D_{-11}+F_3 & \sqrt{2}D_{01} & \eta_{13} & \cdot & \cdot & \cdot & \cdot & S_{12} & S_{11}+S_{-11} \\
\cdot & \cdot & -\sqrt{2}V & \sqrt{2}D_{01} & D_{00}+F_3 & \cdot & \eta_{03} & \cdot & \cdot & \cdot & -\sqrt{2}S_{02} & \sqrt{2}S_{10} \\ \hline
S_{11}-S_{-11} & \cdot & \cdot & \eta_{13} & \cdot & E_{11}-E_{-11}+F_3 & \sqrt{2}E_{01} & E_{12} & \cdot & \cdot & \cdot & \rho_{13} \\
\sqrt{2}S_{01} & \cdot & \cdot & \cdot & \eta_{03} & \sqrt{2}E_{01} & E_{00}+F_3 & \sqrt{2}E_{02} & \cdot & \cdot & \cdot & \cdot \\
S_{12} & \cdot & \cdot & \cdot & \cdot & E_{12} & \sqrt{2}E_{02} & E_{22}+F_3 & \cdot & \cdot & \rho_{23} & \cdot \\ \hline
\cdot & S_{12} & -\sqrt{2}S_{02} & \cdot & \cdot & \cdot & \cdot & \cdot & E_{22}+F_0 & E_{12} & -\sqrt{2}V & \cdot \\
\cdot & S_{11}+S_{-11} & \sqrt{2}S_{10} & \cdot & \cdot & \cdot & \cdot & \cdot & E_{12} & E_{11}+E_{-11}+F_0 & \cdot & -\sqrt{2}V \\ \hline
\cdot & \cdot & \cdot & S_{12} & -\sqrt{2}S_{02} & \cdot & \cdot & \rho_{23} & -\sqrt{2}V & \cdot & E_{22}+F_3 & E_{12} \\
\eta_{13} & \cdot & \cdot & S_{11}+S_{-11} & \sqrt{2}S_{10} & \rho_{13} & \cdot & \cdot & \cdot & -\sqrt{2}V & E_{12} & E_{11}+E_{-11}+F_3
\end{array}\right]$$

The unitary transformations rearrange the wavefunctions into the following. They are relabelled into using signed K and m quantum numbers and then to traditional $K_a K_c$ and v_t.

$$
\begin{bmatrix}
\frac{1}{2}(|1-1-3\rangle + |1+1+3\rangle - |1+1-3\rangle - |1-1+3\rangle) \\
\frac{1}{\sqrt{2}}(|1\ \ 0+3\rangle - |1\ \ 0-3\rangle) \\
\frac{1}{2}(|1-13\rangle + |1+1+3\rangle - |1-1-3\rangle - |1+1-3\rangle) \\
\frac{1}{\sqrt{2}}(|1+1\ \ 0\rangle - |1-1\ \ 0\rangle) \\
|1\ \ 0\ \ 0\rangle \\
\frac{1}{\sqrt{2}}(|1+1\ \ 0\rangle + |1-1\ \ 0\rangle) \\
\frac{1}{2}(|1+1+3\rangle + |1+1-3\rangle - |1-1-3\rangle - |1-1+3\rangle) \\
\frac{1}{\sqrt{2}}(|1\ \ 0+3\rangle + |1\ \ 0-3\rangle) \\
\frac{1}{2}(|1-1-3\rangle + |1+1+3\rangle + |1+1-3\rangle + |1-1+3\rangle) \\
\frac{1}{2}(|2-2-3\rangle - |2-2+3\rangle - |2+2-3\rangle + |2+2+3\rangle) \\
\frac{1}{2}(|2-2-3\rangle - |2-1+3\rangle - |2+1-3\rangle + |2+2+3\rangle) \\
\frac{1}{\sqrt{2}}(|2\ \ 0+3\rangle - |2\ \ 0-3\rangle) \\
\frac{1}{2}(|2+1+3\rangle + |2-1+3\rangle - |2-1-3\rangle - |2+1-3\rangle) \\
\frac{1}{2}(|2-2+3\rangle + |2+2+3\rangle - |2-2-1\rangle - |2+2-3\rangle) \\
\frac{1}{\sqrt{2}}(|2+2\ \ 0\rangle - |2-2\ \ 0\rangle) \\
\frac{1}{\sqrt{2}}(|2+1\ \ 0\rangle - |2-1\ \ 0\rangle) \\
|2\ \ 0\ \ 0\rangle \\
\frac{1}{\sqrt{2}}(|2-1\ \ 0\rangle + |2+1\ \ 0\rangle) \\
\frac{1}{\sqrt{2}}(|2-2\ \ 0\rangle + |2+2\ \ 0\rangle) \\
\frac{1}{2}(|2+2-3\rangle - |2-2+3\rangle - |2-2-3\rangle + |2+2+3\rangle) \\
\frac{1}{2}(|2+1-3\rangle + |2+1+3\rangle - |2-1-3\rangle - |2-1+3\rangle) \\
\frac{1}{\sqrt{2}}(|2\ \ 0+3\rangle + |2\ \ 0-3\rangle) \\
\frac{1}{2}(|2-1-3\rangle + |2-1+3\rangle + |2+1-3\rangle + |2+1+3\rangle) \\
\frac{1}{2}(|2-2-3\rangle + |2-2+3\rangle + |2+2-3\rangle + |2+2+3\rangle)
\end{bmatrix}
\Rightarrow
\begin{bmatrix}
|1-1-3\ A_1\rangle \\
|1\ \ 0-3\ A_1\rangle \\
|1+1-3\ A_2\rangle \\
|1-1\ \ 0\ A_2\rangle \\
|1\ \ 0\ \ 0\ A_2\rangle \\
|1+1\ \ 0\ A_1\rangle \\
|1-1+3\ A_2\rangle \\
|1\ \ 0+3\ A_2\rangle \\
|1+1+3\ A_1\rangle \\
|2-2-3\ A_1\rangle \\
|2-1-3\ A_1\rangle \\
|2\ \ 0-3\ A_2\rangle \\
|2+1-3\ A_2\rangle \\
|2+2-3\ A_2\rangle \\
|2-2\ \ 0\ A_2\rangle \\
|2-1\ \ 0\ A_2\rangle \\
|2\ \ 0\ \ 0\ A_1\rangle \\
|2+1\ \ 0\ A_1\rangle \\
|2+2\ \ 0\ A_1\rangle \\
|2-2+3\ A_2\rangle \\
|2-1+3\ A_2\rangle \\
|2\ \ 0+3\ A_1\rangle \\
|2+1+3\ A_1\rangle \\
|2+2+3\ A_1\rangle
\end{bmatrix}
\Rightarrow
\begin{bmatrix}
|1_{10}1\rangle \\
|1_{01}1\rangle \\
|1_{11}1\rangle \\
|1_{10}0\rangle \\
|1_{01}0\rangle \\
|1_{11}0\rangle \\
|1_{10}2\rangle \\
|1_{01}2\rangle \\
|1_{11}2\rangle \\
|2_{21}1\rangle \\
|2_{12}1\rangle \\
|2_{02}1\rangle \\
|2_{11}1\rangle \\
|2_{20}1\rangle \\
|2_{21}0\rangle \\
|2_{12}0\rangle \\
|2_{02}0\rangle \\
|2_{11}0\rangle \\
|2_{20}0\rangle \\
|2_{21}2\rangle \\
|2_{12}2\rangle \\
|2_{02}2\rangle \\
|2_{11}2\rangle \\
|2_{20}2\rangle
\end{bmatrix}
\tag{3}
$$

