1 System Description

Here we will consider a molecular crystal with N cites that are indexed somehow by n, with lattice coordinates $\overrightarrow{n}$. We will impose periodic boundary conditions upon the crystal so that we have k-space given by $k = 0, \pi/2a, ..., (N-1)\pi/2a$. Suppose each of these molecules to have their S_0-S_1 exciton coupled to a vibrational degree of freedom on the molecule. We will model as a harmonic oscillator. We will index vibrational quanta with ν or w. When excited, the harmonic oscillator for vibration is shifted in its displacement coordinate by λ, which models the conformation change in the molecule upon electronic excitation. This shifted HO yields Fock states which are *not* orthogonal to the unexcited harmonic oscillators. We will index these excited states with $\tilde{\nu}$. In general,

$$\langle \nu | \tilde{\nu} \rangle = \int_{-\infty}^{\infty} \psi_{\tilde{\nu}}^{*}\left(x-\lambda\right) \psi_{\nu}(x) dx \neq 0$$

where $\psi_n(x)$ is the n^{th} harmonic oscillator wavefunction. In the special case:

$$|\langle 0 | \tilde{\nu} \rangle|^2 = \frac{e^{-\lambda^2/2}\lambda^{2\tilde{\nu}}}{2^{\tilde{\nu}}\tilde{\nu}!} = \frac{e^{-S}S^{\tilde{\nu}}}{\tilde{\nu}!} \tag{1}$$

Where $S = \lambda^2/2$ is the HR factor of the molecule. We will also allow molecules to have an intermolecular coupling (usually due to Coulombic interactions).

2 Hamiltonian

The resulting Hamiltonian for our system has two pieces, the "diagonal" part and the "intermolecular coupling" part:

$$\hat{H} = \hat{H}_D + \hat{H}_{IMC} \tag{2}$$

For the Diagonal Piece, we can express it in two forms:

$$\hat{H}_D = \sum_{n''} \left\{ \left(E_X + E_V \left(b_{n''}^{\dagger} + \lambda \right) \left(b_{n''} + \lambda \right) \right) |e_{n''}\rangle\langle e_{n''}| + E_V b_{n''}^{\dagger} b_{n''} \left(1 - |e_{n''}\rangle\langle e_{n''}| \right) \right\} \tag{3}$$

$$\hat{H}_D = \sum_{n''} \left\{ E_X |e_{n''}\rangle\langle e_{n''}| + E_V b_{n''}^{\dagger} b_{n''} \ + E_V \left(\lambda \left(b_{n''}^{\dagger} + b_{n''} \right) + \lambda^2 \right) |e_{n''}\rangle\langle e_{n''}| \right\} \tag{4}$$

Here E_X is the undressed exciton energy, E_V is the vibrational energy quanta, $|e_n\rangle$ specifies an excitation on the n^{th} molecule, while $b_n^{\dagger}(b_n)$ are the creation (annihilation) operators for unshifted vibrations. By extension, $b_n^{\dagger} + \lambda(b_n + \lambda)$ are the creation (annihilation) operators for shifted vibrations.
The reason for both representations is that eq 3 is easier to calculate matrix elements with, as it clearly delineates the $|\tilde{\nu}\rangle$ energies from the $|wnu\rangle$ energies, however, usually eq 4 is cited in papers, because it has a cleaner representation of what causes each energy contribution. The first term provides the excitonic piece, the second term provides the vibronic piece, and the third is the shift induced by the coupling between the two.
For the coupling term in the Hamiltonian:

$$\hat{H}_{IMC} = \sum_{n'',m} J_{n'',m} |e_{n''}\rangle\langle e_m| \tag{5}$$

Where $J_{n'',m}$ is the energetic coupling between the n''^{th} and m^{th} molecules. In the special case where coupling is isotropic in the crystal, we will express this Hamiltonian as:

$$\hat{H}_{IMC} = \sum_{n'',q} J_{\overrightarrow{q}} |e_{n''}\rangle\langle e_{n''+q}| \tag{6}$$

where $\overrightarrow{q} = \overrightarrow{m} - \overrightarrow{n}''$.

