Setting up for numerical calculations of the tissue signal in the case of vibrationally adiabatic conformational change.

We want to solve

$$i\hbar \dot{|\phi(t)}\rangle = \frac{\hat{p}^2}{2m^2} + V(q) |\phi(t)\rangle$$

starting from an initial condition at $t=0$, we proceed by finding the eigenstates and eigenvalues of the conformational Hamiltonian

$$H_{con} = \frac{\hat{p}^2}{2m^2} + V(q)$$

in a discrete position representation and resolving $|\phi(0)\rangle$ in terms of these eigenstates.

We use a grid of spacing $\delta q$ comprising $2K+1$ points

$$q_j = j\delta q; j = -K, -K+1, \ldots, 0, \ldots, K.$$  

Then an arbitrary matrix element of some operator $\hat{O}$ is rendered as

$$<\phi_1|\hat{O}|\phi_2> = \int dq_1 dq_2 <\phi_1|q_1\hat{O}|q_2> <q_1|\phi_2>$$

$$= (\delta q)^2 \sum_{j} <\phi_1|q_j\hat{O}|q_j> <q_j|\phi_2>$$

$$= \sum_{j} \phi_j^* 0_j \phi_j = \phi^* 0 \phi,$$
where \( \phi_j = (\delta Q)^2 \langle q_j \phi \rangle \)

and \( Q \frac{\partial}{\partial Q} = \delta Q \langle q_j \phi \rangle Q \frac{\partial}{\partial Q} Q \phi \rangle \).

For the conformational coordinate operator we have, in particular,

\[
\langle \phi | Q \phi \rangle = \int dq \int dq' \langle \phi | q \rangle \delta(Q - q) \langle q \phi \rangle = \int dq \langle \phi | q \rangle \langle q | \phi \rangle = \sum_j \langle \phi | q_j \rangle \langle q_j | \phi \rangle
\]

\[
= \sum_j \phi_j^* q_j \phi_j
\]

\[
= \sum_{j_2} \phi_j^* \delta_{j_2} q_{j_2} \phi_{j_2}
\]

so it must be that the matrix representing the coordinate operator has elements

\[
Q_{j_2} = Q_j \delta_{j_2}
\]

For the conformational kinetic energy operator,

\[
\langle \phi | \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \phi \rangle = -\frac{i}{2m} \int dq \langle \phi | q \rangle \frac{\hbar^2}{2m} \langle q | \phi \rangle.
\]

Now \( \frac{\partial}{\partial Q} \langle q | \phi \rangle \approx (\delta Q)^{-1} (\langle q + \frac{\delta Q}{2} | \phi \rangle - \langle q - \frac{\delta Q}{2} | \phi \rangle) \)

and \( \frac{\partial^2}{\partial Q^2} \langle q | \phi \rangle \approx (\delta Q)^{-2} (\langle q + \frac{\delta Q}{2} | \phi \rangle - 2 \langle q | \phi \rangle + \langle q - \frac{\delta Q}{2} | \phi \rangle). \)
\[
\langle \phi \mid \frac{\hat{p}^2}{2m} \mid \phi \rangle = -\frac{1}{2m} \sum_j (\delta q)^2 (\bar{\phi}_{j+1} - 2\bar{\phi}_j + \bar{\phi}_{j-1})^2
\]

and we recognize that

\[
(\frac{\hat{p}^2}{2m})_{j_{\mathbb{R}}} = -\frac{1}{2m(\delta q)^2} (\delta_{j+1} - 2\delta_{j_\mathbb{R}} + \delta_{j-1})^2
\]

How should we set \( \delta q \) and \( \mathbb{R} \) to obtain the largest number of "good" eigenstates and eigenenergies?