The advantage of this approach is that it separates states that had the opposite signs of both K and m. These states are likely the most closely degenerate so hopefully it will help keep things straight

$$
|\psi_n\ A_1\rangle =
\begin{bmatrix}
|1-1-3\ A_1\rangle \\
|1\ \ 0-3\ A_1\rangle \\
|1+1\ \ 0\ A_1\rangle \\
|1+1+3\ A_1\rangle \\
|2-2-3\ A_1\rangle \\
|2-1-3\ A_1\rangle \\
|2\ \ 0\ \ 0\ A_1\rangle \\
|2+1\ \ 0\ A_1\rangle \\
|2+2\ \ 0\ A_1\rangle \\
|2\ \ 0+3\ A_1\rangle \\
|2+1+3\ A_1\rangle \\
|2+2+3\ A_1\rangle
\end{bmatrix}
=
\begin{bmatrix}
|1_{10}1\rangle \\
|1_{01}1\rangle \\
|1_{11}0\rangle \\
|1_{11}2\rangle \\
|2_{21}1\rangle \\
|2_{12}1\rangle \\
|2_{02}0\rangle \\
|2_{11}0\rangle \\
|2_{20}0\rangle \\
|2_{02}2\rangle \\
|2_{11}2\rangle \\
|2_{20}2\rangle
\end{bmatrix}
\neq
\begin{bmatrix}
|1_{11}1\rangle \\
|1_{10}0\rangle \\
|1_{01}0\rangle \\
|1_{10}2\rangle \\
|1_{01}2\rangle \\
|2_{02}1\rangle \\
|2_{11}1\rangle \\
|2_{20}1\rangle \\
|2_{21}0\rangle \\
|2_{12}0\rangle \\
|2_{21}2\rangle \\
|2_{12}2\rangle
\end{bmatrix}
=
\begin{bmatrix}
|1+1-3\ A_2\rangle \\
|1-1\ \ 0\ A_2\rangle \\
|1\ \ 0\ \ 0\ A_2\rangle \\
|1-1+3\ A_2\rangle \\
|1\ \ 0+3\ A_2\rangle \\
|2\ \ 0-3\ A_2\rangle \\
|2+1-3\ A_2\rangle \\
|2+2-3\ A_2\rangle \\
|2-2\ \ 0\ A_2\rangle \\
|2-1\ \ 0\ A_2\rangle \\
|2-2+3\ A_2\rangle \\
|2-1+3\ A_2\rangle
\end{bmatrix}
= |\psi_n\ A_2\rangle
\tag{4}
$$

5 Rotations

Operators for reference:

$$N^2|NK\rangle = N(N+1)|NK\rangle \tag{5}$$

$$N_z|NK\rangle = K|NK\rangle \tag{6}$$

$$N_{\pm}|NK\rangle = \sqrt{N(N+1) - K(K \mp 1)}|NK \mp 1\rangle \tag{7}$$

$$\{N_z, N_x\}|NK\rangle = \sqrt{N(N+1) - K(K \mp 1)}(K \mp 1/2)|NK \mp 1\rangle \tag{8}$$

And now our Hamiltonian and the resulting bands of our matrix:

$$H_{rot}^{(2)} = \left(A - \frac{B+C}{2}\right)N_z^2 + \frac{B+C}{2}N^2 + \frac{B-C}{4}\left(N_+^2 + N_-^2\right) + D_{ab}\{N_z, N_x\} \tag{9}$$

$$\langle NK| H_{rot}^{(2)} |NK\rangle = \left(A - \frac{B+C}{2}\right)K^2 + \frac{B+C}{2}N(N+1) \tag{10}$$

$$\langle N, K+1| H_{rot}^{(2)} |NK\rangle = D_{ab}\sqrt{N(N+1) - K(K+1)}(K+1/2) \tag{11}$$

$$\langle N, K+2| H_{rot}^{(2)} |NK\rangle = \left(\frac{B-C}{4}\right)\sqrt{(N(N+1) - K(K+1))(N(N+1) - (K+1)(K+2))} \tag{12}$$

6 Internal Rotation

We are going to couple the torsion to the molecular rotations, N, rather than J. This will look a lot like the published torsional operators and elements but with N substituted for J. Instead of following BELGI's 2 stage model, we are only using 1 stage.
'

$$|m\sigma\rangle = \frac{1}{\sqrt{2\pi}}e^{i(3m+\sigma)\alpha} \tag{13}$$

Now our reference operators

$$\langle m\sigma|P_\alpha|m\sigma\rangle = 3m + \sigma \tag{14}$$

$$\langle m\sigma|\frac{V_{3n}}{2}(1 - \cos(3n\alpha))|m\sigma\rangle = \frac{V_{3n}}{2} \tag{15}$$

$$\langle m \pm n, \sigma|\frac{V_{3n}}{2}(1 - \cos(3n\alpha))|m\sigma\rangle = -\frac{V_{3n}}{4} \tag{16}$$

And now our Hamiltonian and the bands of our purely torsional stage:

$$H_{tors}^{(2)} = F(P_\alpha - \rho N_z)^2 + \frac{V_3}{2}(1 - \cos(3\alpha)) \tag{17}$$

$$\langle Km\sigma| H_{tors}^{(2)} |Km\sigma\rangle = F(3m+\sigma)^2 - 2F\rho(3m+\sigma)K + \frac{V_3}{2} \tag{18}$$

$$\langle Km+1\sigma| H_{tors}^{(2)} |Km\sigma\rangle = -\frac{V_3}{4} \tag{19}$$

There's also off-diagonal terms in v_t terms in the second diagonalization stage. Deviating from Herbst 1984 but following BELGI, these will multiply the terms by these torsional overlap terms.

$$\langle N'K-2, v_t'| H |NKv_t\rangle = \sum_m A_{3m+\sigma}^{K-2,v_t'} A_{3m+\sigma}^{K,v_t} \langle N'K-2, v_t| H |NKv_t\rangle \tag{20}$$

$$\langle N'K-1, v_t'| H |NKv_t\rangle = \sum_m A_{3m+\sigma}^{K-1,v_t'} A_{3m+\sigma}^{K,v_t} \langle N'K-1, v_t| H |NKv_t\rangle \tag{21}$$

$$\langle N'K, v_t'| H |NKv_t\rangle = \sum_m A_{3m+\sigma}^{K,v_t'} A_{3m+\sigma}^{K,v_t} \langle N'K, v_t| H |NKv_t\rangle \tag{22}$$

$$\langle N'K+1, v_t'| H |NKv_t\rangle = \sum_m A_{3m+\sigma}^{K+1,v_t'} A_{3m+\sigma}^{K,v_t} \langle N'K+1, v_t| H |NKv_t\rangle \tag{23}$$

$$\langle N'K+2, v_t'| H |NKv_t\rangle = \sum_m A_{3m+\sigma}^{K+2,v_t'} A_{3m+\sigma}^{K,v_t} \langle N'K+2, v_t| H |NKv_t\rangle \tag{24}$$