3 Absorption, PL and Transition Dipole Operator

We are primarily interested in the optical properties of this system. We will take the electric dipole approximation and also assume that only the excitons in our system can couple to the field. In that case, the low temperature absorption ($k_BT \ll E_V$) takes the form:

$$A(\hbar\omega) = n\hbar\omega \sum_{|\Psi\rangle} |\langle G|\hat{\mu}|\Psi\rangle|^2 \Gamma_\sigma \left(\hbar\omega - E_{|\Psi\rangle}\right) \tag{7}$$

Here $|\Psi\rangle$ ranges over all the definite energy (with value $E_{|\Psi\rangle}$) states of our system, $|G\rangle$ is the total ground state of our system, Γ is some lineshape with a spread of σ, and $\hat{\mu}$ is the transition dipole operator:

$$\hat{\mu} = \mu \sum_{n''} \left(|g_{n''}\rangle\langle e_{n''}| + |e_{n''}\rangle\langle g_{n''}|\right) \tag{8}$$

Notice that when used in the absorption eq 7, the second term in the sum is always zero, so we usually write:

$$\hat{\mu} = \mu \sum_{n''} |g_{n''}\rangle\langle e_{n''}| \tag{9}$$

4 n-Particle States and the Two Particle Approximation

In this system, a complete orthonormal basis is rather complicated. However, since we are ultimately interested in optically active states, we can get away with using Philpot's n-particle basis and truncate after the second level. First, I'll present the states, then I'll justify why we can truncate.

1-particle State: $|\overrightarrow{k}, \tilde{\nu}\rangle = \frac{1}{\sqrt{N}} \sum_n e^{i\overrightarrow{k}\cdot\overrightarrow{n}} |e_n, \tilde{\nu}_n\rangle$

2-particle State: $|\overrightarrow{k}, \tilde{\nu}, l, \boldsymbol{\nu}\rangle = \frac{1}{\sqrt{N}} \sum_n e^{i\overrightarrow{k}\cdot\overrightarrow{n}} |e_n, \tilde{\nu}_n, \boldsymbol{\nu}_{n+l}\rangle \quad (l \neq 0 \text{ and } \boldsymbol{\nu} \neq 0)$

...

where $|e_n\rangle$ specifies an excitation on molecule n, $|\tilde{\nu}_n\rangle$ specifies shifted vibrational quanta on molecule n, $|\boldsymbol{\nu}_n\rangle$ specifies unshifted vibrational quanta on molecule n. If excitation or vibration for a molecule is not explicitly specified, it is assumed to be unexcited and with zero unshifted vibrational quanta.
For states to optically contribute, they must couple to system ground ($|G\rangle$) through the transistion dipole operator. Notice that the 1-particle states can accomplish this:

$$\begin{aligned}
\langle G|\hat{\mu}|\overrightarrow{k}, \tilde{\nu}\rangle &= \frac{\mu}{\sqrt{N}} \langle G| \sum_{n'',n} e^{i\overrightarrow{k}\cdot\overrightarrow{n}} |g_{n''}\rangle\langle e_{n''}||e_n, \tilde{\nu}_n\rangle \\
&= \frac{\mu}{\sqrt{N}} \langle G| \sum_{n'',n} e^{i\overrightarrow{k}\cdot\overrightarrow{n}} \delta_{n'',n}|g_n, \tilde{\nu}_n\rangle \\
&= \frac{\mu}{\sqrt{N}} \langle G| \sum_{n} e^{i\overrightarrow{k}\cdot\overrightarrow{n}} |g_n, \tilde{\nu}_n\rangle \\
&= \frac{\mu}{\sqrt{N}} \sum_{n} e^{i\overrightarrow{k}\cdot\overrightarrow{n}} \langle G|g_n, \tilde{\nu}_n\rangle \\
&= \frac{\mu}{\sqrt{N}} \sum_{n} e^{i\overrightarrow{k}\cdot\overrightarrow{n}} \langle 0_n|\tilde{\nu}_n\rangle \\
&= \frac{\mu}{\sqrt{N}} \langle 0|\tilde{\nu}\rangle \sum_{n} e^{i\overrightarrow{k}\cdot\overrightarrow{n}}
\end{aligned}$$

So,

$$\langle G|\hat{\mu}|\overrightarrow{k}, \tilde{\nu}\rangle = \mu\langle 0|\tilde{\nu}\rangle \delta_{\overrightarrow{k},0} \sqrt{N} \tag{10}$$

where on the last line we used the form of $\overrightarrow{k}$ given by periodic boundary conditions to equate the sum. Notice, this condition is effectly conservation of momentum–the crystal can only absorb into momentumless states.

