We here the follow certain derivations / comments on the formulation of a Hamiltonian for two fragments as proposed by G. Brocks et. al. in MOLECULAR PHYSICS 50(6) p 1025-1043 (1983)

According to the Born-Oppenheimer approximation, the Hamiltonian describing nuclear motion for an N-nucleus system may be written

$$\hat{H} = \frac{-\hbar^2}{2} \sum_{i=1}^{N} \frac{1}{m_i} \nabla_i^2(\underset{\sim}{x}_i) + V$$

where m_i is the mass of the i^{th} nucleus
$\nabla_i^2(x_i)$ is the Laplacian for the i^{th} nucleus
V is the potential

We can divide the N-nucleus system into 2 fragments, A & B say, containing N_A & N_B nuclei respectively (i.e. $N \equiv N_A + N_B$)

Order the laboratory coordinates:

$$\underset{\sim}{x}_i : \quad i = 1, 2, \cdots, N_A$$

$$= (N_A+1), (N_A+2), \cdots, N$$
$$1, 2, \cdots, N_B$$

We seek to rewrite the Hamiltonian so that we may separate off the overall translation of the system. We do this by utilising the following coordinate transformations:

$\underset{\sim}{t}_i^F = \underset{\sim}{x}_i - \underset{\sim}{X}_F$ — [$\forall$ F = A, B ; $\forall$ i = 1, 2, ⋯, $(N_F - 1)$ coords describing the 1st (N_F-1) nuclei w.r.t c.o.m F

$\underset{\sim}{t}_o = \underset{\sim}{X}_A - \underset{\sim}{X}_B$ — [coords describing c.o.m of A w.r.t c.o.m of B

$\underset{\sim}{X} = \frac{1}{M}(M_A \underset{\sim}{X}_A + M_B \underset{\sim}{X}_B)$ — [coords describing the system's c.o.m.

where $\underset{\sim}{X}_A = \frac{1}{M_A} \sum_{i=1}^{N_A} m_i \underset{\sim}{x}_i$ $\qquad M_A = \sum_{i=1}^{N_A} m_i$

$\underset{\sim}{X}_B = \frac{1}{M_B} \sum_{i=N_{A+1}}^{N} m_i \underset{\sim}{x}_i$ $\qquad M_B = \sum_{i=N_{A+1}}^{N} m_i$

$$M = M_A + M_B$$

Rewrite the laboratory kinetic energy:

$$\nabla_i^2(\underset{\sim}{x}_i) = \frac{\partial^2}{\partial \underset{\sim}{x}_i^2} = \sum_{\substack{\text{trans.} \\ \text{variables}}} \frac{\partial^2}{\partial \underset{\sim}{x}_i^2}$$

$$= \left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{X}} + \left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{t}_0} + \left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{t}_i^A} + \left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{t}_i^B}$$

$$\therefore \sum_{i=1}^{N} \frac{1}{m_i} \nabla_i^2(\underset{\sim}{x}_i) = \sum_{i=1}^{N} \frac{1}{m_i} \sum_{\substack{\text{trans.} \\ \text{variables}}} \frac{\partial^2}{\partial \underset{\sim}{x}_i^2} + \text{differential cross-terms} = 0$$

$$= \sum_{i=1}^{N} \frac{1}{m_i} \left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{X}} + \sum_{i=1}^{N} \frac{1}{m_i} \left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{t}_0} + \sum_{F} \sum_{i=1}^{N} \frac{1}{m_i} \left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{t}_i^F}$$

To simplify further, use the chain rule as it written for coordinate changes:

$$\frac{\partial^2}{\partial Q_j} = \sum_{a,b} \left(\frac{\partial q_a}{\partial Q_j}\right)\left(\frac{\partial q_b}{\partial Q_j}\right) \frac{\partial^2}{\partial q_a \partial q_b} + \sum_{b} \left(\frac{\partial^2 q_b}{\partial Q_j}\right) \frac{\partial}{\partial q_b}$$ — See Barker p. 86 eq 6-9

- Consider $\underset{\sim}{X}$ transformation
  - Since $\underset{\sim}{X}$ is not indexed (as opposed to $\underset{\sim}{t}_i^A = \underset{\sim}{x}_i - \underset{\sim}{X}_A$ for $i = 1, \ldots, N_A - 1$ & similarly for $\underset{\sim}{t}_i^B$)

$$\left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{X}} = \sum_{a,b} \left(\frac{\partial \underset{\sim}{X}_a}{\partial \underset{\sim}{x}_i}\right)\left(\frac{\partial \underset{\sim}{X}_b}{\partial \underset{\sim}{x}_i}\right) \frac{\partial^2}{\partial \underset{\sim}{X}_a \partial \underset{\sim}{X}_b} + \sum_{b} \left(\frac{\partial^2 \underset{\sim}{X}_b}{\partial \underset{\sim}{x}_i^2}\right) \frac{\partial}{\partial \underset{\sim}{X}_b}$$

becomes $\left(\frac{\partial \underset{\sim}{x}}{\partial \underset{\sim}{x}_i}\right)^2 \frac{\partial^2}{\partial \underset{\sim}{X}^2} + \left(\frac{\partial^2 \underset{\sim}{x}}{\partial \underset{\sim}{x}_i^2}\right) \frac{\partial}{\partial \underset{\sim}{X}}$

$$\Rightarrow \left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{x}} = \left[\frac{\partial}{\partial \underset{\sim}{x}_i}\left(\frac{1}{M}\sum_{i=1}^{N} m_i \underset{\sim}{x}_i\right)\right]^2 \frac{\partial^2}{\partial \underset{\sim}{X}^2} + \frac{\partial}{\partial \underset{\sim}{x}_i}\left[\frac{\partial}{\partial \underset{\sim}{x}_i}\left(\frac{\sum_i^N m_i \underset{\sim}{x}_i}{M}\right)\right]\frac{\partial}{\partial \underset{\sim}{X}}$$

$$= \left(\frac{m_i}{M}\right)^2 \frac{\partial^2}{\partial \underset{\sim}{X}^2} + \cancel{\frac{\partial}{\partial \underset{\sim}{x}_i}\left(\frac{m_i}{M}\right)\frac{\partial}{\partial \underset{\sim}{X}}}^{=0}$$

$$\therefore \sum_{i=1}^{N} \frac{1}{m_i}\left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{x}} = \sum_{i=1}^{N} \frac{1}{\cancel{m_i}} \frac{m_i^{\cancel{2}}}{M^2} \frac{\partial^2}{\partial \underset{\sim}{X}^2}$$

$$\Rightarrow \sum_{i=1}^{N} \frac{1}{m_i}\left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{x}} = \frac{\cancel{M}}{M^{\cancel{2}}} \frac{\partial^2}{\partial \underset{\sim}{X}^2} = \frac{1}{M}\frac{\partial^2}{\partial \underset{\sim}{X}^2}$$

- Consider $\underset{\sim}{t}_0$ transformation (likewise not indexed explicitly)

- A result is best obtained by use of induction. Let $N=4$ with $N_A = N_B = 2$ (ie a diner composed of two distances)

$$\frac{\partial \underset{\sim}{t}_0}{\partial \underset{\sim}{x}_1} = \frac{m_1}{M_A} \quad \therefore \quad \left(\frac{\partial \underset{\sim}{t}_0}{\partial \underset{\sim}{x}_1}\right)^2 \frac{\partial^2}{\partial \underset{\sim}{t}_0^2} = \frac{m_1^2}{M_A^2} \frac{\partial^2}{\partial \underset{\sim}{t}_0^2}$$

$$\frac{\partial \underset{\sim}{t}_0}{\partial \underset{\sim}{x}_2} = \frac{m_2}{M_A} \quad \therefore \quad \left(\frac{\partial \underset{\sim}{t}_0}{\partial \underset{\sim}{x}_2}\right)^2 \frac{\partial^2}{\partial \underset{\sim}{t}_0^2} = \frac{m_2^2}{M_A^2} \frac{\partial^2}{\partial \underset{\sim}{t}_0^2}$$

$$\frac{\partial \underset{\sim}{t}_0}{\partial \underset{\sim}{x}_3} = -\frac{m_3}{M_B} \quad \therefore \quad \left(\frac{\partial \underset{\sim}{t}_0}{\partial \underset{\sim}{x}_3}\right)^2 \frac{\partial^2}{\partial \underset{\sim}{t}_0^2} = \frac{m_3^2}{M_B^2} \frac{\partial^2}{\partial \underset{\sim}{t}_0^2}$$

$$\frac{\partial \underset{\sim}{t}_0}{\partial \underset{\sim}{x}_4} = -\frac{m_4}{M_B} \quad \therefore \quad \left(\frac{\partial \underset{\sim}{t}_0}{\partial \underset{\sim}{x}_4}\right)^2 \frac{\partial^2}{\partial \underset{\sim}{t}_0^2} = \frac{m_4^2}{M_B^2} \frac{\partial^2}{\partial \underset{\sim}{t}_0^2}$$

$$\Rightarrow \sum_{i=1}^{N=4} \frac{1}{m_i}\left(\frac{\partial \underset{\sim}{t}_0}{\partial \underset{\sim}{x}_i}\right)^2 \frac{\partial^2}{\partial \underset{\sim}{t}_0^2} \qquad \left(= \sum_{i=1}^{4} \frac{1}{m_i}\left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{t}_0}\right)$$

$$\equiv \sum_{i=1}^{N=4} \frac{1}{m_i}\left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{t}_0} = \sum_{i=1}^{4} \frac{1}{m_i}\left(\frac{\partial \underset{\sim}{t}_0}{\partial \underset{\sim}{x}_i}\right)^2 \frac{\partial^2}{\partial \underset{\sim}{t}_0^2}$$

$$= \left[\frac{m_1+m_2}{M_A^2} + \frac{m_3+m_4}{M_B^2}\right]\frac{\partial^2}{\partial \underset{\sim}{t}_0^2}$$

$$\equiv \left[\frac{M_A}{M_A^2} + \frac{M_B}{M_B^2}\right]\frac{\partial^2}{\partial \underset{\sim}{t}_0^2} = \left(\frac{1}{M_A}+\frac{1}{M_B}\right)\frac{\partial^2}{\partial \underset{\sim}{t}_0^2}$$

$$\equiv \mu^{-1}\frac{\partial^2}{\partial \underset{\sim}{t}_0^2}$$

where μ represents the total reduced mass. This argument is easily extended & can be generalised for any $N, N_A, N_B \ldots$ however, induction is always a good way of seeing just what the hell is going on!

- Consider $\underset{\sim}{t}_i^F$ -transformation (explicitly indexed)

  - Let's use induction again & look at the form of $\left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{t}_i^F}$ for system A. Let $N_A = 3$, ie a triatomic.

$$\left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{t}_i^A} = \sum_{a,b=1}^{N_A-1=2}\left(\frac{\partial \underset{\sim}{t}_a^A}{\partial \underset{\sim}{x}_i}\right)\left(\frac{\partial \underset{\sim}{t}_b^A}{\partial \underset{\sim}{x}_i}\right)\frac{\partial^2}{\partial \underset{\sim}{t}_a^A\,\partial \underset{\sim}{t}_b^A} + \sum_{b=1}^{2}\left(\frac{\partial^2 \underset{\sim}{t}_b^A}{\partial \underset{\sim}{x}_i^2}\right)\left(\frac{\partial}{\partial \underset{\sim}{t}_b^A}\right)$$

$$= \left(\frac{\partial \underset{\sim}{x}_1}{\partial \underset{\sim}{x}_i} - \frac{m_i}{M_A}\right)^2\frac{\partial^2}{\partial \underset{\sim}{t}_1^A\,\partial \underset{\sim}{t}_1^A} + \left(\frac{\partial \underset{\sim}{x}_1}{\partial \underset{\sim}{x}_i} - \frac{m_i}{M_A}\right)\left(\frac{\partial \underset{\sim}{x}_2}{\partial \underset{\sim}{x}_i} - \frac{m_i}{M_A}\right)\frac{\partial^2}{\partial \underset{\sim}{t}_1^A\,\partial \underset{\sim}{t}_2^A} + \cdots$$

$$\cdots + \left(\frac{\partial \underset{\sim}{x}_2}{\partial \underset{\sim}{x}_i} - \frac{m_i}{M_A}\right)\left(\frac{\partial \underset{\sim}{x}_1}{\partial \underset{\sim}{x}_i} - \frac{m_i}{M_A}\right)\frac{\partial^2}{\partial \underset{\sim}{t}_2^A\,\partial \underset{\sim}{t}_1^A} + \left(\frac{\partial \underset{\sim}{x}_2}{\partial \underset{\sim}{x}_i} - \frac{m_i}{M_A}\right)^2\frac{\partial^2}{\partial \underset{\sim}{t}_2^A\,\partial \underset{\sim}{t}_2^A} + \cdots$$

$$\cdots + 0 \quad \text{(corresponding to summation of double derivatives} = 0)$$

$$= \left[\left(\frac{\partial \underset{\sim}{x}_1}{\partial \underset{\sim}{x}_i}\right)^2 - 2\left(\frac{\partial \underset{\sim}{x}_1}{\partial \underset{\sim}{x}_i}\right)\frac{m_i}{M_A} + \frac{m_i^2}{M_A^2}\right]\frac{\partial^2}{\partial \underset{\sim}{t}_1^A\,\partial \underset{\sim}{t}_1^A} + \cdots$$

$$\cdots + \left[\left(\frac{\partial \underset{\sim}{x}_1}{\partial \underset{\sim}{x}_i}\right)\left(\frac{\partial \underset{\sim}{x}_2}{\partial \underset{\sim}{x}_i}\right) - \left(\frac{\partial \underset{\sim}{x}_1}{\partial \underset{\sim}{x}_i}\right)\frac{m_i}{M_A} - \left(\frac{\partial \underset{\sim}{x}_2}{\partial \underset{\sim}{x}_i}\right)\frac{m_i}{M_A} + \frac{m_i^2}{M_A^2}\right]\frac{\partial^2}{\partial \underset{\sim}{t}_1^A\,\partial \underset{\sim}{t}_2^A} + \cdots$$

$$\cdots + \left[\left(\frac{\partial \underset{\sim}{x}_2}{\partial \underset{\sim}{x}_i}\right)\left(\frac{\partial \underset{\sim}{x}_1}{\partial \underset{\sim}{x}_i}\right) - \left(\frac{\partial \underset{\sim}{x}_2}{\partial \underset{\sim}{x}_i}\right)\frac{m_i}{M_A} - \left(\frac{\partial \underset{\sim}{x}_1}{\partial \underset{\sim}{x}_i}\right)\frac{m_i}{M_A} + \frac{m_i^2}{M_A^2}\right]\frac{\partial^2}{\partial \underset{\sim}{t}_2^A\,\partial \underset{\sim}{t}_1^A} + \cdots$$

/...

$$\cdots + \left[\left(\frac{\partial x_2}{\partial x_i}\right)^2 - 2\left(\frac{\partial x_2}{\partial x_i}\right)\frac{m_i}{M_A} + \frac{m_i^2}{M_A^2} \right] \frac{\partial^2}{\partial t_2^A \partial t_2^A}$$

$$\therefore \sum_{i=1}^{N} \frac{1}{m_i}\left(\frac{\partial^2}{\partial x_i^2}\right)_{t_i^A} = \sum_{i=1}^{N} \left[\frac{1}{m_i}\left(\frac{\partial x_1}{\partial x_i}\right)^2 - 2\left(\frac{\partial x_1}{\partial x_i}\right)\frac{1}{M_A} + \frac{m_i}{M_A^2} \right] \frac{\partial^2}{\partial t_1^A \partial t_1^A} + \cdots$$

$$\cdots + \sum_{i=1}^{N} \left[\frac{1}{m_i}\left(\frac{\partial x_1}{\partial x_i}\right)\left(\frac{\partial x_2}{\partial x_i}\right) - \left(\frac{\partial x_1}{\partial x_i}\right)\frac{1}{M_A} - \left(\frac{\partial x_2}{\partial x_i}\right)\frac{1}{M_A} + \frac{m_i}{M_A^2} \right] \frac{\partial^2}{\partial t_1^A \partial t_2^A} +$$

$$\cdots + \sum_{i=1}^{N} \left[\frac{1}{m_i}\left(\frac{\partial x_2}{\partial x_i}\right)\left(\frac{\partial x_1}{\partial x_i}\right) - \left(\frac{\partial x_2}{\partial x_i}\right)\frac{1}{M_A} - \left(\frac{\partial x_1}{\partial x_i}\right)\frac{1}{M_A} + \frac{m_i}{M_A^2} \right] \frac{\partial^2}{\partial t_2^A \partial t_1^A} +$$

$$\cdots + \sum_{i=1}^{N} \left[\frac{1}{m_i}\left(\frac{\partial x_2}{\partial x_i}\right)^2 - 2\left(\frac{\partial x_2}{\partial x_i}\right)\frac{1}{M_A} + \frac{m_i}{M_A^2} \right] \frac{\partial^2}{\partial t_2^A \partial t_2^A}$$

Obviously, over a summation, cross-terms like $\left(\frac{\partial x_1}{\partial x_i}\right)\left(\frac{\partial x_2}{\partial x_i}\right)$ and $\left(\frac{\partial x_2}{\partial x_i}\right)\left(\frac{\partial x_1}{\partial x_i}\right) = 0$; it is also clear that terms like:

$$\left(\frac{\partial x_i^\alpha}{\partial x_j}\right)^\alpha \Big|_{\substack{j=1,2 \\ \alpha=1,2}} \quad \text{are} = 1$$

$$\text{then} \quad \sum_{i=1}^{N} \frac{1}{m_i}\left(\frac{\partial^2}{\partial x_i^2}\right) t_i^A = \left[\frac{1}{m_1} - \frac{2}{M_A} + \frac{M_A}{M_A^2} \right] \frac{\partial^2}{\partial t_1^A \partial t_1^A} + \left[-\frac{2}{M_A} + \frac{M_A}{M_A^2} \right] \frac{\partial^2}{\partial t_1^A \partial t_2^A} +$$

$$\cdots + \left[-\frac{2}{M_A} + \frac{M_A}{M_A^2} \right] \frac{\partial^2}{\partial t_2^A \partial t_1^A} + \left[\frac{1}{m_2} - \frac{2}{M_A} + \frac{M_A}{M_A^2} \right] \frac{\partial^2}{\partial t_2^A \partial t_2^A}$$

$$= \left[\frac{1}{m_1} - \frac{1}{M_A} \right] \frac{\partial^2}{\partial t_1^A \partial t_1^A} + \left[-\frac{1}{M_A} \right] \frac{\partial^2}{\partial t_1^A \partial t_2^A} + \left[-\frac{1}{M_A} \right] \frac{\partial^2}{\partial t_2^A \partial t_1^A}$$

$$\cdots + \left[\frac{1}{m_2} - \frac{1}{M_A} \right] \frac{\partial^2}{\partial t_2^A \partial t_2^A}$$

$$\text{Clearly,} \quad \sum_{i=1}^{N} \frac{1}{m_i}\left(\frac{\partial^2}{\partial x_i^2}\right) t_i^A = \sum_{a,b=1}^{z=(N_A-1)} \left(\frac{\delta_{ab}}{m_b} - \frac{1}{M_A} \right) \frac{\partial^2}{\partial t_a^A \partial t_b^A}$$

This expression may be extended for the B fragment & for any no. of fragment nuclei, Δt:

$$\sum_{i=1}^{N} \frac{1}{m_i}\left(\frac{\partial^2}{\partial x_i^2}\right) t_i^F = \sum_{a,b=1}^{N_F-1} \left(\frac{\delta_{ab}}{m_b} - \frac{1}{M_F} \right) \frac{\partial^2}{\partial t_a^F \partial t_b^F}$$

or $$\sum_{i=1}^{N} \frac{1}{m_i} \left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{t}_i^F} = \sum_{a,b=1}^{N_F-1} G^F_{ab} \frac{\partial^2}{\partial t^F_a \partial t^F_b}$$

where $G^F_{ab} = \frac{\delta_{ab}}{m_b} - \frac{1}{M_F}$

b/c $$\sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial^2}{\partial \underset{\sim}{x}_i^2} = \sum_{i=1}^{N} \frac{1}{m_i} \left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{X}} + \sum_{i=1}^{N} \frac{1}{m_i} \left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{t}_0} + \cdots$$

$$\cdots + \sum_{i=1}^{N} \frac{1}{m_i} \left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{t}_i^A} + \sum_{i=1}^{N} \frac{1}{m_i} \left(\frac{\partial^2}{\partial \underset{\sim}{x}_i^2}\right)_{\underset{\sim}{t}_i^B}$$

becomes ...

$$\sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial^2}{\partial \underset{\sim}{x}_i^2} = \frac{1}{M} \frac{\partial^2}{\partial \underset{\sim}{X}^2} + \frac{1}{\mu} \frac{\partial^2}{\partial \underset{\sim}{t}_0^2} + \sum_{F=A,B} \sum_{a,b=1}^{N_F-1} G^F_{ab} \frac{\partial^2}{\partial t^F_a \partial t^F_b}$$

b/c since $\underset{\sim}{t}_i^F$, $\underset{\sim}{t}_0$, & $\underset{\sim}{X}$ are all coordinate vectors $\Rightarrow$

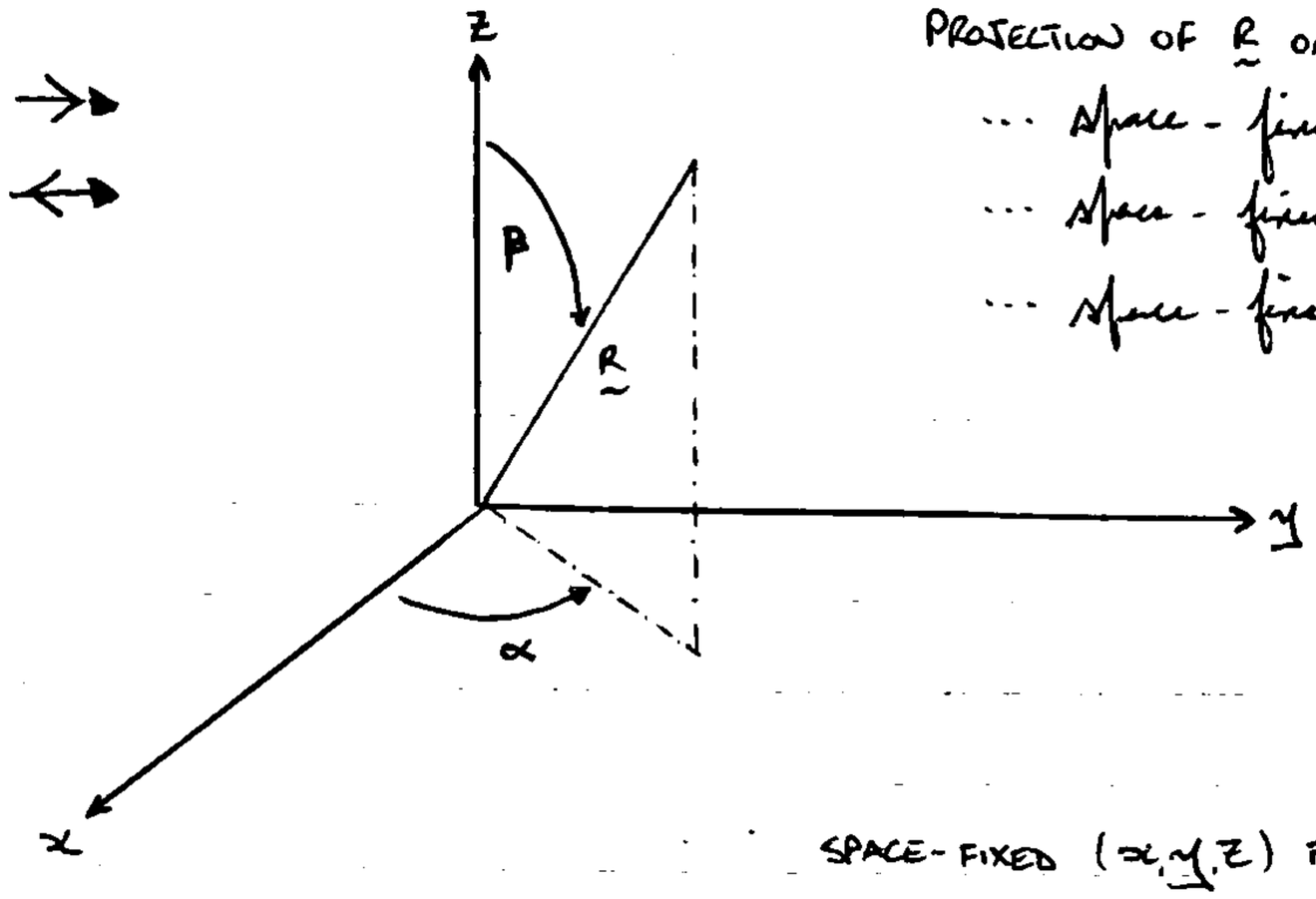
$$\boxed{\sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial^2}{\partial \underset{\sim}{x}_i^2} = \sum_{i=1}^{N} \frac{1}{m_i} \nabla^2(\underset{\sim}{x}_i) = \frac{1}{M} \nabla^2(\underset{\sim}{X}) + \frac{1}{\mu} \nabla^2(\underset{\sim}{t}_0) + \sum_{F} \sum_{ab=1}^{N_F-1} G^F_{ab} \nabla(\underset{\sim}{t}_a) \cdot \nabla(\underset{\sim}{t}_b)}$$

$\frac{1}{M} \nabla^2(\underset{\sim}{X})$ is a description of a free particle of mass M & corresponds to free translation of the total c.o.m. It can be separated off.

The other 3 terms are the K.E. operators for the vibrational Hamiltonian (remember that translation was just disposed of) & are expressed in what's called a space-fixed frame, which is one that's body-fixed w.r.t. translation yet parallel to the lab. frame.

