

Supplementary Information: Can we use on-the-fly quantum simulations to connect molecular structure and sunscreen action?

This document contains additional information relating to the simulations of MAA-like molecules performed in the manuscript.

Active coordinate selection

Tables 1, 3, 5 and 7 contain the calculated gradients and non-adiabatic coupling terms for selected normal-modes for each of the molecules 1a - 4a. Tables 2, 4, 6 and 8 contain the selected mode combinations used in increasingly high-dimensional subsequent DD-MCTDH simulations for each molecule.

Mode	α	No. DVR	Grad. (10^{-3} au)	NACT (10^{-3} au)
39	0.01	11	3.4	-5.5
38	0.01	9	3.2	1.1
16	0.01	19	-2.6	-6.4
37	0.01	9	2.4	-1.4
29	0.01	7	-1.6	-1.4
6	0.01	21	1.5	-5.0
31	0.01	5	-1.4	-0.57
28	0.01	7	-1.3	0.50
2	0.01	7	0.17	10
11	0.01	11	1.3	-8.5
1	0.01	7	-0.13	5.9
9	0.01	5	-0.0043	5.6
8	0.01	21	-0.39	5.3

Table 1: Selected modes for molecule 1a.

No. of dimensions	Mode combinations
6	{39,38}, {16,11}, {37,2}
8	{39,38}, {16,11,1}, {37,2}, {29}
10	{39,38,16}, {37,29,6}, {2,1}, {11,9}
12	{39,38,16}, {37,6}, {29,31}, {2,1}, {11,9,8}

Table 2: Mode combinations for molecule 1a

Mode	α	No. DVR	Grad. (10^{-3} au)	NACT (10^{-3} au)
34	0.02	15	5.5	1.6
36	0.01	19	3.9	-6.6
12	0.01	15	-2.9	-6.2
23	0.01	7	2.0	0.23
35	0.01	7	-2.0	-2.6
5	0.01	21	-1.9	4.9
11	0.01	11	-1.5	5.1
8	0.01	13	1.5	-6.9
9	0.01	13	1.5	0.65
4	0.04	31	-1.4	6.4
2	0.02	7	-0.023	-13
14	0.01	7	-0.51	-7.7
6	0.01	15	-0.50	-6.9
1	0.01	17	-0.47	-5.1

Table 3: Selected modes for molecule 2a.

No. of dimensions	Mode combinations
6	{34,12,23}, {36}, {2,14}
8	{34,35}, {36}, {12,23,8}, {2,14}
10	{34,12,23}, {36}, {35,5}, {2,14}, {8,6}
12	{34,12,23}, {36,11}, {35,5}, {2,14,8}, {6,4}
13	{34,12,23}, {36,35}, {5,4,9}, {11,14,1}, {2,8,6}

Table 4: Mode combinations for molecule 2a

Mode	α	No. DVR	Grad. (10^{-3} au)	NACT (10^{-3} au)
38	0.01	9	3.1	-1.6×10^{-3}
15	0.01	15	-2.3	1.2×10^{-2}
41	0.01	7	2.2	2.3×10^{-2}
37	0.01	7	-1.2	1.2×10^{-2}
9	0.01	11	-1.0	-2.5×10^{-3}
39	0.01	5	0.88	3.0×10^{-5}
20	0.01	7	-0.81	9.2×10^{-3}
40	0.01	9	-9.3×10^{-4}	-34
5	0.01	5	7.0×10^{-4}	15
35	0.01	5	-1.3×10^{-4}	-15
8	0.01	5	1.3×10^{-4}	14
29	0.01	5	3.3×10^{-4}	14
42	0.01	5	-2.5×10^{-4}	-12

Table 5: Selected modes for molecule 3a.