Now, the 2-particle and higher states *cannot* couple to ground via the transition dipole operator. So illustrate why, we can see that for 2-particle states, the derivation will follow exactly the same as for the 1-particle states, until at the fourth step we get the overlap $\langle G|g_n, \tilde{\nu}_n, \text{ɯ}_{n+l}\rangle$. Now, this will yield: $\langle 0_n|\tilde{\nu}_n\rangle\langle 0_{n+l}|\text{ɯ}_{n+l}\rangle$. Now, the first bracket is the same as before, but that second bracket will *always* be zero, because the unshifted vibrational states are orthonormal. So the total matrix element is zero. By extension, if we ever have an unshifted vibrational quantum in our state, it cannot be absorbed into via the transition dipole operator.

I said before that we will use only 1- and 2-particle states. But if the 2-particle states are not absorptively active, why do we need them? Well, it is because of the intermolecular coupling. As we will see, 1- and 2-particle states can couple through the Hamiltonian (specifically $\hat{H}_{IMC}$ couples (n-1)-particle states to n-particle states). So, when we diagonalize our Hamiltonian to get the definite energy states $|\Psi\rangle$, we expect the 1- and 2-particle states to get mixed together. However, the 1- and 3-particle states should be minimally mixed, since we require a second order effect to couple them via $\hat{H}_{IMC}$.

So, of the definite energy states $|\Psi\rangle$, only those whose superposition is dominated by 1-particle states will have appreciable transition dipole operator matrix elements, and if the dominate contribution to the superposition is are 1-particle states, we expect some 2-particle state contributions, but very little 3-particle or higher state contributions.

So, we take this Two-Particle Approximation (TPA), and truncate our bases as 2-particle states. For the remainder of this section, we will adopt the notation:

$$\text{TPA Basis States: } |\overrightarrow{k}, \tilde{\nu}, l, \text{ɯ}\rangle = \frac{1}{\sqrt{N}} \sum_n e^{i\overrightarrow{k}\cdot\overrightarrow{n}} |e_n, \tilde{\nu}_n, \text{ɯ}_{n+l}\rangle \tag{11}$$

to refer to *both* 1- and 2-particle states by adding the additional requirement that: $l = 0 \Leftrightarrow \text{ɯ} = 0$.

5 First Order Perturbation

Diagonalizing the entire Hamiltonian 2 is challenging even with the TPA, and is tractable only using computational methods. However, if we restrict ourselves to only a 1D crystal with lattice spacing a, nearest neighbor interactions (J_{NN}) and assume that $E_V \ll J_{NN}$, then approximate methods can give us a sense of what the absorption should look like.

First notice that the diagonal part of the Hamiltonian 4 is already diagonal in the TPA basis, so we take $\hat{H}_IMC$ as the perturbation. We say:

$$\begin{aligned} E_{|\Psi\rangle} &\approx E^{(0)}_{|\Psi\rangle} + E^{(1)}_{|\Psi\rangle} \\ |\Psi\rangle &\approx |\Psi^{(0)}\rangle + |\Psi^{(1)}\rangle \end{aligned}$$

where:

$$\begin{aligned} |\Psi^{(0)}\rangle &= |\overrightarrow{k}, \tilde{\nu}, l, \text{ɯ}\rangle \\ E^{(0)}_{|\Psi\rangle} &= \langle\Psi^{(0)}|\hat{H}_D|\Psi^{(0)}\rangle \\ E^{(1)}_{|\Psi\rangle} &= \langle\Psi^{(0)}|\hat{H}_{IMC}|\Psi^{(0)}\rangle \\ |\Psi^{(1)}\rangle &= \sum_{\Psi'\neq\Psi} \frac{\langle\Psi'^{(0)}|\hat{H}_{IMC}|\Psi^{(0)}\rangle}{E^{(0)}_{|\Psi\rangle} - E^{(0)}_{|\Psi'\rangle}} |\Psi'^{(0)}\rangle \end{aligned}$$

Let's attack each piece in turn.