With overall translation out of the way, we seek now to separate overall rotation by transforming to a body-fixed frame. For a non-rigid system, it's best to embed the z-axis of the body-fixed frame on the vector connecting the two fragment centres of mass, namely $\underset{\sim}{t}_0 \equiv \underset{\sim}{R}$

Sin →
Cos ←



SPACE-FIXED (x, y, z) FRAME

PROJECTION OF $\underset{\sim}{R}$ ON TO:

… space-fixed $x = R \sin(\beta) \cos(\alpha)$
… space-fixed $y = R \sin(\beta) \sin(\alpha)$
… space-fixed $z = R \cos(\beta)$

ie $\underset{\sim}{t_o} = \underset{\sim}{R} = \begin{pmatrix} R \sin\beta \cos\alpha \\ R \sin\beta \sin\alpha \\ R \cos\beta \end{pmatrix}$

R is mag. of $\underset{\sim}{R}$

NOTE: since we're defining $\underset{\sim}{R}$ as the z-axis of another coordinate system (that shares the space-fixed origin), the polar angles α & β can be called Euler angles [See BUNKER p. 94 fig 6-1]

We embed the z-axis of the body-fixed frame along the space-fixed vector $\underset{\sim}{t_o} = \underset{\sim}{R}$ by using the transformations:

$$\underset{\sim}{z_o} = C^T \underset{\sim}{t_o}$$

$$\underset{\sim}{z}_i^F = C^T \underset{\sim}{t}_i^F \qquad F = A, B$$

where C is a rotation matrix, a product of two Euler-angle rotation matrices, ie

$$C = \begin{bmatrix} \cos(\beta)\cos(\alpha) & -\sin(\alpha) & \sin(\beta)\cos(\alpha) \\ \cos(\beta)\sin(\alpha) & \cos(\alpha) & \sin(\beta)\sin(\alpha) \\ -\sin(\beta) & 0 & \cos(\beta) \end{bmatrix} = \begin{array}{c} \begin{matrix} x & y & z \end{matrix} \\ \begin{bmatrix} C_{xx} & C_{xy} & C_{xz} \\ C_{yx} & C_{yy} & C_{yz} \\ C_{zx} & C_{zy} & C_{zz} \end{bmatrix} \end{array} \begin{matrix} x \\ y \\ z \end{matrix}$$

$\cos = \mathrm{cd}$.

$$= \underbrace{\begin{bmatrix} \cos(\alpha) & -\sin(\alpha) & 0 \\ \sin(\alpha) & \cos(\alpha) & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{\text{Rotation matrix for Euler angle } \alpha} \underbrace{\begin{bmatrix} \cos(\beta) & 0 & \sin(\beta) \\ 0 & 1 & 0 \\ -\sin(\beta) & 0 & \cos(\beta) \end{bmatrix}}_{\text{Rotation matrix for Euler angle } \beta}$$

See Thomson "Angular Momentum ..." pg 15

$$\underset{\sim}{z}_o = C^T \underset{\sim}{t}_o = \begin{bmatrix} \cos(\beta)\cos(\alpha) & \cos(\beta)\sin(\alpha) & -\sin(\beta) \\ -\sin(\alpha) & \cos(\alpha) & 0 \\ \sin(\beta)\cos(\alpha) & \sin(\beta)\sin(\alpha) & \cos(\beta) \end{bmatrix} \begin{bmatrix} R\sin(\beta)\cos(\alpha) \\ R\sin(\beta)\sin(\alpha) \\ R\cos(\beta) \end{bmatrix}$$

$$= \begin{pmatrix} R\sin(\beta)\cos(\alpha)\cos(\beta)\cos(\alpha) + R\sin(\beta)\sin(\alpha)\cos(\beta)\sin(\alpha) - R\cos(\beta)\sin(\beta) \\ -R\sin(\beta)\cos(\alpha)\sin(\alpha) + R\sin(\beta)\sin(\alpha)\cos(\alpha) \\ R\sin^2(\beta)\cos^2(\alpha) + R\sin^2(\beta)\sin^2(\alpha) + R\cos^2(\beta) \end{pmatrix}$$

$$= \begin{pmatrix} R\cos(\beta)\sin(\beta)\left[\cos^2(\alpha) + \sin^2(\alpha) - 1\right] \\ R\sin(\beta)\left(\cos(\alpha)\sin(\alpha) - \cos(\alpha)\sin(\alpha)\right) \\ R\left[\sin^2(\beta)\left(\cos^2(\alpha) + \sin^2(\alpha)\right) + \cos^2(\beta)\right] \end{pmatrix}$$

$$= \begin{pmatrix} R\cos(\beta)\sin(\beta)\left(1 - 1\right) \\ 0 \\ R\left[\sin^2(\beta) + \cos^2(\beta)\right] \end{pmatrix}$$

$$= \begin{pmatrix} 0 \\ 0 \\ R \end{pmatrix}$$ ie z^{th} component of $\underset{\sim}{z}_o$ is R ✓

We now wish to consider what effect rotation C has on the Hamiltonian. We need to express the differential operators of the space-fixed coordinates $\underset{\sim}{t}_o$ & $\underset{\sim}{t}_i^F$ in terms of the new body-fixed coordinates $\underset{\sim}{z}_o$ & $\underset{\sim}{z}_i^F$. Because of the embedding constraints, namely $\underset{\sim}{z}_o = C^T \underset{\sim}{t}_o$ & $\underset{\sim}{z}_i^F = C^T \underset{\sim}{t}_i^F$, the new body-fixed coordinates $\underset{\sim}{z}_i^F$ are functions of $\underset{\sim}{t}_o$ since the C matrix depends on the (polar) Euler angles α & β that occur in $\underset{\sim}{t}_o$. With this in mind, together with the fact that position in the new body-fixed frame depends on the magnitude of $\underset{\sim}{R}$ (as well as the angles α & β) we may use the chain rule:

$$\frac{\partial}{\partial t_{o,\xi}} = \frac{\partial R}{\partial t_{o,\xi}}\frac{\partial}{\partial R} + \frac{\partial \alpha}{\partial t_{o,\xi}}\frac{\partial}{\partial \alpha} + \frac{\partial \beta}{\partial t_{o,\xi}}\frac{\partial}{\partial \beta} + \sum_F \sum_{i=1}^{N_F-1} \sum_\eta \frac{\partial z_{i,\eta}^F}{\partial t_{o,\xi}} \frac{\partial}{\partial z_{i,\eta}^F}$$

where $\xi = x, y$ or z

s.t. for example $t_{o,x} = R\sin(\beta)\cos(\alpha)$

We now make simplifications to the expression for $\frac{\partial}{\partial to,\xi}$. Let's do this term by term.

First recall that: $\underset{\sim}{to} = \underset{\sim}{R} = \begin{pmatrix} R\sin\beta\cos\alpha \\ R\sin\beta\sin\alpha \\ R\cos\beta \end{pmatrix} = \begin{pmatrix} to,x \\ to,y \\ to,z \end{pmatrix}$

$$R = \left(to,x^2 + to,y^2 + to,z^2 \right)^{1/2}$$

$$\alpha = \tan^{-1}\left(to,y / to,x \right)$$

$$\beta = \tan^{-1}\left\{ \frac{(to,x^2 + to,y^2)^{1/2}}{to,z} \right\} = \cos^{-1}\left(\frac{to,z}{R} \right)$$

Good places to find this stuff:
- ZARE, Angular Momentum, pgs 6 → 7
- BYRON & FULLER, Mathematics of Classical & Quantum Physics, p. 258

1ST term: $\frac{\partial R}{\partial to,\xi}\frac{\partial}{\partial R}$

case $\xi = x$; $R = u^{1/2}$ where $u = (to,x^2 + to,y^2 + to,z^2)$

$$\frac{\partial R}{\partial to,x} = \frac{1}{2u^{1/2}}\frac{\partial u}{\partial to,x} = \frac{1}{2R}\,2\,to,x = \frac{2R\sin\beta\cos\alpha}{2R}$$

$$\therefore \quad \frac{\partial R}{\partial to,x}\frac{\partial}{\partial R} = \sin\beta\cos\alpha\,\frac{\partial}{\partial R}$$

recall that (2 pages ago) we put C in the form:

$$C = \begin{bmatrix} C_{xx} & C_{xy} & C_{xz} \\ C_{yx} & C_{yy} & C_{yz} \\ C_{zx} & C_{zy} & C_{zz} \end{bmatrix} = \begin{bmatrix} \cos\beta\cos\alpha & -\sin\alpha & \sin\beta\cos\alpha \\ \cos\beta\sin\alpha & \cos\alpha & \sin\beta\sin\alpha \\ -\sin\beta & 0 & \cos\beta \end{bmatrix}$$

$$\therefore \quad \frac{\partial R}{\partial to,x}\frac{\partial}{\partial R} = C_{xz}\frac{\partial}{\partial R}$$

case $\xi = y$; again, $R = u^{1/2}$

$$\frac{\partial R}{\partial to,y} = \frac{1}{2R}\frac{\partial u}{\partial to,y} \cdot \frac{1}{2R} Z to,y = \frac{2R \sin\beta \sin\alpha}{2R}$$

$$\therefore \frac{\partial R}{\partial to,y}\frac{\partial}{\partial R} \cdot C_{yz}\frac{\partial}{\partial R}$$

case $\xi = z$; again, $R = u^{1/2}$

$$\frac{\partial R}{\partial to,z} = \frac{1}{2R}\frac{\partial u}{\partial to,z} \cdot \frac{1}{2R} Z to,z = \frac{2R\cos\beta}{2R}$$

$$\therefore \frac{\partial R}{\partial to,z}\frac{\partial}{\partial R} = C_{zz}\frac{\partial}{\partial R}$$

So, for the 1st term we have $\boxed{\frac{\partial R}{\partial to,\xi}\frac{\partial}{\partial R} = C_{\xi z}\frac{\partial}{\partial R}}$

2nd term: $\frac{\partial \alpha}{\partial to,\xi}\frac{\partial}{\partial \alpha}$

case $\xi = x$; $\alpha = \tan^{-1}(u)$ where $u = \left(to,y / to,x\right)$

remember the formula for inverse tan derivatives:

$$D_x \tan^{-1}(u) = \frac{1}{1+u^2} D_x$$

See SWOKOWSKI, formula (19) in the inside cover formula sheet.

$$\frac{\partial \alpha}{\partial to,x} = \frac{1}{1+u^2}\frac{\partial}{\partial to,x}\left[to,y \cdot (to,x)^{-1}\right]$$

$$= \frac{1}{1 + to,y^2/to,x^2}\left[\frac{-to,y}{(to,x)^2}\right]$$

$$= \frac{1}{1 + \frac{R^2\sin^2\beta\sin^2\alpha}{R^2\sin^2\beta\cos^2\alpha}}\left[\frac{R\sin\beta\sin\alpha}{R^2\sin^2\beta\cos^2\alpha}\right]$$

$$= \frac{1}{1 + \frac{\sin^2\alpha}{\cos^2\alpha}} \cdot \frac{-\sin\alpha}{R\sin\beta\cos^2\alpha}$$

$$= \frac{-\sin\alpha}{R\sin\beta\cos^2\alpha + \frac{R\sin\beta\cos^2\alpha\sin^2\alpha}{\cos^2\alpha}}$$

$$= \frac{-\sin\alpha}{R\sin\beta(\cos^2\alpha + \sin^2\alpha)} = \frac{-\sin\alpha}{R\sin\beta} = \frac{C_{xy}}{R\sin\beta}$$

$$\therefore \frac{\partial\alpha}{\partial t_{o,x}}\frac{\partial}{\partial\alpha} = (R\sin\beta)^{-1} C_{xy}\frac{\partial}{\partial\alpha}$$

case $\{ = y$; $\alpha = \tan^{-1}(u)$ where $u = (t_{o,y}/t_{o,x})$

$$\frac{\partial\alpha}{\partial t_{o,y}} = \frac{1}{1+u^2}\frac{\partial}{\partial t_{o,y}}\left(\frac{t_{o,y}}{t_{o,x}}\right)$$

$$= \frac{1}{1 + \frac{\sin^2\alpha}{\cos^2\alpha}} \cdot \left(\frac{1}{t_{o,x}}\right)$$

$$= \frac{1}{1 + \frac{\sin^2\alpha}{\cos^2\alpha}} \cdot \left(\frac{1}{R\sin\beta\cos\alpha}\right)$$

$$= \frac{1}{R\sin\beta\cos\alpha + \left(\frac{R\sin\beta\cos\alpha\sin^2\alpha}{\cos^2\alpha}\right)}$$

$$= \frac{1}{R \sin\beta \left(\cos\alpha + \frac{\sin^2\alpha}{\cos\alpha} \right)}$$

$$= \frac{1}{R \sin\beta \left(\cos\alpha + \left(\frac{1}{\cos\alpha} - \frac{\cos^2\alpha}{\cos\alpha} \right) \right)}$$

$$= \frac{1}{R \sin\beta \left(\cos\alpha + \frac{1}{\cos\alpha} - \cos\alpha \right)}$$

$$= \frac{\cos\alpha}{R \sin\beta} = \frac{C_{yy}}{R \sin\beta}$$

$$\therefore \frac{\partial\alpha}{\partial t_{o,y}} \frac{\partial}{\partial\alpha} = (R \sin\beta)^{-1} C_{yy} \frac{\partial}{\partial\alpha}$$

case $\xi = z$; $\alpha = \tan^{-1}(u)$ where $u = \left(t_{o,y} / t_{ox} \right)$

$$\frac{\partial\alpha}{\partial t_{o,z}} = \frac{1}{1+u^2} \frac{\partial}{\partial t_{o,z}} \left(\frac{t_{o,y}}{t_{o,x}} \right)$$

$$= 0$$

$$= (R \sin\beta)^{-1} C_{zy}$$

$$\Rightarrow \frac{\partial\alpha}{\partial t_{o,z}} \frac{\partial}{\partial\alpha} = (R \sin\beta)^{-1} C_{zy} \frac{\partial}{\partial\alpha}$$

for the second term we have

$$\boxed{\frac{\partial\alpha}{\partial t_{o,\xi}} \frac{\partial}{\partial\alpha} = (R \sin\beta)^{-1} C_{\xi y} \frac{\partial}{\partial\alpha}}$$

3rd term: $\frac{\partial\beta}{\partial t_{o,\xi}} \frac{\partial}{\partial\beta}$

case $\xi = x$; $\beta = \tan^{-1}(u)$ where $u = \frac{\left(t_{o,x}^2 + t_{o,y}^2 \right)^{1/2}}{t_{o,z}}$

$$\frac{\partial \beta}{\partial t_{o,x}} = \frac{1}{1+u^2}\,\frac{\partial}{\partial t_{o,x}}(u)$$

$$= \frac{1}{1+\left(\dfrac{t_{o,x}^2 + t_{o,y}^2}{t_{o,z}^2}\right)} \cdot \frac{\not{2}\, t_{o,x}}{\not{2}\, t_{o,z}\left(t_{o,x}^2 + t_{o,y}^2\right)^{1/2}}$$

$$= \frac{1}{R^2/t_{o,z}^2} \cdot \frac{t_{o,x}}{t_{o,z}\left(t_{o,x}^2 + t_{o,y}^2\right)^{1/2}}$$

$$= \frac{t_{o,z}\, t_{o,x}}{R^2\left(t_{o,x}^2 + t_{o,y}^2\right)^{1/2}}$$

$$= \frac{R^2 \cos\beta \sin\beta \cos\alpha}{R^2\left[R^2\left(\sin^2\beta\cos^2\alpha + \sin^2\beta\sin^2\alpha\right)\right]^{1/2}}$$

$$= \frac{\cos\beta \sin\beta \cos\alpha}{R\left[\sin^2\beta\left(\cos^2\alpha + \sin^2\alpha\right)\right]^{1/2}}$$

$$= \frac{\cos\beta \sin\beta \cos\alpha}{R\left(\sin^2\beta\right)^{1/2}}$$

$$= \frac{\cos\beta\cos\alpha}{R} = \frac{C_{xx}}{R}$$

$$\frac{\partial \beta}{\partial t_{o,x}}\,\frac{\partial}{\partial \beta} = R^{-1} C_{xx}\,\frac{\partial}{\partial \beta}$$

case $\xi = y$; $\beta = \tan^{-1}(u)$ where $u = \dfrac{(t_{o,x}^2 + t_{o,y}^2)^{1/2}}{t_{o,z}}$

$$\frac{\partial \beta}{\partial t_{o,y}} = \frac{1}{1+u^2} \frac{\partial}{\partial t_{o,y}}(u)$$

$$= \frac{t_{o,z}^2}{R^2} \cdot \frac{t_{o,y}}{t_{o,z}(t_{o,x}^2 + t_{o,y}^2)^{1/2}}$$

$$= \frac{t_{o,z}\, t_{o,y}}{R^2 (t_{o,x}^2 + t_{o,y}^2)^{1/2}}$$

$$= \frac{R^2 \cos\beta \sin\beta \sin\alpha}{R^2 [R^2 \sin^2\beta (\cos^2\alpha + \sin^2\alpha)]^{1/2}}$$

$$= \frac{\cos\beta \sin\beta \sin\alpha}{R \sin\beta}$$

$$= \frac{\cos\beta \sin\alpha}{R} = \frac{C_{yx}}{R}$$

$$\frac{\partial \beta}{\partial t_{o,y}} \frac{\partial}{\partial \beta} = R^{-1} C_{yx} \frac{\partial}{\partial \beta}$$

case $\xi = z$; $\beta = \tan^{-1}(u)$ where $u = \dfrac{(t_{o,x}^2 + t_{o,y}^2)^{1/2}}{t_{o,z}}$

$$\frac{\partial \beta}{\partial t_{o,z}} = \frac{1}{1+u^2} \frac{\partial}{\partial t_{o,z}}(u)$$

$$= \frac{t_{o,z}^2}{R^2} \cdot \frac{-(t_{o,x}^2 + t_{o,y}^2)^{1/2}}{t_{o,z}^2}$$

$$= -\frac{\left[R^2 \sin^2\beta \left(\cos^2\alpha + \sin^2\alpha\right)\right]^{1/2}}{R^2}$$

$$= -\frac{R\sin\beta}{R^2}$$

$$= -\frac{\sin\beta}{R} = \frac{C_{zx}}{R}$$

$$\frac{\partial\beta}{\partial t_{o,z}}\frac{\partial}{\partial\beta} = R^{-1}C_{zx}\frac{\partial}{\partial\beta}$$

for the 3rd term we have

$$\boxed{\frac{\partial\beta}{\partial t_{o,\eta}}\frac{\partial}{\partial\beta} = R^{-1}C_{\eta x}\frac{\partial}{\partial\beta}}$$

4th term: $\sum_F \sum_{i=1}^{N_F-1} \sum_\eta \frac{\partial z_{i,\eta}^F}{\partial t_{o,\eta}} \frac{\partial}{\partial z_{i,\eta}^F}$

by the product rule $\frac{\partial z_{i,\eta}^F}{\partial t_{o,\eta}} = \sum_\xi \frac{\partial C_{\xi\eta}}{\partial t_{o,\eta}} t_{i,\xi}^F$

To show how this was obtained, consider the matrix representation of the transformation $\underset{\sim}{z}_i^F = C^T \underset{\sim}{t}_i^F$:

$$\begin{pmatrix} z_{i,x}^F \\ z_{i,y}^F \\ z_{i,z}^F \end{pmatrix} = \begin{bmatrix} C_{xx} & C_{yx} & C_{zx} \\ C_{xy} & C_{yy} & C_{zy} \\ C_{xz} & C_{yz} & C_{zz} \end{bmatrix} \begin{pmatrix} t_{i,x}^F \\ t_{i,y}^F \\ t_{i,z}^F \end{pmatrix} = \begin{pmatrix} C_{xx}t_{i,x}^F + C_{yx}t_{i,y}^F + C_{zx}t_{i,z}^F \\ C_{xy}t_{i,x}^F + C_{yy}t_{i,y}^F + C_{zy}t_{i,z}^F \\ C_{xz}t_{i,x}^F + C_{yz}t_{i,y}^F + C_{zz}t_{i,z}^F \end{pmatrix}$$

Clearly $z_{i,\eta}^F = \sum_\xi C_{\xi\eta}\, t_{i,\xi}^F$

& by the product rule, $\frac{\partial z_{i,\eta}^F}{\partial t_{o,\xi}} = \sum_\xi \frac{\partial C_{\xi\eta}}{\partial t_{o,\xi}} t_{i,\xi}^F$ $\left.\begin{array}{l} \eta = x, y, \text{or } z \\ \xi = x, y, \text{or } z \\ \xi = x, y, \text{or } z \end{array}\right\}$ $F = A, B$

We can simplify this further because $\underset{\sim}{t}_i^F = C\,\underset{\sim}{z}_i^F$

ie $$\begin{pmatrix} t_{i,x}^F \\ t_{i,y}^F \\ t_{i,z}^F \end{pmatrix} = \begin{bmatrix} C_{xx} & C_{xy} & C_{xz} \\ C_{yx} & C_{yy} & C_{yz} \\ C_{zx} & C_{zy} & C_{zz} \end{bmatrix} \begin{pmatrix} z_{i,x}^F \\ z_{i,y}^F \\ z_{i,z}^F \end{pmatrix}$$

Which, in a similar spirit to last page gives the generalisation -

$$t_{i,\beta}^F = \sum_{\mu} C_{\beta\mu}\, z_{i,\mu}^F \qquad \mu = x, y, \text{or } z$$

..then
$$\frac{\partial z_{i,\lambda}^F}{\partial t_{0,\beta}} = \sum_{\beta} \frac{\partial C_{\beta\lambda}}{\partial t_{0,\beta}} t_{i,\beta}^F = \sum_{\beta,\mu} \frac{\partial C_{\beta\lambda}}{\partial t_{0,\beta}} C_{\beta\mu}\, z_{i,\mu}^F$$

where
$$\frac{\partial C_{\beta\lambda}}{\partial t_{0,\beta}} = \frac{\partial C_{\beta\lambda}}{\partial \alpha}\frac{\partial \alpha}{\partial t_{0,\beta}} + \frac{\partial C_{\beta\lambda}}{\partial \beta}\frac{\partial \beta}{\partial t_{0,\beta}}$$

because matrix C depends on the Euler angles α & β.

Weiss seen the simplified form of these two from analysis of terms 2 & 3.

At this juncture, weiss explicitly derived the substitutions / simplifications [detailed in Brocks et. al.'s paper as eq.s A (11), (12), & (13)] that will be instrumental in changing the form of the operator $\frac{\partial}{\partial t_{0,\beta}}$ from one given in space-fixed coordinates to one in a body-fixed representation.

We now introduce some angular momentum operator definitions that can be used (in concert with the simplifications just mentioned) to further develop our body-fixed Hoplacians.

Recall from classical mechanics that linear momentum $\underset{\sim}{p} = m\underset{\sim}{v}$ and (orbital) angular momentum is given by: $\hat{l} = \underset{\sim}{R} \times \underset{\sim}{p}$

In quantum mechanics, $\underset{\sim}{p}$ is replaced by $\left(\frac{\hbar}{i}\right)\nabla$ and the

$$\hat{l} = \left(\frac{\hbar}{i}\right) \underset{\sim}{R} \times \nabla = \left(\frac{\hbar}{i}\right) \cdot \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix}$$

ie $$\hat{l} = \frac{\hbar}{i}\left[\hat{i}\,(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}) - \hat{j}\,(x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}) + \hat{k}\,(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})\right]$$

$$= \frac{\hbar}{i}\left[\hat{i}\,(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}) + \hat{j}\,(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}) + \hat{k}\,(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right]$$

$$\Rightarrow \quad \hat{l}_x = \frac{\hbar}{i}\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]$$

$$\hat{l}_y = \frac{\hbar}{i}\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right]$$

$$\hat{l}_z = \frac{\hbar}{i}\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right]$$

Normally the symbol l is reserved for orbital angular momentum. The operator $\hat{j}$ (defined & more generally & extensively than $\hat{l}$) is used describe general angular momentum phenomena (which is advantageous - it permits spin ... don't worry!).

For the problem we're working on, we want the orbital AM operator to have components:

$$\left\{\begin{array}{l} \hat{l}_x = \frac{\hbar}{i}\left[t_{o,y}\frac{\partial}{\partial t_{o,z}} - t_{o,z}\frac{\partial}{\partial t_{o,y}}\right] = \frac{\hbar}{i}\left[R_y\frac{\partial}{\partial R_z} - R_z\frac{\partial}{\partial R_y}\right] \\ \hat{l}_y = \frac{\hbar}{i}\left[t_{o,z}\frac{\partial}{\partial t_{o,x}} - t_{o,x}\frac{\partial}{\partial t_{o,z}}\right] = \frac{\hbar}{i}\left[R_z\frac{\partial}{\partial R_x} - R_x\frac{\partial}{\partial R_z}\right] \\ \hat{l}_z = \frac{\hbar}{i}\left[t_{o,x}\frac{\partial}{\partial t_{o,y}} - t_{o,y}\frac{\partial}{\partial t_{o,x}}\right] = \frac{\hbar}{i}\left[R_x\frac{\partial}{\partial R_y} - R_y\frac{\partial}{\partial R_x}\right] \end{array}\right.$$

analogous to the above 3 components.

We can summarise these in a single expression using the Levi-Civita antisymmetric tensor (sometimes called the alternating tensor or the rank-3 isotropic tensor $\epsilon_{\lambda\mu\nu}$ $\forall \lambda,\mu,\nu$ each equaling x, y, z.

The tensor $\epsilon_{\lambda\mu\nu}$ has the following properties:

① $\epsilon_{\lambda\mu\nu} = 0$ if each index is not unique (e.g. $\lambda = \mu$ etc...)

② $= +1$ for even permutations of indices (e.g. $\epsilon_{xyz} = +1$)

③ $= -1$ for odd permutations of indices (e.g. $\epsilon_{xzy} = -1$)

Then $\hat{l}_x$, $\hat{l}_y$, & $\hat{l}_z$ can be summarised:

$$\boxed{\hat{l}_\lambda = \frac{\hbar}{i} \sum_{\mu,\nu} \epsilon_{\lambda\mu\nu}\, to_{,\mu}\, \frac{\partial}{\partial to_{,\nu}} = \frac{\hbar}{i} \sum_{\mu,\nu} \epsilon_{\lambda\mu\nu} R_\mu \frac{\partial}{\partial R_\nu}}$$

orbital AM component

We can show that this is true simply by expanding...

case $\lambda = x$.

$$\hat{l}_x = \frac{\hbar}{i} \Big[\epsilon_{xxx} R_x \frac{\partial}{\partial R_x} + \epsilon_{xxy} R_x \frac{\partial}{\partial R_y} + \epsilon_{xxz} R_x \frac{\partial}{\partial R_z} + \cdots$$

$$\cdots + \epsilon_{xyx} R_y \frac{\partial}{\partial R_x} + \epsilon_{xyy} R_y \frac{\partial}{\partial R_y} + \epsilon_{xyz} R_y \frac{\partial}{\partial R_z} + \cdots$$

$$\cdots + \epsilon_{xzx} R_z \frac{\partial}{\partial R_x} + \epsilon_{xzy} R_z \frac{\partial}{\partial R_y} + \epsilon_{xzz} R_z \frac{\partial}{\partial R_z} \Big]$$

7 of these 9 terms are $= 0$ by property ① of the Levi-Civita tensor. We're left with,

$$\hat{l}_x = \frac{\hbar}{i} \Big[R_y \frac{\partial}{\partial R_z} - R_z \frac{\partial}{\partial R_y} \Big]$$

which is equivalent to the form given on the previous pg. Expansions of the above boxed formula give the desired forms of $\hat{l}_y$ & $\hat{l}_z$ also. The expansions are not included for brevity, but are extremely similar to the $\hat{l}_x$ expansion.

