

Supplemental Material: Exact states and spectra of vibrationally dressed polaritons

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This supplemental material provides further details of the polynomial-scaling algorithm used to exactly solve the Holstein–Tavis–Cummings model and get the conditional reduced vibrational density matrices for the three conditions discussed in the paper. Section I describes the set of basis states, section II the form of the Hamiltonian matrix elements in this basis, and section III discusses how to extract reduced conditional density matrices from the wavefunction in the given representation.

I. BASIS SET

The basis states can be divided into two distinct subspaces, corresponding to whether one has states $|X\rangle_i$ or $|P\rangle$.

For the states corresponding to $|X\rangle_i$ (which we call the excitonic subspace), one molecule is excited, and $N - 1$ are unexcited. The vibrational state of the excited molecule is represented explicitly by the occupation $m^* \in [0, M]$. For the $N - 1$ unexcited molecules, the vibrational state must be permutationally symmetric, thus we may pick a representative state $\{m_{j \neq i}\}$ to stand for the superposition of all states related by permutation symmetry, $|\mathcal{S}_{N-1}\{m_j\}\rangle$. To uniquely specify the representative state, we choose the state where the occupations are in ascending order. For example, with $N - 1 = 4$, we may denote $|\mathcal{S}_4\{0112\}\rangle$ as representing the linear superposition of all permutations of this pattern of occupations:

$$|\mathcal{S}_4\{0112\}\rangle \equiv \frac{(|0112\rangle + |1012\rangle + |1102\rangle + |1120\rangle + |0211\rangle + |2011\rangle + |2101\rangle + |2110\rangle + |0121\rangle + |1021\rangle + |1201\rangle + |1210\rangle)}{\sqrt{\mathcal{P}_4(\{0112\})}}$$

where $\mathcal{P}_N(\{m_j\})$ counts the number of distinct permutations, i.e. $\mathcal{P}_4(\{0112\}) = 12$ for this example.

The complete vibrational state, where molecule i is excited, can then be written as $|m_i^*, \mathcal{S}_{N-1}\{m_{j \neq i}\}\rangle_V$. Since states with other molecules excited are related by permutation symmetry, the most general state with an excited molecule can be written as:

$$|X\rangle \otimes |m^*, \mathcal{S}_{N-1}\{m\}\rangle_V \equiv \frac{1}{\sqrt{N}} \sum_{i=1}^N |X\rangle_i \otimes |m^*, \mathcal{S}_{N-1}\{m_{j \neq i}\}\rangle_V. \quad (\text{S1})$$

If the occupation of the vibrational modes is restricted to $m \leq M$, then the number of distinct coefficients for

an excited molecule is $(M + 1) \cdot {}^{M+N-1}C_M$, where the combinatoric factor is the number of distinct sets $\{m\}$.

For the states with a photon present (i.e. the photonic subspace), no molecule is electronically excited, so there is full permutation symmetry. These states can thus be written immediately as

$$|P\rangle \otimes |\mathcal{S}_N\{m\}\rangle_V. \quad (\text{S2})$$

As the set of permutations now refers to N molecules, the total number of such states is just ${}^{M+N}C_M$.

II. MATRIX ELEMENTS OF HAMILTONIAN

1. Diagonal Terms

The terms $\hat{a}^\dagger \hat{a}$, $\sum_i \hat{\sigma}_i^+ \hat{\sigma}_i^-$ are diagonal in the above basis, and have the value 0(1) or 1(0) respectively in the photon(exciton) subspace. The term $\sum_i \hat{b}_i^\dagger \hat{b}_i$ is also diagonal, and is given by $m^* + \sum_i m_i$ in the exciton block, and $\sum_i m_i$ in the photon block.

