A.5b) Normal coordinate construction based on internal displacement coordinates

F-G matrix formalism:

Start from $2T = \mathbf{p}_r^t \mathbf{G} \mathbf{p}_r$

$2V = \mathbf{r}^t \mathbf{F}^{(r)} \mathbf{r}$

with $\mathbf{G} = \mathbf{B}\mathbf{M}^{-1}\mathbf{B}^t$

(see lecture notes for detailed definitions).

Hamiltonian:

$$H = T + V = ½\, \mathbf{p}_r^t \mathbf{G} \mathbf{p}_r + ½\, \mathbf{r}^t \mathbf{F}^{(r)} \mathbf{r}$$

Diagonalize real symmetric matrices $\mathbf{G}$ and $\mathbf{F}^{(r)}$ [(3N-6) x (3N-6)] by the following steps:

1) Define orthogonal matrix $\mathbf{Z}$ by $\mathbf{Z}^t\mathbf{Z} = \mathbf{1}$

$$\mathbf{Z}^t\mathbf{G}\mathbf{Z} = \Gamma \quad \text{with } \Gamma = \mathrm{diag}(\gamma_i)$$

Define further $\mathbf{L_0} = \mathbf{Z}\,\Gamma^{½}$ $(\gamma_i \geq 0)$

$$\Rightarrow \quad 2T = \mathbf{p}_r^t \mathbf{Z}\mathbf{Z}^t\mathbf{G}\mathbf{Z}\mathbf{Z}^t\mathbf{p}_r = \mathbf{p}_r^t \mathbf{Z}\Gamma^{½}\Gamma^{½}\mathbf{Z}^t\mathbf{p}_r =$$

$$= \mathbf{p}_r^t \mathbf{L_0}\, \mathbf{L_0}^t \mathbf{p}_r = \tilde{\mathbf{p}}_r^t \tilde{\mathbf{p}}_r$$

with $\tilde{\mathbf{p}}_r = \mathbf{L_0}^t \mathbf{p}_r$ and $\mathbf{r} = \mathbf{L}_0 \tilde{\mathbf{r}}$

$$\Rightarrow \quad 2V = \mathbf{r}^t \mathbf{F}^{(r)} \mathbf{r} = \tilde{\mathbf{r}}^t \mathbf{L}_0^t \mathbf{F}^{(r)} \mathbf{L}_0 \tilde{\mathbf{r}} = \tilde{\mathbf{r}}^t \tilde{\mathbf{F}}^{(r)} \tilde{\mathbf{r}}$$

with $\tilde{\mathbf{F}}^{(r)} = \mathbf{L_0}^t \mathbf{F}^{(r)} \mathbf{L_0}$

being the scaled + transformed "internal" force constant matrix.

2) Diagonalize $\tilde{\mathbf{F}}^{(r)}$ with orthogonal matrix **C** to give ($\mathbf{\Lambda} = \mathrm{diag}(\lambda_i)$)

$$H = T + V = \frac{1}{2}\tilde{\mathbf{p}}_r{}^t \mathbf{C}\mathbf{C}^t \tilde{\mathbf{p}}_r + \frac{1}{2}\tilde{\mathbf{r}}^t \mathbf{C}\mathbf{C}^t \tilde{\mathbf{F}}^{(r)} \mathbf{C}\mathbf{C}^t \tilde{\mathbf{r}}$$

$$= \frac{1}{2}\mathbf{p_q}{}^t \mathbf{p_q} + \frac{1}{2}\mathbf{q}^t \Lambda \mathbf{q}\ ; \quad \mathbf{q} = \mathbf{C}^t \tilde{\mathbf{r}}$$

C is analogous to Cartesian displacements. **q** is the vector of mass-weighted normal coordinates. Re-scaling to define dimensionless normal coordinates same as with Cartesian displacements coordinates.

Overall: $\mathbf{r} = \mathbf{L}_0 \tilde{\mathbf{r}} = \mathbf{L}_0 \mathbf{C}\mathbf{q}$ [all matrices (3N-6)x(3N-6)]

$$\mathbf{r} = \mathbf{Z}\,\mathbf{\Gamma}^{1/2}\,\mathbf{C}\,\mathbf{q} \equiv \mathbf{L}\,\mathbf{q}$$

with $\boxed{\mathbf{L} = \mathbf{Z}\,\mathbf{\Gamma}^{1/2}\,\mathbf{C}}$

L-matrix of Wilson, Decius and Cross
(Molecular Vibrations, McGraw-Hill, 1955)