

0.1 Hessian Diagonalization

Frequencies and normal modes are obtained from Hessian diagonalization, following the method from <https://tinyurl.com/4a75skfm>, which in turn uses (V. Barone, JCP, 2005, 122, 014108; V. Barone et al. IJQ. Chem., 2012, 112, 2185). Without projection frequencies and normal modes are just (transformed) eigenvalues and eigenvectors of the Hessian,

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 E}{\partial x_1^2} & \frac{\partial^2 E}{\partial x_1 y_1} & \frac{\partial^2 E}{\partial x_1 z_1} & \cdots \\ \frac{\partial^2 E}{\partial y_1 x_1} & \frac{\partial^2 E}{\partial y_1^2} & \frac{\partial^2 E}{\partial y_1 z_1} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (1)$$

appropriately mass weighted,

$$\mathbf{H}_w = \begin{pmatrix} \frac{H_{11}}{\sqrt{m_1 m_1}} & \cdots & \frac{H_{1,3i}}{\sqrt{m_1 m_i}} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (2)$$

which is real symmetric so Hermitian ($\mathbf{H} \in \mathbb{R}^{3N \times 3N}$ for a system of N atoms). The frequencies are then square roots of the eigenvalues i.e. $\nu_i = \sqrt{\lambda_i}$ ^a and the normal modes \mathbf{s}_i where,

$$\mathbf{H}_w = \mathbf{S} \mathbf{D} \mathbf{S}^T \quad ; \quad \mathbf{D} = \begin{pmatrix} \lambda_1 & 0 & \cdots \\ 0 & \lambda_2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad ; \quad \mathbf{S} = \begin{pmatrix} \uparrow & \uparrow & \cdots \\ \mathbf{s}_1 & \mathbf{s}_2 & \cdots \\ \downarrow & \downarrow & \cdots \end{pmatrix} \quad (3)$$

To project out translational and rotational motion for a non linear molecule requires a transformation of \mathbf{H}_w ,

$$\mathbf{H}'_w = \mathbf{T}^T \mathbf{H}_w \mathbf{T} \quad ; \quad \mathbf{H}'_w = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \bar{\mathbf{H}}_w \end{pmatrix} \quad (4)$$

where

$$\mathbf{T} = \begin{pmatrix} \uparrow & \uparrow & \cdots \\ \hat{\mathbf{t}}_1 & \hat{\mathbf{t}}_2 & \cdots \\ \downarrow & \downarrow & \cdots \end{pmatrix} \quad (5)$$

and the columns of \mathbf{M} are,

$$\mathbf{t}_1 = \begin{bmatrix} (\hat{\mathbf{e}}_1)_1 \\ \vdots \\ (\hat{\mathbf{e}}_1)_N \end{bmatrix} \quad ; \quad \mathbf{t}_2 = \begin{bmatrix} (\hat{\mathbf{e}}_2)_1 \\ \vdots \\ (\hat{\mathbf{e}}_2)_N \end{bmatrix} \quad ; \quad \mathbf{t}_3 = \begin{bmatrix} (\hat{\mathbf{e}}_3)_1 \\ \vdots \\ (\hat{\mathbf{e}}_3)_N \end{bmatrix} \quad (6)$$

^aWith an appropriate unit conversion.

where $\hat{\mathbf{e}}_k$ is a unit vector in 3D (i.e. $\hat{\mathbf{e}}_1 = (1, 0, 0)^T$). The rotation vectors are

$$\mathbf{t}_4 = \begin{bmatrix} \mathbf{e}_1 \times \mathbf{r}_1 \\ \vdots \\ \mathbf{e}_1 \times \mathbf{r}_N \end{bmatrix} ; \quad \mathbf{t}_5 = \begin{bmatrix} \mathbf{e}_2 \times \mathbf{r}_1 \\ \vdots \\ \mathbf{e}_2 \times \mathbf{r}_N \end{bmatrix} ; \quad \mathbf{t}_6 = \begin{bmatrix} \mathbf{e}_3 \times \mathbf{r}_1 \\ \vdots \\ \mathbf{e}_3 \times \mathbf{r}_N \end{bmatrix} \quad (7)$$

where \mathbf{r}_i is the vector from the centre of mass of the system to the atom i . The remaining \mathbf{t}_n are filled with random vectors that are orthogonal to \mathbf{t}_1 - \mathbf{t}_6 , which can be achieved by QR factorisation once the remaining elements of \mathbb{T} have been seeded with random numbers. Normalisation requires,

$$\hat{\mathbf{t}}_i = \frac{\mathbf{M}^{1/2} \mathbf{t}_i}{|\mathbf{M}^{1/2} \mathbf{t}_i|} ; \quad \mathbf{M} = \begin{pmatrix} m_1 & 0 & 0 & 0 & \cdots \\ 0 & m_1 & 0 & 0 & \cdots \\ 0 & 0 & m_1 & 0 & \cdots \\ 0 & 0 & 0 & m_2 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (8)$$

where m_i is the mass of atom i .

Projected frequencies are then obtained from the submatrix of \mathbf{H}'_w ,

$$\bar{\mathbf{H}}_w = \bar{\mathbf{S}} \bar{\mathbf{D}} \bar{\mathbf{S}}^T ; \quad \bar{\mathbf{S}} = \begin{pmatrix} \uparrow \\ \bar{\mathbf{s}}_7 & \cdots \\ \downarrow \end{pmatrix} ; \quad \bar{\mathbf{D}} = \begin{pmatrix} \bar{\lambda}_7 & 0 & \cdots \\ 0 & \bar{\lambda}_8 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad (9)$$

with $\bar{\nu}_{0-6} = 0 \text{ cm}^{-1}$, while the eigenvectors are,

$$\mathbf{s}_i = \mathbb{T} \mathbf{s}'_i ; \quad \mathbf{S}' = \begin{pmatrix} \uparrow \\ \mathbf{s}'_1 & \cdots \\ \downarrow \end{pmatrix} = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \bar{\mathbf{S}} \end{pmatrix} \quad (10)$$

which correspond to the normal modes in the original coordinates. For a linear molecule the vibrational frequencies are then the $3N - 5$ modes, rather than $3N - 6$, with \mathbf{H}'_w contains a different number of non-zero entries.