No. of dimensions	Mode combinations
6	{38,15}, {41}, {37}, {40,5}
8	{38,15}, {41}, {37,9}, {40,5,35}
10	{38,15,41}, {37,9}, {39}, {40,5,35}, {8}
12	{38,15,41}, {37,9}, {39}, {20}, {40,5,35}, {8,29}

Table 6: Mode combinations for molecule 3a

Mode	α	No. DVR	Grad. (10^{-3} au)	NACT (10^{-3} au)
33	0.01	11	3.8	-1.3×10^{-2}
13	0.01	13	-1.6	-3.4×10^{-2}
10	0.01	11	1.3	0.11
21	0.01	7	-1.3	1.5×10^{-2}
19	0.01	5	0.93	1.0×10^{-2}
37	0.01	5	0.85	1.8×10^{-2}
6	0.01	9	-0.83	-5.6×10^{-2}
38	0.01	7	-1.4×10^{-4}	32
26	0.01	5	-1.5×10^{-3}	-13
39	0.01	5	-1.2×10^{-3}	11
5	0.01	5	2.1×10^{-3}	-11
48	0.04	5	1.6×10^{-3}	-9.5
1	0.01	11	1.9×10^{-3}	3.2
2	0.01	13	0.18	-8.9×10^{-3}

Table 7: Selected modes for molecule 4a.

No. of dimensions	Mode combinations
6	{33,21}, {13,10}, {38,26}
8	{33,2}, {13,10}, {21,1}, {38,26}
10	{33,37}, {13,10}, {21,19}, {38,39,5}, {26}
12	{33,37}, {13,10}, {21,19,2}, {38,39,5}, {26,1}
12	{33,37}, {13,10,6}, {38,39,48}, {21,19}, {26,5}
14	{33,37}, {13,10,6}, {38,39,48}, {21,19}, {26,5,1}, {2}

Table 8: Mode combinations for molecule 4a

Additional DD-MCTDH calculation results

For completeness, Figs. 1 - 4 give the absorption spectra and wavepacket time-correlation functions calculated for molecules 3a and 4a, as determined using DD-MCTDH simulations.

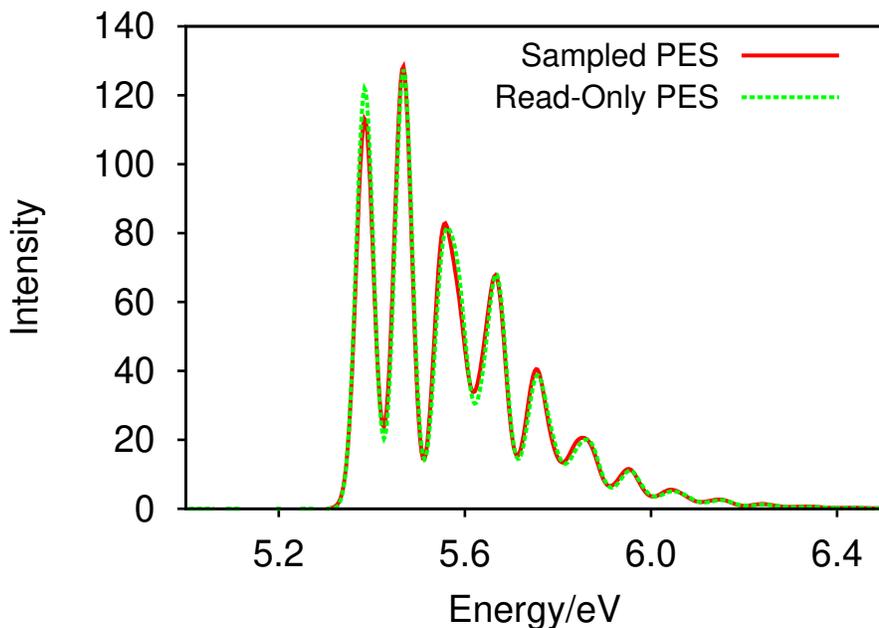


Figure 1: Absorption spectra of molecule 3a after vertical excitation to the S_1 state, calculated using DD-MCTDH with 6 normal modes chosen according to their gradients and non-adiabatic couplings at the Franck-Condon point. The red, solid line is the result from a calculation with the PES being built on-the-fly whilst the green, dashed line is the result from a second calculation using the pre-computed database to construct the PES.

