Cartesian way ("new4")

$$2H = \dot{\mathbf{X}}^t\mathbf{M}\dot{\mathbf{X}} + \mathbf{X}^t\mathbf{F}\mathbf{X}$$

mass weighted coordinates $\mathbf{x} = \sqrt{\mathbf{M}}\mathbf{X}$ $\quad \mathbf{f} = \sqrt{\mathbf{M}}^{-1}\mathbf{F}\sqrt{\mathbf{M}}^{-1}$

$$2H = \dot{\mathbf{x}}^t\dot{\mathbf{x}} + \mathbf{x}^t\mathbf{f}\mathbf{x}$$

normal mode coordinates $\mathbf{x} = \mathbf{s}\mathbf{Q}$ $\quad \mathbf{X} = \mathbf{S}\mathbf{Q}$ $\quad \mathbf{s} = \sqrt{\mathbf{M}}\mathbf{S}$

$$2H = \dot{\mathbf{Q}}^t\mathbf{s}^t\mathbf{s}^t\dot{\mathbf{Q}} + \mathbf{Q}^t\mathbf{s}^t\mathbf{f}\mathbf{s}\mathbf{Q}$$

$$\mathbf{s}\mathbf{s}^t = \mathbf{E} \qquad \boxed{\mathbf{s}\mathbf{f}\mathbf{s}^t = \boldsymbol{\omega}^2}$$

$$2H = \dot{\mathbf{Q}}^2 + \boldsymbol{\omega}^2\mathbf{Q}^2 = \sum_{i=1}^{3N}(\dot{Q}_i^{\,2} + \omega_i^{\,2}Q_i^{\,2})$$

Internal-Cartesian Transformation (new1.f, bumat.f)

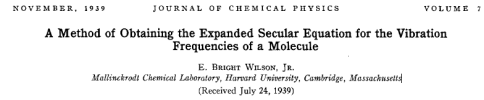
$$\mathbf{I} = \mathbf{B}\mathbf{X}$$

add translations and rotations:

$$\mathbf{X} = \mathbf{B}^{-1}\mathbf{I}$$

"3N = (3N x (3N-6+6) (3N-6+6)"

Harmonic Vibrational Problem in Internal Coordinates



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A Method of Obtaining the Expanded Secular Equation for the Vibration Frequencies of a Molecule

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$$2H = \dot{\mathbf{X}}^t\mathbf{M}\dot{\mathbf{X}} + \mathbf{X}^t\mathbf{F}\mathbf{X}$$

$$2H = \dot{\mathbf{I}}^t\mathbf{B}^{-1t}\mathbf{M}\mathbf{B}^{-1}\mathbf{I} + \mathbf{I}^t\mathbf{B}^{-1t}\mathbf{F}\mathbf{B}^{-1}\mathbf{I}$$

$\mathbf{I} = \mathbf{L}\mathbf{Q}$ $\quad \mathbf{G}^{-1} = \mathbf{B}^{-1t}\mathbf{M}\mathbf{B}^{-1}$ $\quad \mathbf{G} = \mathbf{B}\ {}^t\mathbf{M}^{-1}\mathbf{B}$ $\quad \mathbf{F}_I = \mathbf{B}^{-1t}\mathbf{F}\mathbf{B}^{-1}$

$$2H = \dot{\mathbf{Q}}^t\mathbf{L}^t\mathbf{G}^{-1}\mathbf{L}\dot{\mathbf{Q}} + \mathbf{Q}^t\mathbf{L}^t\mathbf{F}_I\mathbf{L}\mathbf{Q}$$

${}^t\mathbf{L}^t\mathbf{G}^{-1}\mathbf{L} = \mathbf{E}$ $\quad \mathbf{L}^t\mathbf{F}_I\mathbf{L} = \boldsymbol{\omega}^2$

$\mathbf{G} = \mathbf{L}\mathbf{L}^t$ $\quad \mathbf{L}\mathbf{L}^t\mathbf{F}_I\mathbf{L} = \mathbf{L}\boldsymbol{\omega}^2$ $\quad \boxed{\mathbf{G}\mathbf{F}_I\mathbf{L} = \mathbf{L}\boldsymbol{\omega}^2}$

$$2H = \dot{\mathbf{Q}}^2 + \boldsymbol{\omega}^2\mathbf{Q}^2 = \sum_{i=1}^{3N-6}(\dot{Q}_i^{\,2} + \omega_i^{\,2}Q_i^{\,2})$$

