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ABSTRACT

The vacuum field of an optical cavity can potentially modify chemical reactivity and other dynamical properties via vibrational strong coupling (VSC). This intriguing finding has inspired numerous studies, but the underlying mechanisms remain unresolved. While many theoretical efforts focus on solvent or nuclear fluctuations, the tunneling overlap in non-adiabatic processes is usually assumed unperturbed by the cavity field. This paper presents a rigorous calculation of the tunneling splitting and associated ground-state shift resulting from the non-adiabatic coupling between two degenerate, harmonic diabatic surfaces in the ground vibrational state manifold under VSC. Based on this calculation, the tunneling splitting is suppressed by the cavity field for a single-molecule or a few-molecule system, but this cavity-induced effect is neither resonant nor cooperative and vanishes in the thermodynamic limit. This prediction demonstrates the many facets of VSC-induced phenomena and sheds new light on cavity-modified non-adiabatic processes, including charge transfer, Förster resonance energy transfer, energy relaxation, and conical intersection.

I. INTRODUCTION

The effect of an optical cavity on molecular reaction dynamics has intrigued the chemical physics community for a decade. The seminal paper of Ebbesen and co-workers[1] and additional extensive results, as reviewed in Ref. 2, indicate that coupling of molecular systems to the zero-point field of a cavity can significantly alter the reaction dynamics, especially when there is a resonance between the cavity frequency and a molecular mode. These results are still unresolved and have intrigued many researchers. For example, Imperatore *et al.*[3] did not find any substantial influence of the cavity on the rate of cyanate ion hydrolysis. Similarly, Muller *et al.*[4] explored a series of reactions under various solvents and other conditions and did not find that the cavity significantly changed reaction rates. Similar results were also reported by other research groups.[5] Interestingly, Ahn *et al.* carried out a careful rate measurement in a cavity and reported small but observable changes.[6] These are but a few examples; the literature on the topic is quite vast, and the question of whether the vacuum field of a cavity changes chemical reactions remains unsolved, and the underlying mechanisms of resonance and collective effects remain elusive.

The experiments have induced a flurry of theoretical studies. Galego *et al.*[7] find that, under certain circumstances, the cavity can affect the dynamics; however, they do not find a resonance effect. Conversely, Li *et al.*[8,9] find that under equilibrium conditions, one should not expect the cavity to significantly alter reaction rates. Fischer *et al.*[10] studied the tunneling dynamics of a single molecule using exact quantum dynamical simulations and found that the cavity field may alter reaction rates on the single-molecule level. Although Yang and Cao,[11] using a quantum transition state theory approach, do find that the cavity can alter rates and the modified rate exhibits a strong frequency-dependence, the effect is minor; the typical magnitudes are a few percentages, much less than the experimentally measured effects reported earlier. Reichman and co-workers[12,13] used the Kramers turnover theory[14,15] to study cavity effects but did not find order-of-magnitude changes in rates under a broad range of parameters. Studies of vibrational energy transfer[16,17] suggest the key role of VSC-enhanced vibrational energy relaxation and motivate the interpretation of reaction dynamics in a cavity as a relaxation process.[18] In addition, the cavity-modified intermolecular interaction, such as the van der Waals attraction, can change molecular structures in the sample and potentially alter reaction rates.[19]

Of particular interest is the experimentally observed collective VSC in chemical reactions. Inspired by the observation, many theoretical groups have performed detailed numerical simulations with mixed results.[13,20–22] On the one hand, reaction rate calculations demonstrate cavity-induced modifications in an ensemble of a few molecules, but the effect vanishes in the thermodynamical limit. This observation is consistent with the early TST analysis and the prediction of this study. On the other hand, non-equilibrium dynamical simulations reveal the key role of energy dissipation in chemical reactions and can potentially demonstrate collective VSC. As pointed out in the previous paragraph, the non-equilibrium VSC can be rationalized using the Kramers turnover theory in the energy-diffusion regime and the generalized vibrational energy relaxation theory in the quantum regime. The full-dynamics simulation of many-body quantum tunneling in cavities remains challenging and is beyond the scope of this study. A review of many of these approaches used to theoretically study cavity-induced dynamics under VSC can be found in Ref. 23. The upshot of all this is that the theoretical understanding remains an enigma.

With this in mind, we believe it would be useful to study a process that is exponentially sensitive to perturbations and see whether, under such circumstances, the cavity induces significant effects and how these would depend on the resonance between the cavity frequency and the relevant molecular frequency. For this purpose, we undertake here a study of the symmetric tunneling splitting energy induced by a (constant) nonadiabatic coupling between two symmetrically placed diabatic harmonic potentials. In a recent paper,[24] it was shown that the nonadiabatically induced tunneling splitting is readily estimated accurately using a two-state approximation, based on the relevant vibrational wave functions of each of the diabatic Hamiltonians, provided that the nonadiabatic coupling is smaller than the energy spacing between tunneling doublets. The same two-state approximation may also be used to study adiabatic tunneling splitting in symmetric double-well potentials.[25] In the present study, we will use the same approach to examine the effect of a cavity on N non-interacting replicas (i.e., non-interacting identical molecules) of the two-state nonadiabatically induced tunneling splitting. At the outset, we note that although for a single replica the cavity may significantly reduce the magnitude of the tunneling splitting, in the limit of a large number of molecules interacting with the cavity field, we find that the effect vanishes. In all cases, even for a single molecule, there is no resonance effect between the vibrational frequency of the diabatic potential and the cavity frequency.

In Sec. II, we discuss the two-state approximation used to evaluate the tunneling splitting for a single molecule with and without interaction with a cavity. The application of the two-state approximation formalism to the cases of two and three replicas is presented in Sec. III. This prepares the way for the consideration of the general case of N replicas presented in Sec. IV. The casual reader might want to skip Sec. III and go directly to Sec. IV, which is the heart of the paper. We conclude with Sec. V, noting that the present approach may be extended in several different directions and could go beyond the harmonic models adopted in the present derivation.

II. CAVITY EFFECT ON THE SYMMETRIC DIABATIC ENERGY SPLITTING OF A SINGLE REPLICA

A. A single replica without the cavity

To set the framework and get insight into cavity effects, we first review the case without the cavity. We consider a system with two orthogonal electronic states such that the Hamiltonian has the form

$$\hat{H} = \hat{H}_L|L\rangle\langle L| + \hat{H}_R|R\rangle\langle R| + \hat{V}[|L\rangle\langle R| + |R\rangle\langle L|], \tag{2.1}$$

where $\hat{H}_L, \hat{H}_R$, and $\hat{V}$ depend on the "nuclear" coordinate and may also depend on the cavity coordinate. In practice, we will use a harmonic model for the diabatic Hamiltonians such that

$$H_{L,R} = \frac{p^2}{2} + \frac{\omega_0^2}{2}(q \pm q_0)^2, \tag{2.2}$$

where the + sign relates to the left electronic state and the − sign to the right electronic state, and the momentum p and coordinate q are mass weighted. The matrix representation of the "nuclear" Hamiltonian in the diabatic electronic basis set is

$$\hat{H}_{2\times 2} = \begin{pmatrix} \hat{H}_L & \hat{V} \\ \hat{V} & \hat{H}_R \end{pmatrix}, \tag{2.3}$$

and for simplicity, we assume that the nonadiabatic coupling $\hat{V}$ is constant, independent of the nuclear coordinate. For this harmonic model, the eigenstates of the diabatic Hamiltonians are the harmonic oscillator eigenstates; we restrict ourselves to the (normalized) ground states for which

$$\varphi_{0,(L,R)} = \left(\frac{\omega_0}{\pi\hbar}\right)^{\frac{1}{4}} \exp\left[-\frac{\omega_0}{2\hbar}(q \pm q_0)^2\right]. \tag{2.4}$$

The two state approximation implies finding the eigenstates of the Hamiltonian of Eq. (2.3) using the nuclear basis functions $\varphi_{0,(L,R)}$. The representation of the Hamiltonian is then

$$H_{2\times 2} = \begin{pmatrix} \langle\varphi_{0,L}|\hat{H}_L|\varphi_{0,L}\rangle & \langle\varphi_{0,L}|\hat{V}|\varphi_{0,R}\rangle \\ \langle\varphi_{0,R}|V|\varphi_{0,L}\rangle & \langle\varphi_{0,L}|\hat{H}_R|\varphi_{0,R}\rangle \end{pmatrix} = \begin{pmatrix} \frac{\hbar\omega_0}{2} & VS \\ VS & \frac{\hbar\omega_0}{2} \end{pmatrix}, \tag{2.5}$$

where the overlap

$$S = \langle\varphi_{0,L}|\varphi_{0,R}\rangle = \exp\left(-\frac{\omega_0 q_0^2}{\hbar}\right). \tag{2.6}$$

The eigenvalues of the Hamiltonian are readily seen to be $\frac{\hbar\omega_0}{2} \pm VS$ so that the energy splitting between the two lowest states is $2VS$.

