Ladder Operators

Useful formula:

$$a = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i}{m\omega}\hat{p}\right)$$
$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i}{m\omega}\hat{p}\right)$$

This leads to the useful representation of $\hat{x}$ and $\hat{p}$,

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(a^\dagger + a\right)$$
$$\hat{p} = i\sqrt{\frac{\hbar m\omega}{2}}\left(a^\dagger - a\right).$$

The Hamiltonian

The Hamiltonian for the one-vibration DDA system is

$$\hat{H} = \frac{P^2}{2M_s} + \sum_i \frac{M_s\Omega^2}{2}\left(R - \frac{c_i}{M_s\Omega^2}\right)^2 |i\rangle\langle i| + \sum_{ij} E_{ij}|i\rangle\langle j| + \hat{H}_B$$
$$\hat{H}_B = \sum_j \frac{M_B\omega_j^2}{2}\left(Q_j - c'_j\frac{R}{M_B\omega_j^2}\right)^2 + \sum_j \frac{P_j^2}{2M_B}$$

where $\hat{P} = -i\hbar\frac{\partial}{\partial R}$.

Transform the Hamiltonian into the mass-weighted coordinates, that is, $R \to \tilde{R} = \sqrt{M_s}R$ and $P \to \tilde{P} = P/\sqrt{M_s}$ (the same for P_j and R_j).

$$\hat{H} = \frac{\tilde{P}^2}{2} + \sum_i \frac{\Omega^2}{2}\left(\tilde{R} - \frac{c_i}{M_s^{1/2}\Omega^2}\right)^2 |i\rangle\langle i| + \sum_{ij} E_{ij}|i\rangle\langle j| + \hat{H}_{SB}$$
$$\hat{H}_B = \sum_j \frac{\omega_j^2}{2}\left(\tilde{Q}_j - c'_j\frac{\tilde{R}}{\sqrt{M_sM_B}\omega_j^2}\right)^2 + \sum_j \frac{\tilde{P}_j^2}{2}$$

Expand the first equation:

$$\hat{H} = \frac{\tilde{P}^2}{2} + \frac{\Omega^2\tilde{R}^2}{2} + \sum_i \frac{c_i^2}{2M_s\Omega^2}|i\rangle\langle i| + \sum_{ij} E_{ij}|i\rangle\langle j| - \sum_i \frac{c_i}{\sqrt{M_s}}\tilde{R}|i\rangle\langle i| + \hat{H}_{SB}.$$

and move the oscillator terms to the second equation, we have

$$\hat{H} = \sum_i \frac{c_i^2}{2M_s\Omega^2}|i\rangle\langle i| + \sum_{ij} E_{ij}|i\rangle\langle j| - \sum_i \frac{c_i}{\sqrt{M_s}}\tilde{R}|i\rangle\langle i| + \hat{H}_{SB}. \tag{1}$$

Expand the second equation:

$$\frac{\tilde{P}^2}{2}+\left(\Omega^2+\sum_j \frac{c_j'^2}{M_s M_B \omega_j^2}\right)\frac{\tilde{R}^2}{2}+\sum_j \frac{\omega_j^2 \tilde{Q}_j^2}{2}+\sum_j \frac{\tilde{P}_j^2}{2}-\sum_j \frac{c_j'}{\sqrt{M_s M_B}}\tilde{Q}_j \tilde{R}$$

Diagonalize the second equation:

$$\frac{\tilde{P}^2}{2}+\frac{\Omega^2 \tilde{R}^2}{2}+\sum_{j=1}^{N}\frac{\omega_j^2}{2}\left(\tilde{Q}_j-c_j'\frac{\tilde{R}}{\sqrt{M_s M_B \omega_j^2}}\right)^2 \to \sum_{j=1}^{N+1}\frac{\omega_j'}{2}\hat{X}_j$$