Internal way ("ftry.f")

$$\boxed{\mathbf{G}\mathbf{F}_I\mathbf{L} = \mathbf{L}\boldsymbol{\omega}^2}$$

solve $\quad \mathbf{A}^t\mathbf{F}_I\mathbf{A} = \mathbf{t}$

$$\mathbf{F}_I = (\mathbf{A}\sqrt{\mathbf{t}})^t(\mathbf{A}\sqrt{\mathbf{t}}) = \mathbf{a}^t.\mathbf{a}$$

$$\mathbf{a}\mathbf{G}\mathbf{a}^t\mathbf{a}\mathbf{L} = \mathbf{a}\mathbf{L}\boldsymbol{\omega}^2$$

$$\mathbf{Y}\mathbf{l} = \mathbf{l}\boldsymbol{\omega}^2$$

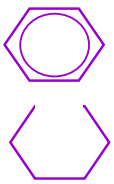
Symmetrically adapted coordinates (new1- FILE.UMA)

when number of internals M > 3N-6

$$\mathbf{Y} = \mathbf{U}\mathbf{I} = \mathbf{U}\mathbf{B}\mathbf{X}$$

3N-6 $\quad$ (3N-6)xM M $\quad$ (3N-6)xM Mx(3N) (3N)

$$\mathbf{B} \rightarrow \mathbf{U}\mathbf{B}$$



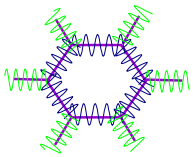
Force field in internals M > 3N

$$\mathbf{F}_I = \mathbf{B}^{-1t}\mathbf{F}\mathbf{B}^{-1}$$

B

M x 3N

F ?



RMS fit (bumatc6.f):

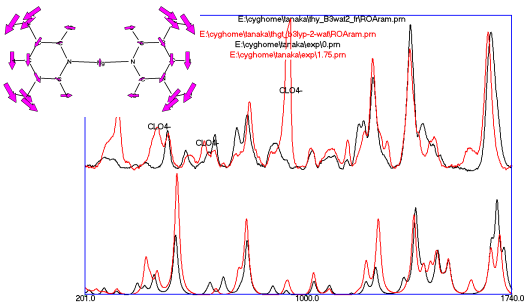
$$\sigma = (\mathbf{B}^t\mathbf{F}_i\mathbf{B} - \mathbf{F}_c)^2 + \alpha\mathbf{F}_c^{\,2} \rightarrow \min$$

$$\sigma = \sum_{i=1}^{N}\sum_{l=1}^{N}\sum_{j=1}^{M}\sum_{k=1}^{M} B_{io}^t B_{pl} B_{ij}^t F_{i,jk} B_{kl} + \alpha F_{i,op} = \sum_i^N \sum_l^N B_{io}^t B_{pl} F_{c,il}$$

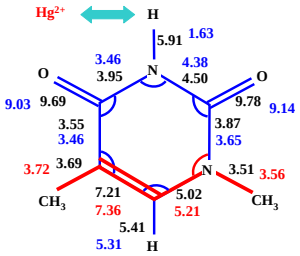
$$\mathbf{A}\mathbf{F}_i = \mathbf{C}$$

$$\mathbf{F}_i = \mathbf{A}^{-1}\mathbf{C}$$

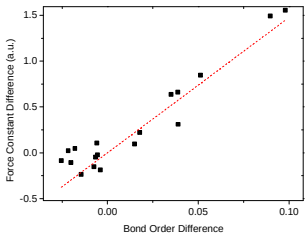
Example: Hg DNA binding



Calculated (B3LYP/6-31+G**/MWB60/PCM(H2O) changes in internal coordinate force field of thymine upon Hg binding



Calculated dependence of changes in stretching force constants on the difference of the bond order



Procedure:

1) calculate FF (by Gaussian, freq)
2) use **gar9** -> FILE.FC, FILE.X
3) "**new1 a**" all possible coordinates
4) (optional) check FILE.UMA
5) use **bumatc6** for all and **bumatd** for diagonals only
6) - INTY.FC (IFC.TXT-diagonal) .. the internal FF
7) (optional) get frequencies and PED via **goin** and **ftry**