B. A single replica interacting with the cavity

The next step is to adapt the two-state approximation to the case in which the system interacts with the cavity. The full Hamiltonian is now

$$\hat{H} = \hat{H}_L|L\rangle\langle L| + \hat{H}_R|R\rangle\langle R| + \hat{V}[|L\rangle\langle R| + |R\rangle\langle L|] + H_c\hat{I}, \tag{2.7}$$

where $\hat{I}$ is the electronic identity operator and the cavity field interacts with the molecular dipole so that the cavity Hamiltonian is

$$H_c = \frac{p_c^2}{2} + \frac{\omega_c^2}{2}(q_c - gq)^2, \tag{2.8}$$

where g is the coupling constant. With this construct, the Hamiltonians $\hat{H}_L + \hat{H}_c$ and $\hat{H}_R + \hat{H}_c$ have potentials that are quadratic in the system (q) and cavity (q_c) coordinates. The resulting force constant matrix for both the right and left cases is the same,

$$K_{2\times 2} = \begin{pmatrix} \omega_0^2 + g^2\omega_c^2 & \omega_c^2 g \\ \omega_c^2 g & \omega_c^2 \end{pmatrix}. \tag{2.9}$$

It has two eigenvalues

$$\lambda_\pm^2 = \frac{1}{2}\left[\omega_0^2 + \omega_c^2\left(1 + g^2\right) \pm \sqrt{\left(\omega_0^2 - \omega_c^2\right)^2 + 2\omega_c^2 g^2\left(\omega_0^2 + \omega_c^2\right) + \omega_c^4 g^4}\right], \tag{2.10}$$

which have the properties

$$\lambda_+^2\lambda_-^2 = \omega_0^2\omega_c^2, \quad \lambda_+^2 + \lambda_-^2 = \omega_0^2 + \omega_c^2\left(1 + g^2\right), \tag{2.11}$$

and

$$\lambda_+ + \lambda_- = \sqrt{(\omega_0 + \omega_c)^2 + \omega_c^2 g^2}. \tag{2.12}$$

The normal mode coordinates are related to the original physical coordinates as

$$y_+ = q\cos\alpha - q_c \sin\alpha, \quad y_- = q\sin\alpha + q_c\cos\alpha, \tag{2.13}$$

and, conversely,

$$q = y_+\cos\alpha + y_-\sin\alpha, \quad q_c = -y_+\sin\alpha + y_-\cos\alpha, \tag{2.14}$$

and we readily find that

$$\sin 2\alpha = -\frac{2\omega_c^2 g}{\left(\lambda_+^2 - \lambda_-^2\right)}, \quad \cos 2\alpha = \frac{\left(\omega_0^2 + g^2\omega_c^2 - \omega_c^2\right)}{\left(\lambda_+^2 - \lambda_-^2\right)}. \tag{2.15}$$

The normal mode transformed Hamiltonians in the vicinity of the wells are then

$$H_{L,R} = \frac{p_{y_+}^2}{2} + \frac{p_{y_-}^2}{2} + \frac{\lambda_+^2}{2}y_{+,(L,R)}'^2 + \frac{\lambda_-^2}{2}y_{-,(L,R)}'^2 - \frac{\omega_0^4}{2\lambda_+^2}q_0^2\cos^2\alpha - \frac{\omega_0^4}{2\lambda_-^2}q_0^2\sin^2\alpha + \frac{\omega_0^2 q_0^2}{2}, \tag{2.16}$$

with

$$y_{+,(L,R)}' = y_+ \pm \frac{\omega_0^2}{\lambda_+^2}q_0\cos\alpha, \quad y_{-,(L,R)}' = y_- \pm \frac{\omega_0^2}{\lambda_-^2}q_0\sin\alpha, \tag{2.17}$$

and we note that either both signs are positive or both are negative. The left (right) subscripts remind us that the plus (minus) signs are for the respective diabatic Hamiltonians. One readily finds that

$$\frac{\omega_0^4}{2\lambda_+^2}q_0^2\cos^2\alpha + \frac{\omega_0^4}{2\lambda_-^2}q_0^2\sin^2\alpha = \frac{\omega_0^2 q_0^2}{2}, \tag{2.18}$$

so that the normal mode transformed diabatic Hamiltonians are

$$H_{(L,R)} = \frac{p_{y_+}^2}{2} + \frac{p_{y_-}^2}{2} + \frac{\lambda_+^2}{2}y_{+,(L,R)}'^2 + \frac{\lambda_-^2}{2}y_{-,(L,R)}'^2. \tag{2.19}$$

The ground state wave function for each of the diabatic states is

$$\Psi_{0,(L,R)}\left(y_{+,(L,R)}', y_{-,(L,R)}'\right) = \varphi_0\left(y_{+,(L,R)}'\right)\varphi_0\left(y_{-,(L,R)}'\right), \tag{2.20}$$

with

$$\begin{aligned} \varphi_0\left(y_+'\right) &= \left(\frac{\lambda_+}{\pi\hbar}\right)^{1/4}\exp\left[-\frac{\lambda_+}{2\hbar}y_+'^2\right], \\ \varphi_0\left(y_-'\right) &= \left(\frac{\lambda_-}{\pi\hbar}\right)^{1/4}\exp\left[-\frac{\lambda_-}{2\hbar}y_-'^2\right], \end{aligned} \tag{2.21}$$

and for the sake of brevity, we left out the (L,R) notation. We then have a basis set of two ground states $\Psi_{0,L}\left(y_{+,L}', y_{-,L}'\right)$ and $\Psi_{0,R}\left(y_{+,R}', y_{-,R}'\right)$ and use it to set up the Hamiltonian matrix. For each state, the ground state energy is the same

$$E_0 = \frac{\hbar(\lambda_+ + \lambda_-)}{2} = \frac{\hbar\sqrt{(\omega_0 + \omega_c)^2 + \omega_c^2 g^2}}{2}, \tag{2.22}$$

where for the second equality, we used Eq. (2.12). The overlap of the left and right functions is

$$\begin{aligned} S_1 &\equiv \left\langle \Psi_{0,L}\left(y_{+,L}', y_{-,L}'\right) \middle| \Psi_{0,R}\left(y_{+,R}', y_{-,R}'\right)\right\rangle \\ &= \exp\left[-\frac{\lambda_+}{\hbar}\left(\frac{\omega_0^2}{\lambda_+^2}q_0\cos\alpha\right)^2 - \frac{\lambda_-}{\hbar}\left(\frac{\omega_0^2}{\lambda_-^2}q_0\sin\alpha\right)^2\right] \\ &= \exp\left[-\frac{\omega_0 q_0^2\left(g^2\omega_c + \omega_c + \omega_0\right)}{\hbar\sqrt{(\omega_0 + \omega_c)^2 + \omega_c^2 g^2}}\right], \end{aligned} \tag{2.23}$$

where the last equality is obtained by noting that [after a bit of manipulation, using Eqs. (2.11) and (2.15)]

$$\frac{\cos^2\alpha}{\lambda_+^3} + \frac{\sin^2\alpha}{\lambda_-^3} = \frac{\left(g^2\omega_c + \omega_c + \omega_0\right)}{\omega_0^3\sqrt{(\omega_0 + \omega_c)^2 + \omega_c^2 g^2}}. \tag{2.24}$$

To summarize, from Eq. (2.22), we note that the coupling to the cavity increases the mean energy of the doublet, while from Eq. (2.23), we find that it decreases the overlap and, therefore, the tunneling splitting, which is given by $2VS_1$. The overlap is a monotonically decreasing function of the coupling constant. There is no resonance effect when the cavity and system frequencies are identical.