5.1 Finding $E^{(0)}_{|\Psi\rangle}$

It is straightforward to show that:

$$E^{(0)}_{|\Psi\rangle} = E_X + (\tilde{\nu} + \boldsymbol{\nu})\, E_V \tag{12}$$

5.2 Finding $E^{(1)}_{|\Psi\rangle}$

$$\begin{aligned}
E^{(1)}_{|\Psi\rangle} &= \langle \Psi^{(0)}|\hat{H}_{IMC}|\Psi^{(0)}\rangle \\
&= \langle k, \tilde{\nu}, l, \boldsymbol{\nu}| \sum_{n''} J_{NN}(|e_{n''}\rangle\langle e_{n''+1}| + |e_{n''}\rangle\langle e_{n''-1}|)|k, \tilde{\nu}, l, \boldsymbol{\nu}\rangle \\
&= \frac{J_{NN}}{N} \sum_{n,n',n''} e^{ika(n-n')}(\langle e_{n'}|e_{n''}\rangle\langle e_{n''+1}|e_n\rangle + \langle e_{n'}|e_{n''}\rangle\langle e_{n''-1}|e_n\rangle)\langle \tilde{\nu}_{n'}, \boldsymbol{\nu}_{n'+l}|\tilde{\nu}_n, \boldsymbol{\nu}_{n+l}\rangle \\
&= \frac{J_{NN}}{N} \sum_{n'} (e^{ika(n'+1-n')}\langle \tilde{\nu}_{n'}, \boldsymbol{\nu}_{n'+l}|\tilde{\nu}_{n'+1}, \boldsymbol{\nu}_{n'+1+l}\rangle + e^{ika(n'-1-n')}\langle \tilde{\nu}_{n'}, \boldsymbol{\nu}_{n'+l}|\tilde{\nu}_{n'-1}, \boldsymbol{\nu}_{n'-1+l}\rangle) \\
&= (e^{ika}\langle \tilde{\nu}_0, \boldsymbol{\nu}_l|\tilde{\nu}_1, \boldsymbol{\nu}_{1+l}\rangle + e^{-ika}\langle \tilde{\nu}_0, \boldsymbol{\nu}_l|\tilde{\nu}_{-1}, \boldsymbol{\nu}_{-1+l}\rangle) \sum_{n'} \frac{J_{NN}}{N} \\
&= (e^{ika}\langle \tilde{\nu}|0\rangle\langle 0|\tilde{\nu}\rangle + e^{-ika}\langle \tilde{\nu}|0\rangle\langle 0|\tilde{\nu}\rangle) J_{NN} \\
&= 2J_{NN}\cos(ka)\,|\langle 0|\tilde{\nu}\rangle|^2
\end{aligned}$$

5.3 Finding $|\Psi^{(1)}\rangle$

$$\begin{aligned}
\langle \Psi'^{(0)}|\hat{H}_{IMC}|\Psi^{(0)}\rangle &= \langle k', \tilde{\nu}', l', \boldsymbol{\nu}'| \sum_{n''} J_{NN}(|e_{n''}\rangle\langle e_{n''+1}| + |e_{n''}\rangle\langle e_{n''-1}|)|k, \tilde{\nu}, l, \boldsymbol{\nu}\rangle \\
&= \frac{J_{NN}}{N} \sum_{n,n',n''} e^{ia(kn-k'n')}(\langle e_{n'}|e_{n''}\rangle\langle e_{n''+1}|e_n\rangle + \langle e_{n'}|e_{n''}\rangle\langle e_{n''-1}|e_n\rangle)\langle \tilde{\nu}'_{n'}, \boldsymbol{\nu}'_{n'+l'}|\tilde{\nu}_n, \boldsymbol{\nu}_{n+l}\rangle \\
&= \frac{J_{NN}}{N} \sum_{n'} e^{ia(k-k')n'+iak}\langle \tilde{\nu}'_{n'}, \boldsymbol{\nu}'_{n'+l'}|\tilde{\nu}_{n'+1}, \boldsymbol{\nu}_{n'+1+l}\rangle + e^{ia(k-k')n'-iak}\langle \tilde{\nu}'_{n'}, \boldsymbol{\nu}'_{n'+l'}|\tilde{\nu}_{n'-1}, \boldsymbol{\nu}_{n'-1+l}\rangle \\
&= \frac{J_{NN}}{N} \left(e^{iak}\langle \tilde{\nu}'_0, \boldsymbol{\nu}'_{l'}|\tilde{\nu}_1, \boldsymbol{\nu}_{1+l}\rangle + e^{-iak}\langle \tilde{\nu}'_0, \boldsymbol{\nu}'_{l'}|\tilde{\nu}_{-1}, \boldsymbol{\nu}_{-1+l}\rangle\right) \sum_{n'} e^{ia(k-k')n'} \\
&= J_{NN} \left(e^{iak}\langle \tilde{\nu}'_0, \boldsymbol{\nu}'_{l'}|\tilde{\nu}_1, \boldsymbol{\nu}_{1+l}\rangle + e^{-iak}\langle \tilde{\nu}'_0, \boldsymbol{\nu}'_{l'}|\tilde{\nu}_{-1}, \boldsymbol{\nu}_{-1+l}\rangle\right) \delta_{k,k'}
\end{aligned}$$