In a similar spirit, the components of the general ~~fragment~~ nuclear/particle angular momentum (for fragment F) are given by:

$$\boxed{\hat{j}_\lambda(\underset{\sim}{t_i^F}) = \frac{\hbar}{i} \sum_{\mu\nu} \epsilon_{\lambda\mu\nu}\, t^F_{i,\mu}\, \frac{\partial}{\partial t^F_{i,\nu}}}$$

- AM components for nucleus belonging to fragment F.

logically, general fragment angular momentum is given by

$$\underset{\sim}{\hat{J}}^F = \sum_{i=1}^{N_F-1} \underset{\sim}{\hat{j}}(t_i^F)$$

GENERAL FRAGMENT AM

where $\hat{j}(t_i^F) = \left(\hat{j}_x^2 + \hat{j}_y^2 + \hat{j}_z^2 \right)^{1/2}$

& total general angular momentum is $\underset{\sim}{\hat{J}} = \sum_F \underset{\sim}{\hat{J}}^F = \underset{\sim}{\hat{J}}^A + \underset{\sim}{\hat{J}}^B$

TOTAL GENERAL AM

Then, total angular momentum is naturally the sum of the total general angular momentum & the orbital angular momentum,

$$\underset{\sim}{\hat{J}} = \underset{\sim}{\hat{l}} + \underset{\sim}{\hat{j}} = \underset{\sim}{\hat{l}} + \underset{\sim}{\hat{j}}^A + \underset{\sim}{\hat{j}}^B$$

TOTAL AM

where $\hat{l} = \left(\hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 \right)^{1/2}$

To be of any use to us, these angular momentum operators need to be able to handle body-fixed coordinates (as opposed to the space-fixed coordinates they're describing in their present form)

Begin by transforming the general angular momenta first.

We are able to write $\frac{\partial}{\partial t_{i,\eta}^F} = \sum_\eta \frac{\partial z_{i,\eta}^F}{\partial t_{i,\eta}^F} \frac{\partial}{\partial z_{i,\eta}^F}$

but $\underset{\sim}{z}_i^F = C^T \underset{\sim}{t}_i^F$

ie $\frac{\partial \underset{\sim}{z}_i^F}{\partial \underset{\sim}{t}_i^F} = C^T \frac{\partial \underset{\sim}{t}_i^F}{\partial \underset{\sim}{t}_i^F} + \cancel{\frac{\partial C^T}{\partial \underset{\sim}{t}_i^F} \underset{\sim}{t}_i^F}$ $= 0$ $\because C$ not a fn of $\underset{\sim}{t}_i^F$

Better to attack the problem by induction! Using $\underset{\sim}{z}_i^F = C^T \underset{\sim}{t}_i^F$

$$z_{i,x}^F = C_{xx} t_{i,x}^F + C_{yx} t_{i,y}^F + C_{zx} t_{i,z}^F$$

$$\Rightarrow \quad \frac{\partial z_{i,x}^F}{\partial t_{i,x}^F} = C_{xx} \; ; \quad \frac{\partial z_{i,x}^F}{\partial t_{i,y}^F} = C_{yx} \; ; \quad \frac{\partial z_{i,x}^F}{\partial t_{i,z}^F} = C_{zx}$$

$$z_{i,y}^F = C_{xy} t_{i,x}^F + C_{yy} t_{i,y}^F + C_{zy} t_{i,z}^F$$

$$\Rightarrow \quad \frac{\partial z_{i,y}^F}{\partial t_{i,y}^F} = C_{yy} \; ; \quad \frac{\partial z_{i,y}^F}{\partial t_{i,x}^F} = C_{xy} \; ; \quad \frac{\partial z_{i,y}^F}{\partial t_{i,z}^F} = C_{zy}$$

$$z_{i,z}^F = C_{xz} t_{i,x}^F + C_{yz} t_{i,y}^F + C_{zz} t_{i,z}^F$$

$$\Rightarrow \quad \frac{\partial z_{i,z}^F}{\partial t_{i,x}^F} = C_{xz} \; ; \quad \frac{\partial z_{i,z}^F}{\partial t_{i,y}^F} = C_{yz} \; ; \quad \frac{\partial z_{i,z}^F}{\partial t_{i,z}^F} = C_{zz}$$

It is now evident that $\dfrac{\partial z_{i,\eta}^F}{\partial t_{i,\xi}^F} = C_{\xi\eta}$

.. then ..

$$\boxed{\frac{\partial}{\partial t_{i,\xi}^F} = \sum_\eta \frac{\partial z_{i,\eta}^F}{\partial t_{i,\xi}^F} \frac{\partial}{\partial z_{i,\eta}^F} = \sum_\eta C_{\xi\eta} \frac{\partial}{\partial z_{i,\eta}^F}}$$

Now consider the λ^{th} component of the i^{th} nucleus' angular momentum:

remember, $\hat{J}_\lambda(\underset{\sim}{t}_i^F) = \frac{\hbar}{i} \sum_{\mu\nu} \epsilon_{\lambda\mu\nu} t_{i,\mu}^F \frac{\partial}{\partial t_{i,\nu}^F}$

but we just found that $\frac{\partial}{\partial t_{i,\nu}^F} = \sum_\eta C_{\nu\eta} \frac{\partial}{\partial z_{i,\eta}^F}$

$$\text{so} \quad \hat{J}_\lambda(\underset{\sim}{t}_i^F) = \frac{\hbar}{i} \sum_{\mu\nu} \epsilon_{\lambda\mu\nu} t_{i,\mu}^F \sum_\eta C_{\nu\eta} \frac{\partial}{\partial z_{i,\eta}^F}$$

but $\underset{\sim}{t}_i^F = C \underset{\sim}{z}_i^F$

ie $$\begin{pmatrix} t^F_{i,x} \\ t^F_{i,y} \\ t^F_{i,z} \end{pmatrix} = \begin{bmatrix} C_{xx} & C_{xy} & C_{xz} \\ C_{yx} & C_{yy} & C_{yz} \\ C_{zx} & C_{zy} & C_{zz} \end{bmatrix} \begin{pmatrix} z^F_{i,x} \\ z^F_{i,y} \\ z^F_{i,z} \end{pmatrix}$$

then, for example: $t^F_{i,x} = C_{xx} z^F_{i,x} + C_{xy} z^F_{i,y} + C_{xz} z^F_{i,z}$

& in general $t^F_{i,\mu} = \sum_\xi C_{\mu\xi} z^F_{i,\xi}$ $\qquad \xi = x, y, \text{or } z$

We can substitute this into our expression for $\hat{j}_\lambda(\underset{\sim}{t}^F_i)$:

$$\hat{j}_\lambda(\underset{\sim}{t}^F_i) = \frac{\hbar}{i} \sum_{\mu\nu} \epsilon_{\lambda\mu\nu} t^F_{i,\mu} \sum_\eta C_{\nu\eta} \frac{\partial}{\partial z^F_{i,\eta}}$$

$$= \frac{\hbar}{i} \sum_{\mu\nu} \epsilon_{\lambda\mu\nu} \sum_\xi C_{\mu\xi} z^F_{i,\xi} \sum_\eta C_{\nu\eta} \frac{\partial}{\partial z^F_{i,\eta}}$$

We can get this into a neater form by expanding this out & using the fact that for scalars, there exists commutativity under multiplication. The job of expansion is made easier (but not much) when we recognise that, as we've seen before, we'll only get non-zero terms in the expansion for even & odd permutations of the Levi-Civita tensor.

<u>case $\lambda = x$</u> : $$\hat{j}_x(\underset{\sim}{t}^F_i) = \frac{\hbar}{i}\left[\epsilon_{xyz} \sum_\xi C_{y,\xi} z^F_{i,\xi} \sum_\eta C_{z,\eta} \frac{\partial}{\partial z^F_{i,\eta}}\right] + \ldots$$

$$\ldots + \frac{\hbar}{i}\left[\epsilon_{xzy} \sum_\xi C_{z,\xi} z^F_{i,\xi} \sum_\eta C_{y,\eta} \frac{\partial}{\partial z^F_{i,\eta}}\right]$$

$$\Rightarrow \hat{j}_x(\underset{\sim}{t}^F_i) = \frac{\hbar}{i}\left[\epsilon_{xyz} \sum_\xi C_{y,\xi} z^F_{i,\xi} \left(C_{zx} \frac{\partial}{\partial z^F_{i,x}} + C_{zy} \frac{\partial}{\partial z^F_{i,y}} + C_{zz} \frac{\partial}{\partial z^F_{i,z}}\right)\right] + \ldots$$

$$\ldots + \frac{\hbar}{i}\left[\epsilon_{xzy} \sum_\xi C_{z,\xi} z^F_{i,\xi} \left(C_{yx} \frac{\partial}{\partial z^F_{i,x}} + C_{yy} \frac{\partial}{\partial z^F_{i,y}} + C_{yz} \frac{\partial}{\partial z^F_{i,z}}\right)\right]$$

$$= \frac{\hbar}{i}\left[\epsilon_{xyz}\left\{C_{yx} z^F_{i,x} + C_{yy} z^F_{i,y} + C_{yz} z^F_{i,z}\right\}\left(C_{zx} \frac{\partial}{\partial z^F_{i,x}} + C_{zy} \frac{\partial}{\partial z^F_{i,y}} + C_{zz} \frac{\partial}{\partial z^F_{i,z}}\right)\right] + \ldots$$

$$\ldots + \frac{\hbar}{i}\left[\epsilon_{xzy}\left\{C_{zx} z^F_{i,x} + C_{zy} z^F_{i,y} + C_{zz} z^F_{i,z}\right\}\left(C_{yx} \frac{\partial}{\partial z^F_{i,x}} + C_{yy} \frac{\partial}{\partial z^F_{i,y}} + C_{yz} \frac{\partial}{\partial z^F_{i,z}}\right)\right]$$

↑ x

$$\hat{j}_x(\underset{\sim}{t}_i^F) = \frac{\hbar}{i}\epsilon_{xyz}\Big\{ C_{yx}z^F_{i,x}C_{zx}\frac{\partial}{\partial z^F_{i,x}} + C_{yx}z^F_{i,x}C_{zy}\frac{\partial}{\partial z^F_{i,y}} + C_{yx}z^F_{i,x}C_{zz}\frac{\partial}{\partial z^F_{i,z}} + \cdots$$
$$\cdots + C_{yy}z^F_{i,y}C_{zx}\frac{\partial}{\partial z^F_{i,x}} + C_{yy}z^F_{i,y}C_{zy}\frac{\partial}{\partial z^F_{i,y}} + C_{yy}z^F_{i,y}C_{zz}\frac{\partial}{\partial z^F_{i,z}} + \cdots$$
$$\cdots + C_{yz}z^F_{i,z}C_{zx}\frac{\partial}{\partial z^F_{i,x}} + C_{yz}z^F_{i,z}C_{zy}\frac{\partial}{\partial z^F_{i,y}} + C_{yz}z^F_{i,z}C_{zz}\frac{\partial}{\partial z^F_{i,z}}\Big\} + \cdots$$

$$\cdots + \frac{\hbar}{i}\epsilon_{xzy}\Big\{ C_{zx}z^F_{i,x}C_{yx}\frac{\partial}{\partial z^F_{i,x}} + C_{zx}z^F_{i,x}C_{yy}\frac{\partial}{\partial z^F_{i,y}} + C_{zx}z^F_{i,x}C_{yz}\frac{\partial}{\partial z^F_{i,z}} + \cdots$$
$$\cdots + C_{zy}z^F_{i,y}C_{yx}\frac{\partial}{\partial z^F_{i,x}} + C_{zy}z^F_{i,y}C_{yy}\frac{\partial}{\partial z^F_{i,y}} + C_{zy}z^F_{i,y}C_{yz}\frac{\partial}{\partial z^F_{i,z}} + \cdots$$
$$\cdots + C_{zz}z^F_{i,z}C_{yx}\frac{\partial}{\partial z^F_{i,x}} + C_{zz}z^F_{i,z}C_{yy}\frac{\partial}{\partial z^F_{i,y}} + C_{zz}z^F_{i,z}C_{yz}\frac{\partial}{\partial z^F_{i,z}}\Big\}$$

Now use scalar multiplication commutativity!

$$\hat{j}_x(\underset{\sim}{t}_i^F) = \frac{\hbar}{i}\cdot^{\epsilon_{xyz}}\Big[C_{yx}C_{zx}z^F_{i,x}\frac{\partial}{\partial z^F_{i,x}} + C_{yx}C_{zy}z^F_{i,x}\frac{\partial}{\partial z^F_{i,y}} + C_{yx}C_{zz}z^F_{i,x}\frac{\partial}{\partial z^F_{i,z}} + \cdots$$
$$\cdots + C_{yy}C_{zx}z^F_{i,y}\frac{\partial}{\partial z^F_{i,x}} + C_{yy}C_{zy}z^F_{i,y}\frac{\partial}{\partial z^F_{i,y}} + C_{yy}C_{zz}z^F_{i,y}\frac{\partial}{\partial z^F_{i,z}} + \cdots$$
$$\cdots + C_{yz}C_{zx}z^F_{i,z}\frac{\partial}{\partial z^F_{i,x}} + C_{yz}C_{zy}z^F_{i,z}\frac{\partial}{\partial z^F_{i,y}} + C_{yz}C_{zz}z^F_{i,z}\frac{\partial}{\partial z^F_{i,z}}\Big] + \cdots$$

$$\cdots + \frac{\hbar}{i}\epsilon_{xzy}\Big\{ C_{zx}C_{yx}z^F_{i,x}\frac{\partial}{\partial z^F_{i,x}} + C_{zx}C_{yy}z^F_{i,x}\frac{\partial}{\partial z^F_{i,y}} + C_{zx}C_{yz}z^F_{i,x}\frac{\partial}{\partial z^F_{i,z}} + \cdots$$
$$\cdots + C_{zy}C_{yx}z^F_{i,y}\frac{\partial}{\partial z^F_{i,x}} + C_{zy}C_{yy}z^F_{i,y}\frac{\partial}{\partial z^F_{i,y}} + C_{zy}C_{yz}z^F_{i,y}\frac{\partial}{\partial z^F_{i,z}} + \cdots$$
$$\cdots + C_{zz}C_{yx}z^F_{i,z}\frac{\partial}{\partial z^F_{i,x}} + C_{zz}C_{yy}z^F_{i,z}\frac{\partial}{\partial z^F_{i,y}} + C_{zz}C_{yz}z^F_{i,z}\frac{\partial}{\partial z^F_{i,z}}\Big]$$

(*)

which now contracts back to:

$$\hat{j}_x(\underset{\sim}{t}_i^F) = \frac{\hbar}{i}\sum_{\mu\nu}\sum_{\xi,\eta}\epsilon_{x\mu\nu}C_{\mu\xi}C_{\nu\eta}z^F_{i,\xi}\frac{\partial}{\partial z^F_{i,\eta}} \qquad \left.\begin{matrix}\mu\\ \nu\\ \xi\\ \eta\end{matrix}\right\} = x,y,z$$

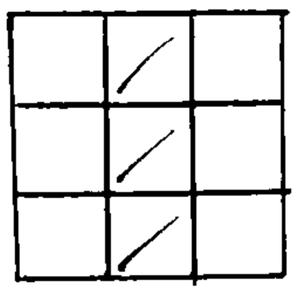
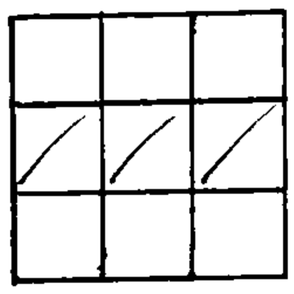
This form is neat, but we can tinker with it more so that when we look at $\hat{\underset{\sim}{j}}(\underset{\sim}{t}_i^F)$, we'll be nicely surprised at how easy it is to transform to $\hat{\underset{\sim}{j}}(\underset{\sim}{z}_i^F)$.

Consider expansion (*) & also C:

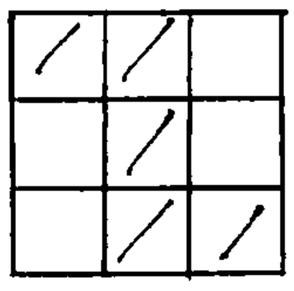
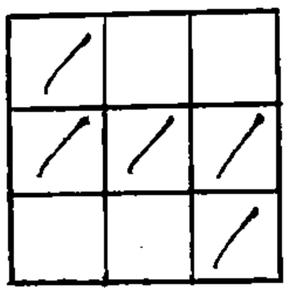
$$C = \begin{bmatrix} \cos\alpha\cos\beta & -\sin\alpha & \sin\beta\cos\alpha \\ \cos\beta\sin\alpha & \cos\alpha & \sin\beta\sin\alpha \\ -\sin\beta & 0 & \cos\beta \end{bmatrix} = \begin{bmatrix} C_{xx} & C_{xy} & C_{xz} \\ C_{yx} & C_{yy} & C_{yz} \\ C_{zx} & C_{zy} & C_{zz} \end{bmatrix}$$

Clearly, the terms in the expansion containing element $C_{ZM}=0$ can be removed.

Graphically, we may represent this:

$$\dot{J}_x(t_i^F) = \frac{k}{i}\epsilon_{xyz}$$  $$+ \frac{k}{i}\epsilon_{xzy}$$ 

Also 'diagonal' terms will cancel each other when the tensor expressions are set to either +1 or −1 (possible too because of scalar multiplication commutivity).

So, $\dot{J}_x(t_i^F) = \frac{k}{i}\epsilon_{xyz}$  $+ \frac{k}{i}\epsilon_{xzy}$ 

We can express the remaining terms:

$$\dot{J}_x(t_i^F) = \frac{k}{i}\epsilon_{xyz}\left[C_{yx}C_{zz}z_{i,x}^F \frac{\partial}{\partial z_{i,z}^F} + C_{yy}C_{zz}z_{i,y}^F \frac{\partial}{\partial z_{i,z}^F} + \cdots \right.$$

$$\left. \cdots + C_{yy}C_{zx}z_{i,y}^F \frac{\partial}{\partial z_{i,x}^F} + C_{yz}C_{zx}z_{i,z}^F \frac{\partial}{\partial z_{i,x}^F} \right] + \cdots$$

$$\cdots + \frac{k}{i}\epsilon_{xzy}\left[C_{zx}C_{yy}z_{i,x}^F \frac{\partial}{\partial z_{i,y}^F} + C_{zx}C_{yz}z_{i,x}^F \frac{\partial}{\partial z_{i,z}^F} + \cdots \right.$$

$$\left. \cdots + C_{zz}C_{yx}z_{i,z}^F \frac{\partial}{\partial z_{i,x}^F} + C_{zz}C_{yy}z_{i,z}^F \frac{\partial}{\partial z_{i,y}^F} \right]$$

$$\dot{J}_x(t_i^F) = \frac{k}{i}\epsilon_{xyz}\left[-\cos^2\beta\, C_{xy}z_{i,x}^F \frac{\partial}{\partial z_{i,z}^F} + C_{xx}z_{i,y}^F \frac{\partial}{\partial z_{i,z}^F} + \cdots \right.$$

$$\left. \cdots + -C_{xz}z_{i,y}^F \frac{\partial}{\partial z_{i,x}^F} + \sin^2\beta\, C_{xy}z_{i,z}^F \frac{\partial}{\partial z_{i,x}^F} \right] + \cdots$$

$$\cdots + \frac{k}{i}\epsilon_{xzy}\left[-C_{xz}z_{i,x}^F \frac{\partial}{\partial z_{i,y}^F} + \sin^2\beta\, C_{xy}z_{i,x}^F \frac{\partial}{\partial z_{i,z}^F} + \cdots \right.$$

$$\left. \cdots + -\cos^2\beta\, C_{xy}z_{i,z}^F \frac{\partial}{\partial z_{i,x}^F} + C_{xx}z_{i,z}^F \frac{\partial}{\partial z_{i,y}^F} \right]$$

Regroup, such that:

$$\dot{J}_x(\underset{\sim}{t}_i^F) = \tfrac{k}{i} C_{xx}\left[z_{i,y}^F \frac{\partial}{\partial z_{i,z}^F} \cdot \epsilon_{xyz} + \epsilon_{xzy} z_{i,z}^F \frac{\partial}{\partial z_{i,y}^F} \right] + \cdots$$

$$\cdots + \tfrac{k}{i} C_{xy}\left[-\epsilon_{xyz}\cos^2\beta\, z_{i,x}^F \frac{\partial}{\partial z_{i,z}^F} + \epsilon_{xyz}\sin^2\beta\, z_{i,z}^F \frac{\partial}{\partial z_{i,x}^F} + \cdots \right.$$

$$\left. \cdots - \epsilon_{xzy}\cos^2\beta\, z_{i,z}^F \frac{\partial}{\partial z_{i,x}^F} + \epsilon_{xzy}\sin^2\beta\, z_{i,x}^F \frac{\partial}{\partial z_{i,z}^F} \right] + \cdots$$

$$\cdots + \tfrac{k}{i} C_{xz}\left[-\epsilon_{xyz} z_{i,y}^F \frac{\partial}{\partial z_{i,x}^F} - \epsilon_{xzy} z_{i,x}^F \frac{\partial}{\partial z_{i,y}^F} \right]$$

but $\epsilon_{xyz} = -\epsilon_{xzy}$

$$\Rightarrow \dot{J}_x(\underset{\sim}{t}_i^F) = \tfrac{k}{i} C_{xx}\left[z_{i,y}^F \frac{\partial}{\partial z_{i,z}^F} \epsilon_{xyz} + \epsilon_{xzy} z_{i,z}^F \frac{\partial}{\partial z_{i,y}^F} \right] + \cdots$$

$$\cdots + \tfrac{k}{i} C_{xy}\left[+\epsilon_{xyz}\underbrace{\left(\sin^2\beta + \cos^2\beta\right)}_{=1} z_{i,z}^F \frac{\partial}{\partial z_{i,x}^F} + \cdots \right.$$

$$\left. \cdots + \epsilon_{xzy}\underbrace{\left(\sin^2\beta + \cos^2\beta\right)}_{=1} z_{i,x}^F \frac{\partial}{\partial z_{i,z}^F} \right] + \cdots$$

$$\cdots + \tfrac{k}{i} C_{xz}\left[+\epsilon_{xyz} z_{i,x}^F \frac{\partial}{\partial z_{i,y}^F} + \epsilon_{xzy} z_{i,y}^F \right]$$

also $\begin{cases} \epsilon_{xyz} = \epsilon_{yzx} = \epsilon_{zxy} \\ \epsilon_{zyx} = \epsilon_{yxz} = \epsilon_{xzy} \end{cases}$

then...

$$\dot{J}_x(\underset{\sim}{t}_i^F) = \tfrac{k}{i} C_{xx}\left[\epsilon_{xyz} z_{i,y}^F \frac{\partial}{\partial z_{i,z}^F} + \epsilon_{xzy} z_{i,z}^F \frac{\partial}{\partial z_{i,y}^F} \right] + \cdots$$

$$\cdots + \tfrac{k}{i} C_{xy}\left[\epsilon_{yzx} z_{i,z}^F \frac{\partial}{\partial z_{i,x}^F} + \epsilon_{yxz} z_{i,x}^F \frac{\partial}{\partial z_{i,z}^F} \right] + \cdots$$

$$\cdots + \tfrac{k}{i} C_{xz}\left[\epsilon_{zxy} z_{i,x}^F \frac{\partial}{\partial z_{i,y}^F} + \epsilon_{zyx} z_{i,y}^F \frac{\partial}{\partial z_{i,x}^F} \right]$$

which is simply the expansion of the following:

$$\dot{J}_x = \sum_{\beta} C_{x\beta} \sum_{\beta\gamma} \epsilon_{\beta\beta\gamma} z_{i,\beta}^F \frac{\partial}{\partial z_{i,\gamma}^F}$$

So, for the x component of the i^{th} nucleus' angular momentum, we found:

$$\hat{j}_x(\underset{\sim}{t}_i^F) = \frac{\hbar}{i}\sum_{\mu,\nu}\sum_{\xi,\eta}\epsilon_{x\mu\nu}C_{\mu\xi}C_{\nu\eta}z_{i,\xi}^F\frac{\partial}{\partial z_{i,\eta}^F}$$

$$= \frac{\hbar}{i}\sum_{\xi}C_{x\xi}\sum_{\xi\eta}\epsilon_{\xi\xi\eta}z_{i,\xi}^F\frac{\partial}{\partial z_{i,\eta}^F}$$

Similar forms ~~$\hat{j}_x$~~ are found for the y & z components $\hat{j}_y(\underset{\sim}{t}_i^F)$ & $\hat{j}_z(\underset{\sim}{t}_i^F)$. The derivations are withheld for conservation reasons (such as ramparts & sanity). Here,

$$\hat{j}_\lambda(\underset{\sim}{t}_i^F) = \frac{\hbar}{i}\sum_{\mu,\nu}\sum_{\xi\eta}\epsilon_{\lambda\mu\nu}C_{\mu\xi}C_{\nu\eta}z_{i,\xi}^F\frac{\partial}{\partial z_{i,\eta}^F}$$

$$= \frac{\hbar}{i}\sum_{\xi}C_{\lambda\xi}\sum_{\xi\eta}\epsilon_{\xi\xi\eta}z_{i,\xi}^F\frac{\partial}{\partial z_{i,\eta}^F}$$

If we recall the original form of $\hat{j}_\lambda(\underset{\sim}{t}_i^F) = \frac{\hbar}{i}\sum_{\mu,\nu}\epsilon_{\lambda\mu\nu}t_{i,\mu}^F\frac{\partial}{\partial t_{i,\nu}^F}$ & replace space-fixed coordinates with body-fixed coordinates, it's clear that:

$$\hat{j}_\lambda(\underset{\sim}{z}_i^F) = \frac{\hbar}{i}\sum_{\mu,\nu}\epsilon_{\lambda\mu\nu}z_{i,\mu}^F\frac{\partial}{\partial z_{i,\nu}^F}$$

$$\Rightarrow \quad \hat{j}_\xi(\underset{\sim}{z}_i^F) = \frac{\hbar}{i}\sum_{\xi\eta}\epsilon_{\xi\xi\eta}z_{i,\xi}^F\frac{\partial}{\partial z_{i,\eta}^F} \qquad (*)$$

$$\therefore \quad \hat{j}_\lambda(\underset{\sim}{t}_i^F) = \frac{\hbar}{i}\sum_{\xi}C_{\lambda\xi}\hat{j}_\xi(\underset{\sim}{z}_i^F)$$

cycle x, y & z:

$$\hat{j}_x(\underset{\sim}{t}_i^F) = C_{xx}\hat{j}_x(\underset{\sim}{z}_i^F) + C_{xy}\hat{j}_y(\underset{\sim}{z}_i^F) + C_{xz}\hat{j}_z(\underset{\sim}{z}_i^F)$$

$$\hat{j}_y(\underset{\sim}{t}_i^F) = C_{yx}\hat{j}_x(\underset{\sim}{z}_i^F) + C_{yy}\hat{j}_y(\underset{\sim}{z}_i^F) + C_{yz}\hat{j}_z(\underset{\sim}{z}_i^F)$$

$$\hat{j}_z(\underset{\sim}{t}_i^F) = C_{zx}\hat{j}_x(\underset{\sim}{z}_i^F) + C_{zy}\hat{j}_y(\underset{\sim}{z}_i^F) + C_{zz}\hat{j}_z(\underset{\sim}{z}_i^F)$$