III. CAVITY EFFECT ON THE SYMMETRIC DIABATIC ENERGY SPLITTING OF TWO AND THREE REPLICAS

A. Two replicas without the cavity

When the two replicas do not interact, each one separately will have the doublet energies of $E_0 \pm VS$ (with $E_0 = \frac{\hbar\omega_0}{2}$). The total energies of the combination of the two replicas that are then possible are $2(E_0 - VS)$ when each replica is in its ground doublet state; $2E_0$—for the ground doublet state of one replica and the upper doublet state of the other and vice versa and, therefore, doubly degenerate; and $2(E_0 + VS)$ when each replica is in its upper doublet state. This is obvious when considering that the two replicas are uncoupled. However, it is instructive to derive this result more formally.

The Hamiltonian of the two noninteracting replicas is

$$\begin{aligned} H_{NI,2} = {} & H_{L_1}|L_1\rangle\langle L_1| + H_{R_1}|R_1\rangle\langle R_1| + H_{L_2}|L_2\rangle\langle L_2| + H_{R_2}|R_2\rangle\langle R_2| \\ & + V[|L_1\rangle\langle R_1| + |R_1\rangle\langle L_1| + |L_2\rangle\langle R_2| + |R_2\rangle\langle L_2|], \end{aligned} \tag{3.1}$$

where the diabatic harmonic Hamiltonians are as in Eq. (2.2), except that with replicas 1 and 2, we now have the respective momenta and coordinates (p_1, q_1) and (p_2, q_2). In the spirit of the two-state approximation, we now have two ground state "nuclear" wave functions, $|\varphi_{0,(L_j,R_j)}\rangle$, $j = 1, 2$, associated with the left and right electronic states. Our composite basis set has four components $|\varphi_{0,L_1}, \varphi_{0,L_2}\rangle|L_1, L_2\rangle$, $|\varphi_{0,L_1}, \varphi_{0,R_2}\rangle|L_1, R_2\rangle$, $|\varphi_{0,R_1}, \varphi_{0,L_2}\rangle|R_1, L_2\rangle$, and $|\varphi_{0,R_1}, \varphi_{0,R_2}\rangle|R_1, R_2\rangle$. Using this basis set, we construct the 4×4-dimensional matrix of the full Hamiltonian,

$$H_{NI,4\times 4} = \begin{pmatrix} \hbar\omega_0 & VS & VS & 0 \\ VS & \hbar\omega_0 & 0 & VS \\ VS & 0 & \hbar\omega_0 & VS \\ 0 & VS & VS & \hbar\omega_0 \end{pmatrix}, \tag{3.2}$$

where the overlap S is given as in the single replica case [Eq. (2.6)]. This matrix is readily diagonalized, and as expected, the eigenvalues are $\hbar\omega_0 - 2VS, \hbar\omega_0, \hbar\omega_0, \hbar\omega_0 + 2VS$. We will see that also in the presence of the cavity, one obtains the same structure; however, the magnitude of the overlap and the mean energy are changed.

B. Two replicas interacting with the cavity

The Hamiltonian of the two replicas interacting with the cavity in this case is

$$H = H_{NI,2} + H_c\hat{I}, \tag{3.3}$$

where $\hat{I}$ is the electronic identity operator. The cavity Hamiltonian has the same structure as in Eq. (2.8), except that the field interacts with the sum of the dipoles of the replicas so that now the cavity not only couples to the two replicas, it also couples the two replicas to each other,

$$H_c = \frac{p_c^2}{2} + \frac{\omega_c^2}{2}[q_c - g(q_1 + q_2)]^2. \tag{3.4}$$

Due to the two replicas, one has four different Hamiltonians, which depend on the sign of q_0. The electronic basis set has four states, $|L_1, L_2\rangle, |L_1, R_2\rangle, |R_1, L_2\rangle, |R_1, R_2\rangle$, so that one gets a four-dimensional Hamiltonian when using the electronic basis set

$$H_{4\times 4} = \begin{pmatrix} H_{L_1} + H_{L_2} + H_c & V & V & 0 \\ V & H_{L_1} + H_{R_2} + H_c & 0 & V \\ V & 0 & H_{R_1} + H_{L_2} + H_c & V \\ 0 & V & V & H_{R_1} + H_{R_2} + H_c \end{pmatrix}. \tag{3.5}$$

The generalization of the two-state model is now a four-state model in which the "nuclear" functions are the ground states of the four Hamiltonians appearing on the diagonal.

The second derivative matrix for each of the four Hamiltonians is the same

$$K_{3\times 3} = \begin{pmatrix} \omega_0^2 + g^2\omega_c^2 & \omega_c^2 g^2 & -\omega_c^2 g \\ \omega_c^2 g^2 & \omega_0^2 + g^2\omega_c^2 & -\omega_c^2 g \\ -\omega_c^2 g & -\omega_c^2 g & \omega_c^2 \end{pmatrix}. \tag{3.6}$$

One of its eigenvalues is ω_0^2; the other two are the solutions of the quadratic equation

$$\begin{aligned} \lambda_\pm^2 = \frac{1}{2}\Big[& \left(\omega_0^2 + \omega_c^2 + 2g^2\omega_c^2\right) \\ & \pm \sqrt{\left(\omega_0^2 - \omega_c^2\right)^2 + 4g^2\omega_c^2\left(\omega_0^2 + \omega_c^2\right) + 4g^4\omega_c^4}\Big], \end{aligned} \tag{3.7}$$

and this is identical to the one replica case [Eq. (2.10)] except that g has been replaced with $\sqrt{2}g$.

In order to evaluate the overlaps, it is necessary to express the physical coordinates in terms of the normal modes. This is performed in two steps. The first is to diagonalize the force constant matrix without the cavity coordinate,

$$K'_{2\times 2} = \begin{pmatrix} \omega_0^2 + g^2\omega_c^2 & \omega_c^2 g^2 \\ \omega_c^2 g^2 & \omega_0^2 + g^2\omega_c^2 \end{pmatrix}. \tag{3.8}$$

Its eigenvalues are ω_0^2 and $\omega_0^2 + 2g^2\omega_c^2$, and the associated eigenvectors are, respectively,

$$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}, \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}.$$