5.3.1 Assume Both are 1-ps

$$\begin{aligned}
\langle \Psi'^{(0)}|\hat{H}_{IMC}|\Psi^{(0)}\rangle &= J_{NN} \left(e^{iak}\langle \tilde{\nu}'_0|\tilde{\nu}_1\rangle + e^{-iak}\langle \tilde{\nu}'_0|\tilde{\nu}_{-1}\rangle\right) \delta_{k,k'} \\
&= J_{NN} \left(e^{iak}\langle \tilde{\nu}'|0\rangle\langle 0|\tilde{\nu}\rangle + e^{-iak}\langle \tilde{\nu}'|0\rangle\langle 0|\tilde{\nu}\rangle\right) \delta_{k,k'} \\
&= 2J_{NN}\cos(ka)\langle \tilde{\nu}'|0\rangle\langle 0|\tilde{\nu}\rangle\delta_{k,k'}
\end{aligned}$$

5.3.2 Assume One is a 2-ps

Without loss of generality, assume $|\Psi^{(0)}\rangle$ is the 2-ps.

$$\begin{aligned}\langle\Psi'^{(0)}|\hat{H}_{IMC}|\Psi^{(0)}\rangle &= J_{NN}\left(e^{iak}\langle\tilde{\nu}'_0|\tilde{\nu}_1,\boldsymbol{\nu}_{1+l}\rangle + e^{-iak}\langle\tilde{\nu}'_0|\tilde{\nu}_{-1},\boldsymbol{\nu}_{-1+l}\rangle\right)\delta_{k,k'}\\ &= J_{NN}\left(e^{iak}\langle\tilde{\nu}'|\boldsymbol{\nu}\rangle\langle 0|\tilde{\nu}\rangle\delta_{l,-1} + e^{-iak}\langle\tilde{\nu}'|\boldsymbol{\nu}\rangle\langle 0|\tilde{\nu}\rangle\delta_{l,1}\right)\delta_{k,k'}\\ &= J_{NN}\langle\tilde{\nu}'|\boldsymbol{\nu}\rangle\langle 0|\tilde{\nu}\rangle\left(e^{iak}\delta_{l,-1} + e^{-iak}\delta_{l,1}\right)\delta_{k,k'}\end{aligned}$$

5.3.3 Assume Both are 2-ps

For completeness (though we will not need this result),

$$\begin{aligned}\langle\Psi'^{(0)}|\hat{H}_{IMC}|\Psi^{(0)}\rangle &== J_{NN}\left(e^{iak}\langle\tilde{\nu}'_0,\boldsymbol{\nu}'_{l'}|\tilde{\nu}_1,\boldsymbol{\nu}_{1+l}\rangle + e^{-iak}\langle\tilde{\nu}'_0,\boldsymbol{\nu}'_{l'}|\tilde{\nu}_{-1},\boldsymbol{\nu}_{-1+l}\rangle\right)\delta_{k,k'}\\ &= J_{NN}\left(e^{iak}\langle\tilde{\nu}'|\boldsymbol{\nu}\rangle\langle\boldsymbol{\nu}'|\tilde{\nu}\rangle\delta_{l',1}\delta_{l,-1} + e^{-iak}\langle\tilde{\nu}'|\boldsymbol{\nu}\rangle\langle\boldsymbol{\nu}'|\tilde{\nu}\rangle\delta_{l',-1}\delta_{l,1}\right)\delta_{k,k'}\\ &= J_{NN}\langle\tilde{\nu}'|\boldsymbol{\nu}\rangle\langle\boldsymbol{\nu}'|\tilde{\nu}\rangle\left(e^{iak}\delta_{l',1}\delta_{l,-1} + e^{-iak}\delta_{l',-1}\delta_{l,1}\right)\delta_{k,k'}\end{aligned}$$

So, by inserting these into the following equation, we find the wavefunction corrections.