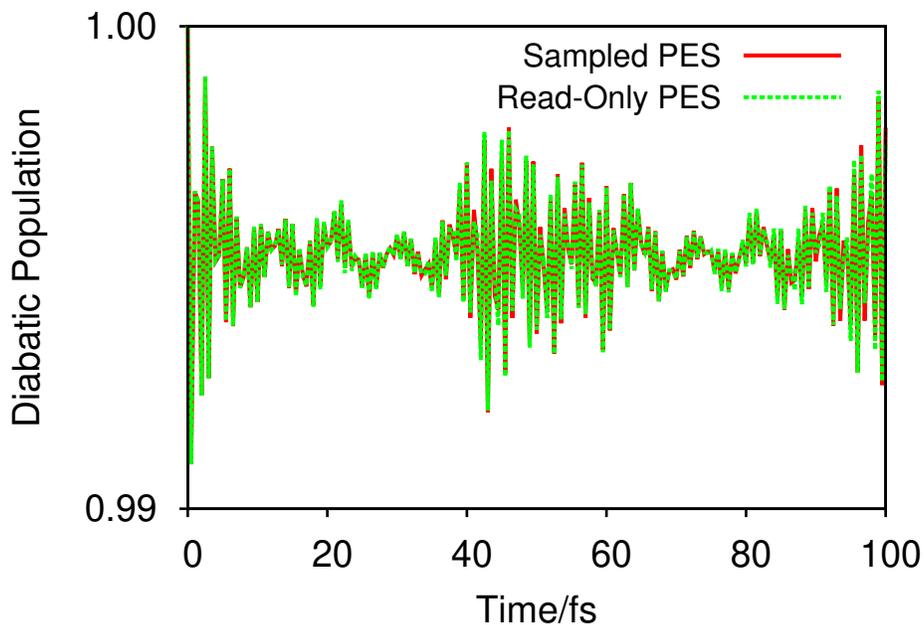


Figure 2: Diabatic state populations of molecule 3a after vertical excitation to the S_1 state with the red, solid line being the population of state S_1 using a PES built on-the-fly and the green, dashed line that using a PES constructed from a pre-computed database of energies, calculated using DD-MCTDH with 6 normal modes chosen according to their gradients and non-adiabatic couplings at the Franck-Condon point.

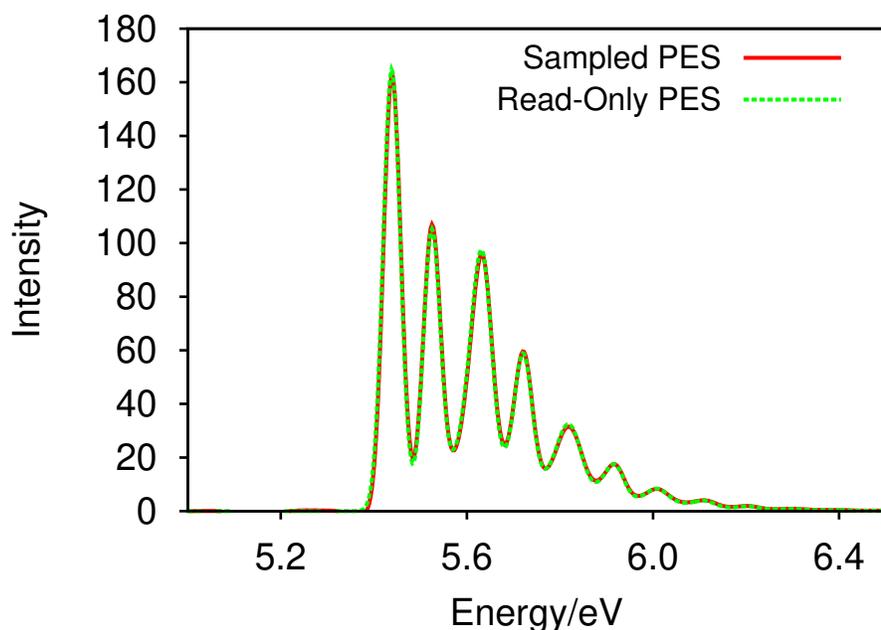


Figure 3: Absorption spectra of molecule 4a after vertical excitation to the S_1 state. The red, solid line is the result from a calculation with the PES being built on-the-fly whilst the green, dashed line is the result from a second calculation using the pre-computed database to construct the PES, calculated using DD-MCTDH with 6 normal modes chosen according to their gradients and non-adiabatic couplings at the Franck-Condon point.