It is then plain to see:

$$\begin{pmatrix} \hat{j}_x(t_i^F) \\ \hat{j}_y(t_i^F) \\ \hat{j}_z(t_i^F) \end{pmatrix} = \begin{bmatrix} C_{xx} & C_{xy} & C_{xz} \\ C_{yx} & C_{yy} & C_{yz} \\ C_{zx} & C_{zy} & C_{zz} \end{bmatrix} \begin{pmatrix} \hat{j}_x(z_i^F) \\ \hat{j}_y(z_i^F) \\ \hat{j}_z(z_i^F) \end{pmatrix}$$

or

$$\boxed{\underset{\sim}{\hat{j}}(t_i^F) = C\,\underset{\sim}{\hat{j}}(z_i^F)}$$

TRANSFORMATION OF GENERAL AM. FOR NUCLEUS IN SPACE-FIXED COORD.S TO GENERAL A.M. OF SAME NUCLEUS IN BODY-FIXED COORDS

This transformation makes it easy to get various angular momenta into body-fixed form, afterall:

$$\underset{\sim}{\hat{j}}^F = \sum_{i=1}^{N_F-1} \underset{\sim}{\hat{j}}(t_i^F) = C \sum_{i=1}^{N_F-1} \underset{\sim}{\hat{j}}(z_i^F)$$

$$\text{&} \quad \underset{\sim}{\hat{j}} = \sum_F \underset{\sim}{\hat{j}}^F = \sum_F C \sum_{i=1}^{N_F-1} \underset{\sim}{\hat{j}}(z_i^F)$$

$$= C \sum_{i=1}^{N_A-1} \underset{\sim}{\hat{j}}(z_i^A) + C \sum_{i=1}^{N_B-1} \underset{\sim}{\hat{j}}(z_i^B)$$

$$= C \left[\left(\sum_{i=1}^{N_A-1} \underset{\sim}{\hat{j}}(z_i^A) \right) + \left(\sum_{i=1}^{N_B-1} \underset{\sim}{\hat{j}}(z_i^B) \right) \right]$$

So, at this point we now have to obtain $\underset{\sim}{\hat{j}}_\lambda(t_i^F)$, $\underset{\sim}{\hat{j}}(t_i^F)$, $\underset{\sim}{\hat{j}}^F$ & $\underset{\sim}{\hat{j}}$ in body-fixed coordinates. We now turn our attention to accomplishing

To accomplish this, first rewrite our relative c.o.m space-fixed differential operator into terms of the simplifications we derived early (see earlier!)

$$\frac{\partial R}{\partial t_{o,\xi}} = C_{\xi,z} \quad \text{(page 10)} \quad ; \quad \frac{\partial \alpha}{\partial t_{o,\xi}} = (R \sin\beta)^{-1} \quad \text{(page 12)};$$

$$\frac{\partial \beta}{\partial t_{o,\xi}} = R^{-1} C_{\xi x} \quad \text{(page 15)} \quad ; \quad \frac{\partial z_{i,\eta}^F}{\partial t_{o,\xi}} = \sum_{\xi,\mu} \frac{\partial C_{\xi\eta}}{\partial t_{o,\xi}} C_{\xi\mu} z_{i,\mu}^F \quad \text{(page 16)}$$

then the operator, $\frac{\partial}{\partial t_{0,\xi}} = \frac{\partial R}{\partial t_{0,\xi}}\frac{\partial}{\partial R} + \frac{\partial \alpha}{\partial t_{0,\xi}}\frac{\partial}{\partial \alpha} + \frac{\partial \beta}{\partial t_{0,\xi}}\frac{\partial}{\partial \beta} + \sum_F \sum_{i=1}^{N_{F-1}} \sum_\eta \frac{\partial z^F_{i,\eta}}{\partial t_{0,\xi}} \frac{\partial}{\partial z^F_{i,\eta}}$

becomes,

$$\frac{\partial}{\partial t_{0,\xi}} = C_{\xi z}\frac{\partial}{\partial R} + (R\sin\beta)^{-1} C_{\xi y}\frac{\partial}{\partial \alpha} + R^{-1}C_{\xi x}\frac{\partial}{\partial \beta} + \sum_F\sum_{i=1}^{N_{F-1}}\sum_\eta\sum_{\zeta\mu} \frac{\partial c_{\zeta\eta}}{\partial t_{0,\xi}} C_{\zeta\mu} z^F_{i,\mu} \frac{\partial}{\partial z^F_{i,\eta}}$$

$$= C_{\xi z}\frac{\partial}{\partial R} + (R\sin\beta)^{-1} C_{\xi y}\frac{\partial}{\partial \alpha} + R^{-1}C_{\xi x}\frac{\partial}{\partial \beta} + \sum_F\sum_{i=1}^{N_{F-1}}\sum_\eta\sum_{\zeta\mu} \left[\frac{\partial c_{\zeta\eta}}{\partial \alpha}\frac{\partial \alpha}{\partial t_{0,\xi}} + \frac{\partial c_{\zeta\eta}}{\partial \beta}\frac{\partial \beta}{\partial t_{0,\xi}} \right] C_{\zeta\mu} z^F_{i,\mu} \frac{\partial}{\partial z^F_{i,\eta}}$$

$$= C_{\xi z}\frac{\partial}{\partial R} + (R\sin\beta)^{-1} C_{\xi y}\frac{\partial}{\partial \alpha} + R^{-1}C_{\xi x}\frac{\partial}{\partial \beta} + \sum_F\sum_{i=1}^{N_{F-1}}\sum_\eta\sum_{\zeta\mu} \left[\frac{\partial c_{\zeta\eta}}{\partial \alpha}\frac{C_{\xi y}}{R\sin\beta} + \frac{\partial c_{\zeta\eta}}{\partial \beta}\frac{C_{\xi x}}{R} \right] C_{\zeta\mu} z^F_{i,\mu} \frac{\partial}{\partial z^F_{i,\eta}}$$

$$= C_{\xi z}\frac{\partial}{\partial R} + (R\sin\beta)^{-1} C_{\xi y}\frac{\partial}{\partial \alpha} + R^{-1}C_{\xi x}\frac{\partial}{\partial \beta} + \textcircled{1}\frac{C_{\xi y}}{R\sin\beta}\sum_F\sum_{i=1}^{N_{F-1}}\sum_\eta\sum_{\zeta\mu} \frac{\partial c_{\zeta\eta}}{\partial \alpha} C_{\zeta\mu} z^F_{i,\mu}\frac{\partial}{\partial z^F_{i,\eta}} + \cdots$$

$$\cdots + \textcircled{2}\frac{C_{\xi x}}{R}\sum_F\sum_{i=1}^{N_{F-1}}\sum_\eta\sum_{\zeta\mu} \frac{\partial c_{\zeta\eta}}{\partial \beta} C_{\zeta\mu} z^F_{i,\mu}\frac{\partial}{\partial z^F_{i,\eta}}$$

Consider ①: $\frac{C_{\xi y}}{R\sin\beta}\sum_F\sum_{i=1}^{N_{F-1}}\sum_\eta\sum_{\zeta\mu} \frac{\partial C_{\zeta\eta}}{\partial \alpha} C_{\zeta\mu} z^F_{i,\mu}\frac{\partial}{\partial z^F_{i,\eta}}$

$$= \frac{C_{\xi y}}{R\sin\beta}\sum_F\sum_{i=1}^{N_{F-1}}\sum_\eta \left\{ \frac{\partial C_{x\eta}}{\partial \alpha}\left[C_{xx} z^F_{i,x} + C_{xy} z^F_{i,y} + C_{xz} z^F_{i,z} \right] + \cdots \right.$$

$$\cdots + \frac{\partial C_{y\eta}}{\partial \alpha}\left[C_{yx} z^F_{i,x} + C_{yy} z^F_{i,y} + C_{yz} z^F_{i,z} \right] + \cdots$$

$$\left. \cdots + \frac{\partial C_{z\eta}}{\partial \alpha}\left[C_{zx} z^F_{i,x} + C_{zy} z^F_{i,y} + C_{zz} z^F_{i,z} \right] \right\} \frac{\partial}{\partial z^F_{i,\eta}}$$

find $\{\cdots\}\frac{\partial}{\partial z^F_{i,\eta}}$ for $\eta = x$:

$$\left\{ -\cos\beta\sin\alpha\left[\cos\beta\cos\alpha z^C_{i,x} - \sin\alpha z^C_{i,y} + \sin\beta\cos\alpha z^F_{i,z} \right] + \cdots \right.$$

$$\cdots + \cos\beta\cos\alpha\left[\cos\beta\sin\alpha z^F_{i,x} + \cos\alpha z^F_i + \sin\beta\sin\alpha z^F_{i,z} \right] + \cdots$$

$$\left. \cdots + 0 \right\} \frac{\partial}{\partial z^F_{i,x}}$$

$$= \left\{ -\left(\cos^2\beta\sin\alpha\cos\alpha - \cos^2\beta\sin\alpha\cos\alpha \right)^{=0} z^F_{i,x} + \cos\beta\left(\sin^2\alpha + \cos^2\alpha \right)^{=1} z^F_{i,y} + \cdots \right.$$

$$\left. \cdots + -\left(\cos\beta\sin\alpha\sin\beta\cos\alpha - \cos\beta\sin\alpha\sin\beta\cos\alpha \right) z^F_{i,z} \right\} \frac{\partial}{\partial z^F_{i,x}}$$

$$= \cos\beta\, z_{i,y}^F \frac{\partial}{\partial z_{i,x}^F}$$

$\eta = y$:

$$\Big\{ -\cos\alpha \Big[\cos\beta\cos\alpha\, z_{i,x}^F + -\sin\alpha\, z_{i,y}^F + \sin\beta\cos\alpha\, z_{i,z}^F \Big] + \ldots$$

$$\ldots - \sin\alpha \Big[\cos\beta\sin\alpha\, z_{i,x}^F + \cos\alpha\, z_{i,y}^F + \sin\beta\sin\alpha\, z_{i,z}^F \Big] + \ldots$$

$$\ldots + 0 \Big\} \frac{\partial}{\partial z_{i,y}^F}$$

$$= \Big\{ -\cos\beta \underbrace{\left(\cos^2\alpha + \sin^2\alpha\right)}_{=1} z_{i,x}^F + 0 \cdot z_{i,y}^F - \sin\beta \underbrace{\left(\cos^2\alpha + \sin^2\alpha\right)}_{=1} z_{i,z} \Big\} \frac{\partial}{\partial z_{i,y}^F}$$

$$= \Big[-\cos\beta\, z_{i,x}^F - \sin\beta\, z_{i,z}^F \Big] \frac{\partial}{\partial z_{i,y}^F}$$

$\eta = z$:

$$\Big\{ -\sin\beta\sin\alpha \Big[\cos\beta\cos\alpha\, z_{i,x}^F - \sin\alpha\, z_{i,y}^F + \sin\beta\cos\alpha\, z_{i,z}^F \Big] + \ldots$$

$$\ldots + \sin\beta\cos\alpha \Big[\cos\beta\sin\alpha\, z_{i,x}^F + \cos\alpha\, z_{i,y}^F + \sin\beta\sin\alpha\, z_{i,z}^F \Big] + \ldots$$

$$\ldots + 0 \Big\} \frac{\partial}{\partial z_{i,z}^F}$$

$$= \Big\{ -\sin\beta\sin\alpha\cos\beta\cos\alpha\, z_{i,x}^F \underbrace{(1-1)}_{=0} + \sin\beta \underbrace{\left(\sin^2\alpha + \cos^2\alpha\right)}_{=1} z_{i,y}^F + \ldots$$

$$\ldots + -\sin^2\beta\sin\alpha\cos\alpha\, z_{i,z}^F \underbrace{(1-1)}_{=0} \Big\} \frac{\partial}{\partial z_{i,z}^F}$$

$$= \sin\beta\, z_{i,y}^F \frac{\partial}{\partial z_{i,z}^F}$$

Therefore ①, $\frac{C_{\beta 1}}{R\sin\beta} \sum_F \sum_{i=1}^{N_F-1} \sum_\eta \sum_{\beta\mu} \frac{\partial C_{\beta\eta}}{\partial\alpha} C_{\beta\mu}\, z_{i,\mu}^F \frac{\partial}{\partial z_{i,\eta}^F}$

$$= \frac{C_{\beta 1}}{R\sin\beta} \sum_F \sum_{i=1}^{N_F-1} \Big[\cos\beta z_{i,y}^F \frac{\partial}{\partial z_{i,x}^F} + \Big\{ -\cos\beta z_{i,x}^F - \sin\beta z_{i,z}^F \Big\} \frac{\partial}{\partial z_{i,y}^F} + \ldots$$

$$\ldots + \sin\beta z_{i,y}^F \frac{\partial}{\partial z_{i,z}^F} \Big]$$

Consider (2),

=

find $\{\cdots\}$ δ

$\{ -$ Sin

$-$ Sin

$-$ Cos

$= \{ [-$ Sin

$-[\sin^2 \beta$

$= -z_{i,z}^F$

$\eta : y$: NO Con

$\eta : z$: $\{$

(!) should read $= -z_{i,z}^F \frac{\partial}{\partial z_{i,x}^F} \longrightarrow$

Consider (2), $\frac{C_{fx}}{R} \sum_F \sum_{i=1}^{N_{F-1}} \sum_\eta \sum_{f_\mu} \frac{\partial C_{f\mu}}{\partial \beta} C_{f\mu} z_{i,\mu}^F \frac{\partial}{\partial z_{i,\eta}^F}$

$$= \frac{C_{fx}}{R} \sum_F \sum_{i=1}^{N_{F-1}} \sum_\eta \Bigg\{ \frac{\partial C_{x\eta}}{\partial \beta} \left[C_{xx} z_{i,x}^F + C_{xy} z_{i,y}^F + C_{xz} z_{i,z}^F \right] + \cdots$$

$$\cdots + \frac{\partial C_{y\eta}}{\partial \beta} \left[C_{yx} z_{i,x}^F + C_{yy} z_{i,y}^F + C_{yz} z_{i,z}^F \right] + \cdots$$

$$\cdots + \frac{\partial C_{z\eta}}{\partial \beta} \left[C_{zx} z_{i,x}^F + C_{zy} z_{i,y}^F + C_{zz} z_{i,z}^F \right] \Bigg\} \frac{\partial}{\partial z_{i,\eta}^F}$$

find $\{\cdots\} \frac{\partial}{\partial z_{i,\eta}^F}$ for $\eta = x$:

$$\Big\{ -\sin\beta\cos\alpha \left[\cos\beta\cos\alpha z_{i,x}^F - \sin\alpha z_{i,y}^F + \sin\beta\cos\alpha z_{i,z}^F \right] + \cdots$$

$$\cdots - \sin\beta\sin\alpha \left[\cos\beta\sin\alpha z_{i,x}^F + \cos\alpha z_{i,y}^F + \sin\beta\sin\alpha z_{i,z}^F \right] + \cdots$$

$$\cdots - \cos\beta \left[-\sin\beta z_{i,x}^F + 0 \cdot z_{i,y}^F + \cos\beta z_{i,z}^F \right] \Big\} \frac{\partial}{\partial z_{i,x}^F}$$

$$= \Big\{ \Big[-\sin\beta\cos\beta \underbrace{\left(\cos^2\alpha + \sin^2\alpha\right)}_{=0} + \sin\beta\cos\beta \Big] z_{i,x}^F + \sin\beta\sin\alpha\cos\alpha \underbrace{(1-1)}_{=0} z_{i,y}^F +$$

$$\cdots - \left[\sin^2\beta(\cos^2\alpha + \sin^2\alpha) + \cos^2\beta \right] z_{i,z}^F \Big\} \frac{\partial}{\partial z_{i,x}^F}$$

$$= -z_{i,z}^F \frac{\partial}{\partial z_{i,x}^F} \leftarrow x$$

$\eta = y$: No contribution $\because C_{\bar{f}1}$ all function of $\alpha \Rightarrow 0$ $\quad \bar{f} = x, y \rightarrow z$.

$\eta = z$: $\Big\{ \cos\beta\cos\alpha \left[\cos\beta\cos\alpha z_{i,x}^F - \sin\alpha z_{i,y}^F + \sin\beta\cos\alpha z_{i,z}^F \right] + \cdots$

$$\cdots + \cos\beta\sin\alpha \left[\cos\beta\sin\alpha z_{i,x}^F + \cos\alpha z_{i,y}^F + \sin\beta\sin\alpha z_{i,z}^F \right] + \cdots$$

$$\cdots + -\sin\beta \left[-\sin\beta z_{i,x}^F + 0 \cdot z_{i,y}^F + \cos\beta z_{i,z}^F \right] \Big\} \frac{\partial}{\partial z_{i,z}^F}$$

$$= \Big\{ \Big[\cos^2\beta \big(\cos^2\alpha + \sin^2\alpha\big)^{=1} \Big]$$

$$\cdots + \Big[\cos\beta \sin\beta \big(\cos^2\alpha$$

$$= Z^F_{i,x} \frac{\partial}{\partial Z^F_{i,z}}$$

Therefore (2) $\frac{C_{qx}}{R} \sum_F^{} \sum_{i=1}^{N_{c-1}} \sum \sum_{\eta} \sum_{jA}$

$$= \frac{C_{qx}}{R} \sum_F^{} \sum_{i=1}^{N_{c-1}} \Big[$$

Combining (1) & (2) into th

$$\frac{\partial}{\partial t_{0,\eta}} = C_{qz} \frac{\partial}{\partial R} + (R \sin\beta)^{-1} C_{q\eta}$$

$$\cdots + \Big(-\cos\beta Z^F_{i,x} - \sin\beta Z$$

$$\cdots + \frac{C_{qx}}{R} \sum_F^{} \sum_{i=1}^{N_{c-1}} - Z^F_{i,z} \frac{\partial}{\partial Z}$$

$$\frac{\partial}{\partial t_{0,\eta}} = C_{qz} \frac{\partial}{\partial R} + (R \sin\beta)^{-1} C$$

$$\cdots + R^{-1} C_{qx} \sum_F^{} \sum_{i=1}^{N_{c-1}} (+$$

(!) should read $\frac{C_{qx}}{R} \sum_F^{} \sum_{i=1}^{N_{c-1}} \Big[-Z^F_{i,z} \frac{\partial}{\partial Z^F_{i,x}} + \cdots \rightarrow$

$$= \Big\{ \big[\cos^2\beta \underbrace{(\cos^2\alpha + \sin^2\alpha)}_{=1} + \sin^2\beta \big] z^F_{i,x} - \cos\beta\cos\alpha\sin\alpha \underbrace{(1-1)}_{=0} z^F_{i,y} + \cdots$$

$$+ \big[\cos\beta\sin\beta \underbrace{(\cos^2\alpha + \sin^2\alpha)}_{=1} - \cos\beta\sin\beta \big] z^F_{i,z} \Big\} \frac{\partial}{\partial z^F_{i,z}}$$

$$= z^F_{i,x} \frac{\partial}{\partial z^F_{i,z}}$$

Therefore (2) $$\frac{C_{\xi x}}{R} \sum_F \sum_{i=1}^{N_F-1} \sum_\eta \sum_{\xi\mu} \frac{\partial x_{\xi\eta}}{\partial\beta} C_{\xi\mu} z^F_{i,\mu} \frac{\partial}{\partial z^F_{i,\eta}}$$

$$= \frac{C_{\xi x}}{R} \sum_F \sum_{i=1}^{N_F-1} \Big[-z^F_{i,z} \frac{\partial}{\partial z^F_{i,x}} + z^F_{i,x} \frac{\partial}{\partial z^F_{i,z}} \Big]$$

$\uparrow x$

Combining (1) & (2) into the expression for the differential operator,

$$\frac{\partial}{\partial x_{0,\xi}} = C_{\xi z} \frac{\partial}{\partial R} + (R\sin\beta)^{-1} C_{\xi y} \frac{\partial}{\partial\alpha} + R^{-1} C_{\xi x} \frac{\partial}{\partial\beta} + \frac{C_{\xi y}}{R\sin\beta} \sum_F \sum_{i=1}^{N_F-1} \Big[\cos\beta\, z^F_{i,y} \frac{\partial}{\partial z^F_{i,x}} +$$

$$\cdots + \big(-\cos\beta\, z^F_{i,x} - \sin\beta z^F_{i,z} \big) \frac{\partial}{\partial z^F_{i,y}} + \sin\beta\, z^F_{i,y} \frac{\partial}{\partial z^F_{i,z}} \Big] + \cdots$$

$$\cdots + \frac{C_{\xi x}}{R} \sum_F \sum_{i=1}^{N_F-1} -z^F_{i,z} \frac{\partial}{\partial z^F_{i,x}} + z^F_{i,x} \frac{\partial}{\partial z^F_{i,z}}$$

$$\frac{\partial}{\partial x_{0,\xi}} = C_{\xi z} \frac{\partial}{\partial R} + (R\sin\beta)^{-1} C_{\xi y} \frac{\partial}{\partial\alpha} + R^{-1} C_{\xi x} \frac{\partial}{\partial\beta} + \cdots$$

$$\cdots + R^{-1} C_{\xi x} \sum_F \sum_{i=1}^{N_F-1} (+1) z^F_{i,x} \frac{\partial}{\partial z^F_{i,z}} + (-1) z^F_{i,z} \frac{\partial}{\partial z^F_{i,x}} + \cdots +$$

$$\cdots + R^{-1} C_{\xi y} \frac{\cos\beta}{\sin\beta} \sum_F \sum_{i=1}^{N_F-1} (+1) z^F_{i,y} \frac{\partial}{\partial z^F_{i,x}} + (-1) z^F_{i,z} \frac{\partial}{\partial z^F_{i,y}} + \cdots$$

$$\cdots + R^{-1} C_{\xi y} \frac{\sin\beta}{\sin\beta} \sum_F \sum_{i=1}^{N_F-1} (+1) z^F_{i,y} \frac{\partial}{\partial z^F_{i,z}} + (-1) z^F_{i,z} \frac{\partial}{\partial z^F_{i,y}} .$$

Recall from pg 25 eq. (*) that:

$$\hat{j}_\lambda(\underset{\sim}{z}_i^F) = \frac{\hbar}{i} \sum_{\mu\nu} \epsilon_{\lambda\mu\nu} z^F_{i,\mu} \frac{\partial}{\partial z^F_{i,\nu}}$$

$$\hat{j}_\lambda(\underline{z}_i^F) = \frac{\hbar}{i}(+1)\, z_{i,\mu}^F \frac{\partial}{\partial z_{i,\nu}^F} + \frac{\hbar}{i}(-1)\, z_{i,\nu}^F \frac{\partial}{\partial z_{i,\mu}^F} \qquad \lambda \neq \mu \neq \nu$$

Also, recall that $\frac{\cos\theta}{\sin\theta} = \frac{1}{\tan\theta} = \cot\theta$; $\frac{1}{\sin\theta} = \operatorname{csc}\theta$

then ... $$\frac{\partial}{\partial t_{0,\zeta}} = R^{-1} C_{\zeta x}\left(\frac{\partial}{\partial\beta} - \sum_F \sum_{i=1}^{N_F-1} (+1)\, z_{i,z}^F \frac{\partial}{\partial z_{i,x}^F} + (-1)\, z_{i,x}^F \frac{\partial}{\partial z_{i,z}^F}\right) + \cdots$$

$$\cdots + R^{-1} C_{\zeta y}\left(\frac{1}{\sin\beta}\frac{\partial}{\partial\alpha} - \frac{\cos\beta}{\sin\beta}\sum_F\sum_{i=1}^{N_F-1}(+1) z_{i,x}^F \frac{\partial}{\partial z_{i,y}^F} + (-1)\, z_{i,y}^F \frac{\partial}{\partial z_{i,x}^F}\right) + \cdots$$

$$\cdots + R^{-1} C_{\zeta y}\left(\sum_F \sum_{i=1}^{N_F-1} (+1)\, z_{i,y}^F \frac{\partial}{\partial z_{i,z}^F} + (-1)\, z_{i,z}^F \frac{\partial}{\partial z_{i,y}^F}\right) + \cdots$$

$$\cdots + R R^{-1} C_{\zeta z} \frac{\partial}{\partial R}$$

$$\therefore \quad \frac{\partial}{\partial t_{0,\zeta}} = R^{-1} C_{\zeta x}\left(\frac{\partial}{\partial\beta} - \sum_F\sum_{i=1}^{N_F-1} \epsilon_{yzx}\, z_{i,z}^F \frac{\partial}{\partial z_{i,x}^F} + \epsilon_{yxz}\, z_{i,x}^F \frac{\partial}{\partial z_{i,z}^F}\right) + \cdots$$

$$\cdots + R^{-1} C_{\zeta y}\left(\operatorname{csc}\beta\frac{\partial}{\partial\alpha} - \cot\beta \sum_F\sum_{i=1}^{N_F-1} \epsilon_{zxy}\, z_{i,x}^F \frac{\partial}{\partial z_{i,y}^F} + \epsilon_{zyx}\, z_{i,y}^F \frac{\partial}{\partial z_{i,x}^F}\right) +$$

$$\cdots + R^{-1} C_{\zeta y}\left(\sum_F\sum_{i=1}^{N_F-1} \epsilon_{xyz}\, z_{i,y}^F \frac{\partial}{\partial z_{i,z}^F} + \epsilon_{xzy}\, z_{i,z}^F \frac{\partial}{\partial z_{i,y}^F}\right) + \cdots$$

$$\cdots + C_{\zeta z}\frac{\partial}{\partial R}$$

$$\Rightarrow \quad \frac{\partial}{\partial t_{0,\zeta}} = R^{-1} C_{\zeta x}\left(\frac{\partial}{\partial\beta} - \sum_F\sum_{i=1}^{N_F-1} \frac{i}{\hbar}\hat{j}_y(\underset{\sim}{z}_i^F)\right) + \cdots$$

$$+ R^{-1} C_{\zeta y}\left(\operatorname{csc}\beta\frac{\partial}{\partial\alpha} - \left[\cot\beta \sum_F\sum_{i=1}^{N_F-1} \frac{i}{\hbar}\hat{j}_z(\underline{z}_i^F)\right] + \sum_F\sum_{i=1}^{N_F-1}\frac{i}{\hbar}\hat{j}_x(\underline{z}_i^F)\right) +$$

$$+ C_{\zeta z}\frac{\partial}{\partial R}$$

to clearly,

$$\frac{\partial}{\partial t_{0,\zeta}} = R^{-1} C_{\zeta x}\left(\frac{\partial}{\partial\beta} - \sum_F \hat{j}_y(\underset{\sim}{z}^F)\frac{i}{\hbar}\right) + \cdots$$

$$\cdots + R^{-1} C_{\zeta y}\left(\operatorname{csc}\beta\frac{\partial}{\partial\alpha} - \cot\beta\sum_F \frac{i}{\hbar}\hat{j}_z(\underset{\sim}{z}^F) + \sum_F \frac{i}{\hbar}\hat{j}_x(\underset{\sim}{z}^F)\right) +$$