$$|\Psi^{(1)}\rangle = \sum_{\Psi'\neq\Psi}\frac{\langle\Psi'^{(0)}|\hat{H}_{IMC}|\Psi^{(0)}\rangle}{E^{(0)}_{|\Psi\rangle} - E^{(0)}_{|\Psi'\rangle}}|\Psi'^{(0)}\rangle$$

6 Absorption to First Order

To find the absorption inside this first order perturbation, we must find the transition dipole operator matrix elements: $\langle G|\hat{\mu}|\Psi\rangle \approx \langle G|\hat{\mu}|\Psi^{(0)}\rangle + \langle G|\hat{\mu}|\Psi^{(1)}\rangle$. We have already worked out the first term:

$$\langle G|\hat{\mu}|\Psi^{(0)}\rangle = \mu\langle 0|\tilde{\nu}\rangle\delta_{k,0}\delta_{l,0}\delta_{\boldsymbol{\nu},0}\sqrt{N} \tag{13}$$

So it remains to find the second term:

$$\begin{aligned}\langle G|\hat{\mu}|\Psi^{(1)}\rangle &= \sum_{\Psi'\neq\Psi}\frac{\langle\Psi'^{(0)}|\hat{H}_{IMC}|\Psi^{(0)}\rangle}{E^{(0)}_{|\Psi\rangle} - E^{(0)}_{|\Psi'\rangle}}\langle G|\hat{\mu}|\Psi'^{(0)}\rangle\\ &= \sum_{\Psi'\neq\Psi}\frac{\langle k',\tilde{\nu}',l',\boldsymbol{\nu}'|\hat{H}_{IMC}|\Psi^{(0)}\rangle}{E^{(0)}_{|\Psi\rangle} - E^{(0)}_{|\Psi'\rangle}}\mu\langle 0|\tilde{\nu}'\rangle\delta_{k',0}\delta_{l',0}\delta_{\boldsymbol{\nu}',0}\sqrt{N}\\ &= \sum_{\Psi'\neq\Psi}\frac{\langle k'=0,\tilde{\nu}'|\hat{H}_{IMC}|\Psi^{(0)}\rangle}{E^{(0)}_{|\Psi\rangle} - E^{(0)}_{|\Psi'\rangle}}\mu\langle 0|\tilde{\nu}'\rangle\sqrt{N}\end{aligned}$$

6.1 Assume $|\Psi^{(0)}\rangle$ is a 1-ps

$$\begin{aligned}
\langle G|\hat{\mu}|\Psi^{(1)}\rangle &= \sum_{\Psi'\neq\Psi} \frac{\langle k'=0,\tilde{\nu}'|\hat{H}_{IMC}|k,\tilde{\nu}\rangle}{E^{(0)}_{|\Psi\rangle} - E^{(0)}_{|\Psi'\rangle}} \mu\langle 0|\tilde{\nu}'\rangle\sqrt{N} \\
&= \sum_{\Psi'\neq\Psi} \frac{2J_{NN}\cos(ka)\langle\tilde{\nu}'|0\rangle\langle 0|\tilde{\nu}\rangle\delta_{k,0}}{(\tilde{\nu}-\tilde{\nu}')E_V} \mu\langle 0|\tilde{\nu}'\rangle\sqrt{N} \\
&= \sum_{\Psi'\neq\Psi} \frac{2J_{NN}\langle\tilde{\nu}'|0\rangle\langle 0|\tilde{\nu}\rangle\delta_{k,0}}{(\tilde{\nu}-\tilde{\nu}')E_V} \mu\langle 0|\tilde{\nu}'\rangle\sqrt{N} \\
&= 2\mu\sqrt{N}\langle 0|\tilde{\nu}\rangle\delta_{k,0}\frac{J_{NN}}{E_V}\sum_{\tilde{\nu}'\neq\tilde{\nu}} \frac{|\langle 0|\tilde{\nu}'\rangle|^2}{(\tilde{\nu}-\tilde{\nu}')} \\
&= 2\mu\sqrt{N}\langle 0|\tilde{\nu}\rangle\delta_{k,0}\frac{J_{NN}}{E_V}\sum_{\tilde{\nu}'\neq\tilde{\nu}} \frac{e^{-S}S^{\tilde{\nu}'}}{\tilde{\nu}'!(\tilde{\nu}-\tilde{\nu}')}
\end{aligned}$$