7 Spin-Rotation

The rotations of a free radical induce a sufficient magnetic field for the unpaired electron's spin projections to have differing energy levels.

$$H_{sr}^{(2)}|JNKS\rangle = \sum_{\alpha,\beta}\{N_\alpha, S_\beta\}|JNKS\rangle \tag{25}$$

I will use Hund's case (b) under the following coupling scheme:

$$\mathbf{N} = \mathbf{J} - \mathbf{S} \tag{26}$$

Need to be able to articulate why case (b). The purpose of the subtraction construction is it makes the spin-rotation matrix elements make more sense in derivation. Lastly, for reference and the derivation of the spin-torsion operators, here are the odd ordered S operators in our coupled basis set. They are paired with the functions and full explicit.

$$\langle JNKS|\, S_z\, |JNKS\rangle = K\theta(N) \tag{27a}$$

$$\langle JNKS|\, S_z\, |JNKS\rangle = K\frac{N(N+1)+S(S+1)-J(J+1)}{2N(N+1)} \tag{27b}$$

$$\langle JN+1,KS|\, S_z\, |JNKS\rangle = \sqrt{(N+1)^2 - K^2}\,\phi(N+1) \tag{28a}$$

$$\langle JN+1,KS|\, S_z\, |JNKS\rangle = -\frac{\sqrt{(N+1)^2-K^2}}{N}\left(\frac{(N-J+S+1)(N+J+S+2)(S+J-N)(N+J-S+1)}{(2N+1)(2N+3)}\right)^{1/2} \tag{28b}$$

Below are the matrix elements for $S = 1/2$ from the Jinjun Liu paper:

$$\langle JNK|H_{sr}^{(2)}|JNK\rangle = -\frac{1}{2}a_0(J(J+1)-N(N+1)-S(S+1)) + A(3K^2 - N(N+1))\theta(N) \tag{29}$$

$$\langle JNK+1|H_{sr}^{(2)}|JNK\rangle = (d + \imath e)(K + \frac{1}{2})f(N,K)\theta(N) \tag{30}$$

$$\langle JNK+2|H_{sr}^{(2)}|JNK\rangle = \frac{1}{2}(b + \imath c)f(N,K+1)\theta(N) \tag{31}$$

Now the off-diagonal in N (Note: for $S = 1/2$, $N = J - 1/2$q):

$$\langle JN+1,K-2|H_{sr}^{(2)}|JNK\rangle = \frac{1}{4}(b - \imath c)f(N+1,K-2)g(N+1,K-1)\phi(N+1) \tag{32}$$

$$\langle JN+1,K-1|H_{sr}^{(2)}|JNK\rangle = \frac{1}{4}(d - \imath e)(N+2K)g(N+1,K-1)\phi(N+1) \tag{33}$$

$$\langle JN+1,K|H_{sr}^{(2)}|JNK\rangle = \frac{3}{2}aK((N+1)^2 - K^2)^{1/2}\phi(N+1) \tag{34}$$

$$\langle JN+1,K+1|H_{sr}^{(2)}|JNK\rangle = \frac{1}{4}(d + \imath e)(N-2K)g(N+1,-K-1)\phi(N+1) \tag{35}$$

$$\langle JN+1,K+2|H_{sr}^{(2)}|JNK\rangle = -\frac{1}{4}(b + \imath c)f(N+1,K+1)g(N+1,-K-1)\phi(N+1) \tag{36}$$

And the associated functions:

$$f(x,y) = (x(x+1) - y(y+1))^{1/2} \tag{37}$$

$$g(x,y) = ((x-y)(x-y-1))^{1/2} \tag{38}$$

$$\theta(N) = \frac{N(N+1)+S(S+1)-J(J+1)}{2N(N+1)} \tag{39}$$

$$\phi(N) = -\frac{1}{N}\left(\frac{(N-J+S)(N+J+S+1)(S+J-N+1)(N+J-S)}{(2N-1)(2N+1)}\right)^{1/2} \tag{40}$$

And, of course, the connection between the spin-rotation tensor and the parameters above:

$$T_0^0(\epsilon) = (-1/\sqrt{3})(\epsilon_{zz} + \epsilon_{xx} + \epsilon_{yy}) = \sqrt{3}a_0 \tag{41}$$

$$T_0^2(\epsilon) = (1/\sqrt{6})(2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy}) = -\sqrt{6}a \tag{42}$$

$$T_{\pm 1}^2(\epsilon) = \mp(1/2)((\epsilon_{zx} + \epsilon_{xz}) \pm \imath(\epsilon_{zy} + \epsilon_{yz})) = \pm(d \pm \imath e) \tag{43}$$

$$T_{\pm 2}^2(\epsilon) = (1/2)((\epsilon_{xx} - \epsilon_{yy}) \pm \imath(\epsilon_{xy} + \epsilon_{yx})) = b \pm \imath c \tag{44}$$

8 Spin-Torsion

Our wavefunction here is $|JNKSv_t\sigma\rangle$. Any matching quantum numbers will be removed for compactness in the following if needed. There is only one torsional operator of first order, P_α, and it belongs to A_2 for $\mathbf{G}_6$. In order to construct a second order spin-torsion operator, we can multiply with either S_z or S_x. Since we are working in RAM, we can ignore $P_\alpha S_x$ and focus solely on $P_\alpha S_z$. The $A_{3m+\sigma}^{K,v_t}$ factors are the coefficients of the torsional wavefunctions from the first diagonalization stage.

$$\langle JNKSv_t'\sigma|\eta\hat{P}_\alpha\hat{S}_z|JNKSv_t\sigma\rangle = \eta\sum_m A_{3m+\sigma}^{K,v_t'}A_{3m+\sigma}^{K,v_t}(3m+\sigma)K\frac{S(S+1)+N(N+1)-J(J+1)}{2N(N+1)} \tag{45a}$$

$$\langle JNKSv_t'\sigma|\eta\hat{P}_\alpha\hat{S}_z|JNKSv_t\sigma\rangle = \eta\sum_m A_{3m+\sigma}^{K,v_t'}A_{3m+\sigma}^{K,v_t}(3m+\sigma)K\theta(N) \tag{45b}$$

$$\langle N+1,v_t'|\eta\hat{P}_\alpha\hat{S}_z|Nv_t\rangle = \sum_m \frac{\eta A_{3m+\sigma}^{K,v_t'}A_{3m+\sigma}^{K,v_t}(3m+\sigma)}{-N}$$
$$\left(\frac{((N+1)^2-K^2)(N-J+S+1)(N+J+S+2)(S+J-N)(N+J-S+1)}{(2N+1)(2N+3)}\right)^{1/2} \tag{46a}$$

$$\langle N+1,v_t'|\eta\hat{P}_\alpha\hat{S}_z|Nv_t\rangle = \sum_m \eta A_{3m+\sigma}^{K,v_t'}A_{3m+\sigma}^{K,v_t}(3m+\sigma)\sqrt{(N+1)^2-K^2}\phi(N+1) \tag{46b}$$