Then, with R.M. described in terms of body-fixed coordinates $\underset{\sim}{z}^F$,

$$\frac{\partial}{\partial \xi_{0,q}} = R^{-1} C_{qx}\left(\frac{\partial}{\partial \beta} - \frac{i}{\hbar}\hat{j}_y\right) + R^{-1} C_{qy}\left(\csc\beta \frac{\partial}{\partial \alpha} - \cot\beta \frac{i}{\hbar}\hat{j}_z + \frac{i}{\hbar}\hat{j}_x\right) + \cdots$$

$$\cdots + C_{qz}\frac{\partial}{\partial \gamma}$$

RELATIVE C.O.M DIFFERENTIAL OPERATOR EXPRESSED IN BODY-FIXED COORDINATES

We know: the transform of $\underset{\sim}{\hat{j}}$ is $\underset{\sim}{\hat{j}}(\underset{\sim}{t}) = C\,\underset{\sim}{\hat{j}}(\underset{\sim}{z})$; the form of the orbital angular momentum function $\hat{l}_\lambda$ (component); & the relative C.O.M operator in body-fixed coordinates

Earlier, we defined $\underset{\sim}{\hat{J}} = \hat{l} + \hat{j}$

$$\Rightarrow \quad \hat{J}_\lambda(\underset{\sim}{t}_i) = \hat{l}_\lambda(\underset{\sim}{t}_0) + \hat{j}_\lambda(\underset{\sim}{t}_i) \qquad \because \underset{\sim}{t}_i \text{ are functions of } \underset{\sim}{t}_0$$

from pg (25) we know that $\underset{\sim}{\hat{j}}_\lambda(t) = \frac{\hbar}{i}\sum_q C_{\lambda q}\,\underset{\sim}{\hat{j}}_q(\underset{\sim}{z}_i)$

$$\Rightarrow \quad \hat{J}_\lambda(t_i) = \frac{\hbar}{i}\sum_{\mu,\nu}\epsilon_{\lambda\mu\nu}\,t_{0\mu}\frac{\partial}{\partial t_{0,\nu}} + \frac{\hbar}{i}\sum_q C_{\lambda q}\,\hat{j}_q(\underset{\sim}{z}_i) \qquad \text{see pg (18) too!}$$

$$= \frac{\hbar}{i}\sum_{\mu,\nu}\epsilon_{\lambda\mu\nu}\sum_q C_{\mu q} z_q \frac{\partial}{\partial t_{0,\nu}} + \frac{\hbar}{i}\sum_q C_{\lambda q}\,\hat{j}_q(\underset{\sim}{z}_i)$$

$$= \frac{\hbar}{i}\sum_{\mu,\nu}\epsilon_{\lambda\mu\nu}\sum_q C_{\mu q} C_{\nu q} z_{0q}\frac{\partial}{\partial z_{0,q}} + \frac{\hbar}{i}\sum_q C_{\lambda q}\,\hat{j}_q(\underset{\sim}{z}_i)$$

recall how we manipulated $\hat{j}_\lambda(\underset{\sim}{t}^F_i)$ using scalar multiplication commutativity on pages 21 & 22...

$$\hat{J}_\lambda(t_i) = \frac{\hbar}{i}\sum_{\mu,\nu}\sum_q \epsilon_{\lambda\mu\nu} C_{\mu q} C_{\nu q} z_{0,q}\frac{\partial}{\partial z_{0,q}} + \frac{\hbar}{i}\sum_q C_{\lambda q}\,\hat{j}_q(\underset{\sim}{z}_i)$$

Also, by the same procedure applied on pages 22-25,

$$\hat{J}_\lambda(t_i) = \frac{\hbar}{i}\sum_\gamma C_{\lambda\gamma}\sum_{\gamma\eta}\epsilon_{\gamma\gamma\eta}\,z_{o,\gamma}\frac{\partial}{\partial z_{o,\eta}} + \frac{\hbar}{i}\sum_\gamma C_{\lambda\gamma}\,\hat{j}_\gamma(z_i)$$

$$= \frac{\hbar}{i}\sum_\gamma C_{\lambda\gamma}\,\hat{l}_\gamma(\underset{\sim}{z}_o) + \frac{\hbar}{i}\sum_\gamma C_{\lambda\gamma}\,\hat{j}_\gamma(\underset{\sim}{z}_i)$$

$$= \frac{\hbar}{i}\sum_\gamma C_{\lambda\gamma}\left(\hat{l}_\gamma(\underset{\sim}{z}_o) + \hat{j}_\gamma(\underset{\sim}{z}_i)\right)$$

$\lambda = x$: $\hat{J}_x(\underset{\sim}{t}_i) = C_{xx}\left(\hat{l}_x(\underset{\sim}{z}_o) + \hat{j}_x(\underset{\sim}{z}_i)\right) + C_{xy}\left(\hat{l}_y(\underset{\sim}{z}_o) + \hat{j}_y(\underset{\sim}{z}_i)\right) + C_{xz}\left(\hat{l}_z(\underset{\sim}{z}_o) + \hat{j}_z(\underset{\sim}{z}_i)\right)$

$\lambda = y$ $\hat{J}_y(\underset{\sim}{t}_i) = C_{yx}\left(\hat{l}_x(\underset{\sim}{z}_o) + \hat{j}_x(\underset{\sim}{z}_i)\right) + C_{yy}\left(\hat{l}_y(\underset{\sim}{z}_o) + \hat{j}_y(\underset{\sim}{z}_i)\right) + C_{yz}\left(\hat{l}_z(\underset{\sim}{z}_o) + \hat{j}_z(\underset{\sim}{z}_i)\right)$

$\lambda = z$ $\hat{J}_z(\underset{\sim}{t}_i) = C_{zx}\left(\hat{l}_x(\underset{\sim}{z}_o) + \hat{j}_x(\underset{\sim}{z}_i)\right) + C_{zy}\left(\hat{l}_y(\underset{\sim}{z}_o) + \hat{j}_y(\underset{\sim}{z}_i)\right) + C_{zz}\left(\hat{l}_z(\underset{\sim}{z}_o) + \hat{j}_z(\underset{\sim}{z}_i)\right)$

ie
$$\begin{pmatrix} \hat{J}_x(\underset{\sim}{t}_i) \\ \hat{J}_x(\underset{\sim}{t}_i) \\ \hat{J}_x(\underset{\sim}{t}_i) \end{pmatrix} = \begin{bmatrix} C_{xx} & C_{xy} & C_{xz} \\ C_{yx} & C_{yy} & C_{yz} \\ C_{zx} & C_{zy} & C_{zz} \end{bmatrix} \begin{pmatrix} \hat{l}_x(\underset{\sim}{z}_o) + \hat{j}_x(\underset{\sim}{z}_i) \\ \hat{l}_y(\underset{\sim}{z}_o) + \hat{j}_y(\underset{\sim}{z}_i) \\ \hat{l}_z(\underset{\sim}{z}_o) + \hat{j}_z(\underset{\sim}{z}_i) \end{pmatrix}$$

but $\hat{l}_\lambda(\underset{\sim}{z}_o) + \hat{j}_\lambda(\underset{\sim}{z}_i) \equiv \hat{J}_\lambda(\underset{\sim}{z}_i)$ $\therefore$ $\underset{\sim}{z}_i$ are functions $\underset{\sim}{to}$ $\hookrightarrow$ $\underset{\sim}{z}_o$

ie
$$\boxed{\hat{J}(t_i) = C\,\hat{J}(\underset{\sim}{z}_i)}$$

TRANSFORMATION OF TOTAL AM FROM SPACE-FIXED COORDINATES TO BODY-FIXED COORDINATES.

We can use this transform to find the components $\hat{J}_x$, $\hat{J}_y$, & $\hat{J}_z$ in body-fixed coordinates. The diagonalization is facilitated by an knowledge of $\hat{J}_{o,\gamma}$ in body-fixed form.

Normally one would now proceed to develop $\hat{J}_\lambda$ in body-fixed form for λ general. I found it particularly instructive to use induction:

- Consider $\hat{J}_x(t_i) \cdot \hat{l}_x(t_o) + \dot{\hat{j}}_x(t_i)$

$$\hat{l}_x(t_o) = \frac{t_n}{i} \sum_{\mu\nu} \epsilon_{x\mu\nu}\, to_{,\mu} \frac{\partial}{\partial to_{,\nu}}$$

$$= \frac{t_n}{i} \left[to_{,y} \frac{\partial}{\partial to_{,z}} - to_{,z} \frac{\partial}{\partial to_{,y}} \right] = \frac{t_n}{i} \left[① - ② \right]$$

$$① \; to_{,y} \frac{\partial}{\partial to_{,z}} = R \sin\beta \sin\alpha \left[\frac{1}{R} - \sin\beta \left(\frac{\partial}{\partial\beta} - \frac{i}{k} \hat{j}_y \right) + 0 + \cos\beta \frac{\partial}{\partial R} \right]$$

$$= -\sin^2\beta \sin\alpha \left(\frac{\partial}{\partial\beta} - \frac{i}{k} \hat{j}_y \right) + R \sin\beta \sin\alpha \cos\beta \frac{\partial}{\partial R}$$

$$② \; to_{,z} \frac{\partial}{\partial to_{,y}} = R \cos\beta \left[\frac{1}{R} \cos\beta \sin\alpha \left(\frac{\partial}{\partial\beta} - \frac{i}{k} \hat{j}_y \right) + \frac{1}{R} \cos\alpha \left(\operatorname{cosec}\beta \frac{\partial}{\partial\alpha} - \cot\beta \frac{i}{k} \hat{j}_z + \cdots \right. \right.$$

$$\left. \left. \cdots + \frac{i}{k} \hat{j}_x \right) + \sin\beta \sin\alpha \frac{\partial}{\partial R} \right]$$

where angular momenta are in body-fixed coordinates

$$\therefore \hat{l}_x(t_o) = \frac{t_n}{i} \left[① - ② \right] = \frac{t_n}{i} \left[-\sin\alpha \left(\frac{\partial}{\partial\beta} - \frac{i}{k} \hat{j}_y \right) \left(\sin^2\beta + \cos^2\beta \right) + \cdots \right.$$

$$\left. \cdots + \cos\beta \cos\alpha \left(\operatorname{cosec}\beta \frac{\partial}{\partial\alpha} - \cot\beta \frac{i}{k} \hat{j}_z + \frac{i}{k} \hat{j}_x \right) \right]$$

& $\hat{j}_x(t_i) = \frac{t_n}{i} \sum_\xi C_{x\xi}\, \hat{j}_\xi(\underline{z}_i) = \cos\beta\cos\alpha\, \hat{j}_x(\underline{z}_i) - \sin\alpha\, \hat{j}_y(\underline{z}_i) + \cos\alpha\sin\beta\, \hat{j}_z(\underline{z}_i)$

then $\hat{J}_x(t_i) = -\frac{t_n}{i} \sin\alpha \frac{\partial}{\partial\beta} + \sin\alpha\, \hat{j}_y(\underline{z}_i) + \frac{t_n}{i} \cos\beta\cos\alpha \left(-\operatorname{cosec}\beta \frac{\partial}{\partial\alpha} + \cot\beta \frac{i}{k} \hat{j}_z \right) + \cdots$

$$\cdots - \cos\beta\cos\alpha\, \hat{j}_x(\underline{z}_i) + \cos\beta\cos\alpha\, \hat{j}_x(\underline{z}_i) - \sin\alpha\, \hat{j}_y(\underline{z}_i) + \cos\alpha\sin\beta\, \hat{j}_z(\underline{z}_i)$$

$$\hat{J}_x(t_i) = (-\sin\alpha) \frac{t_n}{i} \frac{\partial}{\partial\beta} + \cos\beta\cos\alpha \left(-\frac{t_n}{i} \operatorname{cosec}\beta \frac{\partial}{\partial\alpha} + \cot\beta\, \hat{j}_z(\underline{z}_i) \right) + \cdots$$

$$\cdots + (\cos\alpha \sin\beta)\, \hat{j}_z(\underline{z}_i)$$

$$\underline{\underline{\alpha}} \quad \hat{J}_x(t_i) = C_{xy} \frac{t_n}{i} \frac{\partial}{\partial\beta} + C_{xx} \left(-\frac{t_n}{i} \operatorname{cosec}\beta \frac{\partial}{\partial\alpha} + \cot\beta\, \hat{j}_z(\underline{z}_i) \right) + C_{xz}\, \hat{j}_z(\underline{z}_i)$$

$$= C_{xx} \left(-\frac{t_n}{i} \operatorname{cosec}\beta \frac{\partial}{\partial\alpha} + \cot\beta\, \hat{j}_z(\underline{z}_i) \right) + C_{xy} \frac{t_n}{i} \frac{\partial}{\partial\beta} + C_{xz}\, \hat{j}_z(\underline{z}_i)$$

Similarly, $\hat{J}_y(\underset{\sim}{t}_i) = C_{yx}\left(-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha} + \cot\beta\,\hat{j}_z(\underset{\sim}{z}_i)\right) + C_{yy}\frac{\hbar}{i}\frac{\partial}{\partial\beta} + C_{yz}\,\hat{j}_z(\underset{\sim}{z}_i)$

& $\hat{J}_z(\underset{\sim}{t}_i) = C_{zx}\left(-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha} + \cot\beta\,\hat{j}_z(\underset{\sim}{z}_i)\right) + C_{zy}\frac{\hbar}{i}\frac{\partial}{\partial\beta} + C_{zz}\,\hat{j}_z(\underset{\sim}{z}_i)$

All three components have the form described on Pg 33, that is

$$\hat{J}_\lambda(\underset{\sim}{t}_i) = C_{\lambda x}\,\hat{J}_x(\underset{\sim}{z}_i) + C_{\lambda y}\,\hat{J}_y(\underset{\sim}{z}_i) + C_{\lambda z}\,\hat{J}_z(\underset{\sim}{z}_i)$$

Therefore:

$$\hat{J}_x = -\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha} + \cot\beta\,\hat{j}_z$$

$$\hat{J}_y = \frac{\hbar}{i}\frac{\partial}{\partial\beta}$$

$$\hat{J}_z = \hat{j}_z$$

COMPONENTS OF TOTAL AM EXPRESSED IN BODY FIXED COORDINATES

NB: Bunker has found a similar result in the analogous case of a diatomic molecule (what we consider a fragment, he considers an atom; what we call grand particle AM he calls electron spin AM; orbital AM is independent for both cases). See Pg 132 eq.A 7-80 → 7-82.

Now investigate commutation relations. The definition of a commutator of two operators $\hat{A}$ & $\hat{B}$ is: $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$. For observables A & B to be simultaneously measurable, their corresponding operators must commute; ie $[\hat{A},\hat{B}] = 0$.

$$[\hat{J}_x,\hat{J}_z] = \left[-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha} + \cot\beta\,\hat{j}_z\,,\,\hat{j}_z\right]$$

$$= \left[-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}\,,\,\hat{j}_z\right] + \left[\cot\beta\,\hat{j}_z\,,\,\hat{j}_z\right]$$

$$= -\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}\hat{j}_z + \frac{\hbar}{i}\hat{j}_z\operatorname{cosec}\beta\frac{\partial}{\partial\alpha} + \cot\beta(\hat{j}_z)^2 + -\hat{j}_z\cot\beta\,\hat{j}_z$$

but $\hat{j}_z$ denotes on 3rd ~~non-dotted~~ fragment Euler angle, χ, ie not

on polar angles α & β. (see ZARE p 83, 3.44)

$$\therefore \left[\hat{J}_x, \hat{J}_z\right] = -\frac{\hbar}{i}\operatorname{cosec}\beta \frac{\partial}{\partial\alpha}\hat{j}_z + \frac{\hbar}{i}\operatorname{cosec}\beta\, \hat{j}_z \frac{\partial}{\partial\alpha} + \cot\beta(\hat{j}_z)^2 - \cot\beta(\hat{j}_z)^2$$

$$= -\frac{\hbar}{i}\operatorname{cosec}\beta \frac{\partial}{\partial\alpha}\hat{j}_z + \frac{\hbar}{i}\operatorname{cosec}\beta \frac{\partial}{\partial\alpha}\hat{j}_z \quad \text{(since order of operation is arbitrary)}$$

$$= 0$$

Similar arguments are applied to:

$$\left[\hat{J}_y, \hat{J}_z\right] = \left[\frac{\hbar}{i}\frac{\partial}{\partial\beta}, \hat{j}_z\right] = \frac{\hbar}{i}\frac{\partial}{\partial\beta}\hat{j}_z - \frac{\hbar}{i}\hat{j}_z\frac{\partial}{\partial\beta}$$

$$= \frac{\hbar}{i}\frac{\partial}{\partial\beta}\hat{j}_z - \frac{\hbar}{i}\frac{\partial}{\partial\beta}\hat{j}_z$$

$$= 0$$

Also, $\left[\hat{J}_x, \hat{J}_y\right] = \left[-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}, \frac{\hbar}{i}\frac{\partial}{\partial\beta}\right] + \left[\cot\beta\,\hat{j}_z, \frac{\hbar}{i}\frac{\partial}{\partial\beta}\right]$

where $\left[-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}, \frac{\hbar}{i}\frac{\partial}{\partial\beta}\right] = \hbar^2\operatorname{cosec}\beta\frac{\partial^2}{\partial\alpha\partial\beta} - \hbar^2\frac{\partial}{\partial\beta}\left(\overset{u}{\operatorname{cosec}\beta}\overset{v'}{\frac{\partial}{\partial\alpha}}\right)$

$$= \hbar^2\operatorname{cosec}\beta\frac{\partial^2}{\partial\alpha\partial\beta} - \hbar^2\operatorname{cosec}\beta\frac{\partial^2}{\partial\beta\partial\alpha} + \hbar^2\left(\frac{\partial}{\partial\beta}\operatorname{cosec}\beta\right)\frac{\partial}{\partial\alpha}$$

uv' + $u'v$

PRODUCT RULE

$$= -\hbar^2\left(\frac{\partial}{\partial\beta}\operatorname{cosec}\beta\right)\frac{\partial}{\partial\alpha}$$

$$= +\hbar^2\operatorname{cosec}\beta\cot\beta\frac{\partial}{\partial\alpha}$$

& $\left[\cot\beta\,\hat{j}_z, \frac{\hbar}{i}\frac{\partial}{\partial\beta}\right] = \frac{\hbar}{i}\cot\beta\,\hat{j}_z\frac{\partial}{\partial\beta} - \frac{\hbar}{i}\frac{\partial}{\partial\beta}\left(\overset{u}{\cot\beta}\,\overset{v}{\hat{j}_z}\right)$

$$= \frac{\hbar}{i}\cot\beta\,\hat{j}_z\frac{\partial}{\partial\beta} - \frac{\hbar}{i}\cot\beta\frac{\partial}{\partial\beta}\hat{j}_z - \frac{\hbar}{i}\left(\frac{\partial}{\partial\beta}\cot\beta\right)\hat{j}_z$$

$$= +\frac{\hbar}{i}\operatorname{cosec}^2\beta\,\hat{j}_z$$

$$= +\frac{\hbar}{i}\left(1+\cot^2\beta\right)\hat{j}_z \quad \text{via trig identity}$$

$$\therefore \left[\hat{J}_x, \hat{J}_y\right] = t^2 \operatorname{cosec}\beta \cot\beta \frac{\partial}{\partial\alpha} + \frac{t}{i}\left(1+\cot^2\beta\right)\hat{j}_z$$

$$= \left(-\frac{t}{i}\right)\frac{t}{i}\operatorname{cosec}\beta\cot\beta\frac{\partial}{\partial\alpha} + \frac{t}{i}\hat{j}_z + \frac{t}{i}\cot^2\beta\,\hat{j}_z$$

$$= \frac{t}{i}\cot\beta\left(-\frac{t}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha} + \cot\beta\,\hat{j}_z\right) + \frac{t}{i}\hat{j}_z$$

$$= \frac{t}{i}\cot\beta\,\hat{J}_x + \frac{t}{i}\hat{j}_z$$

Summarising:

$$\left[\hat{J}_x, \hat{J}_z\right] = 0$$

$$\left[\hat{J}_y, \hat{J}_z\right] = 0$$

$$\left[\hat{J}_x, \hat{J}_y\right] = \frac{t}{i}\cot\beta\,\hat{J}_x + \frac{t}{i}\hat{j}_z$$

BODY-FIXED TOTAL AM COMMUTATION RELATIONS

Because the components of our body-fixed total angular momentum operator do not satisfy anomalous commutator relations (see Brahs et. al. eq. A7 on p. 1039) or the relation $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$ (see later), we call $\underset{\sim}{\hat{J}}$ a PSEUDO-ANGULAR MOMENTUM operator.

Before progressing on to more commutator relations, it is worthwhile to note that, just as $\hat{j}_z$ operates only on fragment Euler angle χ, $\hat{j}_x$ depends on fragment Euler angles ϕ, θ, & χ as does $\hat{j}_y$ (see equation 3.45 on page 83 of ZARE)

Let's now investigate the form of the commutators of type $\left[\hat{J}_\xi, \hat{j}_\eta\right]$ $\forall \xi,\eta = x,y,z$. Firstly, understand form the general form of the body-fixed fragment AM component,

$$\hat{j}_\lambda(\underset{\sim}{r}_i) = \sum_{\mu\nu} \epsilon_{\lambda\mu\nu}\, r_{i,\mu}\frac{\partial}{\partial r_{i,\nu}}$$

that it is elementary to find the following commutators:

$$[\hat{J}_x, \hat{J}_y] = -\frac{\hbar}{i}\hat{J}_z \;;\; [\hat{J}_y, \hat{J}_z] = -\frac{\hbar}{i}\hat{J}_x \;;\; [\hat{J}_z, \hat{J}_x] = -\frac{\hbar}{i}\hat{J}_y$$

b,

$$[\hat{T}_x, \hat{J}_x] = \left[-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}, \hat{J}_x\right] + \left[\cot\beta\hat{J}_z, \hat{J}_x\right]$$

$$= -\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}\hat{J}_x + \frac{\hbar}{i}\hat{J}_x\left(\overset{u}{\operatorname{cosec}\beta}\overset{v}{\frac{\partial}{\partial\alpha}}\right) + \cot\beta\hat{J}_z\hat{J}_x - \hat{J}_x\overset{u}{\cot\beta}\overset{v}{\hat{J}_z}$$

$$= -\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}\hat{J}_x + \frac{\hbar}{i}\operatorname{cosec}\beta\hat{J}_x\frac{\partial}{\partial\alpha} + \cot\beta\hat{J}_z\hat{J}_x - \cot\beta\hat{J}_x\hat{J}_z$$

$$= \cot\beta\left(\hat{J}_z\hat{J}_x - \hat{J}_x\hat{J}_z\right)$$

$$= \cot\beta\,[\hat{J}_z, \hat{J}_x]$$

$$= -\frac{\hbar}{i}\cot\beta\hat{J}_y$$

$$[\hat{T}_x, \hat{J}_y] = \left[-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}, \cancel{\frac{\hbar}{i}\frac{\partial}{\partial\beta}\hat{J}_y}\right] + \left[\cot\beta\hat{J}_z, \hat{J}_y\right]$$

$$= -\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}\hat{J}_y + \frac{\hbar}{i}\hat{J}_y\left(\overset{u}{\operatorname{cosec}\beta}\overset{v}{\frac{\partial}{\partial\alpha}}\right) + \cot\beta\hat{J}_z\hat{J}_y - \hat{J}_y\left(\overset{u}{\cot\beta}\overset{v}{\hat{J}_z}\right)$$

$$= -\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}\hat{J}_y + \frac{\hbar}{i}\operatorname{cosec}\beta\hat{J}_y\frac{\partial}{\partial\alpha} + \cot\beta\hat{J}_z\hat{J}_y - \cot\beta\hat{J}_y\hat{J}_z$$

$$= \cot\beta\left(\hat{J}_z\hat{J}_y - \hat{J}_y\hat{J}_z\right)$$

$$= -\cot\beta\left(\hat{J}_y\hat{J}_z - \hat{J}_z\hat{J}_y\right)$$

$$= -\cot\beta\,[\hat{J}_y, \hat{J}_z]$$

$$= +\frac{\hbar}{i}\cot\beta\hat{J}_x$$

$[\hat{J}_x, \hat{J}_z] = [\hat{T}_x, \hat{T}_z] = 0$ (see page 36)

$$\Rightarrow \quad [\hat{T}_x, \hat{J}_\lambda] = -\frac{\hbar}{i}\cot\beta\,\epsilon_{z\lambda\mu}\hat{J}_\mu$$

$$[\hat{J}_y, \hat{j}_x] = \left[\frac{\hbar}{i}\frac{\partial}{\partial\beta}, \hat{j}_x\right] = \frac{\hbar}{i}\frac{\partial}{\partial\beta}\hat{j}_x - \frac{\hbar}{i}\hat{j}_x\frac{\partial}{\partial\beta} = 0$$

$$[\hat{J}_y, \hat{j}_y] = \left[\frac{\hbar}{i}\frac{\partial}{\partial\beta}, \hat{j}_y\right] = \frac{\hbar}{i}\frac{\partial}{\partial\beta}\hat{j}_y - \frac{\hbar}{i}\hat{j}_y\frac{\partial}{\partial\beta} = 0$$

$$[\hat{J}_y, \hat{j}_z] = 0 \quad \text{from page 36}$$

$$\Rightarrow \quad [\hat{J}_y, \hat{j}_\lambda] = 0$$

$$[\hat{J}_z, \hat{j}_x] = [\hat{j}_z, \hat{j}_x] = -\frac{\hbar}{i}\hat{j}_y$$

$$[\hat{J}_z, \hat{j}_y] = [\hat{j}_z, \hat{j}_y] = -[\hat{j}_y, \hat{j}_z] + \frac{\hbar}{i}\hat{j}_x$$

} see page 38 (15th line)

$$[\hat{J}_z, \hat{j}_z] = [\hat{j}_z, \hat{j}_z] = (\hat{j}_z)^2 - (\hat{j}_z)^2 = 0$$

$$\Rightarrow \quad [\hat{J}_z, \hat{j}_\lambda] = -\frac{\hbar}{i}\epsilon_{z\lambda\mu}\hat{j}_\mu$$

Summarising:

$$[\hat{J}_x, \hat{j}_\lambda] = -\frac{\hbar}{i}\cot\beta\,\epsilon_{z\lambda\mu}\hat{j}_\mu$$

$$[\hat{J}_y, \hat{j}_\lambda] = 0$$

$$[\hat{J}_z, \hat{j}_\lambda] = -\frac{\hbar}{i}\epsilon_{z\lambda\mu}\hat{j}_\mu$$

TOTAL FRAGMENT AM COMMUTATION RELATIONS

At last we're now in a position to make substitutions to the space-fixed KE operator given on page 6.