So,

$$\begin{aligned}
|\langle G|\hat{\mu}|\Psi\rangle|^2 &\approx |\langle G|\hat{\mu}|\Psi^{(0)}\rangle + \langle G|\hat{\mu}|\Psi^{(1)}\rangle|^2 \\
&= N\mu^2\delta_{k,0}|\langle 0|\tilde{\nu}\rangle|^2\left|1 + 2\frac{J_{NN}}{E_V}\sum_{\tilde{\nu}'\neq\tilde{\nu}}\frac{e^{-S}S^{\tilde{\nu}'}}{\tilde{\nu}'!(\tilde{\nu}-\tilde{\nu}')}\right|^2
\end{aligned}$$

6.2 Assume $|\Psi^{(0)}\rangle$ is a 2-ps

$$\begin{aligned}
\langle G|\hat{\mu}|\Psi^{(1)}\rangle &= \sum_{\Psi'\neq\Psi} \frac{\langle k'=0,\tilde{\nu}'|\hat{H}_{IMC}|k,\tilde{\nu},l,\boldsymbol{w}\rangle}{E^{(0)}_{|\Psi\rangle} - E^{(0)}_{|\Psi'\rangle}} \mu\langle 0|\tilde{\nu}'\rangle\sqrt{N} \\
&= \sum_{\Psi'\neq\Psi} \frac{J_{NN}\langle\tilde{\nu}'|\boldsymbol{w}\rangle\langle 0|\tilde{\nu}\rangle\left(e^{iak}\delta_{l,-1} + e^{-iak}\delta_{l,1}\right)\delta_{k,0}}{(\tilde{\nu}+\boldsymbol{w}-\tilde{\nu}')E_V} \mu\langle 0|\tilde{\nu}'\rangle\sqrt{N} \\
&= \sum_{\Psi'\neq\Psi} \frac{J_{NN}\langle\tilde{\nu}'|\boldsymbol{w}\rangle\langle 0|\tilde{\nu}\rangle\left(\delta_{l,-1} + \delta_{l,1}\right)\delta_{k,0}}{(\tilde{\nu}+\boldsymbol{w}-\tilde{\nu}')E_V} \mu\langle 0|\tilde{\nu}'\rangle\sqrt{N} \\
&= \mu\sqrt{N}\langle 0|\tilde{\nu}\rangle\delta_{k,0}\left(\delta_{l,-1} + \delta_{l,1}\right)\frac{J_{NN}}{E_V}\sum_{\tilde{\nu}'} \frac{\langle 0|\tilde{\nu}'\rangle\langle\tilde{\nu}'|\boldsymbol{w}\rangle}{(\tilde{\nu}+\boldsymbol{w}-\tilde{\nu}')}
\end{aligned}$$

So,

$$\begin{aligned}
|\langle G|\hat{\mu}|\Psi\rangle|^2 &\approx |\langle G|\hat{\mu}|\Psi^{(0)}\rangle + \langle G|\hat{\mu}|\Psi^{(1)}\rangle|^2 \\
&= \left|0 + \mu\sqrt{N}\langle 0|\tilde{\nu}\rangle\delta_{k,0}\left(\delta_{l,-1} + \delta_{l,1}\right)\frac{J_{NN}}{E_V}\sum_{\tilde{\nu}'}\frac{\langle 0|\tilde{\nu}'\rangle\langle\tilde{\nu}'|\boldsymbol{w}\rangle}{(\tilde{\nu}+\boldsymbol{w}-\tilde{\nu}')}\right|^2 \\
&= N\mu^2\delta_{k,0}|\langle 0|\tilde{\nu}\rangle|^2\left(\delta_{l,-1} + \delta_{l,1}\right)\left(\frac{J_{NN}}{E_V}\right)^2\left|\sum_{\tilde{\nu}'}\frac{\langle 0|\tilde{\nu}'\rangle\langle\tilde{\nu}'|\boldsymbol{w}\rangle}{(\tilde{\nu}+\boldsymbol{w}-\tilde{\nu}')}\right|^2
\end{aligned}$$

The important feature to notice here is that $|\langle G|\hat{\mu}|\Psi\rangle|^2$ is second order in J_{NN}/E_V, and so is neglected in our first order expansion.