2. Vibrational Coupling

The term coupling the electronic and vibrational states,

$$H_\lambda = \sum_i \sigma_i^+ \hat{\sigma}_i^- (\hat{b}_i^\dagger + \hat{b}_i),$$

is not diagonal, but is straightforward. It vanishes when acting on states involving $|P\rangle$. For states involving $|X\rangle_i$, it is diagonal in the vibrational state of the other $N - 1$ molecules, and so takes the form:

$$\begin{aligned} & \left(\langle X | \otimes \langle m^* |, \mathcal{S}_{N-1}\{m\} | \right)_V H_\lambda \left(|X\rangle \otimes |m^*, \mathcal{S}_{N-1}\{m\}\rangle_V \right) \\ & = \sqrt{m^*} \delta_{m^*-1, m^*} + \sqrt{m^*} \delta_{m^*, m^*-1} \end{aligned}$$

where m^* and $m^{*'}$ are vibrational occupations of the excited molecule.

3. Matter-Light Coupling

The only complicated term is the matter-light coupling:

$$H_R = \sum_i (\hat{\sigma}_i^+ \hat{a} + \hat{\sigma}_i^- \hat{a}^\dagger),$$

as this mixes the two sectors, which are labeled differently.

We focus on the photon emission term, as the other term follows by conjugation. We need to find:

$$\begin{aligned} & \left(\langle P | \otimes \langle \mathcal{S}_N \{m'\} | \right)_V \sum_i \hat{\sigma}_i^- \hat{a}^\dagger \left(|X\rangle \otimes |m^*, \mathcal{S}_{N-1} \{m\} \rangle_V \right) \\ & \equiv O_{\{m'\}, m^*, \{m\}} \quad (\text{S3}) \end{aligned}$$

In order for this not to vanish, the set of final occupations $\{m'\}$ must have an element equal to m^* and the rest of the set equal to $\{m\}$. If this is true, then we have:

$$O_{\{m'\}, m^*, \{m\}} = \frac{N \mathcal{P}_{N-1}(\{m\})}{\sqrt{N \mathcal{P}_{N-1}(\{m\})} \sqrt{\mathcal{P}_N(\{m'\})}}$$

where $\mathcal{P}_{N-1}(\{m\})$ is the count of distinct permutations as defined above. The factors $\sqrt{N \mathcal{P}_{N-1}(\{m\})}$ and $\sqrt{\mathcal{P}_N(\{m'\})}$ in the denominator come from the normalization of $|m^*, \mathcal{S}_{N-1} \{m\}\rangle_V$ and $|\mathcal{S}_N \{m'\}\rangle_V$. The factors in the numerator come from the distinct ways in which the overlap may occur — a choice of N molecules that may be excited, and $\mathcal{P}_{N-1}(\{m\})$ ways of arranging the unexcited molecules in the overlap.

The conditions given above means that by taking a single element m^* out of $\{m'\}$, the rest should become equal to $\{m\}$. Since coefficients are indexed over these sets, we can consider this as requiring a mapping $\mathcal{M}_{N-1 \rightarrow N}$ from the pair of integers $(m^*, \mathcal{I}_{N-1}(\{m\}))$, to the integer $\mathcal{I}_N(\{m'\})$, where $\mathcal{I}_N(\{m\})$ is the index of an ordered set of N occupations. We compute this mapping once and store for later use.

III. CONDITIONAL DENSITY MATRICES

In the paper, we plot the conditional Wigner functions of the vibrational state of a single molecule. These correspond to the reduced density matrices subject to the three possible conditions, denoted by $|P\rangle$, $|X\rangle_i$ and $|X\rangle_{j \neq i}$ in the paper. By using the basis states described above, we can numerically diagonalize to find the ground state wavefunction $|\psi\rangle$ in the basis of states described above. This section discusses how to extract the corresponding reduced conditional density matrices from such a representation of the state.