We know $\underset{\sim}{t}_i^F = C\,\underset{\sim}{z}_i^F \Rightarrow \nabla(\underset{\sim}{t}_i^F) = C\,\nabla(\underset{\sim}{z}_i^F)$

Now use identity $\underset{\sim}{a}\cdot\underset{\sim}{b} = \underset{\sim}{a}^T\underset{\sim}{b}$ to simplify $\nabla(\underset{\sim}{t}_i^F)\cdot\nabla(\underset{\sim}{t}_j^F)$:

$$\nabla(\underset{\sim}{t}_i^F)\cdot\nabla(\underset{\sim}{t}_j^F) = C(\nabla(\underset{\sim}{z}_i^F))\cdot C(\nabla(\underset{\sim}{z}_j^F))$$

$$= (\nabla(\underset{\sim}{z}_i^F))^T C^T C\, \nabla(\underset{\sim}{z}_j^F) \qquad \text{but } C^T C \triangleq 1$$

$$= (\nabla(\underset{\sim}{z}_i^F))^T \nabla(\underset{\sim}{z}_j^F)$$

$$= \nabla(\underset{\sim}{z}_i^F)\cdot\nabla(\underset{\sim}{z}_j^F)$$

Rusty on vector stuff? See 1.5 of "Computational Dynamics" A.A. SHABANA QA845. S44 1994

Thus, the term $\sum_F \sum_{a,b=1}^{N_F-1} \zeta_{ab}^F \nabla(\underset{\sim}{t}_a^F)\cdot\nabla(\underset{\sim}{t}_b^F)$ is form invariant, i.e.

$$\hat{K}_{ROT}^F = -\frac{\hbar^2}{2}\sum_{a,b=1}^{N_F-1}\zeta_{ab}^F\,\nabla(\underset{\sim}{t}_a^F)\cdot\nabla(\underset{\sim}{t}_b^F) = -\frac{\hbar^2}{2}\sum_{a,b=1}^{N_F-1}\zeta_{ab}^F\,\nabla(\underset{\sim}{z}_a^F)\cdot\nabla(\underset{\sim}{z}_b^F)$$

FORM-INVARIANT FRAGMENT K.E. OPERATOR

We're also in a position to rewrite the operator describing the orbital rotational kinetic energy:

$$\hat{K}_{ORB} = -\frac{\hbar^2}{2\mu}\nabla^2(\underset{\sim}{t}_0)$$

Before, we found $\frac{\partial}{\partial t_{0,\xi}} = \frac{1}{R}C_{\xi x}\left(\frac{\partial}{\partial\beta} - \frac{i}{\hbar}\hat{J}_y\right) + \frac{1}{R}C_{\xi y}\left(\csc\beta\frac{\partial}{\partial\alpha} - \cot\beta\frac{i}{\hbar}\hat{J}_z \cdots\right.$

$$\left. \cdots + \frac{i}{\hbar}\hat{J}_x\right) + C_{\xi z}\frac{\partial}{\partial R}$$

This can easily be rewritten in terms of total angular momentum components in body-fixed coordinates (pg 35):

$$\frac{\partial}{\partial t_{0,\xi}} = \frac{1}{R}C_{\xi x}\frac{i}{\hbar}\left(\hat{J}_y - \hat{j}_y\right) - \frac{1}{R}C_{\xi y}\frac{i}{\hbar}\left(\hat{J}_x - \hat{j}_x\right) + C_{\xi z}\frac{\partial}{\partial R}$$

$$\text{if } \left(\frac{\partial}{\partial\underset{\sim}{t}_0}\right)^2 = \nabla^2(\underset{\sim}{t}_0) = \sum_\xi\left(\frac{\partial}{\partial t_{0,\xi}}\right)^2$$

$\sum_\xi\left(\frac{\partial}{\partial t_{0,\xi}}\right)^2$ is a product yielding 9 terms:

$$\sum_\zeta \left(\frac{\partial}{\partial \xi_{0,\zeta}}\right)^2 = \sum_\zeta \Bigg\{ -\frac{1}{R^2}\frac{1}{k^2} C_{\zeta x}\left(\hat{J}_\lambda - \hat{j}_\lambda\right) C_{\zeta x}\left(\hat{J}_\lambda - \hat{j}_\lambda\right) \quad (1)$$

$$+ \frac{1}{R^2}\frac{1}{k^2} C_{\zeta x}\left(\hat{J}_\lambda - \hat{j}_\lambda\right) C_{\zeta y}\left(\hat{J}_x - \hat{j}_x\right) \quad (2)$$

$$+ \frac{1}{R}\frac{i}{k} C_{\zeta x}\left(\hat{J}_\lambda - \hat{j}_\lambda\right) C_{\zeta z}\frac{\partial}{\partial R} \quad (3)$$

$$+ \frac{1}{R^2}\frac{1}{k^2} C_{\zeta y}\left(\hat{J}_x - \hat{j}_x\right) C_{\zeta x}\left(\hat{J}_\lambda - \hat{j}_\lambda\right) \quad (4)$$

$$- \frac{1}{R^2}\frac{1}{k^2} C_{\zeta y}\left(\hat{J}_x - \hat{j}_x\right) C_{\zeta y}\left(\hat{J}_x - \hat{j}_x\right) \quad (5)$$

$$- \frac{1}{R}\frac{i}{k} C_{\zeta y}\left(\hat{J}_x - \hat{j}_x\right) C_{\zeta z}\frac{\partial}{\partial R} \quad (6)$$

$$+ \frac{i}{k} C_{\zeta z}\frac{\partial}{\partial R}\frac{1}{R} C_{\zeta x}\left(\hat{J}_\lambda - \hat{j}_\lambda\right) \quad (7)$$

$$- \frac{i}{k} C_{\zeta z}\frac{\partial}{\partial R}\frac{1}{R} C_{\zeta y}\left(\hat{J}_x - \hat{j}_x\right) \quad (8)$$

$$+ \left(C_{\zeta z}\right)^2 \frac{\partial^2}{\partial R^2} \Bigg\} \quad (9)$$

Keep in mind that $\hat{j}_\lambda$ doesn't act on elements of C $(\lambda = x, y, z)$

(1) $$= -\sum_\zeta \frac{1}{R^2}\frac{1}{k^2} C_{\zeta x}\left(\hat{J}_\lambda - \hat{j}_\lambda\right) C_{\zeta x}\left(\hat{J}_\lambda - \hat{j}_\lambda\right)$$

$$= -\frac{1}{R^2}\frac{1}{k^2}\left[\sum_\zeta C_{\zeta x}^2\left(\hat{J}_\lambda - \hat{j}_\lambda\right)^2 + \sum_\zeta C_{\zeta x}\left(\hat{J}_\lambda C_{\zeta x}\right)\left(\hat{J}_\lambda - \hat{j}_\lambda\right)\right] \quad \text{- product rule}$$

$$= -\frac{1}{R^2 k^2}\left[\left(\cos^2\beta\cos^2\alpha + \sin^2\alpha + \sin^2\beta\cos^2\alpha\right)\left(\hat{J}_\lambda - \hat{j}_\lambda\right)^2 + \sum_\zeta C_{\zeta x}\left(\frac{k}{i}\frac{\partial}{\partial\beta} C_{\zeta x}\right)\left(\hat{J}_\lambda - \hat{j}_\lambda\right)\right]$$

$$= -\frac{1}{R^2 k^2}\left[\left(\hat{J}_\lambda - \hat{j}_\lambda\right)^2 + \left(-\cos\beta\cos\alpha\sin\beta + \sin\beta\cos\alpha\cos\beta\right)\left(\hat{J}_\lambda - \hat{j}_\lambda\right)\right]$$

$$= -\frac{1}{R^2 k^2}\left(\hat{J}_\lambda - \hat{j}_\lambda\right)^2$$

(2) $$+ \frac{1}{R^2 k^2}\sum_\zeta C_{\zeta x}\left(\hat{J}_\lambda - \hat{j}_\lambda\right) C_{\zeta y}\left(\hat{J}_x - \hat{j}_x\right)$$

$$= \frac{1}{R^2 k^2}\left[\sum_\zeta C_{\zeta x} C_{\zeta y}\left(\hat{J}_\lambda - \hat{j}_\lambda\right)\left(\hat{J}_x - \hat{j}_x\right) + \sum_\zeta C_{\zeta x}\left(\frac{k}{i}\frac{\partial}{\partial\beta} C_{\zeta y}\right)\left(\hat{J}_x - \hat{j}_x\right)\right]$$

$$= \frac{1}{R^2 t^2}\Big[\Big(-\cos\beta\cos\alpha\sin\alpha + \cos\beta\sin\alpha\cos\alpha + 0\Big)\Big(\hat{J}_y - \hat{j}_y\Big)\Big(\hat{J}_x - \hat{j}_x\Big) + \cdots$$

$$\cdots + \Big(-\sin\beta\sin^2\alpha\cos\beta + 0 + \sin\beta\sin^2\alpha\cos\beta\Big)\Big(\hat{J}_x - \hat{j}_x\Big)\Big]$$

$$= \frac{1}{R^2 t^2}\Big[0 + 0\Big]$$

$$= 0$$

③ $$+ \frac{1}{R}\frac{i}{t}\sum_j C_{jx}\overset{u}{\big(\hat{J}_y - \hat{j}_y\big)}C_{jz}\overset{v}{\frac{\partial}{\partial R}}$$

$$= + \frac{i}{Rt}\sum_j\Big[C_{jx}C_{jz}\big(\hat{J}_y - \hat{j}_y\big)\frac{\partial}{\partial R} + C_{jx}\Big(\frac{t}{i}\frac{\partial}{\partial\beta}C_{jz}\Big)\frac{\partial}{\partial R}\Big]$$

$$= + \frac{i}{Rt}\Big[\Big(\cos\beta\cos^2\alpha\sin\beta + \cos\beta\sin^2\alpha\sin\beta - \cos\beta\sin\beta\Big)\Big(\hat{J}_y - \hat{j}_y\Big)\frac{\partial}{\partial R} + \cdots$$

$$\cdots + \frac{t}{i}\big(\cos^2\beta\cos^2\alpha + \cos^2\beta\sin^2\alpha + \sin^2\beta\big)\frac{\partial}{\partial R}\Big]$$

$$= + \frac{i}{Rt}\Big[0 + \frac{t}{i}\frac{\partial}{\partial R}\Big]$$

$$= \frac{1}{R}\frac{\partial}{\partial R}$$

④ $$\frac{1}{R^2 t^2}\sum_j C_{jy}\overset{u}{\big(\hat{J}_x - \hat{j}_x\big)}C_{jx}\overset{v}{\big(\hat{J}_y - \hat{j}_y\big)}$$

$$= \frac{1}{R^2 t^2}\Big[\sum_j C_{jy}C_{jx}\big(\hat{J}_x - \hat{j}_x\big)\big(\hat{J}_y - \hat{j}_y\big) + \sum_j C_{jy}\big(\hat{J}_x C_{jx}\big)\big(\hat{J}_y - \hat{j}_y\big)\Big]$$

$$= \frac{1}{R^2 t^2}\Big[0\ (\text{see } ②) + \sum_j C_{jy}\Big(-\frac{t}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}C_{jx} + \cot\beta\,\hat{j}_z C_{jx}\Big)\big(\hat{J}_y - \hat{j}_y\big)\Big]$$

$$= \frac{1}{R^2 t^2}\Big[\Big(+\sin\alpha\frac{t}{i}\operatorname{cosec}\beta\,(-\cos\beta\sin\alpha) - \cos\alpha\frac{t}{i}\operatorname{cosec}\beta\,(\cos\beta\cos\alpha)(")\Big]$$

$$= \frac{-1}{R^2 t^2}\frac{k}{i}\Big[\operatorname{cosec}\beta\cos\beta\big(\sin^2\alpha + \cos^2\alpha\big)\Big]\big(\hat{J}_y - \hat{j}_y\big)$$

$$= \frac{-1}{iR^2 k}\cot\beta\big(\hat{J}_y - \hat{j}_y\big)$$

⑤ $-\frac{1}{R^2}\frac{1}{k^2}\sum_\gamma C_{\gamma\gamma}(\hat{J}_x-\hat{j}_x)\overset{\circ}{C}_{\gamma\gamma}(\hat{J}_x-\hat{j}_x)$

$= -\frac{1}{R^2}\frac{1}{k^2}\left[\sum_\gamma C_{\gamma\gamma}^2(\hat{J}_x-\hat{j}_x)^2 + \sum_\gamma C_{\gamma\gamma}\left(-\frac{k}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}C_{\gamma\gamma}\right)(\hat{J}_x-\hat{j}_x)\right]$

$= -\frac{1}{R^2}\frac{1}{k^2}\left[(\sin^2\alpha+\cos^2\alpha)(\hat{J}_x-\hat{j}_x)^2 + \frac{k}{i}\left(-\sin\alpha\operatorname{cosec}\beta\cos\alpha+\cos\alpha\operatorname{cosec}\beta\sin\alpha\right)_x \times(\hat{J}_x-\hat{j}_x)\right]$

$= -\frac{1}{R^2}\frac{1}{k^2}(\hat{J}_x-\hat{j}_x)^2 + \frac{k}{i}\cdot 0\cdot(\hat{J}_x-\hat{j}_x)$

$= -\frac{1}{R^2}\frac{1}{k^2}(\hat{J}_x-\hat{j}_x)^2$

⑥ $-\frac{i}{Rk}\sum_\gamma C_{\gamma\gamma}(\hat{J}_x-\hat{j}_x)\overset{\circ}{C}_{\gamma z}\overset{\circ}{\frac{\partial}{\partial R}}$

$= \frac{-i}{Rk}\left[\sum_\gamma C_{\gamma\gamma}C_{\gamma z}\left(-\frac{k}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}\right)\frac{\partial}{\partial R} + \sum_\gamma C_{\gamma\gamma}\left(-\frac{k}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}C_{\gamma z}\right)\frac{\partial}{\partial R}\right]$

$= \frac{-i}{Rk}\left[\left(-\sin\alpha\sin\beta\cos\alpha+\cos\alpha\sin\beta\sin\alpha\right)\left(-\frac{k}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}\frac{\partial}{\partial R}\right)+\cdots\right.$

$\left.\cdots+\frac{-k}{i}\left(+\sin^2\alpha\operatorname{cosec}\beta\sin\beta+\cos^2\alpha\operatorname{cosec}\beta\sin\beta\right)\frac{\partial}{\partial R}\right]$

$= \frac{-i}{Rk}\left[0+\frac{-k}{i}\operatorname{cosec}\beta\sin\beta\frac{\partial}{\partial R}\right]$

$= \frac{1}{R}\frac{\sin\beta}{\sin\beta}\frac{\partial}{\partial R}$

$= \frac{1}{R}\frac{\partial}{\partial R}$

⑦ $\sum_\gamma + \frac{i}{k}C_{\gamma z}\frac{\partial}{\partial R}\frac{1}{R}C_{\gamma x}(\hat{J}_y-\hat{j}_y)$

$= +\frac{i}{k}\sum_\gamma C_{\gamma z}C_{\gamma x}\frac{\partial}{\partial R}\frac{1}{R}(\hat{J}_y-\hat{j}_y)$

$= +\frac{i}{k}\left(\sin\beta\cos^2\alpha\cos\beta+\sin\beta\sin^2\alpha\cos\beta-\cos\beta\sin\beta\right)\frac{\partial}{\partial R}\frac{1}{R}(\hat{J}_y-\hat{j}_y)$

$= +\frac{i}{k}\left(\sin\beta\cos\beta-\cos\beta\sin\beta\right)\frac{\partial}{\partial R}\frac{1}{R}(\hat{J}_y-\hat{j}_y)$

$= 0$

⑧ $-\frac{i}{k}\sum_j C_{jz}\frac{\partial}{\partial R}\frac{1}{R}C_{jy}(\hat{J}_x-\hat{j}_x)$

$= -\frac{i}{k}\sum_j C_{jz}C_{jy}\frac{\partial}{\partial R}\frac{1}{R}(\hat{J}_x-\hat{j}_x)$

$= -\frac{i}{k}\left(-\sin\alpha\sin\beta\cos\alpha+\cos\alpha\sin\beta\sin\alpha\right)\frac{\partial}{\partial R}\frac{1}{R}(\hat{J}_x-\hat{j}_x)$

$= 0$

⑨ $\sum_j (C_{jz})^2\frac{\partial^2}{\partial R^2}$

$= (\sin^2\beta+\cos^2\beta)\frac{\partial^2}{\partial R^2}$

$= \frac{\partial}{\partial R^2}$

$\therefore \nabla^2(t_0) = ① + \cdots + ⑨$

$= -\frac{1}{R^2k^2}(\hat{J}_y-\hat{j}_y)^2 + 0 + \frac{1}{R}\frac{\partial}{\partial R} - \frac{1}{iR^2k}\cot\beta(\hat{J}_y-\hat{j}_y)\cdots$

$-\frac{1}{R^2k^2}(\hat{J}_x-\hat{j}_x)^2 + \frac{1}{R}\frac{\partial}{\partial R} + 0 + 0 + \frac{\partial^2}{\partial R^2}$

$= -\frac{1}{R^2k^2}\left[(\hat{J}_y-\hat{j}_y)^2+(\hat{J}_x-\hat{j}_x)^2\right] + \frac{2}{R}\frac{\partial}{\partial R} - \frac{1}{iR^2k}\cot\beta(\hat{J}_y-\hat{j}_y)$

$+\frac{\partial^2}{\partial R^2}$

$\therefore \hat{K}_{ORB} = -\frac{k^2}{2\mu}\left[\frac{2}{R}\frac{\partial}{\partial R}+\frac{\partial^2}{\partial R^2}-\frac{1}{R^2k^2}\left\{(\hat{J}_y-\hat{j}_y)^2+(\hat{J}_x-\hat{j}_x)^2\cdots\right.\right.$

$\left.\left.-\frac{k}{i}\cot\beta(\hat{J}_y-\hat{j}_y)\right\}\right]$

working the product rule backwards:

$\frac{1}{R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} = \frac{1}{R^2}R^2\frac{\partial^2}{\partial R^2}+\frac{1}{R^2}2R\frac{\partial}{\partial R} = \frac{\partial^2}{\partial R^2}+\frac{2}{R}\frac{\partial}{\partial R}\cdots$

$$\hat{K}_{ORB} = -\frac{\hbar^2}{2\mu}\frac{1}{R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{1}{2\mu R^2}\left[(\hat{J}_x - \hat{j}_x)^2 + (\hat{J}_y - \hat{j}_y)^2 + \frac{\hbar}{i}\cot\beta(\hat{J}_y - \hat{j}_y)\right]$$

ORBITAL KE OPERATOR

It's possible to simplify this further. First, in order to make a substitution later on, we need to expand the space-fixed total angular momentum operator. Recall from page 33 that we found $\hat{\underset{\sim}{J}}(t_{\sim i}) = C\hat{\underset{\sim}{J}}(z_{\sim i})$

$$\Rightarrow \hat{\underset{\sim}{J}}^2(t_{\sim i}) = C\hat{\underset{\sim}{J}}(z_{\sim i}) \cdot C\hat{\underset{\sim}{J}}(z_{\sim i})$$

$$= \begin{pmatrix} C_{xx}\hat{J}_x + C_{xy}\hat{J}_y + C_{xz}\hat{J}_z \\ C_{yx}\hat{J}_x + C_{yy}\hat{J}_y + C_{yz}\hat{J}_z \\ C_{zx}\hat{J}_x + C_{zy}\hat{J}_y + C_{zz}\hat{J}_z \end{pmatrix} \cdot \begin{pmatrix} C_{xx}\hat{J}_x + C_{xy}\hat{J}_y + C_{xz}\hat{J}_z \\ C_{yx}\hat{J}_x + C_{yy}\hat{J}_y + C_{yz}\hat{J}_z \\ C_{zx}\hat{J}_x + C_{zy}\hat{J}_y + C_{zz}\hat{J}_z \end{pmatrix}$$

$$= \begin{pmatrix} \sum_f C_{xf}\hat{J}_f \\ \sum_f C_{yf}\hat{J}_f \\ \sum_f C_{zf}\hat{J}_f \end{pmatrix} \cdot \begin{pmatrix} C_{xx}\hat{J}_x + C_{xy}\hat{J}_y + C_{xz}\hat{J}_z \\ C_{yx}\hat{J}_x + C_{yy}\hat{J}_y + C_{yz}\hat{J}_z \\ C_{zx}\hat{J}_x + C_{zy}\hat{J}_y + C_{zz}\hat{J}_z \end{pmatrix}$$

$$\hat{\underset{\sim}{J}}^2(t_{\sim i}) = \underbrace{\sum_f C_{xf}\hat{J}_f C_{xx}\hat{J}_x}_{①} + \underbrace{\sum_f C_{xf}\hat{J}_f C_{xy}\hat{J}_y}_{②} + \underbrace{\sum_f C_{xf}\hat{J}_f C_{xz}\hat{J}_z}_{③} + \cdots$$
$$\cdots + \underbrace{\sum_f C_{yf}\hat{J}_f C_{yx}\hat{J}_x}_{④} + \underbrace{\sum_f C_{yf}\hat{J}_f C_{yy}\hat{J}_y}_{⑤} + \underbrace{\sum_f C_{yf}\hat{J}_f C_{yz}\hat{J}_z}_{⑥} + \cdots$$
$$\cdots + \underbrace{\sum_f C_{zf}\hat{J}_f C_{zx}\hat{J}_x}_{⑦} + \underbrace{\sum_f C_{zf}\hat{J}_f C_{zy}\hat{J}_y}_{⑧} + \underbrace{\sum_f C_{zf}\hat{J}_f C_{zz}\hat{J}_z}_{⑨}$$

which, when using the product rule, is a $6 \times 9 = 54$ term sum !!

Now expand each of the above 9 terms. Don't bother with redundant terms of the total component AM operators:

eg. $\hat{J}_x = -\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha} + \cot\beta\hat{j}_z$ $\hat{j}_z$ doesn't act on elements of C!

so, effectively we can write $\hat{J}_x = -\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}$

① $C_{xx}\hat{J}_x C_{xx}\hat{J}_x + C_{xy}\hat{J}_y C_{xx}\hat{J}_x + C_{xz}\hat{J}_z C_{xx}\hat{J}_x$

$= C_{xx}^2\hat{J}_x^2 + C_{xx}\left(-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}C_{xx}\right)\hat{J}_x + \ldots$

$\ldots + C_{xy}C_{xx}\hat{J}_y\hat{J}_x + C_{xy}\left(\frac{\hbar}{i}\frac{\partial}{\partial\beta}C_{xx}\right)\hat{J}_x + \ldots$

$\ldots + C_{xz}C_{xx}\hat{J}_z\hat{J}_x + C_{xz}\left(\cancel{\hat{J}_z C_{xx}}\right)\hat{J}_x$ $\quad = 0$

② $C_{xx}\hat{J}_x C_{xy}\hat{J}_y + C_{xy}\hat{J}_y C_{xy}\hat{J}_y + C_{xz}\hat{J}_z C_{xy}\hat{J}_y$

$= C_{xx}C_{xy}\hat{J}_x\hat{J}_x + C_{xx}\left(-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}C_{xy}\right)\hat{J}_y + \ldots$

$\ldots + C_{xy}^2\hat{J}_y^2 + C_{xy}\left(\frac{\hbar}{i}\frac{\partial}{\partial\beta}C_{xy}\right)\hat{J}_y + \ldots$

$\ldots + C_{xz}C_{xy}\hat{J}_z\hat{J}_y + C_{xz}\left(\cancel{\hat{J}_z C_{xy}}\right)\hat{J}_y$ $\quad = 0$

③ $C_{xx}\hat{J}_x C_{xz}\hat{J}_z + C_{xy}\hat{J}_y C_{xz}\hat{J}_z + C_{xz}\hat{J}_z C_{xz}\hat{J}_z$

$= C_{xx}C_{xz}\hat{J}_x\hat{J}_z + C_{xx}\left(-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}C_{xz}\right)\hat{J}_z + \ldots$

$\ldots + C_{xy}C_{xz}\hat{J}_y\hat{J}_z + C_{xy}\left(\frac{\hbar}{i}\frac{\partial}{\partial\beta}C_{xz}\right)\hat{J}_z + \ldots$

$\ldots + C_{xz}^2\hat{J}_z^2 + C_{xz}\left(\cancel{\hat{J}_z C_{xz}}\right)\hat{J}_z$ $\quad = 0$

④ $C_{yx}\hat{J}_x C_{yx}\hat{J}_x + C_{yy}\hat{J}_y C_{yx}\hat{J}_x + C_{yz}\hat{J}_z C_{yx}\hat{J}_x$

$= C_{yx}^2\hat{J}_x^2 + C_{yx}\left(-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}C_{yx}\right)\hat{J}_x + \ldots$

$\ldots + C_{yy}C_{yx}\hat{J}_y\hat{J}_x + C_{yy}\left(\frac{\hbar}{i}\frac{\partial}{\partial\beta}C_{yx}\right)\hat{J}_x + \ldots$

$\ldots + C_{yz}C_{yx}\hat{J}_z\hat{J}_x + C_{yz}\left(\cancel{\hat{J}_z C_{yx}}\right)\hat{J}_x$

⑤ $C_{yx}\hat{J}_x C_{yy}\hat{J}_y + C_{yy}\hat{J}_y C_{yy}\hat{J}_y + C_{yz}\hat{J}_z C_{yy}\hat{J}_y$

$= C_{yx}C_{yy}\hat{J}_x\hat{J}_y + C_{yx}\left(-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}C_{yy}\right)\hat{J}_y + \cdots$

$\cdots + C_{yy}^2\hat{J}_y^2 + C_{yy}\left(\frac{\hbar}{i}\frac{\partial}{\partial\beta}C_{yy}\right)\hat{J}_y + \cdots$

$\cdots + C_{yz}C_{yy}\hat{J}_z\hat{J}_y + C_{yz}\left(\cancel{\hat{J}_z C_{yy}}_{=0}\right)\hat{J}_y$

⑥ $C_{yx}\hat{J}_x C_{yz}\hat{J}_z + C_{yy}\hat{J}_y C_{yz}\hat{J}_z + C_{yz}\hat{J}_z C_{yz}\hat{J}_z$

$= C_{yx}C_{yz}\hat{J}_x\hat{J}_z + C_{yx}\left(-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}C_{yz}\right)\hat{J}_z + \cdots$

$\cdots + C_{yy}C_{yz}\hat{J}_y\hat{J}_z + C_{yy}\left(\frac{\hbar}{i}\frac{\partial}{\partial\beta}C_{yz}\right)\hat{J}_z + \cdots$

$\cdots + C_{yz}^2\hat{J}_z^2 + C_{yz}\left(\cancel{\hat{J}_z C_{yz}}_{=0}\right)\hat{J}_z$

⑦ $C_{zx}\hat{J}_x C_{zx}\hat{J}_x + C_{zy}\hat{J}_y C_{zx}\hat{J}_x + C_{zz}\hat{J}_z C_{zx}\hat{J}_x$

$= C_{zx}^2\hat{J}_x^2 + C_{zx}\left(-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}C_{zx}\right)\hat{J}_x + \cdots$

$\cdots + C_{zy}C_{zx}\hat{J}_y\hat{J}_x + C_{zy}\left(\frac{\hbar}{i}\frac{\partial}{\partial\beta}C_{zx}\right)\hat{J}_x + \cdots$

$\cdots + C_{zz}C_{zx}\hat{J}_z\hat{J}_x + C_{zz}\left(\cancel{\hat{J}_z C_{zx}}_{=0}\right)\hat{J}_x$