We thus construct an orthogonal matrix

$$O_{3\times 3} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{3.9}$$

and transform the full force constant matrix as

$$\begin{pmatrix} \omega_0^2 + g^2\omega_c^2 & \omega_c^2 g^2 & -\omega_c^2 g \\ \omega_c^2 g^2 & \omega_0^2 + g^2\omega_c^2 & -\omega_c^2 g \\ -\omega_c^2 g & -\omega_c^2 g & \omega_c^2 \end{pmatrix} = O_{3\times 3}\begin{pmatrix} \omega_0^2 & 0 & 0 \\ 0 & \left(\omega_0^2 + 2g^2\omega_c^2\right) & -\omega_c^2\sqrt{2}g \\ 0 & -\omega_c^2\sqrt{2}g & \omega_c^2 \end{pmatrix} O_{3\times 3}^T, \tag{3.10}$$

so that it remains to diagonalize a two-dimensional matrix, which is identical in form to the single replica case [Eq. (2.9)] with the identification that the coupling constant is now $g_2 = \sqrt{2}g$. This diagonalization is achieved with the matrix

$$U_{3\times 3} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & \sin\alpha \\ 0 & -\sin\alpha & \cos\alpha \end{pmatrix}, \tag{3.11}$$

such that

$$\begin{pmatrix} \omega_0^2 & 0 & 0 \\ 0 & \left(\omega_0^2 + 2g^2\omega_c^2\right) & -\omega_c^2\sqrt{2}g \\ 0 & -\omega_c^2\sqrt{2}g & \omega_c^2 \end{pmatrix} = U_{3\times 3}\begin{pmatrix} \omega_0^2 & 0 & 0 \\ 0 & \lambda_+^2 & 0 \\ 0 & 0 & \lambda_-^2 \end{pmatrix} U_{3\times 3}^T, \tag{3.12}$$

and, therefore, the orthogonal matrix that diagonalizes the full three dimensional force constant matrix [Eq. (3.2)] is

$$W_{3\times 3} = O_{3\times 3}U_{3\times 3} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}}\cos\alpha & \frac{1}{\sqrt{2}}\sin\alpha \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}}\cos\alpha & \frac{1}{\sqrt{2}}\sin\alpha \\ 0 & -\sin\alpha & \cos\alpha \end{pmatrix}. \tag{3.13}$$

This, in turn, implies that the normal modes may be expressed in terms of the physical coordinates as

$$y_0 = \frac{1}{\sqrt{2}}(q_1 - q_2), \tag{3.14}$$

$$y_+ = \frac{1}{\sqrt{2}}(q_1 + q_2)\cos\alpha - q_c\sin\alpha, \tag{3.15}$$

$$y_- = \frac{1}{\sqrt{2}}(q_1 + q_2)\sin\alpha + q_c\cos\alpha, \tag{3.16}$$

and, inversely,

$$q_1 = \frac{1}{\sqrt{2}}(y_+\cos\alpha + y_-\sin\alpha + y_0), \tag{3.17}$$

$$q_2 = \frac{1}{\sqrt{2}}(y_+\cos\alpha + y_-\sin\alpha - y_0), \tag{3.18}$$

$$q_c = y_-\cos\alpha - y_+\sin\alpha. \tag{3.19}$$

The transformation angle α is given as in the single replica case except for the change in the coupling constant so that now

$$\sin 2\alpha = -\frac{2\omega_c^2\sqrt{2}g}{\left(\lambda_+^2 - \lambda_-^2\right)}, \quad \cos 2\alpha = \frac{\left(\omega_0^2 + 2g^2\omega_c^2 - \omega_c^2\right)}{\left(\lambda_+^2 - \lambda_-^2\right)}. \tag{3.20}$$

We are now in a position to express the four Hamiltonians in terms of the normal modes as

$$H_{L_1} + H_{L_2} + H_c = \frac{p_1^2 + p_2^2 + p_c^2}{2} + \frac{\omega_0^2 y_0^2}{2} + \frac{\lambda_+^2}{2}\left(y_+ + \frac{\sqrt{2}q_0\omega_0^2}{\lambda_+^2}\cos\alpha\right)^2 + \frac{\lambda_-^2}{2}\left(y_- + \frac{\sqrt{2}q_0\omega_0^2}{\lambda_-^2}\sin\alpha\right)^2, \tag{3.21}$$

$$H_{R_1} + H_{R_2} + H_c = \frac{p_1^2 + p_2^2 + p_c^2}{2} + \frac{\omega_0^2 y_0^2}{2} + \frac{\lambda_+^2}{2}\left(y_+ - \frac{\sqrt{2}q_0\omega_0^2}{\lambda_+^2}\cos\alpha\right)^2 + \frac{\lambda_-^2}{2}\left(y_- - \frac{\sqrt{2}q_0\omega_0^2}{\lambda_-^2}\sin\alpha\right)^2, \tag{3.22}$$

$$H_{L_1} + H_{R_2} + H_c = \frac{p_1^2 + p_2^2 + p_c^2}{2} + \frac{\lambda_+^2 y_+^2 + \lambda_-^2 y_-^2}{2} + \frac{\omega_0^2}{2}\left(y_0 + \sqrt{2}q_0\right)^2, \tag{3.23}$$

$$H_{R_1} + H_{L_2} + H_c = \frac{p_1^2 + p_2^2 + p_c^2}{2} + \frac{\lambda_+^2 y_+^2 + \lambda_-^2 y_-^2}{2} + \frac{\omega_0^2}{2}\left(y_0 - \sqrt{2}q_0\right)^2. \tag{3.24}$$

The ground state eigenfunctions of the four Hamiltonians are

$$\Psi_{L_1,L_2}(y_+, y_-, y_0) = \left(\frac{\lambda_-}{\pi\hbar}\frac{\lambda_+}{\pi\hbar}\frac{\omega_0}{\pi\hbar}\right)^{\frac{1}{4}}\exp\left[-\frac{\lambda_+}{2\hbar}\left(y_+ + \frac{\sqrt{2}q_0\omega_0^2}{\lambda_+^2}\cos\alpha\right)^2 - \frac{\lambda_-}{2\hbar}\left(y_- + \frac{\sqrt{2}q_0\omega_0^2}{\lambda_+^2}\sin\alpha\right)^2 - \frac{\omega_0}{2\hbar}y_0^2\right], \tag{3.25}$$

$$\Psi_{R_1,R_2}(y_+, y_-, y_0) = \left(\frac{\lambda_-}{\pi\hbar}\frac{\lambda_+}{\pi\hbar}\frac{\omega_0}{\pi\hbar}\right)^{\frac{1}{4}}\exp\left[-\frac{\lambda_+}{2\hbar}\left(y_+ - \frac{\sqrt{2}q_0\omega_0^2}{\lambda_+^2}\cos\alpha\right)^2 - \frac{\lambda_-}{2\hbar}\left(y_- - \frac{\sqrt{2}q_0\omega_0^2}{\lambda_+^2}\sin\alpha\right)^2 - \frac{\omega_0}{2\hbar}y_0^2\right], \tag{3.26}$$

$$\Psi_{L_1,R_2}(y_+, y_-, y_0) = \left(\frac{\lambda_-}{\pi\hbar}\frac{\lambda_+}{\pi\hbar}\frac{\omega_0}{\pi\hbar}\right)^{\frac{1}{4}}\exp\left[-\frac{\lambda_+}{2\hbar}y_+^2 - \frac{\lambda_-}{2\hbar}y_-^2 - \frac{\omega_0}{2\hbar}\left(y_0 + \sqrt{2}q_0\right)^2\right], \tag{3.27}$$

$$\Psi_{R_1,L_2}(y_+, y_-, y_0) = \left(\frac{\lambda_-}{\pi\hbar}\frac{\lambda_+}{\pi\hbar}\frac{\omega_0}{\pi\hbar}\right)^{\frac{1}{4}}\exp\left[-\frac{\lambda_+}{2\hbar}y_+^2 - \frac{\lambda_-}{2\hbar}y_-^2 - \frac{\omega_0}{2\hbar}\left(y_0 - \sqrt{2}q_0\right)^2\right]. \tag{3.28}$$

The corresponding diagonal energies are all the same

$$E_0 = \frac{\hbar(\lambda_+ + \lambda_- + \omega_0)}{2}. \tag{3.29}$$

It then remains to evaluate the overlaps and, interestingly, one finds that they are all identical

$$\begin{aligned}\langle\Psi_{L_1,L_2}|\Psi_{L_1,R_2}\rangle &= \langle\Psi_{L_1,L_2}|\Psi_{R_1,L_2}\rangle = \langle\Psi_{L_1,R_2}|\Psi_{R_1,R_2}\rangle\\ &= \langle\Psi_{R_1,L_2}|\Psi_{R_1,R_2}\rangle\\ &= \exp\left[-\frac{q_0^2\omega_0^4}{2\hbar}\left(\frac{1}{\lambda_+^3}\cos^2\alpha+\frac{1}{\lambda_-^3}\sin^2\alpha\right)-\frac{\omega_0}{2\hbar}q_0^2\right]\\ &\equiv S_2. \end{aligned}\tag{3.30}$$