I growingly suspect a single diagonalization stage approach would be more appropriate. Below are the matrix elements in such form:

$$\langle JNKSm\sigma|\eta\hat{P}_\alpha\hat{S}_z|JNKSm\sigma\rangle = \eta(3m+\sigma)K\frac{S(S+1)+N(N+1)-J(J+1)}{2N(N+1)} \tag{47a}$$

$$\langle JNKSm\sigma|\eta\hat{P}_\alpha\hat{S}_z|JNKSm\sigma\rangle = \eta(3m+\sigma)K\theta(N) \tag{47b}$$

$$\langle JN+1,KSm\sigma|\eta\hat{P}_\alpha\hat{S}_z|JNKSm\sigma\rangle =$$
$$\frac{\eta(3m+\sigma)}{-N}\left(\frac{((N+1)^2-K^2)(N-J+S+1)(N+J+S+2)(S+J-N)(N+J-S+1)}{(2N+1)(2N+3)}\right)^{1/2} \tag{48a}$$

$$\langle JN+1,KSm|\eta\hat{P}_\alpha\hat{S}_z|JNKSm\rangle = \eta(3m+\sigma)\sqrt{(N+1)^2-K^2}\phi(N+1) \tag{48b}$$

9 Distortion Terms

Pure Rotational Watson A-Reduced 4th order terms

$$\mathscr{H}_r^{(4)} = \Delta_N\hat{N}^4 + \Delta_{NK}\hat{N}^2\hat{N}_z^2 + \Delta_K\hat{N}_z^4 + \frac{1}{2}\{\delta_N\hat{N}^2+\delta_K\hat{N}_z^2,\hat{N}_+^2+\hat{N}_-^2\} \tag{49}$$

Torsion-Rotation Nakagawa Reduced 4th order terms:

$$\mathscr{H}_t^{(4)} = F_m\hat{P}_\alpha^4 + \frac{V_6}{2}(1-\cos 6\alpha) + V_{3m}\{1-\cos 3\alpha,\hat{P}_\alpha^2\} + \rho_m\hat{P}_\alpha^3\hat{N}_z + \rho_3\{1-\cos 3\alpha,\hat{P}_\alpha\}\hat{N}_z + F_N\hat{P}_\alpha^2\hat{N}^2 + F_K\hat{P}_\alpha^2\hat{N}_z^2$$
$$+ F_{bc}\hat{P}_\alpha^2\left(\hat{N}_+^2+\hat{N}_-^2\right) + F_{ab}\hat{P}_\alpha^2\{\hat{N}_z,\hat{N}_x\} + V_{3N}\hat{N}^2(1-\cos 3\alpha) + V_{3K}\hat{N}_z^2(1-\cos 3\alpha) + V_{3ab}(1-\cos 3\alpha)\{\hat{N}_z,\hat{N}_x\}$$
$$+ V_{3bc}(1-\cos 3\alpha)(\hat{N}_+^2+\hat{N}_-^2) + \rho_N\hat{P}_\alpha\hat{N}_z\hat{N}^2 + \rho_K\hat{P}_\alpha\hat{N}_z^3 + \rho_{ab}\hat{P}_\alpha\{\hat{N}_z^2,N_x\} + \rho_{bN}\hat{P}_\alpha\hat{N}_x\hat{N}^2 \tag{50}$$

Spin-Rotation Brown & Sears A-Reduced 4th order terms:

$$\mathscr{H}_{sr}^{(4)} = +\Delta_N^s\hat{N}^2(\hat{N}\cdot\hat{S}) + \frac{\Delta_{NK}^s}{2}\{\hat{N}^2,\hat{N}_z\hat{S}_z\} + \Delta_{KN}^s\hat{N}_z^2(\hat{N}\cdot\hat{S}) + \Delta_K^s\hat{N}_z^3\hat{S}_z + \delta_N^s(\hat{N}_+^2+\hat{N}_-^2)(\hat{N}\cdot\hat{S}) + \frac{\delta_K^s}{2}\{\hat{N}_+^2+\hat{N}_-^2,\hat{N}_z\hat{S}_z\} \tag{51}$$

10 The Combined Hamiltonian

$$\mathscr{H} = H_{rot}^{(2)} + H_{tor}^{(2)} + H_{sr}^{(2)} + H_{rot}^{(4)} + H_{tor}^{(4)} + H_{sr}^{(4)} + H_{rot}^{(2)}H_{tor}^{(2)} + H_{rot}^{(2)}H_{sr}^{(2)} + H_{tor}^{(2)}H_{sr}^{(2)} \tag{52}$$

Rotational portions of the Hamiltonian are solved as per the Watson-A. Torsional will follow from BELGI's RAM. Spin-rotation of 2nd order is from Brown & Sears 1979.

$$\mathscr{H}^{(2)} = A\hat{N}_z^2 + B\hat{N}_x^2 + C\hat{N}_y^2 + D_{ab}\{\hat{N}_z, \hat{N}_x\} + F\hat{P}_\alpha^2 - 2\rho\hat{P}_\alpha\hat{N}_z + V_3\cos 3\alpha +$$
$$\epsilon_{zz}\hat{N}_z\hat{S}_z + \epsilon_{xx}\hat{N}_x\hat{S}_x + \epsilon_{yy}\hat{N}_y\hat{S}_y + \overline{\epsilon_{zx}}(\{\hat{N}_z, \hat{S}_x\} + \{\hat{N}_x, \hat{S}_z\}) + \eta_{z\alpha}\hat{P}_\alpha\hat{S}_z \tag{53}$$

Next is to begin reducing the full Hamiltonian to remove redundant parameters via contact transformation. Most sources use $S^{(n)}$ or $F^{(n)}$ for the contact transforming term but I will be using $G^{(n)}$ since S looks like spin and F looks like internal momentum. The second order reduction will be as follows (Brown & Sears (1979)):

$$\widetilde{\mathscr{H}^{(2)}} = \mathscr{H}^{(2)} + i[\mathscr{H}^{(2)}, G^{(1)}] - \frac{i}{2}[[[\mathscr{H}, G^{(1)}], G^{(1)}], G^{(1)}] \tag{54}$$

$G^{(1)}$ is composed of the A_1 operators of first order. This is just Sy and Ny as there are no torsional terms of first order with A_1 symmetry. The terms $P_\alpha N_x$ and $P_\alpha S_x$ have been removed by reduction with the S_y operator.