⑧ $C_{zx}\hat{J}_x C_{zy}\hat{J}_y + C_{zy}\hat{J}_y C_{zy}\hat{J}_y + C_{zz}\hat{J}_z C_{zy}\hat{J}_y$

$= C_{zx}C_{zy}\hat{J}_x\hat{J}_y + C_{zx}\left(-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}C_{zy}\right)\hat{J}_y + \cdots$

$\cdots + C_{zy}^2\hat{J}_y^2 + C_{zy}\left(\frac{\hbar}{i}\frac{\partial}{\partial\beta}C_{zy}\right)\hat{J}_y + \cdots$

$\cdots + C_{zz}C_{zy}\hat{J}_z\hat{J}_y + C_{zz}\left(\cancel{\hat{J}_z C_{zy}}_{=0}\right)\hat{J}_y$

⑨ $C_{zx}\hat{J}_x C_{zz}\hat{J}_z + C_{zy}\hat{J}_y C_{zz}\hat{J}_z + C_{zz}\hat{J}_z C_{zz}\hat{J}_z$

$= C_{zx}C_{zz}\hat{J}_x\hat{J}_z + C_{zx}\left(-\frac{\hbar}{i}\operatorname{cosec}\beta\frac{\partial}{\partial\alpha}C_{zz}\right)\hat{J}_z + \cdots$

$\cdots + C_{zy}C_{zz}\hat{J}_y\hat{J}_z + C_{zy}\left(\frac{\hbar}{i}\frac{\partial}{\partial\beta}C_{zz}\right)\hat{J}_z + \cdots$

$\cdots + C_{zz}^2\hat{J}_z^2 + C_{zz}\underbrace{\left(\hat{J}_z C_{zz}\right)}_{=0}\hat{J}_z$

As can be seen, the sixth term of each expansion has been cancelled out. This is because $\hat{J}_\lambda$ do NOT act on elements of C. We're left with 45 terms, easily grouped into 12 (denoted by Roman numerals):

$\hat{J}^2(t_{\underset{\sim}{i}}) = ① + \cdots + ⑨$

$= \underbrace{\left(C_{xx}^2 + C_{yx}^2 + C_{zx}^2\right)}_{\text{I}}\hat{J}_x^2 + \underbrace{\left(C_{xy}^2 + C_{yy}^2 + C_{zy}^2\right)}_{\text{II}}\hat{J}_y^2 + \underbrace{\left(C_{xz}^2 + C_{yz}^2 + C_{zz}^2\right)}_{\text{III}}\hat{J}_z^2 +$

$\cdots + \left\{C_{xy}C_{xx} + C_{yy}C_{yx} + C_{zy}C_{zx}\right\}\left(\hat{J}_y\hat{J}_x + \hat{J}_x\hat{J}_y\right)$ IV $+ \cdots$

$\cdots + \left\{C_{xz}C_{xx} + C_{yz}C_{yx} + C_{zz}C_{zx}\right\}\left(\hat{J}_z\hat{J}_x + \hat{J}_x\hat{J}_z\right)$ V $+ \cdots$

$\cdots + \left\{C_{xz}C_{xy} + C_{yz}C_{yy} + C_{zz}C_{zy}\right\}\left(\hat{J}_z\hat{J}_y + \hat{J}_y\hat{J}_z\right)$ VI $+ \cdots$

$\cdots + -\frac{\hbar}{i}\operatorname{cosec}\beta\left[C_{xx}\frac{\partial}{\partial\alpha}C_{xx} + C_{yx}\frac{\partial}{\partial\alpha}C_{yx} + C_{zx}\frac{\partial}{\partial\alpha}C_{zx}\right]\hat{J}_x$ VII $+ \cdots$

$\cdots + -\frac{\hbar}{i}\operatorname{cosec}\beta\left[C_{xx}\frac{\partial}{\partial\alpha}C_{xy} + C_{yx}\frac{\partial}{\partial\alpha}C_{yy} + C_{zx}\frac{\partial}{\partial\alpha}C_{zy}\right]\hat{J}_y$ VIII $+ \cdots$

$\cdots + -\frac{\hbar}{i}\operatorname{cosec}\beta\left[C_{xx}\frac{\partial}{\partial\alpha}C_{xz} + C_{yx}\frac{\partial}{\partial\alpha}C_{yz} + C_{zx}\frac{\partial}{\partial\alpha}C_{zz}\right]\hat{J}_z$ IX $+ \cdots$

$\cdots + \frac{\hbar}{i}\left[C_{xy}\frac{\partial}{\partial\beta}C_{xx} + C_{yy}\frac{\partial}{\partial\beta}C_{yx} + C_{zy}\frac{\partial}{\partial\beta}C_{zx}\right]\hat{J}_x$ X $+ \cdots$

$\cdots + \frac{\hbar}{i}\left[C_{xy}\frac{\partial}{\partial\beta}C_{xy} + C_{yy}\frac{\partial}{\partial\beta}C_{yy} + C_{zy}\frac{\partial}{\partial\beta}C_{zy}\right]\hat{J}_y$ XI $+ \cdots$

$\cdots + \frac{\hbar}{i}\left[C_{xy}\frac{\partial}{\partial\beta}C_{xz} + C_{yy}\frac{\partial}{\partial\beta}C_{yz} + C_{zy}\frac{\partial}{\partial\beta}C_{zz}\right]\hat{J}_z$ XII

Examine each term:

(I) $(C_{xx}^2 + C_{yx}^2 + C_{zx}^2)\hat{J}_x^2$

$= (\cos^2\beta\cos^2\alpha + \cos^2\beta\sin^2\alpha + \sin^2\beta)\hat{J}_x^2$

$= (\cos^2\beta[\cos^2\alpha + \sin^2\alpha] + \sin^2\beta)\hat{J}_x^2$

$= \hat{J}_x^2$

(II) $(C_{xy}^2 + C_{yy}^2 + C_{zy}^2)\hat{J}_y^2$

$= (\sin^2\alpha + \cos^2\alpha + 0)\hat{J}_y^2$

$= \hat{J}_y^2$

(III) $(C_{xz}^2 + C_{yz}^2 + C_{zz}^2)\hat{J}_z^2$

$= (\sin^2\beta\cos^2\alpha + \sin^2\beta\sin^2\alpha + \cos^2\beta)\hat{J}_z$

$= (\sin^2\beta[\cos^2\alpha + \sin^2\alpha] + \cos^2\beta)\hat{J}_z$

$= \hat{J}_z^2$

(IV) $\{C_{xy}C_{xx} + C_{yy}C_{yx} + C_{zy}C_{zx}\}(\hat{J}_y\hat{J}_x + \hat{J}_x\hat{J}_y)$

$= \{-\sin\alpha\cos\beta\cos\alpha + \cos\alpha\cos\beta\sin\alpha + 0\}(\hat{J}_y\hat{J}_x + \hat{J}_x\hat{J}_y)$

$= 0$

(V) $\{C_{xz}C_{xx} + C_{yz}C_{yx} + C_{zz}C_{zx}\}(\hat{J}_z\hat{J}_x + \hat{J}_x\hat{J}_z)$

$= \{\sin\beta\cos^2\alpha\cos\beta + \sin\beta\sin^2\alpha\cos\beta - \sin\beta\cos\beta\}(\hat{J}_z\hat{J}_x + \hat{J}_x\hat{J}_z)$

$= \{\sin\beta\cos\beta(\cos^2\alpha + \sin^2\alpha) - \sin\beta\cos\beta\}(\hat{J}_z\hat{J}_x + \hat{J}_x\hat{J}_z)$

$= 0$

(VI) $\left[C_{xz} C_{xy} + C_{yz} C_{yy} + C_{zz} C_{zy} \right] \left(\hat{J}_z \hat{J}_y + \hat{J}_y \hat{J}_z \right)$

$= \left[-\sin\beta \cos\alpha \sin\alpha + \sin\beta \sin\alpha \cos\alpha + 0 \right] \left(\hat{J}_z \hat{J}_y + \hat{J}_y \hat{J}_z \right)$

$= 0$

(VII) $-\frac{t}{i} \operatorname{cosec}\beta \left[C_{xx} \frac{\partial}{\partial\alpha} C_{xx} + C_{yx} \frac{\partial}{\partial\alpha} C_{yx} + C_{zx} \frac{\partial}{\partial\alpha} C_{zx} \right] \hat{J}_x$

$= -\frac{t}{i} \operatorname{cosec}\beta \left[-\cos^2\beta \cos\alpha \sin\alpha + \cos^2\beta \sin\alpha \cos\alpha + -\sin\beta \cdot 0 \right] \hat{J}_x$

$= 0$

(VIII) $-\frac{t}{i} \operatorname{cosec}\beta \left[C_{xx} \frac{\partial}{\partial\alpha} C_{xy} + C_{yx} \frac{\partial}{\partial\alpha} C_{yy} + C_{zx} \frac{\partial}{\partial\alpha} C_{zy} \right] \hat{J}_y$

$= -\frac{t}{i} \operatorname{cosec}\beta \left[-\cos\beta \cos^2\alpha - \cos\beta \sin^2\alpha + -\sin\beta \cdot 0 \right] \hat{J}_y$

$= +\frac{t}{i} \operatorname{cosec}\beta \left[\cos\beta \left(\cos^2\alpha + \sin^2\alpha \right) \right] \hat{J}_y$

$= \frac{t}{i} \frac{1}{\sin\beta} \cos\beta \hat{J}_y$

$= \frac{t}{i} \cot\beta \hat{J}_y$

(IX) $-\frac{t}{i} \operatorname{cosec}\beta \left[C_{xx} \frac{\partial}{\partial\alpha} C_{xz} + C_{yx} \frac{\partial}{\partial\alpha} C_{yz} + C_{zx} \frac{\partial}{\partial\alpha} C_{zz} \right] \hat{J}_z$

$= -\frac{t}{i} \operatorname{cosec}\beta \left[-\cos\beta \cos\alpha \sin\beta \sin\alpha + \cos\beta \sin\alpha \sin\beta \cos\alpha + 0 \right] \hat{J}_z$

$= 0$

(X) $\frac{t}{i} \left[C_{xy} \frac{\partial}{\partial\beta} C_{xx} + C_{yy} \frac{\partial}{\partial\beta} C_{yx} + C_{zy} \frac{\partial}{\partial\beta} C_{zx} \right] \hat{J}_x$

$= \frac{t}{i} \left[+\sin\alpha \sin\beta \cos\alpha + -\cos\alpha \sin\beta \sin\alpha + 0 \cdot \frac{\partial}{\partial\beta}(-\sin\beta) \right] \hat{J}_x$

$= 0$

(XI) $\frac{\hbar}{i}\left[C_{xy}\frac{\partial}{\partial\beta}C_{xy} + C_{yy}\frac{\partial}{\partial\beta}C_{yy} + C_{zy}\frac{\partial}{\partial\beta}C_{zy}\right]\hat{J}_y$

$= \frac{\hbar}{i}\left[-\sin\alpha\cdot 0 + \cos\alpha\cdot 0 + 0\cdot 0\right]\hat{J}_y$

$= 0$

(XII) $\frac{\hbar}{i}\left[C_{xy}\frac{\partial}{\partial\beta}C_{xz} + C_{yy}\frac{\partial}{\partial\beta}C_{yz} + C_{zy}\frac{\partial}{\partial\beta}C_{zz}\right]\hat{J}_z$

$= \frac{\hbar}{i}\left[-\sin\alpha\cos\beta\cos\alpha + \cos\alpha\cos\beta\sin\alpha + 0\cdot\frac{\partial}{\partial\beta}(\cos\beta)\right]\hat{J}_z$

Of the 12 (grouped) terms examined, only 4 were found to be non-zero

$\Rightarrow \hat{J}^2(\underset{\sim}{t_i}) = C\hat{J}(\underset{\sim}{t_i})\cdot C\hat{J}(\underset{\sim}{t_i}) = (1) + \cdots + (9)$

$= (I) + \cdots + (XII)$

ie $\hat{J}^2(\underset{\sim}{t_i}) = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 + \frac{\hbar}{i}\cot\beta\hat{J}_y$ (*)

By the product rule, $\operatorname{cosec}\beta\hat{J}_y\sin\beta\hat{J}_y$

$= \operatorname{cosec}\beta\left(\sin\beta\hat{J}_y^2 + \frac{\hbar}{i}\left(\frac{\partial}{\partial\beta}\sin\beta\right)\hat{J}_y\right)$

$= \frac{1}{\sin\beta}\left(\sin\beta\hat{J}_y^2 + \frac{\hbar}{i}\cos\beta\hat{J}_y\right)$

$= \hat{J}_y^2 + \frac{\hbar}{i}\cot\beta\hat{J}_y$

so, $\operatorname{cosec}\beta\hat{J}_y\sin\beta\hat{J}_y = \hat{J}_y^2 + \frac{\hbar}{i}\cot\beta\hat{J}_y$ is a nice substitution term for (*)

$\Rightarrow$ $\hat{J}^2(\underset{\sim}{t_i}) = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 + \frac{\hbar}{i}\cot\beta\hat{J}_y$

$= \hat{J}_x^2 + \operatorname{cosec}\beta\hat{J}_y\sin\beta\hat{J}_y + \hat{J}_z^2$

Return now to the orbital KE orbital operator, $\hat{K}_{ORB}$ (see p. 45):

$$\hat{K}_{ORB} = -\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{1}{2\mu R^2}\left[(\hat{J}_x - \hat{j}_x)^2 + (\hat{J}_y - \hat{j}_y)^2 + \frac{\hbar}{i}\cot\beta(\hat{J}_y - \hat{j}_y)\right]$$

where $(\hat{J}_x - \hat{j}_x)^2 = \hat{J}_x^2 - \hat{J}_x\hat{j}_x - \hat{j}_x\hat{J}_x + \hat{j}_x^2$

$$= \hat{J}_x^2 - 2\hat{j}_x\hat{J}_x - (\hat{J}_x\hat{j}_x - \hat{j}_x\hat{J}_x) + \hat{j}_x^2$$

$$= \hat{J}_x^2 - 2\hat{j}_x\hat{J}_x - [\hat{J}_x, \hat{j}_x] + \hat{j}_x^2$$

$(\hat{J}_y - \hat{j}_y)^2 = \hat{J}_y^2 - \hat{J}_y\hat{j}_y - \hat{j}_y\hat{J}_y + \hat{j}_y^2$

$$= \hat{J}_y^2 - 2\hat{j}_y\hat{J}_y - (\hat{J}_y\hat{j}_y - \hat{j}_y\hat{J}_y) + \hat{j}_y^2$$

$$= \hat{J}_y^2 - 2\hat{j}_y\hat{J}_y - [\hat{J}_y, \hat{j}_y] + \hat{j}_y^2$$

$$\Rightarrow \hat{K}_{ORB} = -\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{1}{2\mu R^2}\left[\hat{J}_x^2 - 2\hat{j}_x\hat{J}_x - [\hat{J}_x, \hat{j}_x] + \hat{j}_x^2 + \hat{J}_y^2 + \cdots\right.$$

$$\left. \cdots + -2\hat{j}_y\hat{J}_y - [\hat{J}_y, \hat{j}_y] + \hat{j}_y^2 + \frac{\hbar}{i}\cot\beta\hat{J}_y - \frac{\hbar}{i}\cot\beta\hat{j}_y\right]$$

but $[\hat{J}_x, \hat{j}_x] = -\frac{\hbar}{i}\cot\beta\hat{j}_y$

$[\hat{J}_y, \hat{j}_y] = 0$

} from p. 39

$$\hat{K}_{ORB} = -\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{1}{2\mu R^2}\left[\hat{J}_x^2 - 2\hat{j}_x\hat{J}_x + \frac{\hbar}{i}\cot\beta\hat{j}_y + \hat{j}_x^2 + \hat{J}_y^2 + \cdots\right.$$

$$\left. -\frac{\hbar}{i}\cot\beta\hat{j}_y \cdots + -2\hat{j}_y\hat{J}_y - 0 + \hat{j}_y^2 + \frac{\hbar}{i}\cot\beta\hat{J}_y\right]$$

Using the fact that $\hat{J}_z = \hat{j}_z$, we can add a term of the form:

$$\frac{1}{2\mu R^2}\left(\hat{J}_z^2 + \hat{j}_z^2 - 2\hat{j}_z\hat{J}_z\right) \quad \text{because it} = 0$$

$$\therefore \hat{K}_{ORB} = -\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{1}{2\mu R^2}\left[\hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 + \frac{\hbar}{i}\omega t\,\beta\hat{J}_y + \cdots\right.$$

$$\left.\cdots + \dot{J}_x^2 + \dot{J}_y^2 + \dot{J}_z^2 - 2\dot{J}_x\hat{J}_x - 2\dot{J}_y\hat{J}_y - 2\dot{J}_z\hat{J}_z\right]$$

but we recently found $\hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 + \frac{\hbar}{i}\omega t\,\hat{J}_y = \hat{J}^2(t_i)$ (see p. 51), so,

$$\hat{K}_{ORB} = -\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{1}{2\mu R^2}\left[\hat{J}^2(t_i) + \dot{J}_x^2 + \dot{J}_y^2 + \dot{J}_z^2 + \cdots\right.$$

$$\left.\cdots - 2\dot{J}_x\hat{J}_x - 2\dot{J}_y\hat{J}_y - 2\dot{J}_z\hat{J}_z\right]$$

..then,

$$\boxed{\hat{K}_{ORB} = -\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{1}{2\mu R^2}\left[\hat{J}^2(t_i) + \dot{J}^2 - 2\dot{J}\cdot\hat{J}\right]}$$

ORBITAL KE OPERATOR

Before deriving matrix elements for the operators $\hat{K}^F_{ROT}$ & $\hat{K}_{ORB}$, we can make further simplifications. At this juncture, the Hamiltonian may be written:

$$\hat{H} = \hat{K}^A_{ROT} + \hat{K}^B_{ROT} + \hat{K}_{ORB} + \hat{V}_{TOTAL}$$

The potential, as yet undiscussed, is given by:

$$\hat{V}_{TOTAL} = \hat{V}^A_{ROT}(\underset{\sim}{Z}_i^A) + \hat{V}^B_{ROT}(\underset{\sim}{Z}_i^B) + \hat{V}_{INT}(\underset{\sim}{Z}_i^F, \underset{\sim}{R})$$

$$\Rightarrow \hat{H} = \hat{H}^A_{ROT} + \hat{H}^B_{ROT} + \hat{K}_{ORB} + \hat{V}_{INT}$$

where $\hat{H}^F_{ROT} = \hat{K}^F_{ROT} + \hat{V}^F_{ROT} \qquad F = A, B$

Recall from p. 40 that $\hat{K}^F_{ROT} = -\frac{\hbar^2}{2}\sum_{a,b=1}^{N_F-1} G^F_{ab}\,\nabla(\underset{\sim}{Z}_a^F)\cdot\nabla(\underset{\sim}{Z}_b^F)$

form of $\nabla(\tilde{Z}_i^F)$, we may manipulate $\hat{K}^F_{ROT}$ such that it's written in terms of the angular momentum projections on the fragments' three principal axes: a, b, & c. Essentially, this amounts to writing a rigid rotor Hamiltonian [see ZARE pages 253 → 258]

ie $\hat{K}^F_{ROT} = A_F(\hat{j}_a^F)^2 + B_F(\hat{j}_b^F)^2 + C_F(\hat{j}_c^F)^2$

where $(A_F \propto I^F_{aa}) \geq (B_F \propto I^F_{bb}) \geq (C_F \propto I^F_{cc})$ are rotational constants. I_{jj} are called the principal moments of inertia.

Consider fragment F to be a prolate top (see Hanson fig 6.14 on p. 245). Prolate tops have $I_{aa} < I_{bb} = I_{cc}$ & the principal a axis is superimposed on the fragment-fixed z-axis... see ZARE table 6.2 on p. 268

Prolate top creation / raising operator $\hat{j}_+ = \hat{j}_b + i\hat{j}_c$

Prolate top annihilation / destruction / lowering operator $\hat{j}_- = \hat{j}_b - i\hat{j}_c$

(NB for info on the physics of raising & lowering operators see Hanson pages 59 → 62).

So, $\hat{K}^F_{ROT} = A_F(\hat{j}_a^F)^2 + B_F(\hat{j}_b^F)^2 + C_F(\hat{j}_c^F)^2$

$= A_F(\hat{j}_a^F)^2 + \frac{B_F}{2}\left((\hat{j}_b^F)^2 + (\hat{j}_c^F)^2 + (\hat{j}_b^F)^2 - (\hat{j}_c^F)^2\right) + \cdots$

$\cdots + \frac{C_F}{2}\left((\hat{j}_b^F)^2 + (\hat{j}_c^F)^2 - (\hat{j}_b^F)^2 + (\hat{j}_c^F)^2\right)$

$= A_F(\hat{j}_a^F)^2 + \frac{B_F}{2}\left((\hat{j}_b^F)^2 + (\hat{j}_c^F)^2 + \frac{1}{2}\left[(\hat{j}_b^F + i\hat{j}_c^F)^2 + (\hat{j}_b^F - i\hat{j}_c^F)^2\right]\right) + \cdots$

$\cdots + \frac{C_F}{2}\left((\hat{j}_b^F)^2 + (\hat{j}_c^F)^2 - \frac{1}{2}\left[(\hat{j}_b^F + i\hat{j}_c^F)^2 + (\hat{j}_b^F - i\hat{j}_c^F)^2\right]\right)$

$= A_F(\hat{j}_a^F)^2 + \frac{B_F}{2}\left((\hat{j}_b^F)^2 + (\hat{j}_c^F)^2 + \frac{1}{2}\left(\hat{j}_+^2 + \hat{j}_-^2\right)\right) + \cdots$

$\cdots + \frac{C_F}{2}\left((\hat{j}_b^F)^2 + (\hat{j}_c^F)^2 - \frac{1}{2}\left(\hat{j}_+^2 + \hat{j}_-^2\right)\right)$

$$\hat{K}^F_{ROT} = A_F(\hat{j}^F_a)^2 + \frac{B_F}{2}\left((\hat{j}^F_b)^2 + (\hat{j}^F_c)^2\right) + \frac{B_F}{4}\left(\hat{j}^2_+ + \hat{j}^2_-\right) + \cdots$$

$$\cdots + \frac{C_F}{2}\left((\hat{j}^F_b)^2 + (\hat{j}^F_c)^2\right) - \frac{C_F}{4}\left(\hat{j}^2_+ + \hat{j}^2_-\right)$$

$$= \tfrac{1}{2}\left[2A_F(\hat{j}^F_a)^2 + (B_F + C_F)\left((\hat{j}^F_b)^2 + (\hat{j}^F_c)^2\right) + \tfrac{1}{2}(B_F - C_F)\left(\hat{j}^2_+ + \hat{j}^2_-\right)\right]$$

$$= \tfrac{1}{2}\left[2A_F(\hat{j}^F_a)^2 + (B_F + C_F)\left((\hat{j}^F_a)^2 + (\hat{j}^F_b)^2 + (\hat{j}^F_c)^2 - (\hat{j}^F_a)^2\right) + \cdots\right.$$

$$\left.\cdots + \tfrac{1}{2}(B_F - C_F)\left(\hat{j}^2_+ + \hat{j}^2_-\right)\right]$$

$$= \tfrac{1}{2}\left[2A_F(\hat{j}^F_a)^2 + (B_F + C_F)(\hat{j}^F)^2 - B_F(\hat{j}^F_a)^2 - C_F(\hat{j}^F_a)^2 + \cdots\right.$$

$$\left.\cdots + \tfrac{1}{2}(B_F - C_F)\left(\hat{j}^2_+ + \hat{j}^2_-\right)\right]$$

$$= \tfrac{1}{2}\left[(B_F + C_F)(\hat{j}^F)^2 + (2A_F - B_F - C_F)(\hat{j}^F_a)^2 + \tfrac{1}{2}(B_F - C_F)\left(\hat{j}^2_+ + \hat{j}^2_-\right)\right]$$

But, as mentioned before, for prolate tops - the a principal axis lies on the fragment's z-axis $\Rightarrow (\hat{j}^F_a)^2 \equiv (\hat{j}^F_z)^2$. Thus,

$$\hat{K}^F_{ROT} = \tfrac{1}{2}\left[(B_F + C_F)(\hat{j}^F)^2 + (2A_F - B_F - C_F)(\hat{j}^F_z)^2 + \tfrac{1}{2}(B_F - C_F)\left(\hat{j}^2_+ + \hat{j}^2_-\right)\right]$$

We can nicely incorporate $\hat{V}^F_{ROT}$ into the expression for $\hat{H}^F_{ROT}$ by specifying the rotational constants for the rigid equilibrium fragment geometry ie $A_F \to Ae^{(F)}$; $B_F \to Be^{(F)}$; $C_F \to Ce^{(F)}$ where the subscript e denotes equilibrium. These equilibrium rotational constants can easily be obtained by performing a geometry optimisation using a package like GAUSSIAN or SPARTAN etc.. to, for a prolate top; $\hat{H}^F_{ROT}$ is given:

$\hat{H} \longrightarrow$ $$\hat{H}^F_{ROT}(\text{prolate}) = \tfrac{1}{2}\left[(Be^{(F)} + Ce^{(F)})(\hat{j}^F)^2 + (2Ae^{(F)} - Be^{(F)} - Ce^{(F)})(\hat{j}^F_z) + \tfrac{1}{2}(Be^{(F)} - Ce^{(F)})\left(\hat{j}^2_+ + \hat{j}^2_-\right)\right]$$

where $(\hat{j}^F)^2 = (\hat{j}^F_a)^2 + (\hat{j}^F_b)^2 + (\hat{j}^F_c)^2$

c.f. Bunker eq. 8-114 p. 185

$\hat{j}^F$ is total fragment angular momentum operator.

Can find a similar expression for the oblate top case (c principal axis superimposed on fragment-fixed z-axis & $\hat{J}_\pm = \hat{J}_a^F \pm i\hat{J}_b^F$):

$$\hat{H}^F_{ROT}(\text{oblate}) = \tfrac{1}{2}\left[(A_e^{(F)} + B_e^{(F)})(\hat{J}^F)^2 + (2C_e^{(F)} - A_e^{(F)} - B_e^{(F)})(\hat{J}_z^F)^2 + \tfrac{1}{2}(A_e^{(F)} - B_e^{(F)})(\hat{J}_+^2 + \hat{J}_-^2)\right]$$

c.f. Bunker
eq. 8-140 p. 188

At this stage, $\hat{H} = \hat{H}^A_{ROT} + \hat{H}^B_{ROT} + \hat{K}_{ORB} + \hat{V}_{INT}$

where $\hat{V}_{INT}$ is yet to be discussed
$\hat{K}_{ORB}$ is on p 53 but soon to be slightly altered
$\hat{H}^A_{ROT}$ & $\hat{H}^B_{ROT}$ are summarised below -

$$\hat{H}^F_{ROT}(\text{prolate}) = \tfrac{1}{2}\left[(B_e^{(F)} + C_e^{(F)})(\hat{J}^F)^2 + (2A_e^{(F)} - B_e^{(F)} - C_e^{(F)})(\hat{J}_z^F)^2 + \tfrac{1}{2}(B_e^{(F)} - C_e^{(F)})(\hat{J}_+^2 + \hat{J}_-^2)\right]$$

$$\hat{J}_\pm^F = \hat{J}_\pm = \hat{J}_b^F \pm i\hat{J}_c^F$$

$$\hat{H}^F_{ROT}(\text{oblate}) = \tfrac{1}{2}\left[(A_e^{(F)} + B_e^{(F)})(\hat{J}^F)^2 + (2C_e^{(F)} - A_e^{(F)} - B_e^{(F)})(\hat{J}_z^F)^2 + \tfrac{1}{2}(A_e^{(F)} - B_e^{(F)})(\hat{J}_+^2 + \hat{J}_-^2)\right]$$

$$\hat{J}_\pm^F = \hat{J}_\pm = \hat{J}_a^F \pm i\hat{J}_b^F$$

RIGID-ROTOR ENERGY OPERATOR FOR FRAGMENT F

NB for the unimolecular dissociation of ketene $H_2C{=}C{=}O$ into methylene & carbon-monoxide fragments, it is best to use the prolate top formalism. The scalar t^2 has been incorporated into the rotational constants temporarily - when matrix elements are found the factor is removed.