Using Eq. (2.23), replacing g with $\sqrt{2}g$, we find that the overlap is

$$S_2=\exp\left(-\frac{\omega_0}{2\hbar}q_0^2\left[1+\frac{(\omega_0+\omega_c+2g^2\omega_c)}{\sqrt{(\omega_0+\omega_c)^2+2g^2\omega_c^2}}\right]\right).\tag{3.31}$$

The Hamiltonian matrix using the four ground state wave functions is identical to the independent replica case as given in Eq. (2.3) except that the diagonal energy $\hbar\omega_0$ is replaced by E_0 as given in Eq. (3.29), and the overlap S must be replaced by S_2. The eigenvalues are then $E_0, E_0, E_0 \pm 2VS_2$. The effect of the coupling to the cavity is twofold. It changes the mean energy and the overlap. However, as in the single replica case, there is no noticeable change when the cavity and system frequencies are identical—there is no resonance effect.

C. Three replicas interacting with the cavity

As further preparation for the general result with N replicas, it is instructive to consider also in some detail the case with three replicas. In this case, the Hamiltonian becomes

$$H=\sum_{j=1}^{3}\hat{H}_{L,j}|L_j\rangle\langle L_j|+\hat{H}_{R,j}|R_j\rangle\langle R_j|+\hat{V}[|L_j\rangle\langle R_j|+|R_j\rangle\langle L_j|]+H_c\hat{I},\tag{3.32}$$

and the cavity Hamiltonian couples bilinearly all three replicas

$$H_c=\frac{p_c^2}{2}+\frac{\omega_c^2}{2}[q_c-g(q_1+q_2+q_3)]^2.\tag{3.33}$$

Due to the alternating signs of the shift q_0, we will now have 2^3 Hamiltonians with identical second derivative matrices but with different signs of q_0. The electronic basis thus has eight states: $|L_1,L_2,L_3\rangle$, $|L_1,L_2,R_3\rangle$, $|L_1,R_2,L_3\rangle$, $|R_1,L_2,L_3\rangle$, $|R_1,R_2,L_3\rangle$, $|R_1,L_2,R_3\rangle$, $|L_1,R_2,R_3\rangle$, and $|R_1,R_2,R_3\rangle$. The nonadiabatic coupling couples only the left and right states of the same replica. This implies that when representing the Hamiltonian in the electronic states, one obtains an eight-dimensional Hamiltonian matrix

$$H=\begin{pmatrix} H_{L_1,L_2,L_3} & V & V & V & 0 & 0 & 0 & 0\\ V & H_{L_1,L_2,R_3} & 0 & 0 & 0 & V & V & 0\\ V & 0 & H_{L_1,R_2,L_3} & 0 & V & 0 & V & 0\\ V & 0 & 0 & H_{R_1,L_2,L_3} & V & V & 0 & 0\\ 0 & 0 & V & V & H_{R_1,R_2,L_3} & 0 & 0 & V\\ 0 & V & 0 & V & 0 & H_{R_1,L_2,R_3} & 0 & V\\ 0 & V & V & 0 & 0 & 0 & H_{L_1,R_2,R_3} & V\\ 0 & 0 & 0 & 0 & V & V & V & H_{R_1,R_2,R_3} \end{pmatrix},\tag{3.34}$$

where we used the shorthand $H_{L_1,L_2,L_3}=H_{L_1}+H_{L_2}+H_{L_3}+H_c$, etc.

As in the previous case, we will use the ground state wave functions for each of the diabatic Hamiltonians to obtain a representation of the Hamiltonian in the "nuclear" states as well. For this purpose, it remains to find the overlap matrix elements. We follow the previous strategy and first diagonalize the force constant matrix without the cavity coordinate, which now has three eigenvalues ω_0^2, ω_0^2 and $\omega_0^2+3g^2\omega_c^2$ so that

$$\begin{aligned}K'_{3\times3}&=\begin{pmatrix}\omega_0^2+g^2\omega_c^2 & \omega_c^2g^2 & \omega_c^2g^2\\ \omega_c^2g^2 & \omega_0^2+g^2\omega_c^2 & \omega_c^2g^2\\ \omega_c^2g^2 & \omega_c^2g^2 & \omega_0^2+\omega_c^2g^2\end{pmatrix}\\ &=O_{3\times3}^T\begin{pmatrix}\omega_0^2+3\omega_c^2g^2 & 0 & 0\\ 0 & \omega_0^2 & 0\\ 0 & 0 & \omega_0^2\end{pmatrix}O_{3\times3},\end{aligned}\tag{3.35}$$

and the orthogonal transformation matrix is readily found to be such that

$$O_{4\times4}=\begin{pmatrix}O_{3\times3} & 0\\ 0 & 1\end{pmatrix}=\begin{pmatrix}\frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{6}} & 0\\ \frac{1}{\sqrt{3}} & 0 & -\frac{2}{\sqrt{6}} & 0\\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{6}} & 0\\ 0 & 0 & 0 & 1\end{pmatrix}.\tag{3.36}$$

The full force constant matrix is then rewritten as

$$\begin{aligned}O_{4\times4}^TK_{4\times4}O_{4\times4}&=O_{4\times4}^T\begin{pmatrix}\omega_0^2+g^2\omega_c^2 & \omega_c^2g^2 & \omega_c^2g^2 & \omega_c^2g\\ \omega_c^2g^2 & \omega_0^2+g^2\omega_c^2 & \omega_c^2g^2 & \omega_c^2g\\ \omega_c^2g^2 & \omega_c^2g^2 & \omega_0^2+\omega_c^2g^2 & \omega_c^2g\\ \omega_c^2g & \omega_c^2g & \omega_c^2g & \omega_c^2\end{pmatrix}O_{4\times4}\\ &=\begin{pmatrix}\omega_0^2+3g^2\omega_c^2 & 0 & 0 & \sqrt{3}\omega_c^2g\\ 0 & \omega_0^2 & 0 & 0\\ 0 & 0 & \omega_0^2 & 0\\ \sqrt{3}g\omega_c^2 & 0 & 0 & \omega_c^2\end{pmatrix}.\end{aligned}\tag{3.37}$$

The orthogonal matrix that diagonalizes the transformed force constant matrix is such that

$$\begin{pmatrix} \omega_0^2+3g^2\omega_c^2 & 0 & 0 & \sqrt{3}\omega_c^2 g \\ 0 & \omega_0^2 & 0 & 0 \\ 0 & 0 & \omega_0^2 & 0 \\ \sqrt{3}g\omega_c^2 & 0 & 0 & \omega_c^2 \end{pmatrix} = U_{4\times 4}\begin{pmatrix} \lambda_+^2 & 0 & 0 & 0 \\ 0 & \omega_0^2 & 0 & 0 \\ 0 & 0 & \omega_0^2 & 0 \\ 0 & 0 & 0 & \lambda_-^2 \end{pmatrix} U_{4\times 4}^T, \tag{3.38}$$

and

$$U_{4\times 4} = \begin{pmatrix} \cos\alpha & 0 & 0 & \sin\alpha \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -\sin\alpha & 0 & 0 & \cos\alpha \end{pmatrix}. \tag{3.39}$$