Now on to the 4th order terms. For rotations, I will take from the Watson-A and torsions will of course be address from BELGI-Cs. The Brown paper that everyone vaguely cites has the $H_{rot}^{(2)}H_{sr}^{(2)}$ terms. I will need to solve for $H_{tor}^{(2)}H_{sr}^{(2)}$.

$$\mathscr{H}^{(4)} = \hat{H}_{tsr}^{(4)} + \Delta_N\hat{N}^4 + \Delta_{NK}\hat{N}^2\hat{N}_z^2 + \Delta_K\hat{N}_z^4 + \delta_N\{\hat{N}^2, \hat{N}_+^2 + \hat{N}_-^2\} + \delta_K\{\hat{N}_z^2, \hat{N}_+^2 + \hat{N}_-^2\}$$
$$+ \Delta_N^s\hat{N}^2(\hat{N}\cdot\hat{S}) + \frac{\Delta_{NK}^s}{2}\{\hat{N}^2, \hat{N}_z\hat{S}_z\} + \Delta_{KN}^s\hat{N}_z^2(\hat{N}\cdot\hat{S}) + \Delta_k^s\hat{N}_z^3\hat{S}_z + \delta_N^s(\hat{N}_+^2 + \hat{N}_-^2)(\hat{N}\cdot\hat{S}) + \frac{\delta_K^s}{2}\{\hat{N}_+^2 + \hat{N}_-^2, \hat{N}_z\hat{S}_z\}$$
$$+ F_m\hat{P}_\alpha^4 + \frac{V_6}{2}(1 - \cos 3\alpha) + \rho_m\hat{P}_\alpha^3\hat{N}_z + F_N\hat{P}_\alpha^2\hat{N}^2 + F_K\hat{P}_\alpha^2\hat{N}_z^2 + F_{ab}\hat{P}_\alpha^2\{\hat{N}_z, \hat{N}_x\} + F_{bc}\hat{P}_{alpha}^2(\hat{N}_+^2 + \hat{N}_-^2)$$
$$+ V_{3N}(1 - \cos 3\alpha)\hat{N}^2 + V_{3K}(1 - \cos 3\alpha)\hat{N}_z^2 + V_{3ab}(1 - \cos 3\alpha)\{\hat{N}_z, \hat{N}_x\} + \frac{V_{3bc}}{2}(1 - \cos 3\alpha)(\hat{N}_+^2 + \hat{N}_-^2)$$
$$+ D_{3ac}\sin 3\alpha\{\hat{N}_z, \hat{N}_y\} + D_{3bc}\sin 3\alpha\{\hat{N}_x, \hat{N}_y\} + \rho_N\hat{P}_\alpha\hat{N}_z\hat{N}^2 + \rho_K\hat{P}_\alpha\hat{N}_z^3 + \rho_{ab}\hat{P}_\alpha\{\hat{N}_z^2, \hat{N}_x\} + \frac{\rho_{bc}}{2}\hat{P}_\alpha\{\hat{N}_z, \hat{N}_+^2 + \hat{N}_-^2\}$$
$$+ D_{abN}\{\hat{N}_z, \hat{N}_x\}\hat{N}^2 + D_{abK}\{\hat{N}_z^3, \hat{N}_x\} \tag{55}$$

11 Intensity Calculations

From Gopalakrishnan 2003, spin-rotation line strengths:

$$S(\tau'J'; \tau''J'') = \left| \sum_{N'N''} (-1)^{N''+S+J'+1}\sqrt{(2J'+1)(2J''+1)} \begin{Bmatrix} N'' & J'' & S \\ J' & N' & 1 \end{Bmatrix} \bar{S}^{1/2}(\tau'N'; \tau''N'') \right|^2 \tag{56}$$

$$\bar{S}^{1/2}(\tau'N'; \tau''N'') = \sqrt{2N''+1}\sum_{K'K''}\sum_q a_{\tau'K'}a_{\tau''K''}(-1)^{N''-1-K'}(2N'+1)\begin{pmatrix} N'' & 1 & N' \\ K'' & q & -K' \end{pmatrix} T_q^1(\mu) \tag{57}$$

Now applying some simplifications based on lower K value, K''. Based on the 3j symbol, $K'' + q - K' = 0$ so $K' = K'' + q$.

$$\bar{S}^{1/2}(\tau'N'; \tau''N'') = \sqrt{2N''+1}\sum_{K''}\sum_q a_{\tau',K''+q}a_{\tau''K''}(-1)^{N''-1-K'}(2N'+1)\begin{pmatrix} N'' & 1 & N' \\ K'' & q & -K''-q \end{pmatrix} T_q^1(\mu) \tag{58}$$

From Kleiner 2010, torsional rotation strengths:

$$S(L'; L) = \frac{1}{\mu^2}\sum_M 3\left| \sum_\gamma \sum_{K',K,v_t''',v_t''} C_{K',v_t'''}^{J'\tau v_t'\sigma'} C_{K,v_t''}^{J\tau v_t\sigma} \langle K'v_t'''\sigma'|\mu_\gamma|Kv_t''\sigma\rangle \langle J'K'M|\Phi_{Z\gamma}|JKM\rangle \right|^2 \tag{59}$$

Sloppy combo:

$$S(L'; L) = \left| \sum_{N'N}(-1)^{N+S+J'+1}\sqrt{(2J'+1)(2J+1)}\begin{Bmatrix} N & J & S \\ J' & N' & 1 \end{Bmatrix}\sqrt{2N+1} \right.$$
$$\left. \sum_{K',K,v_t''',v_t''}\sum_q C_{K',v_t'''}^{J'\tau v_t'\sigma'} C_{K,v_t''}^{J\tau v_t\sigma}(-1)^{N-1-K'}(2N'+1)\begin{pmatrix} N & 1 & N' \\ K & 1 & -K' \end{pmatrix}T_q^1(\mu) \right|^2 \tag{60}$$

Reapplying that simplification,

12 Parameter Definitions

I need to find that spin-rotation paper. And then change the I tensor to 4D. Also what the fuck would $\eta_{\alpha\alpha}$ mean. $\eta_{z\alpha}$ makes plenty of sense though. Hmm they should be the same in RAM as it's the interaction of the z component of the electron spin and the internal rotor angular momentum

This combines the PAM derivation from Kroto with the foundations of XIAM. The purpose of this is to allow the users to input PAM parameters which are more readily calculated & physically interprettable and then use the RAM internally.

We start with the follwing expression for kinetic energy, T:

$$T = \frac{1}{2}\omega^\dagger \mathbf{I}\omega \tag{61}$$

Here ω is the vector of angular velocities and $\mathbf{I}$ is the 4x4 inertial tensor. Thus:

$$2T = \omega^\dagger \begin{bmatrix} I_z & . & . & \lambda_z I_\alpha \\ . & I_x & . & \lambda_x I_\alpha \\ . & . & I_z & . \\ \lambda_z I_\alpha & \lambda_x I_\alpha & . & I_\alpha \end{bmatrix} \begin{bmatrix} \omega_z \\ \omega_x \\ \omega_y \\ \omega_\alpha \end{bmatrix} \tag{62}$$

The direction cosines, λ_z & λ_x, are determined from the angle between the methyl rotor and the molecular z-axis. A fortunate trait of the $\mathbf{G}_6$ case is that only one angle is needed to define the methyl rotor position.

$$\lambda_z = \cos\delta \tag{63}$$
$$\lambda_x = \sin\delta \tag{64}$$

We now want to rotate the inertial tensor about the y-axis to remove the coupling between the x-axis and the methyl rotor.

