## 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,

$$
\mathsf{H} = \begin{pmatrix} \frac{\partial^2 E}{\partial x_1^2} & \frac{\partial^2 E}{\partial x_1 y_1} & \frac{\partial^2 E}{\partial x_1 z_1} & \cdots \\ \frac{\partial^2 E}{\partial y_1 x_1} & \frac{\partial^2 E}{\partial y_1^2} & \frac{\partial^2 E}{\partial y_1 z_1} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{1}
$$

appropriately mass weighted,

$$
\mathsf{H}_{\mathrm{w}} = \begin{pmatrix} \frac{\mathsf{H}_{11}}{\sqrt{m_1 m_1}} & \cdots & \frac{\mathsf{H}_{1,3i}}{\sqrt{m_1 m_i}} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{2}
$$

which is real symmetric so Hermitian ($\mathsf{H} \in \mathbb{R}^{3N \times 3N}$ 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 $\boldsymbol{v}_i$ where,

$$
\mathsf{H}_{\mathrm{w}} = \mathsf{S} \mathsf{D} \mathsf{S}^T \quad ; \quad \mathsf{D} = \begin{pmatrix} \lambda_1 & 0 & \cdots \\ 0 & \lambda_2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad ; \quad \mathsf{S} = \begin{pmatrix} \uparrow & \uparrow & \\ \boldsymbol{s}_1 & \boldsymbol{s}_2 & \cdots \\ \downarrow & \downarrow & \end{pmatrix} \tag{3}
$$

To project out translational and rotational motion for a non linear molecule requires a transformation of $\mathsf{H}_{\mathrm{w}}$,

$$
\mathsf{H}'_{\mathrm{w}} = \mathsf{T}^T \mathsf{H}_{\mathrm{w}} \mathsf{T} \quad ; \quad \mathsf{H}'_{\mathrm{w}} = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \bar{\mathsf{H}}_{\mathrm{w}} \end{pmatrix} \tag{4}
$$

where

$$
\mathsf{T} = \begin{pmatrix} \uparrow & \uparrow & \\ \hat{\boldsymbol{t}}_1 & \hat{\boldsymbol{t}}_2 & \cdots \\ \downarrow & \downarrow & \end{pmatrix} \tag{5}
$$

and the columns of $\mathsf{M}$ are,

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

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[a]With an appropriate unit conversion.

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

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

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

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

where $m_i$ is the mass of atom $i$.

Projected frequencies are then obtained from the submatrix of $\mathsf{H}'_{\mathrm{w}}$,

$$\bar{\mathsf{H}}_{\mathrm{w}} = \bar{\mathsf{S}}\bar{\mathsf{D}}\bar{\mathsf{S}}^T \quad ; \quad \bar{\mathsf{S}} = \begin{pmatrix} \uparrow \\ \bar{\boldsymbol{s}}_7 & \cdots \\ \downarrow \end{pmatrix} \quad ; \quad \bar{\mathsf{D}} = \begin{pmatrix} \bar{\lambda}_7 & 0 & \cdots \\ 0 & \bar{\lambda}_8 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \tag{9}$$

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

$$\boldsymbol{s}_i = \mathsf{T}\boldsymbol{s}'_i \quad ; \quad \mathsf{S}' = \begin{pmatrix} \uparrow \\ \boldsymbol{s}'_1 & \cdots \\ \downarrow \end{pmatrix} = \begin{pmatrix} \boldsymbol{0} & \boldsymbol{0} \\ \boldsymbol{0} & \bar{\mathsf{S}} \end{pmatrix} \tag{10}$$

which correspond to the normal modes in the original coordinates.