The orthogonal matrix that diagonalizes the full four dimensional force constant matrix is

$$W_{4\times 4} = O_{4\times 4}U_{4\times 4} = \begin{pmatrix} \frac{\cos\alpha}{\sqrt{3}} & -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{6}} & \frac{\sin\alpha}{\sqrt{3}} \\ \frac{\cos\alpha}{\sqrt{3}} & 0 & -\frac{2}{\sqrt{6}} & \frac{\sin\alpha}{\sqrt{3}} \\ \frac{\cos\alpha}{\sqrt{3}} & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{6}} & \frac{\sin\alpha}{\sqrt{3}} \\ -\sin\alpha & 0 & 0 & \cos\alpha \end{pmatrix}, \tag{3.40}$$

and this gives us the relationship between the normal mode coordinates and the physical coordinates such that

$$q_1 = \frac{\cos\alpha}{\sqrt{3}}y_+ - \frac{1}{\sqrt{2}}y_1 + \frac{1}{\sqrt{6}}y_2 + y_-\frac{\sin\alpha}{\sqrt{3}}, \tag{3.41}$$

$$q_2 = \frac{\cos\alpha}{\sqrt{3}}y_+ - \frac{2}{\sqrt{6}}y_2 + y_-\frac{\sin\alpha}{\sqrt{3}}, \tag{3.42}$$

$$q_3 = \frac{\cos\alpha}{\sqrt{3}}y_+ + \frac{1}{\sqrt{2}}y_1 + \frac{1}{\sqrt{6}}y_2 + y_-\frac{\sin\alpha}{\sqrt{3}}, \tag{3.43}$$

$$q_c = -y_+\sin\alpha + y_-\cos\alpha. \tag{3.44}$$

The transformation angle is given as in the single replica case, except for the change in the coupling constant, so that now, due to the three replicas,

$$\sin 2\alpha = -\frac{2\omega_c^2\sqrt{3}g}{\left(\lambda_+^2-\lambda_-^2\right)}, \quad \cos 2\alpha = \frac{\left(\omega_0^2+3g^2\omega_c^2-\omega_c^2\right)}{\left(\lambda_+^2-\lambda_-^2\right)}. \tag{3.45}$$

We have eight different combinations of the diabatic potential depending on the sign of q_0 in each of them. These correspond to V_{L_1,L_2,L_3}, V_{L_1,L_2,R_3}, V_{L_1,R_2,L_3}, V_{R_1,L_2,L_3}, V_{R_1,R_2,L_3}, V_{R_1,L_2,R_3}, V_{L_1,R_2,R_3}, and V_{R_1,R_2,R_3} but they all have the same second derivative matrix. For example,

$$V_{L_1,L_2,L_3} = \frac{\omega_0^2\left(y_1^2+y_2^2\right)}{2} + \frac{\lambda_+^2}{2}\left(y_+ + \frac{\sqrt{3}q_0\omega_0^2}{\lambda_+^2}\cos\alpha\right)^2 + \frac{\lambda_-^2}{2}\left(y_- + \frac{\sqrt{3}q_0\omega_0^2}{\lambda_-^2}\sin\alpha\right)^2, \tag{3.46}$$

$$V_{L_1,L_2,R_3} = \frac{\lambda_+^2}{2}\left(y_+ + \frac{q_0\omega_0^2}{\sqrt{3}\lambda_+^2}\cos\alpha\right)^2 + \frac{\omega_0^2}{2}\left(y_1-\sqrt{2}q_0\right)^2 + \frac{\omega_0^2}{2}\left(y_2-\frac{2}{\sqrt{6}}q_0\right)^2 + \frac{\lambda_-^2}{2}\left(y_- + \frac{q_0\omega_0^2}{\sqrt{3}\lambda_-^2}\sin\alpha\right)^2, \tag{3.47}$$

$$V_{L_1,R_2,L_3} = \frac{\lambda_+^2}{2}\left(y_+ + \frac{q_0\omega_0^2}{\sqrt{3}\lambda_+^2}\cos\alpha\right)^2 + \frac{\omega_0^2}{2}y_1^2 + \frac{\omega_0^2}{2}\left(y_2+\frac{4}{\sqrt{6}}q_0\right)^2 + \frac{\lambda_-^2}{2}\left(y_- + \frac{q_0\omega_0^2}{\sqrt{3}\lambda_-^2}\sin\alpha\right)^2, \tag{3.48}$$

$$V_{R_1,L_2,L_3} = \frac{\lambda_+^2}{2}\left(y_+ + \frac{q_0\omega_0^2}{\sqrt{3}\lambda_+^2}\cos\alpha\right)^2 + \frac{\omega_0^2}{2}\left(y_1+\sqrt{2}q_0\right)^2 + \frac{\omega_0^2}{2}\left(y_2-\frac{2}{\sqrt{6}}q_0\right)^2 + \frac{\lambda_-^2}{2}\left(y_- + \frac{q_0\omega_0^2}{\sqrt{3}\lambda_-^2}\sin\alpha\right)^2, \tag{3.49}$$

and the other four potentials are the same except that the plus and minus signs interchange.

The ground state wave functions are, for example,

$$\varphi_{L_1,L_2,L_3} = \left(\frac{\lambda_+\lambda_-}{\pi^2\hbar^2}\right)^{\frac{1}{4}}\sqrt{\frac{\omega_0}{\pi\hbar}}\cdot\exp\left[-\frac{\lambda_+}{2\hbar}\left(y_+ + \frac{\sqrt{3}q_0\omega_0^2}{\lambda_+^2}\cos\alpha\right)^2 - \frac{\lambda_-}{2\hbar}\left(y_- \pm \frac{\sqrt{3}q_0\omega_0^2}{\lambda_-^2}\sin\alpha\right)^2 - \frac{\omega_0\left(y_1^2+y_2^2\right)}{2\hbar}\right], \tag{3.50}$$

and the expressions for the remaining seven wave functions are self-evident. The ground state energies are all the same

$$E_0 = \frac{\hbar(\lambda_+ + 2\omega_0 + \lambda_-)}{2} = \hbar\omega_0 + \frac{\hbar}{2}\sqrt{(\omega_0+\omega_c)^2 + 3g^2\omega_c^2}, \tag{3.51}$$

and have the same structure as in the previous one and two replica cases except that now g has been replaced with $\sqrt{3}g$. The possible overlaps due to the nonadiabatic coupling must have only one index that changes sign and, as before, one finds after some algebra that all of these are identical; the overlap with three replicas is

$$S_3 = \exp\left[-\frac{2\omega_0}{3\hbar}q_0^2 - \frac{\omega_0 q_0^2}{3\hbar}\left(\frac{\omega_0^3}{\lambda_+^3}\cos^2\alpha + \frac{\omega_0^3}{\lambda_-^3}\sin^2\alpha\right)\right] = \exp\left[-\frac{2\omega_0}{3\hbar}q_0^2 - \frac{\omega_0 q_0^2}{3\hbar}\left(\frac{\left(3g^2\omega_c+\omega_c+\omega_0\right)}{\sqrt{(\omega_0+\omega_c)^2+\omega_c^2 3g^2}}\right)\right]. \tag{3.52}$$

The full Hamiltonian in the ground state basis becomes

$$H = \begin{pmatrix} E_0 & VS_3 & VS_3 & VS_3 & 0 & 0 & 0 & 0 \\ VS_3 & E_0 & 0 & 0 & 0 & VS_3 & VS_3 & 0 \\ VS_3 & 0 & E_0 & 0 & VS_3 & 0 & VS_3 & 0 \\ VS_3 & 0 & 0 & E_0 & VS_3 & VS_3 & 0 & 0 \\ 0 & 0 & VS_3 & VS_3 & E_0 & 0 & 0 & VS_3 \\ 0 & VS_3 & 0 & VS_3 & 0 & E_0 & 0 & VS_3 \\ 0 & VS_3 & VS_3 & 0 & 0 & 0 & E_0 & VS_3 \\ 0 & 0 & 0 & 0 & VS_3 & VS_3 & VS_3 & E_0 \end{pmatrix}, \tag{3.53}$$

and the eigenvalues are $E_0 \pm 3VS_3$, and a threefold degeneracy of $E_0 \pm VS_3$. Here, too, this is the same structure as in the case without the cavity. This feature cannot be overstressed. It is a result of the fact that the nonadiabatic coupling is always between two states of the same replica. In the uncoupled case, the three independent replicas have the energies $\frac{\hbar\omega_0}{2} \pm VS$. This gives, for the lowest state, the total energy of $3\left(\frac{\hbar\omega_0}{2} - VS\right)$; the next energies are $3\frac{\hbar\omega_0}{2} - VS$, and they appear three times. Similarly, the next energies appear three times: $3\frac{\hbar\omega_0}{2} + VS$, and the highest energy is $3\left(\frac{\hbar\omega_0}{2} + VS\right)$. As in the two-replica case, the effect of the coupling to the cavity changes the mean energy and the overlap, but the structure of the energy levels remains the same.