$$2T = \omega^\dagger R_y^\dagger(\delta) \begin{bmatrix} I_z & . & . & \lambda_z I_\alpha \\ . & I_x & . & \lambda_x I_\alpha \\ . & . & I_z & . \\ \lambda_z I_\alpha & \lambda_x I_\alpha & . & I_\alpha \end{bmatrix} \begin{bmatrix} \cos\delta & -\sin\delta & . & . \\ \sin\delta & \cos\delta & . & . \\ . & . & 1 & . \\ . & . & . & 1 \end{bmatrix} \begin{bmatrix} \omega_z \\ \omega_x \\ \omega_y \\ \omega_\alpha \end{bmatrix} \tag{65}$$

This gives us

$$2T = \omega^\dagger \begin{bmatrix} I_z\cos^2\delta + I_x\sin^2\delta & (I_x - I_z)\cos\delta\sin\delta & . & I_\alpha \\ (I_x - I_z)\cos\delta\sin\delta & I_x\cos^2\delta + I_z\sin^2\delta & . & . \\ . & . & I_y & . \\ I_\alpha & . & . & I_\alpha \end{bmatrix} \begin{bmatrix} \omega_z \\ \omega_x \\ \omega_y \\ \omega_\alpha \end{bmatrix} \tag{66}$$

For simplicity we will rename some of the changed variables with $'$ to mark the change to the new axis system. This rotation can also cause I_x' to be come less than I_z' which will cause the code to change from a I^r to a II^r representation.

$$2T = \omega^\dagger \begin{bmatrix} I_z' & I_{xz}' & . & I_\alpha \\ I_{xz}' & I_x' & . & . \\ . & . & I_y & . \\ I_\alpha & . & . & I_\alpha \end{bmatrix} \begin{bmatrix} \omega_z \\ \omega_x \\ \omega_y \\ \omega_\alpha \end{bmatrix} \tag{67}$$

$$2T = \omega^\dagger \begin{bmatrix} I_z'\omega_z + I_{xz}'\omega_x + I_\alpha\omega_\alpha \\ I_x'\omega_x + I_{xz}'\omega_z \\ I_y\omega_y \\ I_\alpha\omega_\alpha + I_\alpha\omega_z \end{bmatrix} \tag{68}$$

$$2T = I_\alpha\omega_\alpha^2 + I_z'\omega_z^2 + I_y\omega_y^2 + I_x'\omega_x^2 + \omega_x I_{xz}'\omega_z + \omega_z I_{xz}'\omega_x + \omega_\alpha I_\alpha\omega_z + \omega_z I_\alpha\omega_\alpha \tag{69}$$

Our projections of angular momentum are connected to the total energy via the derivatives with respect to the angular velocities:

$$N_z = \partial T/\partial\omega_z = I_z'\omega_z + \frac{1}{2}\omega_x I_{xz}' + I_\alpha\omega_\alpha \tag{70}$$

$$N_x = \partial T/\partial\omega_x = I_x'\omega_x + \frac{1}{2}I_{xz}'\omega_z + \frac{1}{2}\omega_z I_{xz}' \tag{71}$$

$$N_y = \partial T/\partial\omega_y = I_y\omega_y \tag{72}$$
$$P_\alpha = \partial T/\partial\omega_\alpha = I_\alpha\omega_\alpha + I_\alpha\omega_z \tag{73}$$

Now let us define a few substitutions:

$$N_a = I'_z \omega_z + I_\alpha \omega_\alpha \tag{74}$$

$$\omega_z = \frac{1}{I'_z}(N_a - I_\alpha \omega_\alpha) \tag{75}$$

$$N_b = I'_x \omega_x \tag{76}$$

$$N_c = I_y \omega_y = N_y \tag{77}$$

$$\pi = \frac{I_\alpha}{I'_z} N_a = \rho N_a \tag{78}$$

Now if we apply these:

$$P_\alpha - \pi = I_\alpha \omega_\alpha + I_\alpha \omega_z - \rho N_a = I_\alpha \omega_\alpha + I_\alpha \omega_z - \frac{I_\alpha}{I'_z}(I'_z \omega_z + I_\alpha \omega_\alpha) = I_\alpha(1 - \rho)\omega_\alpha = r I_\alpha \omega_\alpha \tag{79}$$

$$\omega_\alpha = \frac{P_\alpha - \pi}{r I_\alpha} \tag{80}$$

$$r = 1 - \rho \tag{81}$$

Finally we can begin reconstructing the Hamiltonian:

$$2T = I'_z \omega_z^2 + \frac{1}{I_y} N_c^2 + \frac{1}{I'_x} N_b^2 + \frac{I'_{xz}}{I'_x I'_z}(N_a N_b + N_b N_a) + I_\alpha \omega_\alpha^2 + \omega_\alpha I_\alpha \omega_z + \omega_z I_\alpha \omega_\alpha \tag{82}$$

$$2T = \frac{1}{I_y} N_c^2 + \frac{1}{I'_x} N_b^2 + \frac{I'_{xz}}{I'_x I'_z}(N_a N_b + N_b N_a) + \omega_\alpha(I_\alpha \omega_\alpha + I_\alpha \omega_z) + \omega_z(I'_z \omega_z + I_\alpha \omega_\alpha) \tag{83}$$

$$2T = \frac{1}{I_y} N_c^2 + \frac{1}{I'_x} N_b^2 + \frac{I'_{xz}}{I'_x I'_z}(N_a N_b + N_b N_a) + \omega_\alpha P_\alpha + \omega_z N_a \tag{84}$$

$$2T = \frac{1}{I_y} N_c^2 + \frac{1}{I'_x} N_b^2 + \frac{I'_{xz}}{I'_x I'_z}(N_a N_b + N_b N_a) + \frac{1}{r I_\alpha} P_\alpha(P_\alpha - \pi) + \frac{1}{I'_z}(N_a - I_\alpha \omega_\alpha) N_a \tag{85}$$

$$2T = \frac{1}{I_y} N_c^2 + \frac{1}{I'_x} N_b^2 + \frac{I'_{xz}}{I'_x I'_z}(N_a N_b + N_b N_a) + \frac{1}{r I_\alpha} P_\alpha(P_\alpha - \pi) + \frac{1}{I'_z} N_a^2 - \frac{1}{I'_z} I_\alpha \omega_\alpha N_a \tag{86}$$

$$2T = \frac{1}{I'_z} N_a^2 + \frac{1}{I_y} N_c^2 + \frac{1}{I'_x} N_b^2 + \frac{I'_{xz}}{I'_x I'_z}(N_a N_b + N_b N_a) + \frac{1}{r I_\alpha} P_\alpha(P_\alpha - \pi) - \frac{I_\alpha}{I'_z} \frac{P_\alpha - \pi}{r I_\alpha} N_a \tag{87}$$

$$2T = 2\mathscr{H}_{rr}^{(2)} + \frac{1}{r I_\alpha}(P_\alpha^2 - \rho P_\alpha N_a - \frac{I_\alpha}{I'_z} P_\alpha N_a + \frac{\rho I_\alpha}{I'_z} N_a^2) \tag{88}$$

$$2T = 2\mathscr{H}_{rr}^{(2)} + \frac{1}{r I_\alpha}(P_\alpha^2 - 2\rho P_\alpha N_a + \rho^2 N_a^2) \tag{89}$$

$$T = \frac{1}{2I'_z} N_a^2 + \frac{1}{2I_y} N_c^2 + \frac{1}{2I'_x} N_b^2 + \frac{I'_{xz}}{2I'_x I'_z}(N_a N_b + N_b N_a) + \frac{1}{2r I_\alpha}(P_\alpha - \rho N_a)^2 \tag{90}$$