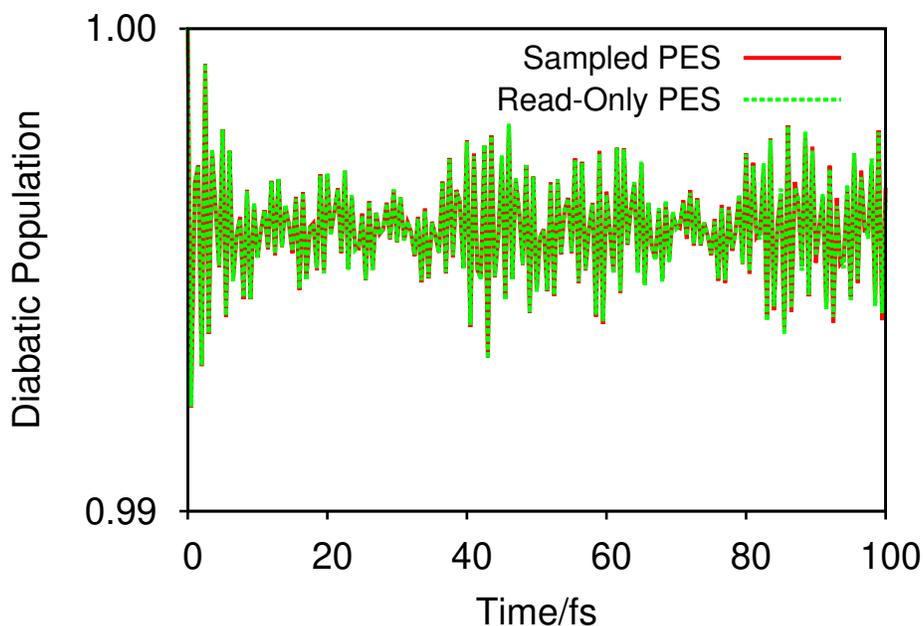


Figure 4: Diabatic state populations of molecule 4a after vertical excitation to the S_1 state with the red, solid line being the population of state S_1 using a PES built on-the-fly and the green, dashed line that using a PES constructed from a pre-computed database of energies, calculated using DD-MCTDH with 6 normal modes chosen according to their gradients and non-adiabatic couplings at the Franck-Condon point.