Comparing the overlaps for the case of one, two, and three interacting replicas indicates that in the general case of N replicas, all overlaps that are nonzero are the same and would have the form

$$S_N = \exp\left[-\frac{\omega_0}{N\hbar}q_0^2\left(N - 1 + \frac{(\omega_0 + \omega_c + Ng^2\omega_c)}{\sqrt{(\omega_0 + \omega_c)^2 + Ng^2\omega_c^2}}\right)\right], \tag{3.54}$$

such that

$$\lim_{N\to\infty} S_N = \exp\left[-\frac{\omega_0}{\hbar}q_0^2\right] = S, \tag{3.55}$$

implying that the interaction with the cavity does not change the magnitude of the overlaps, and they are just the result for each replica separately, without coupling to the cavity.

Similarly, one may expect that the mean energy for the N replica case is

$$E_0 = (N - 1)\frac{\hbar\omega_0}{2} + \frac{\hbar}{2}\sqrt{(\omega_0 + \omega_c)^2 + Ng^2\omega_c^2}, \tag{3.56}$$

so that the interaction with the cavity shifts the ground state energy by an amount that, as we shall see below, is related to the Rabi splitting induced by the cavity. In Sec. IV, we will deal with the general case and show that indeed, Eqs. (3.55) and (3.56) are the results for the N replica case.

IV. CAVITY EFFECT ON THE SYMMETRIC DIABATIC ENERGY SPLITTING OF *N* REPLICAS

A. *N* identical replicas without the cavity

In this case, each replica will have the doublet of energy levels $\frac{\hbar\omega_0}{2} \pm VS$. The ground state energy of all replicas combined will be $N\left(\frac{\hbar\omega_0}{2} - VS\right)$; the next level will have one replica in the upper state and all other replicas in the ground state. Since there are altogether N replicas, this may occur N different times, so that one will have the energy $(N - 1)\left(\frac{\hbar\omega_0}{2} - VS\right) + \left(\frac{\hbar\omega_0}{2} + VS\right) = N\frac{\hbar\omega_0}{2} - (N - 2)VS$. If one has K replicas in the upper state and $N - K$ in the ground state, the energy will be $N\frac{\hbar\omega_0}{2} + (2K - N)VS$, and it will occur with the multiplicity given by the binomial factor $\frac{N!}{K!(N-K)!}$. The total number of states will be given by the sum $\sum_{K=0}^{N}\frac{N!}{K!(N-K)!} = 2^N$, as expected. Due to the fact that the nonadiabatic term couples only left and right states of a single replica, and provided that we can prove that all allowed overlaps are identical, then also in the presence of coupling to the cavity, the energy matrix obtained with all the ground states of the diabatic Hamiltonians will have the same structure, irrespective of the fact that the replicas are or are not coupled to the cavity. The coupling to the cavity will only change the magnitude of the mean energy and the allowed overlaps.

B. The transformation to normal modes in the presence of the cavity

In this case, the diabatic Hamiltonians become

$$H_D = \sum_{j=1}^{N} \hat{H}_{Lj}|L_j\rangle\langle L_j| + \hat{H}_{R,j}|R_j\rangle\langle R_j| + \hat{V}\left[|L_j\rangle\langle R_j| + |R_j\rangle\langle L_j|\right] + H_c\hat{I}, \tag{4.1}$$

and the cavity Hamiltonian is

$$H_c = \frac{p_c^2}{2} + \frac{\omega_c^2}{2}\left(q_c - g\sum_{j=1}^{N} q_j\right)^2. \tag{4.2}$$

Due to the two states of each of the N replicas, one has 2^N different Hamiltonians that depend on the signs of q_0, and this creates an enormous basis set. However, as in the previous specific examples, the nonadiabatic coupling between any two states is nonzero only when one pair of states has a different sign for the same Hamiltonian; this leads to simplification.

As a first step, we consider the normal mode transformation. The second derivative matrix of the potentials coupling all $N + 1$ degrees of freedom has the form

$$K_{(N+1)\times(N+1)} = \begin{pmatrix} \omega_0^2 + g^2\omega_c^2 & g^2\omega_c^2 & g^2\omega_c^2 & \dots & g^2\omega_c^2 & g\omega_c^2 \\ g^2\omega_c^2 & \omega_0^2 + g^2\omega_c^2 & g^2\omega_c^2 & \dots & g^2\omega_c^2 & g\omega_c^2 \\ g^2\omega_c^2 & g^2\omega_c^2 & \omega_0^2 + g^2\omega_c^2 & \dots & g^2\omega_c^2 & g\omega_c^2 \\ \vdots & \vdots & \vdots & \dots & \vdots & \vdots \\ g^2\omega_c^2 & g^2\omega_c^2 & g^2\omega_c^2 & \dots & \omega_0^2 + g^2\omega_c^2 & g\omega_c^2 \\ g\omega_c^2 & g\omega_c^2 & g\omega_c^2 & \dots & g\omega_c^2 & \omega_c^2 \end{pmatrix}$$

$$= \begin{pmatrix} K_{N\times N} & \underline{\mathrm{g}}\omega_c^2 \\ \underline{\mathrm{g}}\omega_c^2 & \omega_c^2 \end{pmatrix} = \begin{pmatrix} \omega_0^2 I_{N\times N} + g^2\omega_c^2 W_{N\times N} & \underline{\mathrm{g}}\omega_c^2 \\ \underline{\mathrm{g}}\omega_c^2 & \omega_c^2 \end{pmatrix}, \tag{4.3}$$

where $\underline{g}\omega_c^2$ is an N dimensional constant vector of ones multiplied by $g\omega_c^2$ and the final equality defines the matrix $W_{N\text{x}N}$. It has one eigenvalue N with a normalized eigenvector of N entries of $\frac{1}{\sqrt{N}}$ and $N-1$ null eigenvalues. The orthogonal matrix $O_{N\text{x}N}$ that diagonalizes $W_{N\text{x}N}$ has the following structure:

$$O_{N\text{x}N} = \begin{pmatrix} \frac{1}{\sqrt{N}} & -\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{12}} & -\frac{1}{\sqrt{20}} & \cdots & -\frac{1}{\sqrt{N(N-1)}} \\ \frac{1}{\sqrt{N}} & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{12}} & -\frac{1}{\sqrt{20}} & \cdots & -\frac{1}{\sqrt{N(N-1)}} \\ \frac{1}{\sqrt{N}} & 0 & \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{12}} & -\frac{1}{\sqrt{20}} & \cdots & -\frac{1}{\sqrt{N(N-1)}} \\ \frac{1}{\sqrt{N}} & 0 & 0 & \frac{3}{\sqrt{12}} & -\frac{1}{\sqrt{20}} & \cdots & -\frac{1}{\sqrt{N(N-1)}} \\ \frac{1}{\sqrt{N}} & 0 & 0 & 0 & \frac{4}{\sqrt{20}} & \cdots & -\frac{1}{\sqrt{N(N-1)}} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \frac{1}{\sqrt{N}} & 0 & 0 & 0 & 0 & \cdots & \sqrt{\frac{N-1}{N}} \end{pmatrix}. \tag{4.4}$$