$$\begin{bmatrix}\tilde{Q}_1 & \tilde{Q}_2 & \cdots & \tilde{Q}_{N-1} & \tilde{Q}_N & \tilde{R}\end{bmatrix}\begin{bmatrix}\frac{\omega_1^2}{2} & 0 & \cdots & 0 & \frac{c_1'}{2\sqrt{M_s M_B}} \\ 0 & \frac{\omega_2^2}{2} & \cdots & 0 & \frac{c_2'}{2\sqrt{M_s M_B}} \\ 0 & \vdots & \ddots & 0 & \vdots \\ 0 & 0 & \cdots & \frac{\omega_N^2}{2} & \frac{c_N'}{2\sqrt{M_s M_B}} \\ \frac{c_1'}{2\sqrt{M_s M_B}} & \frac{c_2'}{2\sqrt{M_s M_B}} & \cdots & \frac{c_N'}{2\sqrt{M_s M_B}} & (\Omega^2+\sum_j \frac{c_j'^2}{M_s M_B \omega_j^2})/2\end{bmatrix}\begin{bmatrix}\tilde{Q}_1 \\ \tilde{Q}_2 \\ \vdots \\ \tilde{Q}_{N-1} \\ \tilde{Q}_N \\ \tilde{R}\end{bmatrix}.$$

We obtain a set of frequencies $\mathrm{diag}(\frac{\omega_j'^2}{2})$ and a unitary matrix U (U is returned by numpy.linalg.eig()):

$$\begin{bmatrix}\tilde{Q}_1' \\ \tilde{Q}_2' \\ \vdots \\ \tilde{Q}_{N-1}' \\ \tilde{Q}_N' \\ \tilde{Q}'\end{bmatrix}=U\begin{bmatrix}\tilde{Q}_1 \\ \tilde{Q}_2 \\ \vdots \\ \tilde{Q}_{N-1} \\ \tilde{Q}_N \\ \tilde{R}\end{bmatrix}.$$

so that

$$\tilde{R}=U^T[N+1,:]\begin{bmatrix}\tilde{Q}_1' \\ \tilde{Q}_2' \\ \vdots \\ \tilde{Q}_{N-1}' \\ \tilde{Q}_N' \\ \tilde{Q}'\end{bmatrix}=\sum_j U_{j,N+1}\tilde{Q}_j.$$

Substitute the expansion $\tilde{R}=\sum_j U_{j,N+1}\tilde{Q}_j$ into (1) we have

$$\hat{H}=\sum_{ij}E_{ij}\left|i\right\rangle\left\langle j\right|+\sum_i \frac{c_i^2}{2M_s\Omega^2}\left|i\right\rangle\left\langle i\right|-\sum_i\left(\sum_j U_{j,N+1}\frac{c_i}{\sqrt{M_s}}\right)\tilde{Q}_j\left|i\right\rangle\left\langle i\right|+\hat{H}_B.$$

Use the ladder operators[1] $\tilde{Q}_j = \sqrt{\frac{\hbar}{2\omega'_j}}\left(a_j^\dagger + a_j\right)$ we obtain

$$\hat{H} = \sum_{ij} E_{ij}|i\rangle\langle j| + \sum_i \frac{c_i^2}{2M_s\Omega^2}|i\rangle\langle i| - \sum_i \underbrace{\left(\sum_j U_{j,N+1}\sqrt{\frac{\hbar}{2M_s\omega'_j}}\right)}_{c_j} c_i|i\rangle\langle i|\left(a_j^\dagger + a_j\right) + \hat{H}_B. \quad (2)$$

$$= \sum_{ij} E_{ij}|i\rangle\langle j| + \sum_i \frac{c_i^2}{2M_s\Omega^2}|i\rangle\langle i| - \sum_{ij} c_i c_j|i\rangle\langle i|\left(a_j^\dagger + a_j\right) + \hat{H}_B \quad (3)$$