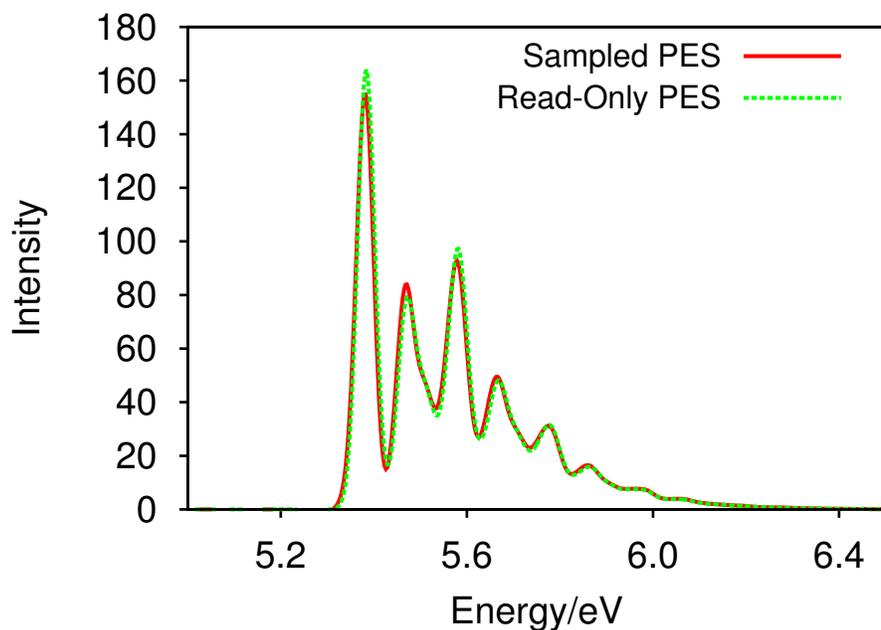


Figure 5: Absorption spectra of molecule 4a after vertical excitation to the S_1 state, calculated using DD-MCTDH with 6 normal modes, 5 chosen according to their gradients at the Franck-Condon point, the sixth and seventh spanning the same space as those pointing between the FC point and (1) the conical intersection and (2) the first step along the S_1 geometry optimisation. The red, solid line is the result from a calculation with the PES being built on-the-fly whilst the green, dashed line is the result from a second calculation using the pre-computed database to construct the PES.

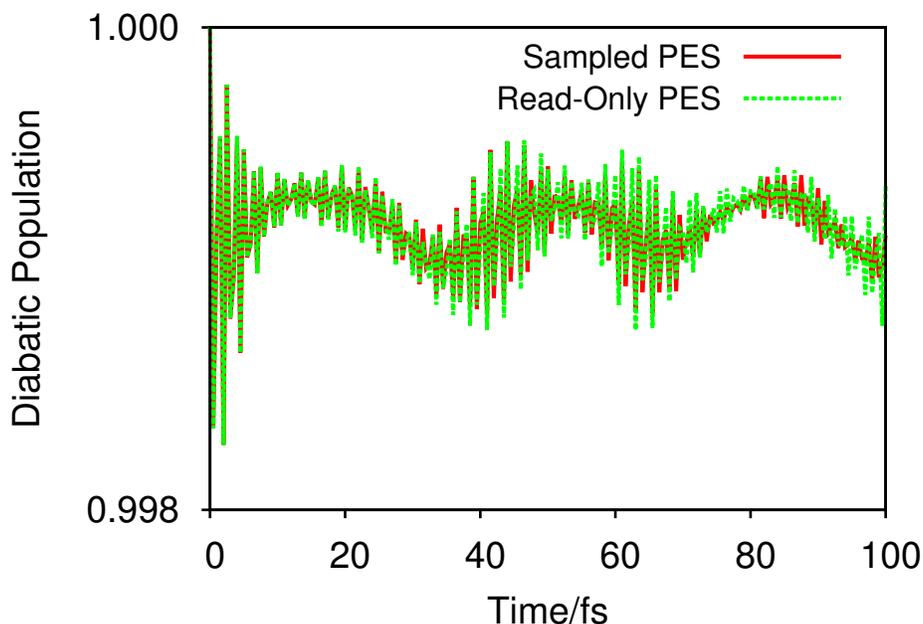


Figure 6: Diabatic state populations of molecule 4a after vertical excitation to the S_1 state with the red, solid line being the population of state S_1 using a PES built on-the-fly and the green, dashed line that using a PES constructed from a pre-computed database of energies, calculated using DD-MCTDH with 6 normal modes, 5 chosen according to their gradients at the Franck-Condon point, the sixth and seventh spanning the same space as those pointing between the FC point and (1) the conical intersection and (2) the first step along the S_1 geometry optimisation.