And at long last we have our tidy little Rho Axis Hamiltonian:

$$\mathscr{H}_{rt}^{(2)} = A_{RAM} N_a^2 + B_{RAM} N_b^2 + C N_c^2 + D_{ab}(N_a N_b + N_b N_a) + F_{RAM}(P_\alpha - \rho N_a)^2 \tag{91}$$

We can calculate the RAM parameters from the PAM values using the following relations:

$$A_{RAM} = \frac{A_{PAM} B_{PAM}}{B_{PAM} \cos^2 \delta + A_{PAM} \sin^2 \delta} \tag{92}$$

$$B_{RAM} = \frac{A_{PAM} B_{PAM}}{A_{PAM} \cos^2 \delta + B_{PAM} \sin^2 \delta} \tag{93}$$

$$C_{RAM} = C_{PAM} \tag{94}$$

$$D_{ab} = \frac{(B_{PAM}^{-1} - A_{PAM}^{-1}) \cos \delta \sin \delta}{2 A_{RAM} B_{RAM}} \tag{95}$$

$$F_{RAM} = \frac{F^2}{F - A_{RAM}} \tag{96}$$

$$\rho = \frac{A_{RAM}}{F} \tag{97}$$

13　The Program

hard coded parameters
three diagonalization stages. Torsional, Spin-Rot, Rot+Int
Could consider 2. Torsional, R+SR+I
Going with two. It's coded up
It's going to make more sense to consider PAM with a singular diagonalization stage
Did RAM anyways
reminder for how Julia maps on to Dirac notation

$$H[i,j] \rightarrow \langle j|H|i \rangle \tag{98}$$

Okay so here's how it's going to go. I'm going to make a function for the matrix blocks that are independent of m and J. Then one for just those independent of m. That'll allow for Hrot and Hspi to be handled only once and twice, respectively per J. Lastly will come the functions that vary with m for Htor.

The final diagonalization stage has 4 types of blocks, as observed in Table 3. They are $[N, v_t|N, v_t]$, $[N, v_t'|N, v_t]$, $[N+1, v_t|N, v_t]$, and $[N+1, v_t'|N, v_t]$. Each will get their own construction function.

14　Methyl Hyperfine

15　Spin-Spin Coupling

16　Perturbative Hyperfine

From BBC:

$$\langle N'K'SJ'IF'| H_Q |NKSJIF \rangle = \frac{eQ}{2} \begin{pmatrix} I & 2 & I \\ -I & 0 & I \end{pmatrix}^{-1} (-1)^{J+I+F} \begin{Bmatrix} I & J' & F \\ J & I & 2 \end{Bmatrix} (-1)^{N'+S+J} \sqrt{(2J'+1)(2J+1)}$$
$$\begin{Bmatrix} N' & J' & S \\ J & N & S \end{Bmatrix} \sqrt{(2N'+1)(2N+1)} \sum_q (-1)^{N'-K'} \begin{pmatrix} N' & 2N \\ -K' & q & K \end{pmatrix} T_q^2(\nabla E) \tag{99}$$

The perturbative treatment will use only the purely diagonal terms. K will be replaced with K_a for the prolate case and below. This will be substituted for K_c in the oblate case.

$$\langle NK_aSJIF |H_Q| NKSJIF \rangle = \frac{eQ}{2}(-1)^{2J+2N+I+F+S-K_a}(2J+1)(2N+1)T_0^2(\nabla E)$$
$$\begin{pmatrix} I & 2 & I \\ -I & 0 & I \end{pmatrix}^{-1} \begin{Bmatrix} I & J & F \\ J & I & 2 \end{Bmatrix} \begin{Bmatrix} N & J & S \\ J & N & S \end{Bmatrix} \begin{pmatrix} N & 2 & N \\ -K_a & 0 & K_a \end{pmatrix} \tag{100}$$

Replacing with some explicit symbols:

$$\langle NK_aSJIF| H_Q |NKSJIF \rangle = \frac{eQ}{2}(-1)^{FJ+2N+2I+2F+S-K_a}(2J+1)(2N+1)T_0^2(\nabla E)$$
$$\left(\frac{\sqrt{(2I+1)(I+1)I}}{2(3I^2-I(I+1))} \right) \begin{Bmatrix} N & J & S \\ J & N & S \end{Bmatrix} \left(\frac{2(3K_a^2-N(N+1))}{\sqrt{(2N+1)(N+1)N}} \right)$$
$$\left(\frac{2(3(I(I+1)+J(J+1)-F(F+1))(I(I+1)+J(J+1)-F(F+1)-1)-4I(I+1)J(J+1))}{\sqrt{(2I-1)2I(2I+1)(2I+2)(2I+3)(2J-1)2J(2J+1)(2J+2)(2J+3)}} \right) \tag{101}$$

17　Vibrational States

As my pursuit of of the white whale that is isoprene continues, I have begun to conceive of vibcalc. This will employ a two stage diagonalization procedure with the purely vibrational terms on one stage and the Coriolis terms will be integrated into the rotational stage.

$$\mathscr{H}_{vib} = U_0p^2 + U_1q + U_2q^2 + U_3q^3 + U_4q^4 + U_5q^5 + U_6q^6 + U_7q^7 + U_8q^8 \tag{102}$$

$$p^2|n\rangle = -\frac{1}{2}\sqrt{n(n-1)}|n-2\rangle + \frac{1}{2}(2n+1)|n\rangle - \frac{1}{2}\sqrt{(n+1)(n+2)}|n+2\rangle \tag{103}$$

18 Analytic Derivatives

Derivatives of operators for Hamiltonian matrices is actually surprisingly straight-forward thanks to the Hellmann-Feynman Theorem:

$$\frac{dE_\lambda}{d\lambda} = \left\langle \psi_\lambda \left| \frac{d\mathscr{H}_\lambda}{d\lambda} \right| \psi_\lambda \right\rangle \tag{104}$$