Initial Density Matrix, Shifting the Coordinate System

Suppose the initial density matrix for the vibrational modes is $\rho_B = \exp[-\beta(\frac{\tilde{P}^2}{2} + \frac{\Omega^2(\tilde{R}-\tilde{R}_0)^2}{2}) - \beta(\sum_j \frac{\omega_j^2}{2}\left(\tilde{Q}_j - c'_j\frac{\tilde{R}}{\sqrt{M_sM_B\omega_j^2}}\right)^2 + \sum_j \frac{\tilde{P}_j^2}{2})]$. We set $\tilde{\mathcal{R}} = \tilde{R} - \tilde{R}_0$ ($\tilde{R} = \tilde{\mathcal{R}} + \tilde{R}_0$) and $\tilde{\mathcal{Q}} = \tilde{Q} - c'_j\frac{\tilde{\mathcal{R}}_0}{\sqrt{M_sM_B\omega_j^2}}$. Put them back to the density matrix we get

$$\begin{aligned}\rho_B =& \exp[-\beta(\frac{\tilde{P}^2}{2} + \frac{\Omega^2\tilde{\mathcal{R}}^2}{2}) - \beta(\sum_j \frac{\omega_j^2}{2}\left(\tilde{\mathcal{Q}}_j - c'_j\frac{\tilde{\mathcal{R}}}{\sqrt{M_sM_B\omega_j^2}}\right)^2 + \sum_j \frac{\tilde{P}_j^2}{2})] \\ =& e^{-\beta H_R}\end{aligned}$$

where

$$H_R = \frac{\tilde{P}^2}{2} + \frac{\Omega^2\tilde{\mathcal{R}}^2}{2} + \sum_j \frac{\omega_j^2}{2}\left(\tilde{\mathcal{Q}}_j - c'_j\frac{\tilde{\mathcal{R}}}{\sqrt{M_sM_B\omega_j^2}}\right)^2 + \sum_j \frac{\tilde{P}_j^2}{2}$$

Accordingly, the Hamiltonian becomes

$$\hat{H} = \sum_i \frac{\Omega^2}{2}\left(\tilde{R}_0 - \frac{c_i}{M_s^{1/2}\Omega^2}\right)^2|i\rangle\langle i| + \sum_i \Omega^2\left(\tilde{R}_0 - \frac{c_i}{M_s^{1/2}\Omega^2}\right)\tilde{\mathcal{R}}|i\rangle\langle i| + \sum_{ij} E_{ij}|i\rangle\langle j| + \hat{H}_{SB}$$

$$\hat{H}_B = \frac{\tilde{P}^2}{2} + \left(\Omega^2 + \sum_j \frac{c_j'^2}{M_sM_B\omega_j^2}\right)\frac{\tilde{\mathcal{R}}^2}{2} + \sum_j \frac{\omega_j^2\tilde{\mathcal{Q}}_j^2}{2} + \sum_j \frac{\tilde{P}_j^2}{2} - \sum_j \frac{c'_j}{\sqrt{M_sM_B}}\tilde{\mathcal{Q}}_j\tilde{\mathcal{R}}$$

Compared to the Hamiltonian in the last section, the only difference is that the reorganization energy and vibration coupling change by $\tilde{R}_0 = R_0\sqrt{M_s}$. Thus, we can replace the c'_js in the last section with $(c'_j - \tilde{R}_0\sqrt{M_s}\Omega^2) = (c'_j - R_0M_s\Omega^2)$ to make the initial density matrix shifted.

Ohmic to Lorentzian

If the spectral density for the bath-reaction-coordinate coupling is Ohmic:

$$J(\omega) = \frac{1}{2}\pi\xi\omega e^{\omega/\omega_c}$$

[1] $\tilde{Q}_j$'s are mass-weighted coordinates so there's no mass in this equation.

The effective bath that the electronic system senses has the following spectral density

$$J_{\mathrm{eff}} = \sum_i \frac{\pi \xi \omega \Omega^4}{2(\Omega^2 - \omega^2)^2 + \pi^2 \omega^2 \xi^2 / (2M_s^2)} R_0^i \left| i \right\rangle \left\langle i \right| \tag{4}$$