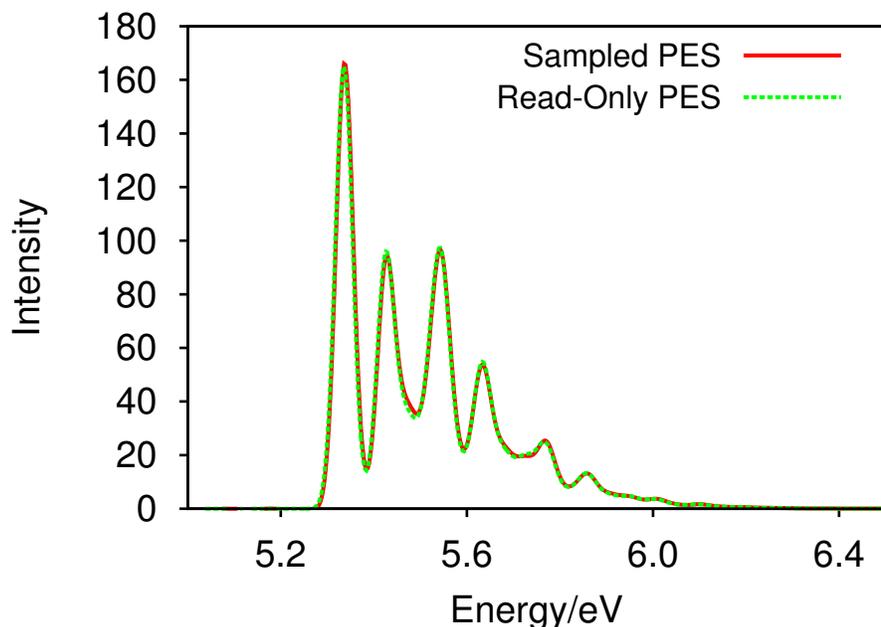


Figure 7: Absorption spectra of molecule 4a after vertical excitation to the S_1 state, calculated using DD-MCTDH with 6 normal modes, 5 chosen according to their gradients at the Franck-Condon point, the sixth and seventh spanning the same space as those pointing between the FC point and (1) the conical intersection and (2) the 17th step along the S_1 geometry optimisation. The red, solid line is the result from a calculation with the PES being built on-the-fly whilst the green, dashed line is the result from a second calculation using the pre-computed database to construct the PES.

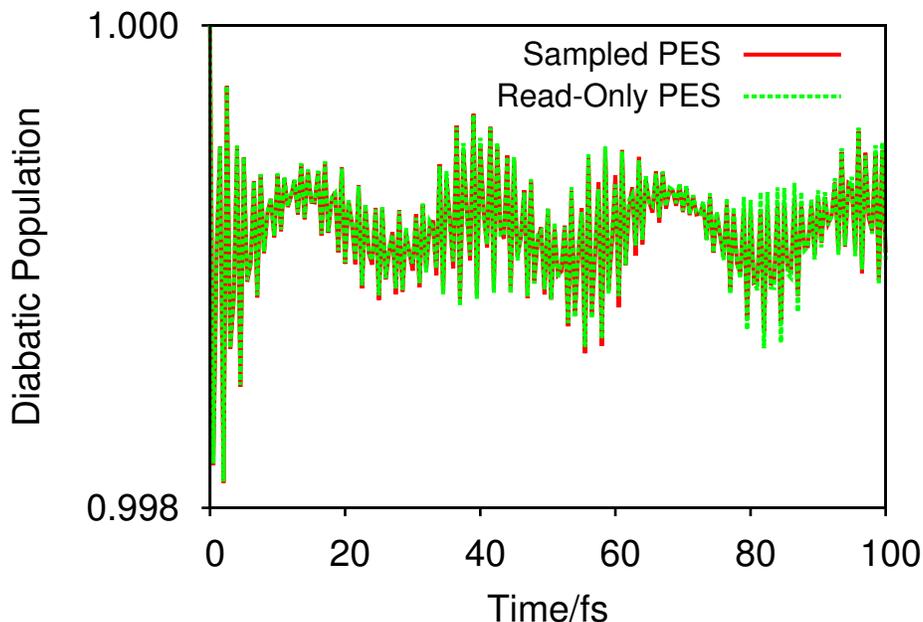


Figure 8: Diabatic state populations of molecule 4a after vertical excitation to the S_1 state with the red, solid line being the population of state S_1 using a PES built on-the-fly and the green, dashed line that using a PES constructed from a pre-computed database of energies, calculated using DD-MCTDH with 6 normal modes, 5 chosen according to their gradients at the Franck-Condon point, the sixth and seventh spanning the same space as those pointing between the FC point and (1) the conical intersection and (2) the 17th step along the S_1 geometry optimisation.