The expanded Hamiltonian of the coupled terms:

$$\mathscr{H} = \frac{F}{r}P_\alpha^2 - 2\frac{F}{r}\rho P_\alpha N_z - 2\frac{F}{r}\gamma P_\alpha N_x + (A + \frac{F}{r}\rho)N_z^2 + (B + \frac{F}{r}\rho)N_x^2 \tag{105}$$

$$\rho = \frac{\lambda A}{F} \tag{106}$$

$$\gamma = \frac{\sqrt{(1-\lambda)^2}B}{F} \tag{107}$$

$$r = 1 - \frac{\lambda^2 A}{F} \tag{108}$$

Here are the key non-unity first derivatives:

$$\frac{\partial \mathscr{H}}{\partial A} = Nz^2 + \frac{\lambda^2 \frac{\left(Pa + \frac{-ANz\lambda}{F} + \frac{-BNx\sqrt{(1-\lambda)^2}}{F}\right)^2 F}{\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)^2}}{F} + \frac{-FNz\lambda\left(2Pa + \frac{-2ANz\lambda}{F} + \frac{-2BNx\sqrt{(1-\lambda)^2}}{F}\right)}{F\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)} \tag{109}$$

$$\frac{\partial \mathscr{H}}{\partial F} =$$

$$\frac{1}{1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}} - \frac{F}{\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)^2}\left(\frac{\lambda^2 A}{F^2} + \frac{(1-\lambda)^2 B}{F^2}\right)P_\alpha^2$$

$$+\frac{-2A\lambda}{F\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)} - \left(1 + F\left(\frac{\lambda^2 A}{F^2} + \frac{(1-\lambda)^2 B}{F^2}\right) + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)\frac{-2AF\lambda}{\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)^2 F^2}P_\alpha N_z$$

$$+\frac{-2\lambda}{1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}} - \left(\frac{\lambda^2 A}{F^2} + \frac{(1-\lambda)^2 B}{F^2}\right)\frac{-2F\lambda}{\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)^2}P_\alpha N_x$$

$$+\frac{\left(\frac{A\lambda}{F}\right)^2 + \frac{-2AF\lambda\frac{A\lambda}{F^2}}{F}}{1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}} - \frac{\left(\frac{A\lambda}{F}\right)^2 F}{\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)^2}\left(\frac{\lambda^2 A}{F^2} + \frac{(1-\lambda)^2 B}{F^2}\right)N_z^2$$

$$+\frac{\left(\frac{B\sqrt{(1-\lambda)^2}}{F}\right)^2 + \frac{-2BF\frac{B\sqrt{(1-\lambda)^2}}{F^2}\sqrt{(1-\lambda)^2}}{F}}{1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}} - \frac{\left(\frac{B\sqrt{(1-\lambda)^2}}{F}\right)^2 F}{\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)^2}\left(\frac{\lambda^2 A}{F^2} + \frac{(1-\lambda)^2 B}{F^2}\right)N_x^2$$

$$+\frac{AB\lambda\sqrt{(1-\lambda)^2}}{F^2\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)} - \left(F^2\left(\frac{\lambda^2 A}{F^2} + \frac{(1-\lambda)^2 B}{F^2}\right) + 2F\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)\right)\frac{ABF\lambda\sqrt{(1-\lambda)^2}}{\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)^2 F^4}\{N$$

$$\frac{\partial \mathcal{H}}{\partial A} =$$

$$\frac{\lambda^2}{\left(\frac{F-B-\lambda^2 A-\lambda^2 B+2B\lambda}{F}\right)^2}P_\alpha^2$$

$$+\frac{-2\lambda}{1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}}+\lambda^2\frac{-2A\lambda}{\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)^2 F}P_\alpha N_z$$

$$+\frac{-2\lambda^3}{\left(\frac{F-B-\lambda^2 A-\lambda^2 B+2.0B\lambda}{F}\right)^2}P_\alpha N_x$$

$$+1+\lambda^2\frac{\left(\frac{A\lambda}{F}\right)^2 F}{\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)^2}+\frac{2\lambda^2 A}{F\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)}N_z^2$$

$$+\frac{\lambda^2\frac{\left(\frac{B\sqrt{(1-\lambda)^2}}{F}\right)^2 F}{\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)^2}}{F}N_x^2$$

$$+\frac{\lambda^2 F^2\frac{ABF\lambda\sqrt{(1-\lambda)^2}}{\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)^2 F^4}}{F}+\frac{BF\lambda\sqrt{(1-\lambda)^2}}{F^2\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)}\{N_z,N_x\}$$

$$\frac{\partial \mathcal{H}}{\partial B} =$$

$$\frac{(1-\lambda)^2\frac{F}{\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)^2}}{F}P_\alpha^2$$

$$+\frac{(1-\lambda)^2 F\frac{-2AF\lambda}{\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)^2 F^2}}{F}P_\alpha N_z$$

$$+\frac{(1-\lambda)^2\frac{-2F\lambda}{\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)^2}}{F}P_\alpha N_x$$

$$+\frac{(1-\lambda)^2\frac{\left(\frac{A\lambda}{F}\right)^2 F}{\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)^2}}{F}N_z^2$$

$$+1+\frac{(1-\lambda)^2\frac{\left(\frac{B\sqrt{(1-\lambda)^2}}{F}\right)^2 F}{\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)^2}}{F}+\frac{2\left(\sqrt{(1-\lambda)^2}\right)^2 BF}{F^2\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)}N_x^2$$

$$+\frac{(1-\lambda)^2 F^2\frac{ABF\lambda\sqrt{(1-\lambda)^2}}{\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)^2 F^4}}{F}+\frac{AF\lambda\sqrt{(1-\lambda)^2}}{F^2\left(1+\frac{-\lambda^2 A}{F}+\frac{-(1-\lambda)^2 B}{F}\right)}\{N_z,N_x\}$$

$$\frac{\partial \mathscr{H}}{\partial \lambda} =$$

$$-\frac{F}{\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)^2}\left(\frac{-B\left(-2 + 2\lambda\right)}{F} + \frac{-2A\lambda}{F}\right)P_\alpha^2$$

$$+\frac{-2AF}{F\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)} - F\left(\frac{-B\left(-2 + 2\lambda\right)}{F} + \frac{-2A\lambda}{F}\right)\frac{-2AF\lambda}{\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)^2 F^2}P_\alpha N_z$$

$$+\frac{-2F}{1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}} - \left(\frac{-B\left(-2 + 2\lambda\right)}{F} + \frac{-2A\lambda}{F}\right)\frac{-2F\lambda}{\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)^2}P_\alpha N_x$$

$$+\frac{2A^2 F\lambda}{F^2\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)} - \frac{\left(\frac{A\lambda}{F}\right)^2 F}{\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)^2}\left(\frac{-B\left(-2 + 2\lambda\right)}{F} + \frac{-2A\lambda}{F}\right)N_z^2$$

$$+\frac{B^2 F\left(-2 + 2\lambda\right)}{F^2\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)} - \frac{\left(\frac{B\sqrt{(1-\lambda)^2}}{F}\right)^2 F}{\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)^2}\left(\frac{-B\left(-2 + 2\lambda\right)}{F} + \frac{-2A\lambda}{F}\right)N_x^2$$

$$+\frac{ABF\sqrt{(1-\lambda)^2} + \frac{\frac{1}{2}ABF\lambda(-2 + 2\lambda)}{\sqrt{(1-\lambda)^2}}}{F^2\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)} - F^2\left(\frac{-B\left(-2 + 2\lambda\right)}{F} + \frac{-2A\lambda}{F}\right)\frac{ABF\lambda\sqrt{(1-\lambda)^2}}{\left(1 + \frac{-\lambda^2 A}{F} + \frac{-(1-\lambda)^2 B}{F}\right)^2 F^4}\{N_z, N_x\}$$