a. Photonic sector $|P\rangle$ We calculate the conditional reduced density matrix $\rho^{|P\rangle}$ which corresponds to restricting to the subspace involving $|P\rangle$. We then need to trace out the vibrational state of $N-1$ of the molecules. To do this, we can re-use the map $\mathcal{M}_{N-1 \rightarrow N}$. This mapping finds which set of indices for the $N-1$ molecules we trace out combine with the state m of the molecule of interest to find a given index for the full N molecule problem. To find the element $\rho_{m, m'}^{|P\rangle}$, we need to find all pairs of states of the N molecule problem which are reduced to the same $N-1$ molecule state when m, m' are taken out. For example, if we denote $j_N = \mathcal{I}_N(\{m\})$ as

an index of a state of N molecules, we need to find states such that

$$\begin{aligned} k_N &= \mathcal{M}_{N-1 \rightarrow N}(m, j_{N-1}), \\ k'_N &= \mathcal{M}_{N-1 \rightarrow N}(m', j_{N-1}). \end{aligned} \quad (\text{S4})$$

This is so that we can trace over j_{N-1} , describing the state of the other molecules. Using these labels we can then write

$$\rho_{m, m'}^{|P\rangle} = \sum_{j_{N-1}=1}^{\mathcal{N}_{N-1}} \frac{\psi_{P, k_N}^* \psi_{P, k'_N} \mathcal{P}_{N-1}(j_{N-1})}{\sqrt{\mathcal{P}_N(k_N) \mathcal{P}_N(k'_N)}} \quad (\text{S5})$$

where the summation is over all $\mathcal{N}_{N-1} \equiv N-1+M C_M$ vibrational states of $N-1$ molecules. Note that the indices k_N, k'_N appearing here are related to j_N by Eq. (S4). As defined above, ψ_{P, k_N} is the coefficient of the state with index k_N in the $|P\rangle$ subspace, and we have used the number of distinct permutations $\mathcal{P}_N(k_N)$ as shorthand for $\mathcal{P}_N(\{m\})$ where $k_N = \mathcal{I}_N(\{m\})$. The factors in the denominator come from the normalization of the basis states, and the factor in the numerator comes from counting the number of terms contributing to the trace.

b. Excited molecule, $|X\rangle_i$ For $\rho^{|X\rangle_i}$, the conditional reduced density matrix is straightforward, as the vibrational state of the excited molecule is represented explicitly. We need only to trace over the other $N-1$ molecules. Using j_{N-1} as the index of these states we find

$$\rho_{m, m'}^{|X\rangle_i} = \frac{1}{N} \sum_{j_{N-1}=1}^{\mathcal{N}_{N-1}} \psi_{X, m, j_{N-1}}^* \psi_{X, m', j_{N-1}} \quad (\text{S6})$$

Here $\psi_{X, m, j_{N-1}}$ is the coefficient of the state in with index (m, j_{N-1}) in the $|X\rangle$ subspace, and the factor of N appears from the normalization of basis states.

c. Other molecule excited, $|X\rangle_{j \neq i}$ To calculate $\rho^{|X\rangle_{j \neq i}}$, the conditional reduced density matrix corresponding a different molecule being electronically excited, we must trace over the excited molecule, and over $N-2$ of the $N-1$ unexcited molecules. This is similar to the case for $|P\rangle$, but this time we must use the mapping $\mathcal{M}_{N-2 \rightarrow N-1}$, from the indexing of distinct patterns of $N-2$ molecules and one explicit index, to the indexing of $N-1$ molecules.

$$\begin{aligned} k_{N-1} &= \mathcal{M}_{N-2 \rightarrow N-1}(m, j_{N-2}), \\ k'_{N-1} &= \mathcal{M}_{N-2 \rightarrow N-1}(m', j_{N-2}). \end{aligned} \quad (\text{S7})$$

Then, using similar notation to Eq. (S5) we may write:

$$\begin{aligned} \rho_{m, m'}^{|X\rangle_{j \neq i}} &= \sum_{j_{N-2}=1}^{\mathcal{N}_{N-2}} \sum_{m''=0}^M \psi_{X, m'', k_{N-1}}^* \psi_{X, m'', k'_{N-1}} \\ &\times \frac{N-1}{N} \frac{\mathcal{P}_{N-2}(j_{N-2})}{\sqrt{\mathcal{P}_{N-1}(k_{N-1}) \mathcal{P}_{N-1}(k'_{N-1})}}. \end{aligned} \quad (\text{S8})$$