As promised above, the orbital KE operator, $\hat{K}_{ORB}$ can be further simplified. For total fragment angular momentum, we may define the usual shift operator:

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$$

- don't confuse with the above fragment shift operators

It is convenient to define the shift operators corresponding to the pseudo total angular momentum operator, $\hat{\underset{\sim}{J}}$:

$$\hat{J}_\pm = \hat{J}_x \mp i\hat{J}_y \quad \text{such that,}$$

$$\hat{K}_{ORB} = \frac{-\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{1}{2\mu R^2}\left[\hat{\underset{\sim}{J}}^2(\underset{\sim}{t}_i) + \hat{\underset{\sim}{j}}^2 - 2\hat{\underset{\sim}{j}}\cdot\hat{\underset{\sim}{J}}\right]$$

$$= \frac{-\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{1}{2\mu R^2}\left[\hat{\underset{\sim}{J}}^2(\underset{\sim}{t}_i) + \hat{\underset{\sim}{j}}^2 - 2\hat{j}_x\hat{J}_x - 2\hat{j}_y\hat{J}_y - 2\hat{j}_z\hat{J}_z\right]$$

Now $\hat{j}_+\hat{J}_+ = (\hat{j}_x + i\hat{j}_y)(\hat{J}_x - i\hat{J}_y) = \hat{j}_x\hat{J}_x - i\hat{j}_x\hat{J}_y + i\hat{j}_y\hat{J}_x + \hat{j}_y\hat{J}_y$

& $\hat{j}_-\hat{J}_- = (\hat{j}_x - i\hat{j}_y)(\hat{J}_x + i\hat{J}_y) = \hat{j}_x\hat{J}_x + i\hat{j}_x\hat{J}_y - i\hat{j}_y\hat{J}_x + \hat{j}_y\hat{J}_y$

$$\therefore \hat{j}_+\hat{J}_+ + \hat{j}_-\hat{J}_- = 2\hat{j}_x\hat{J}_x + 2\hat{j}_y\hat{J}_y$$

ie

$$\boxed{\hat{K}_{ORB} = \frac{-\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{1}{2\mu R^2}\left[\hat{\underset{\sim}{J}}^2(\underset{\sim}{t}_i) + \hat{\underset{\sim}{j}}^2 - 2\hat{j}_z\hat{J}_z - 2\hat{j}_+\hat{J}_- - 2\hat{j}_-\hat{J}_+\right]}$$

ORBITAL KE OPERATOR IN TERMS AZIMUTHAL & SHIFT OPERATORS

The advantage of having $\hat{H}^A_{ROT}$, $\hat{H}^B_{ROT}$, & $\hat{K}_{ORB}$ in their present form is that they're built from the following operators: $\hat{\underset{\sim}{j}}$, $\hat{\underset{\sim}{j}}^F$, $\hat{\underset{\sim}{J}}$, $\hat{j}_z$, $\hat{j}^F_z$, $\hat{J}_z$, $\hat{j}_\pm$, & $\hat{J}_\pm$. The fragment-fixed & total fragment AM operators, when acting on an acceptable basis, yield the usual "textbook" eigenvalues & matrix elements (see ZARE ch 1; BUNKER p 175 → 186; THOMPSON p 242 → 245). The remaining body-fixed pseudo AM operators $\hat{J}$, $\hat{J}_z$, & $\hat{J}_\pm$ ~~rotor~~ were shown by Brocks et. al. (their Appendix B) to act on a basis containing the Wigner function $D^{(J)*}_{M\Omega}(\alpha, \beta, \gamma=0)$ & give the regular eigenvalues & matrix elements just mentioned. The implications of their finding make life easy - we can use simple known matrix elements & orthonormality conditions to construct our matrix elements provided we choose a J-M resolved basis (ie a basis containing the $D^{(J)*}_{M\Omega}$ function ... J & M should appear nowhere else.

For the hetero problem, we chose a direct-product basis of body-fixed Wigner functions. Unlike Brahs et. al., we have not assumed a Clebsch-Gordan coupled basis. It is my feeling that Brahs et. al. used vector-coupling as it was convenient to handle their arbitrarily averaged interaction potential. We'll attack the potential operator with a different strategy not requiring C-G coupling; more about this later.
Our basis is:

$$|JM\Omega\, j_A k_A\, j_B k_B \Omega_B\rangle = N^{-1} D^{(J)*}_{M\Omega}(\alpha,\beta,\gamma=0)\, D^{(j_A)*}_{\Omega_A k_A}(\phi_A,\theta_A,\chi_A)\, D^{(j_B)*}_{\Omega_B k_B}(\phi_B,\theta_B,\chi_B)$$

DIRECT-PRODUCT BASIS OF BODY-FIXED WIGNER FUNCTIONS

where: N is a normalising factor

$\alpha,\beta,\gamma=0$ are body-fixed Euler angles (they orient body-fixed Z-axis $\equiv \underset{\sim}{R}$ relative to space-fixed frame) recall $\underset{\sim}{R}$ joins the two fragment centres of mass

ϕ_F,θ_F,χ_F are internal fragment-fixed Euler angles (orienting the geometry of fragment F relative to body-fixed $Z \equiv \underset{\sim}{R}$)

J is total AM quantum no. (for the entire dimer)

M is quantum number for projection of $\hat{\underset{\sim}{J}}$ on to space-fixed Z-axis

Ω is quantum no. associated with $\hat{J}_z$ operator for projection of $\hat{\underset{\sim}{J}}$ on to body-fixed Z-axis. NB $\Omega = \Omega_A + \Omega_B$

j_F is total fragment AM quantum no.

Ω_F is quantum no. associated with fragments F's contribution to projection of $\hat{\underset{\sim}{J}}$ on to body-fixed Z-axis

k_F is quantum no. for projection of $\hat{\underset{\sim}{j}}_F$ on to fragment-fixed Z-axis (associated with $\hat{j}^F_z$)

Wigner functions take the general form: $D^j_{m'm}(\alpha,\beta,\gamma) = e^{-im'\alpha}\, d^j_{m'm}(\beta)\, e^{-im\gamma}$

the symmetry of the Wigner function & the role of β ($\equiv\theta$) will be shown over the page when the above quantum numbers & (some) angles are schematically detailed. [See also Thompson figure 6.1. on pp 212]

The functional form of the reduced matrix element $d^{j}_{m'm}(\beta)$ can be found by visualising a rotating system in the majorana representation & using spinors & the binomial theorem for power-expansion to give

$$d^{j}_{m'm}(\beta) = \sqrt{(j+m')!\,(j-m')!\,(j+m)!\,(j-m)!} \times \sum_{x} \frac{(-1)^{x}\,[\cos\beta/2]^{2j+m'-m-2x}\,[\sin(\beta/2)]^{2x+m-m'}}{(j+m'-x)!\,(j-m-x)!\,x!\,(x+m-m')!}$$

where the summation index x is valid for those values not giving rise to division by zero

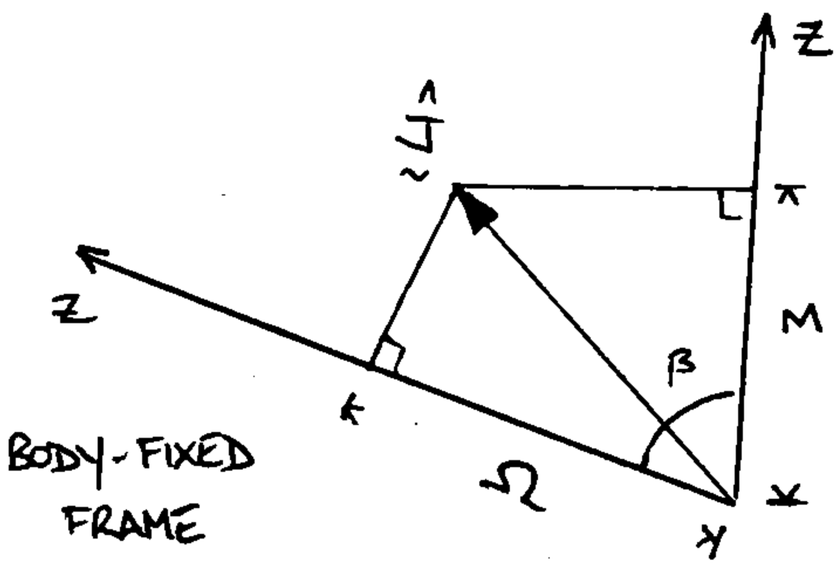
$$\Rightarrow \qquad (m'-m) \leq x \leq \min(j-m,\ j+m')$$

Alternatively for minimisation of for-do loops, $d^{j}_{m'm}(\beta)$ may be expressed in terms a Jacobi polynomial:

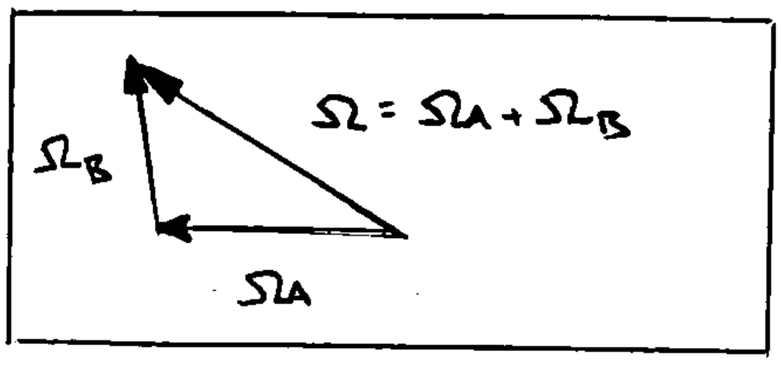
$$d^{j}_{m'm}(\beta) = \sqrt{\frac{(j+m)!\,(j-m)!}{(j+m')!\,(j-m')!}} \times [\cos(\beta/2)]^{m+m'}\,[\sin(\beta/2)]^{m-m'}\,P_{j-m}^{(m-m',\,m+m')}(\cos\beta)$$

Thompson is pretty good for reduced rotation matrix elements (p 218 → 222)

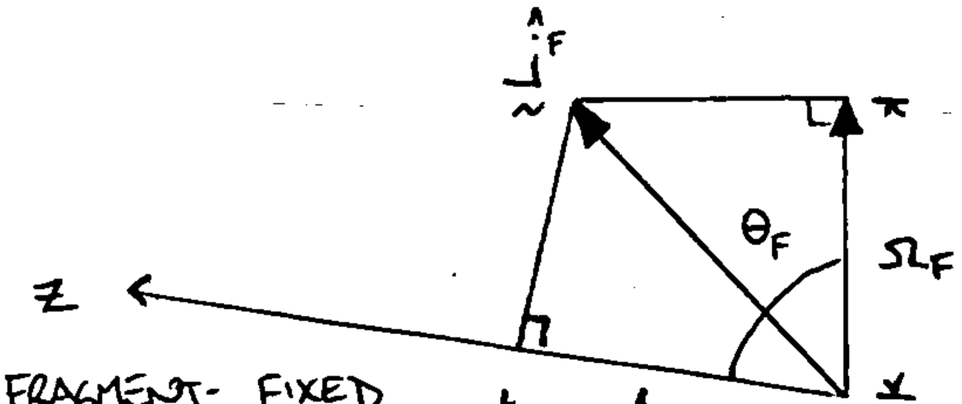
As promised, the schematics of the quantum NO. A etc... : ↗ axis ↗ vector



SPACE-FIXED FRAME



VECTOR IDENITY FOR Ω QUANTUM NO.



Using both the eigenvalues for regular AM operators & orthonormality conditions, we obtain the following matrix elements for the operators appearing in the $\hat{H}^F_{ROT}$ expression. [NB See BUNKER pp 184→185 but make sure you understand his notation: non-existing matrix element $\langle a'|\hat{O}|a\rangle$ $= \langle a-z|\hat{O}|a\rangle = \delta(a' \stackrel{?}{=} a-z) \times \text{eigenvalue} = \delta_{a'(a-z)} \times \text{eigenvalue}$]

$$\langle \Omega' j_A' k_A' j_B' k_B' \Omega_B' | (\hat{j}^F)^2 | \Omega j_A k_A j_B k_B \Omega_B \rangle$$

$$= \delta_{\Omega'\Omega}\, \delta_{j_A' j_A}\, \delta_{k_A' k_A}\, \delta_{j_B' j_B}\, \delta_{k_B' k_B}\, \delta_{\Omega_B' \Omega_B} \cdot j_F(j_F+1)$$

$$\langle \cdots | (\hat{j}^F_z)^2 | \cdots \rangle = \delta_{\Omega'\Omega}\, \delta_{j_A' j_A}\, \delta_{k_A' k_A}\, \delta_{j_B' j_B}\, \delta_{k_B' k_B}\, \delta_{\Omega_B' \Omega_B} \cdot k_F^2$$

$$\langle \cdots | (\hat{j}_+)^2 | \cdots \rangle = \delta_{\Omega'\Omega}\, \delta_{j_A' j_A}\, \delta_{k_F' k_F}\, \delta_{j_B' j_B}\, \delta_{\Omega_B' \Omega_B}\, \delta_{k_F' k_{F-2}}\, C^-_{j_F k_F}\, C^-_{j_F k_{F-1}}$$

$$\langle \cdots | (\hat{j}_-)^2 | \cdots \rangle = \delta_{\Omega'\Omega}\, \delta_{j_A' j_A}\, \delta_{k_F' k_F}\, \delta_{j_B' j_B}\, \delta_{\Omega_B' \Omega_B}\, \delta_{k_F' k_{F+2}}\, C^+_{j_F k_F}\, C^+_{j_F k_{F+1}}$$

where: $C^{\pm}_{j_F k_F} = [j_F(j_F+1) - k_F(k_F \pm 1)]^{1/2}$

$$C^{\pm}_{j_F k_F \pm 1} = [j_F(j_F+1) - (k_F \pm 1)(k_F \pm 2)]^{1/2}$$

$\bar{F}$ denotes the label for the other fragment (e.g. $\bar{A} = B$). The scalar t^2 has been omitted (see note on p. 56)

Recall, $\hat{H}^F_{ROT} = \frac{1}{2}[(Be^{(F)} + Ce^{(F)})(\hat{j}^F)^2 + (2Ae^{(F)} - Be^{(F)} - Ce^{(F)})(\hat{j}^F_z)^2 + \frac{1}{2}(Be^{(F)} - Ce^{(F)})(\hat{j}_+^2 + \hat{j}_-^2)]$

so,

$$\langle \Omega' j_A' k_A' j_B' k_B' \Omega_B' | \hat{H}^A_{ROT} | \Omega j_A k_A j_B k_B \Omega_B \rangle$$

$$= \delta_{\Omega'\Omega}\, \delta_{j_A' j_A}\, \delta_{j_B' j_B}\, \delta_{\Omega_B' \Omega_B} (\delta_{k_B' k_B} h_{j_A k_A' k_A} + \delta_{k_A' k_A} h_{j_B k_B' k_B})$$

where $h_{j_F k_F' k_F} = \frac{1}{2}\delta_{k_F' k_F}[(Be^{(F)} + Ce^{(F)}) j_F(j_F+1) + (2Ae^{(F)} - Be^{(F)} - Ce^{(F)}) k_F^2] + \ldots$

$$\ldots + \frac{1}{4}[\delta_{k_F' k_{F+2}} (Be^{(F)} - Ce^{(F)})\, C^+_{j_F k_F} C^+_{j_F k_{F+1}} + \delta_{k_F' k_{F-2}} (Be^{(F)} - Ce^{(F)})\, C^-_{j_F k_F} C^-_{j_F k_{F-1}}]$$

COMULATIVE FRAGMENT KINETIC ENERGY MATRIX ELEMENTS

NOTE TWO
STRIKE OUTS

At the time of writing, the Watson code has been set up to handle a fixed value for R. Thus, we may immediately truncate our expression for $\hat{K}_{ORB}$ by removing the differential radial contribution.

$$\hat{K}_{ORB}\big|_{\text{fixed } R} = \frac{1}{2\mu R^2}\left[\hat{J}^2 + \hat{j}^2 - 2\hat{j}_z\hat{J}_z - \hat{j}_+\hat{J}_+ - \hat{j}_-\hat{J}_-\right]$$

which may be rewritten with the use of the following identities

$$\hat{j}^2 = \hat{j}_A^2 + \hat{j}_B^2 + 2\hat{j}_z^A\hat{j}_z^B + \hat{j}_+^A\hat{j}_-^B + \hat{j}_-^A\hat{j}_+^B$$

$$\hat{j}_\pm = \hat{j}_\pm^A + \hat{j}_\pm^B$$

$$\therefore \hat{K}_{ORB} = \frac{1}{2\mu R^2}\left[\hat{J}^2 + \hat{j}_A^2 + \hat{j}_B^2 + 2\hat{j}_z^A\hat{j}_z^B + \hat{j}_+^A\hat{j}_-^B + \hat{j}_-^A\hat{j}_+^B - 2\hat{j}_z\hat{J}_z - \hat{j}_+\hat{J}_+ - \hat{j}_-\hat{J}_-\right]$$

$$\langle \Sigma\, j_A' k_A' j_B' k_B' \Sigma_B' \,|\, \hat{J}^2 \,|\, \Sigma\, j_A k_A j_B k_B \Sigma_B\rangle$$

$$= \delta_{\Sigma'\Sigma}\delta_{j_A' j_A}\delta_{k_A' k_A}\delta_{j_B' j_B}\delta_{k_B' k_B}\delta_{\Sigma_B'\Sigma_B}\cdot \hbar^2 J(J+1)$$

$$\langle \cdots |(\hat{j}_A)^2| \cdots\rangle = \delta_{\Sigma'\Sigma}\delta_{j_A' j_A}\delta_{k_A' k_A}\delta_{j_B' j_B}\delta_{k_B' k_B}\delta_{\Sigma_B'\Sigma_B}\cdot \hbar^2 j_A(j_A+1)$$

$$\langle \cdots |(\hat{j}_B)^2| \cdots\rangle = \delta_{\Sigma'\Sigma}\delta_{j_A' j_A}\delta_{k_A' k_A}\delta_{j_B' j_B}\delta_{k_B' k_B}\delta_{\Sigma_B'\Sigma_B}\,\hbar^2 j_B(j_B+1)$$

$$\langle \cdots |\,\hat{j}_z^A\,| \cdots\rangle = \delta_{\Sigma'\Sigma}\delta_{j_A' j_A}\delta_{k_A' k_A}\delta_{j_B' j_B}\delta_{k_B' k_B}\delta_{\Sigma_B'\Sigma_B}\,\hbar\Sigma_A$$

$$\langle \cdots |\,\hat{j}_z^B\,| \cdots\rangle = \delta_{\Sigma'\Sigma}\delta_{j_A' j_A}\delta_{k_A' k_A}\delta_{j_B' j_B}\delta_{k_B' k_B}\delta_{\Sigma_B'\Sigma_B}\,\hbar\Sigma_B$$

$$\langle \cdots |\,\hat{j}_z\hat{J}_z\,| \cdots\rangle \equiv \langle \cdots |\,\hat{J}_z^2\,| \cdots\rangle = \delta_{\Sigma'\Sigma}\delta_{j_A' j_A}\delta_{k_A' k_A}\delta_{j_B' j_B}\delta_{k_B' k_B}\delta_{\Sigma_B'\Sigma_B}\,\hbar^2\Sigma^2$$

$$\langle \cdots |\,\hat{J}_+\,| \cdots\rangle = \delta_{\Omega'\Sigma-1}\delta_{j_A' j_A}\delta_{k_A' k_A}\delta_{j_B' j_B}\delta_{k_B' k_B}\delta_{\Sigma_B'\Sigma_B}\,\hbar\, C^-_{J\Sigma}$$

$$\langle \cdots |\,\hat{J}_-\,| \cdots\rangle = \delta_{\Omega'\Sigma+1}\delta_{j_A' j_A}\delta_{k_A' k_A}\delta_{j_B' j_B}\delta_{k_B' k_B}\delta_{\Sigma_B'\Sigma_B}\,\hbar\, C^+_{J\Sigma}$$

$$\langle \cdots |\,\hat{j}_+^F\,| \cdots\rangle = \delta_{\Sigma'\Sigma}\delta_{j_A' j_A}\delta_{k_A' k_A}\delta_{j_B' j_B}\delta_{k_B' k_B}\cancel{\delta_{S_F' S_F}}\,\delta_{\Sigma_F'\Sigma_{F-1}}\, C^-_{j_F\Omega_F}\cdot\hbar$$

$$\langle \cdots |\,\hat{j}_-^F\,| \cdots\rangle = \delta_{\Sigma'\Sigma}\delta_{j_A' j_A}\delta_{k_A' k_A}\delta_{j_B' j_B}\delta_{k_B' k_B}\cancel{\delta_{S_F' S_F}}\,\delta_{\Sigma_F'\Sigma_{F+1}}\, C^+_{j_F\Sigma_F}\,\hbar$$

Using the fact that $(\delta_{ij})^2 = \delta_{ij}$

$\therefore$

then

but $\delta_{\Sigma' \Sigma_A - 1} = \delta_{\Sigma_B' \Sigma_B + 1}$, such that:

$$\langle \cdots | \hat{J}_\pm^A | \cdots \rangle = \delta_{\Sigma'\Sigma} \delta_{j'_A j_A} \delta_{k'_A k_A} \delta_{j'_B j_B} \delta_{k'_B k_B} \delta_{\Sigma'_B \Sigma_B \pm 1} C^{\mp}_{j_A \Sigma_A} \hbar$$

$$\langle \cdots | \hat{J}_\pm^B | \cdots \rangle = \delta_{\Sigma'\Sigma} \delta_{j'_A j_A} \delta_{k'_A k_A} \delta_{j'_B j_B} \delta_{k'_B k_B} \delta_{\Sigma'_B \Sigma_B \mp 1} C^{\mp}_{j_B \Sigma_B} \hbar$$

$$\therefore \langle \cdots | \hat{J}_+^A \hat{J}_-^B | \cdots \rangle = \hbar^2 \delta_{\Sigma'\Sigma} \delta_{j'_A j_A} \delta_{k'_A k_A} \delta_{j'_B j_B} \delta_{k'_B k_B} \delta_{\Sigma'_B \Sigma_B + 1} C^{-}_{j_A \Sigma_A} C^{+}_{j_B \Sigma_B}$$

$$\langle \cdots | \hat{J}_-^A \hat{J}_+^B | \cdots \rangle = \hbar^2 \delta_{\Sigma'\Sigma} \delta_{j'_A j_A} \delta_{k'_A k_A} \delta_{j'_B j_B} \delta_{k'_B k_B} \delta_{\Sigma'_B \Sigma_B - 1} C^{+}_{j_A \Sigma_A} C^{-}_{j_B \Sigma_B}$$

$$\langle \cdots | \hat{J}_\pm^A \hat{J}_\pm^B | \cdots \rangle = \hbar^2 \delta_{\Sigma' \Sigma \mp 1} \delta_{j'_A j_A} \delta_{k'_A k_A} \delta_{j'_B j_B} \delta_{k'_B k_B} \delta_{\Sigma'_B \Sigma_B} C^{\mp}_{J\Sigma} C^{\mp}_{j_A \Omega_A}$$

$$\langle \cdots | \hat{J}_\pm^B \hat{J}_\pm^B | \cdots \rangle = \hbar^2 \delta_{\Sigma' \Sigma \mp 1} \delta_{j'_A j_A} \delta_{k'_A k_A} \delta_{j'_B j_B} \delta_{k'_B k_B} \delta_{\Sigma'_B \mp 1} C^{\mp}_{J\Sigma} C^{\mp}_{j_B \Sigma_B}$$

then

$$\langle \Sigma' j'_A k'_A j'_B k'_B \Sigma'_B | \hat{K}_{OR_B} | \Sigma j_A k_A j_B k_B \Sigma_B \rangle$$

$$= \delta_{j'_A j_A} \delta_{k'_A k_A} \delta_{j'_B j_B} \delta_{k'_B k_B} \frac{\hbar^2}{2\mu R^2} \Big\{ \delta_{\Sigma'\Sigma} \delta_{\Sigma'_B \Sigma_B} [J(J+1) + \cdots$$

$$\cdots + j_A(j_A+1) + j_B(j_B+1) + 2\Sigma_A \Sigma_B - 2\Sigma^2] + \cdots$$

$$\cdots + \delta_{\Sigma'\Sigma} \delta_{\Sigma'_B \Sigma_B + 1} C^{-}_{j_A \Sigma_A} C^{+}_{j_B \Sigma_B} + \delta_{\Sigma'\Sigma} \delta_{\Sigma'_B \Sigma_B - 1} C^{+}_{j_A \Sigma_A} C^{-}_{j_B \Sigma_B} + \cdots$$

$$\cdots - \delta_{\Sigma' \Sigma + 1} C^{+}_{J\Sigma} [\delta_{\Sigma'_B \Sigma_B} C^{+}_{j_A \Sigma_A} + \delta_{\Sigma_B' \Sigma_B + 1} C^{+}_{j_B \Sigma_B}] + \cdots$$

$$\cdots - \delta_{\Sigma' \Sigma - 1} C^{-}_{J\Sigma} [\delta_{\Sigma'_B \Sigma_B} C^{-}_{j_A \Sigma_A} + \delta_{\Sigma_B' \Sigma_B - 1} C^{-}_{j_B \Sigma_B}] \Big\}$$

MATRIX ELEMENTS FOR THE ORBITAL KINETIC ENERGY OPERATOR

The matrix elements of $\hat{V}_{INT}$ can be handled by a discrete variable representation (DVR). I will write about that process elsewhere. Once the DVR issue is understood, the Schrödinger eq. for the intermolecular dissociation of ketene may be attacked with

$$\hat{H} = \hat{H}^A_{ROT} + \hat{H}^B_{ROT} + \hat{K}_{ROT} + \hat{V}_{INT}$$

QED