Procedure for determining pseudo normal-mode coordinates

In the main text, we noted that we had generated additional pseudo normal-mode coordinates which could be added to the standard normal-mode coordinate set in order to (potentially) improve the description of the dynamics. The procedure used to generate these additional normal-modes was as follows:

1. Let \vec{x}_0 be the reference geometry and \vec{c}_0 its centre of mass, in mass weighted cartesian coordinates.
2. Select the n_V vectors that we are interested in describing, eg. minima, CI, some geometry along the reaction coordinate, etc. Even more useful, one could use the principal components obtained from the covariance matrix of some large collection of vectors describing dynamics from a few surface hopping trajectories.
3. Let the matrix of these vectors in weighted cartesian coordinates be \mathbf{V} (dimensions $n_V \times n$). Note that the centre of mass of these vectors has to be made to equal \vec{c}_0 .
4. Let the orthogonal projection operator that projects onto the space of these important vectors be $\mathbf{P}^i = \mathbf{V}(\mathbf{V}^T \mathbf{V})^{-1} \mathbf{V}^T$ (note $\mathbf{P}^i = (\mathbf{P}^i)^T$). It is worth noting that orthogonal projection operators leave the vectors acted on as close as possible to the original ones, within the space of projection.
5. Let \mathbf{N} be the $(n - 6) \times n$ matrix of eigenvectors of the Hessian matrix in the basis of mass weighted cartesian coordinates (i.e normal modes). We will partition the columns of \mathbf{N} into two submatrices $\mathbf{N} = \mathbf{N}^t || \mathbf{N}^u$. The set of modes we wish to leave untouched is \mathbf{N}^u ; these could be important to include during the dynamics, or high frequency modes that we might wish to also omit altogether. The set of "touchable" modes \mathbf{N}^t are the ones we will use to construct better coordinates for the problem under consideration. Important vectors in \mathbf{V} will typically be constituted of many small displacements along these, so our final aim is to create new coordinates that turn these small displacements into a fewer, more manageable and succinct set of coordinates. It can be shown that the kinetic energy (KE) operator of the mass weighted cartesian coordinates is invariant with respect to *orthogonal transformations*. If we use orthogonal transformations to mix these touchable modes into the more succinct representation, we shall have gain the added bonus of not worrying about the form of the KE; this is our aim here.

6. Let the orthogonal projection operator of the touchable modes be $\mathbf{P}^t = \mathbf{N}^t((\mathbf{N}^t)^T\mathbf{N}^t)^{-1}(\mathbf{N}^t)^T$ (note $\mathbf{P}^t = (\mathbf{P}^t)^T$). We can construct the covariant matrix of touchable modes *within the space of vectors* \mathbf{V} . Its given by

$$\begin{aligned}\mathbf{P}^{it} &= \mathbf{P}^i\mathbf{P}^t \\ \mathbf{G} &= (\mathbf{P}^{it}\mathbf{N})^T(\mathbf{P}^{it}\mathbf{N})\end{aligned}\tag{1}$$

The eigendecomposition of \mathbf{G} , a *symmetric* matrix, gives a set of *orthogonal* eigenvectors.

$$\mathbf{U}^T\mathbf{G}\mathbf{U} = \mathbf{D}^T\mathbf{D} = (\mathbf{P}^{it}\mathbf{N}\mathbf{U})^T(\mathbf{P}^{it}\mathbf{N}\mathbf{U}) = \mathbf{\Lambda}\tag{2}$$

Note that the dimensions of \mathbf{U} are $(n-6) \times (n-6)$. \mathbf{D} is a $(n-6) \times n$ matrix of orthogonal vectors, *within the space of vectors* \mathbf{V} . The resulting n_s significant eigenvalues ($\lambda_i > \delta$, δ typically less than 1.0) are an indication of how many linearly independent vectors exist in the space of vectors \mathbf{V} , which, if there are many of them, may be fewer than n_V . A typical eigenvalue decomposition algorithm will sort these out in some order, here we shall assume descending order $\lambda_i > \lambda_{i+1}$.