For a given eigenstate \( \psi_n \) with energy \( E_n \) to be accurate, our grid must be large enough so that

\( V(\mathbb{R}) \) and \( V(\mathbb{R} - \mathbb{R}) = V(-\mathbb{R}) \) are both somewhat higher than \( E_n \). Since the wave function of the \( n \)th eigenstate has \( n \) nodes, and our grid must include several points between each pair of nodes in order to accurately portray that wave function, we also require

\[ 2\mathbb{R} + 1 \geq 3n \]

Loosely speaking, then, we expect about the lowest-lying third of our eigenstates and eigenenergies to be accurate, provided that our spatial grid extends over a range slightly larger than the region of nonnegligible
probability amplitude in $\psi_n \equiv (2\pi)^{1/2} \left( \frac{2\pi}{m}\right)^{1/4} n^{1/2} e^{i(-n/2)}$

$E_n \equiv (2\pi)^{1/2} \left( \frac{2\pi}{m}\right)^{1/4} n^{1/2} (3n)^{1/4} \cong \frac{\hbar}{2m} \frac{2}{15} \frac{2}{\sqrt{13}} \cong \frac{\hbar}{4\sqrt{2m}}.$

If we wish to accurately portray $n_{\text{max}}$ states of a harmonic oscillator, we choose $2n+1 = 3n_{\text{max}}$, or $n$ equal to the integer part of $3n_{\text{max}}/2$ and set the grid spacing so that

$$\frac{\hbar}{2} (n_{\text{max}} + \frac{1}{2}) \leq \frac{m \cdot \frac{\hbar}{2}}{2} \left( \frac{3}{2} n_{\text{max}} \right)^2 \delta Q^2$$

or

$$\delta Q \geq \frac{1}{n_{\text{max}}} \left( \frac{\hbar}{m \cdot \frac{\hbar}{2}} \right)^{1/2}.$$

In order to capture $n_{\text{max}}$ states of a particle in a box of width $L$, we simply choose

\begin{align*}
X &= \text{IntegerPart} \left( 3n_{\text{max}}/2 \right) \\
\delta Q &= \frac{L}{2X+2} \cong \frac{L/3}{n_{\text{max}}}.
\end{align*}

We can use these example systems to estimate the grid size and spacing needed to correctly calculate the lowest, say, 15 (i.e., $n = \frac{1}{5} \left( \frac{12\pi}{m} \right)^{-1}$) conformational eigenfunctions and eigenenergies of $\hat{P}^2/2m + \hbar \epsilon_0 (\hat{A})$ and $\hat{P}^2/2m + \hbar \epsilon_2 (\hat{A})$.

We choose $2X+1 = 3 \cdot 15 = 45 \Rightarrow X = 22$. The harmonic-oscillator model suggests that we should set

$$\delta Q = \frac{1}{15} \left( \frac{\hbar}{m} \right)^{1/2} \left( \frac{m \cdot \frac{\hbar}{2}}{12\pi} \right)^{1/4} = \frac{1}{15} \left( \frac{\hbar}{m \cdot \frac{\hbar}{2}} \right)^{1/2} (36)^{1/4} = \left( \frac{\hbar}{2m} \right)^{1/2} \frac{2}{15} \frac{2}{\sqrt{13}} \cong \frac{\hbar}{4\sqrt{2m}}.$$
The particle-in-a-box example recommends a somewhat larger grid spacing,

$$
\delta x = \frac{1}{45} \approx \frac{11}{11/2 \text{m}} \frac{1}{2 \text{m}} \frac{1}{45} = \frac{11}{0.282} \frac{1}{45} \frac{1}{2 \text{m}} \approx \frac{3.9}{45} \frac{1}{2 \text{m}}.
$$

Notice that 44 times the H.O.-recommended grid spacing gives a grid length of only \(11 \frac{1}{2 \text{m}}\), which is clearly much too small to cover the spatial range visited by the conformational eigenfunctions of interest.

The most prudent course of action will be to use a grid spacing \(\delta x = \frac{1}{5 \frac{1}{2 \text{m}}^{\frac{1}{2}}}\) slightly smaller than

The smaller recommendation and a grid size \(50 \frac{1}{2 \text{m}}\) slightly larger than seems necessary, so that

\((2\kappa + 1) \frac{1}{5 \frac{1}{2 \text{m}}^{\frac{1}{2}}} \approx 50 \frac{1}{2 \text{m}}\) or \(\kappa = 125\). The adequacy of these initial choices must of course be tested by decreasing the grid spacing and increasing the grid length (say, by simultaneously halving \(\delta x\) and quadrupling \(\kappa\)).