6.3 Putting it all together

When we combine all of our results, then:

$$\begin{aligned}
A(\hbar\omega) &= n\hbar\omega \sum_{|\Psi\rangle} |\langle G|\hat{\mu}|\Psi\rangle|^2 \Gamma_\sigma\left(\hbar\omega - E_{|\Psi\rangle}\right) \\
&\approx n\hbar\omega \sum_{|\Psi\rangle} |\langle G|\hat{\mu}|\Psi^{(0)}\rangle + \langle G|\hat{\mu}|\Psi^{(1)}\rangle|^2 \Gamma_\sigma\left(\hbar\omega - E_{|\Psi\rangle}\right) \\
&\approx n\hbar\omega \sum_{|\Psi^{(0)}\rangle = |k,\tilde{\nu}\rangle} |\langle G|\hat{\mu}|\Psi^{(0)}\rangle + \langle G|\hat{\mu}|\Psi^{(1)}\rangle|^2 \Gamma_\sigma\left(\hbar\omega - E_{|\Psi\rangle}\right) \\
&= n\hbar\omega N\mu^2 \sum_{\tilde{\nu}} |\langle 0|\tilde{\nu}\rangle|^2 \left| 1 + 2\frac{J_{NN}}{E_V} \sum_{\tilde{\nu}' \neq \tilde{\nu}} \frac{e^{-S} S^{\tilde{\nu}'}}{\tilde{\nu}'!(\tilde{\nu} - \tilde{\nu}')} \right|^2 \Gamma_\sigma\left(\hbar\omega - E_X - \tilde{\nu}E_V - 2J_{NN}\left|\langle 0|\tilde{\nu}\rangle\right|^2\right)
\end{aligned}$$

Thus:

$$\frac{A(\hbar\omega)}{\hbar\omega} \approx nN\mu^2 \sum_{\tilde{\nu}} |\langle 0|\tilde{\nu}\rangle|^2 \left| 1 + 2\frac{J_{NN}}{E_V} \sum_{\tilde{\nu}' \neq \tilde{\nu}} \frac{e^{-S} S^{\tilde{\nu}'}}{\tilde{\nu}'!(\tilde{\nu} - \tilde{\nu}')} \right|^2 \Gamma_\sigma\left(\hbar\omega - E_X - E_V\left(\tilde{\nu} - 2\frac{J_{NN}}{E_V}\left|\langle 0|\tilde{\nu}\rangle\right|^2\right)\right) \quad (14)$$

Which we can implement computationally as:

$$\frac{A(\hbar\omega)}{\hbar\omega} = C \sum_{\tilde{\nu}} \frac{e^{-S} S^{\tilde{\nu}}}{\tilde{\nu}!} \left| 1 + 2\frac{J_{NN}}{E_V} \sum_{\tilde{\nu}' \neq \tilde{\nu}} \frac{e^{-S} S^{\tilde{\nu}'}}{\tilde{\nu}'!(\tilde{\nu} - \tilde{\nu}')} \right|^2 \Gamma_\sigma\left(\hbar\omega - E_X - E_V\left(\tilde{\nu} - 2\frac{J_{NN}}{E_V}\frac{e^{-S} S^{\tilde{\nu}}}{\tilde{\nu}!}\right)\right) \quad (15)$$

with 6 free parameters: $C, E_X, E_V, S, \sigma, J_{NN}$.
However, it is common to include a phenomenological parameterization of σ to increase the broadening for higher vibrational states. That is: $\sigma = \sigma_0(1 + \tilde{\nu}\Delta\sigma)$ with $\Delta\sigma \sim 0.5$. So,

$$\frac{A(\hbar\omega)}{\hbar\omega} = C \sum_{\tilde{\nu}} \frac{e^{-S} S^{\tilde{\nu}}}{\tilde{\nu}!} \left| 1 + 2\frac{J_{NN}}{E_V} \sum_{\tilde{\nu}' \neq \tilde{\nu}} \frac{e^{-S} S^{\tilde{\nu}'}}{\tilde{\nu}'!(\tilde{\nu} - \tilde{\nu}')} \right|^2 \Gamma_{\sigma_0(1+\tilde{\nu}\Delta\sigma)}\left(\hbar\omega - E_X - E_V\left(\tilde{\nu} - 2\frac{J_{NN}}{E_V}\frac{e^{-S} S^{\tilde{\nu}}}{\tilde{\nu}!}\right)\right) \quad (16)$$

with 7 free parameters: $C, E_X, E_V, S, \sigma_0, \Delta\sigma, J_{NN}$.