7. The first n_s vectors in \mathbf{D} will therefore contain the principal components of the space of vectors in \mathbf{V} . The set of *orthogonal* eigenvectors \mathbf{U} can be applied to mix (in a orthogonal transformation sense) the touchable normal modes to generate a new set of *orthogonal* vectors $\mathbf{N}\mathbf{U}$. Similarly to \mathbf{D} , the top n_s vectors have the property of maximising the overlap with the space of vectors in \mathbf{V} . This can be demonstrated by considering the product $(\mathbf{N}\mathbf{U})^T\mathbf{D}$

$$\begin{aligned}(\mathbf{N}\mathbf{U})^T\mathbf{D} &= \\ (\mathbf{P}^{it}\mathbf{N}\mathbf{U} + (\mathbf{1} - \mathbf{P}^{it})\mathbf{N}\mathbf{U})^T\mathbf{D} &= \\ (\mathbf{D} + (\mathbf{1} - \mathbf{P}^{it})\mathbf{N}\mathbf{U})^T\mathbf{D} &= \\ (\mathbf{\Lambda} - (\mathbf{D}^T\mathbf{P}(\mathbf{1} - \mathbf{P}^{it})\mathbf{N}\mathbf{U})^T) &= \mathbf{\Lambda} - 0\end{aligned}\tag{3}$$

Note that $\mathbf{P}\mathbf{D} = \mathbf{D}$. Where the first n_s vectors in $\mathbf{N}\mathbf{U}$, with significant λ_i maximise the overlap within the space of \mathbf{V} .

8. Let the matrix of the first n_s (significant) vectors in $\mathbf{N}\mathbf{U}$ be \mathbf{N}^s . We could finally rotate this subspace of coordinates \mathbf{N}^s to make them resemble as much as possible normal modes. This can be achieved by first transforming to a normal mode basis: $\mathbf{N}^s\mathbf{N}^{sT}$ and we can then inspect which is the largest normal coordinate making up each vector in \mathbf{N}^s .
9. Let the matrix of selected normal mode vectors with biggest contribution (absolute coefficient), one for each of the n_s vectors in \mathbf{N}^s , be \mathbf{N}^{Sel} . The orthogonal transformation matrix \mathbf{O} that will make \mathbf{N}^s resemble as much as possible \mathbf{N}^{Sel} , is given by the procrustes problem (since the space of vectors in \mathbf{N}^s and \mathbf{N}^{Sel} are not the same):

$$\begin{aligned}\mathbf{A}^T\mathbf{s}\mathbf{B} &= (\mathbf{N}^s)^T\mathbf{N}^{Sel} \\ \mathbf{O} &= \mathbf{A}^T\mathbf{B}\end{aligned}\tag{4}$$

Where the first line is the SVD decomposition of $(\mathbf{N}^s)^T\mathbf{N}^{Sel}$. The final set of coordinates in mass weighted cartesian bases is given by $\mathbf{F} = \mathbf{O}\mathbf{N}^s$. given that we arrived at \mathbf{F} by solely rotations of normal coordinates, the KE operator remains invariant. \mathbf{F} has the property of most succinctly describing the space of vectors in \mathbf{V} while remaining orthogonal to \mathbf{N}^u , the untouchable normal modes.

10. Finally, we can estimate the frequency of the new coordinates by averaging over the frequencies of the normal modes making up each coordinate in \mathbf{F} , these are given by the first n_s diagonal elements of $\mathbf{F}^T\mathbf{N}\mathbf{\Omega}\mathbf{N}^T\mathbf{F}$, where $\mathbf{\Omega}$ is the Hessian eigenvalue matrix.