We then rewrite

$$O_{N\times N}^T W_{N\times N} O_{N\times N} = w_{N\times N}, \tag{4.5}$$

with $w_{N\text{x}N}$ being diagonal so that the diagonal form of the second order derivative matrix without the cavity coordinate is written as

$$\begin{aligned} v_2(N\times N) &= O_{N\times N}^T\left[\omega_0^2 I_{N\times N} + g^2\omega_c^2 W_{N\times N}\right]O_{N\times N} \\ &= \omega_0^2 I_{N\times N} + g^2\omega_c^2 w_{N\times N}. \end{aligned} \tag{4.6}$$

The full second derivative matrix may then be transformed by defining

$$O_{N+1\times N+1} = \begin{pmatrix} O_{N\times N} & 0 \\ 0 & 1 \end{pmatrix}, \tag{4.7}$$

so that

$$\begin{aligned} K'_{(N+1)\times(N+1)} &= O_{N+1\times N+1}^T K_{(N+1)\times(N+1)} O_{N+1\times N+1} \\ &= \begin{pmatrix} w_2(N\text{x}N) & O_{N\text{x}N}^T \underline{g}\omega_c^2 \\ \underline{g}\omega_c^2 O_{N\text{x}N} & \omega_c^2 \end{pmatrix}. \end{aligned} \tag{4.8}$$

Since all columns of $O_{N\text{x}N}$ sum to zero except for the first, which sums to $\sqrt{N}$, one readily finds that

$$O_{N\times N}^T \underline{g}\omega_c^2 = O_{N\times N}^T g\omega_c^2 \begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix} = \begin{pmatrix} \sqrt{N}g\omega_c^2 \\ 0 \\ \vdots \\ 0 \end{pmatrix}. \tag{4.9}$$

The transformed second derivative matrix then has the following form:

$$K'_{(N+1)\times(N+1)} = \begin{pmatrix} \omega_0^2 + Ng^2\omega_c^2 & 0 & 0 & \cdots & 0 & \sqrt{N}g\omega_c^2 \\ 0 & \omega_0^2 & 0 & \cdots & 0 & 0 \\ 0 & 0 & \omega_0^2 & \cdots & 0 & 0 \\ \vdots & \vdots & 0 & \ddots & \vdots & \vdots \\ 0 & 0 & \vdots & \cdots & \omega_0^2 & 0 \\ \sqrt{N}g\omega_c^2 & 0 & 0 & 0 & 0 & \omega_c^2 \end{pmatrix}. \tag{4.10}$$

Diagonalizing this matrix is relatively straightforward; the eigenvalue ω_0^2 has a degeneracy of $N-1$, and the remaining two eigenvalues are

$$\begin{aligned} \lambda_\pm^2 &= \frac{\left(\omega_0^2 + \omega_c^2 + Ng^2\omega_c^2\right)}{2} \\ &\quad \pm \frac{1}{2}\sqrt{\left(\omega_0^2 - \omega_c^2\right)^2 + 2Ng^2\omega_c^2\left(\omega_0^2 + \omega_c^2\right) + \left(Ng^2\omega_c^2\right)^2}, \end{aligned} \tag{4.11}$$

and these are identical to the eigenvalues in Eq. (2.10) except that having N replicas implies that the coupling constant goes as $\sqrt{N}g$. On resonance ($\omega_0 = \omega_c$), we have that

$$\lambda_\pm^2(\omega_0 = \omega_c) = \omega_0^2\left(1 + \frac{Ng^2}{2} \pm \sqrt{N}g\sqrt{1 + \frac{Ng^2}{4}}\right), \tag{4.12}$$

which implies that the Rabi splitting is

$$\begin{aligned} \Delta\omega_{\text{Rabi}} &= \lambda_+ - \lambda_- \\ &= \omega_0\sqrt{1 + \frac{Ng^2}{2}}\left(\sqrt{1 + \frac{\sqrt{N}g\sqrt{1 + \frac{Ng^2}{4}}}{1 + \frac{Ng^2}{2}}}\right. \\ &\qquad \left. - \sqrt{1 - \frac{\sqrt{N}g\sqrt{1 + \frac{Ng^2}{4}}}{1 + \frac{Ng^2}{2}}}\right) \\ &= \omega_0\sqrt{N}g + O\left(\omega_0 Ng^2\right), \end{aligned} \tag{4.13}$$

and this gives us an estimate for the magnitude of $\sqrt{N}g$.

It remains to express the normal modes in terms of the physical coordinates and vice versa. The orthogonal matrix that diagonalizes $K'_{(N+1)\times(N+1)}$ is

$$U_{N+1\times N+1} = \begin{pmatrix} \cos\alpha & 0 & 0 & \cdots & 0 & \sin\alpha \\ 0 & 1 & 0 & \cdots & 0 & 0 \\ 0 & 0 & 1 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 1 & 0 \\ -\sin\alpha & 0 & 0 & \cdots & 0 & \cos\alpha \end{pmatrix}, \tag{4.14}$$

and the angle α is given by the usual relations

$$\sin 2\alpha = \frac{2\omega_c^2\sqrt{N}g}{\left(\mu_+^2 - \mu_-^2\right)}, \quad \cos 2\alpha = \frac{\left(\omega_0^2 + Ng^2\omega_c^2 - \omega_c^2\right)}{\left(\mu_+^2 - \mu_-^2\right)}, \tag{4.15}$$

where the constant g has been replaced with $\sqrt{N}g$.

The orthogonal matrix that diagonalizes the full second derivative matrix $K_{(N+1\times N+1)}$ is then

$$O_{N+1\times N+1}U_{N+1\times N+1}=\begin{pmatrix} \frac{\cos\alpha}{\sqrt{N}} & -\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{12}} & -\frac{1}{\sqrt{20}} & \cdots & -\frac{1}{\sqrt{N(N-1)}} & \frac{\sin\alpha}{\sqrt{N}}\\ \frac{\cos\alpha}{\sqrt{N}} & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{12}} & -\frac{1}{\sqrt{20}} & \cdots & -\frac{1}{\sqrt{N(N-1)}} & \frac{\sin\alpha}{\sqrt{N}}\\ \frac{\cos\alpha}{\sqrt{N}} & 0 & \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{12}} & -\frac{1}{\sqrt{20}} & \cdots & -\frac{1}{\sqrt{N(N-1)}} & \frac{\sin\alpha}{\sqrt{N}}\\ \frac{\cos\alpha}{\sqrt{N}} & 0 & 0 & \frac{3}{\sqrt{12}} & -\frac{1}{\sqrt{20}} & \cdots & -\frac{1}{\sqrt{N(N-1)}} & \frac{\sin\alpha}{\sqrt{N}}\\ \frac{\cos\alpha}{\sqrt{N}} & 0 & 0 & 0 & \frac{4}{\sqrt{20}} & \cdots & -\frac{1}{\sqrt{N(N-1)}} & \frac{\sin\alpha}{\sqrt{N}}\\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots\\ \frac{\cos\alpha}{\sqrt{N}} & 0 & 0 & 0 & 0 & \cdots & \sqrt{\frac{N-1}{N}} & \frac{\sin\alpha}{\sqrt{N}}\\ -\sin\alpha & 0 & 0 & 0 & 0 & \cdots & 0 & \cos\alpha \end{pmatrix}, \tag{4.16}$$

and one readily finds that the physical coordinates may be expressed in terms of the normal modes as

$$\begin{pmatrix} q_1\\ q_2\\ q_3\\ \vdots\\ q_N\\ q_c \end{pmatrix} = Z_{N+1\times N+1}\begin{pmatrix} y_+\\ y_1\\ y_2\\ \vdots\\ y_{N-1}\\ y_- \end{pmatrix} = O_{N+1\times N+1}U_{N+1\times N+1}\begin{pmatrix} y_+\\ y_1\\ y_2\\ \vdots\\ y_{N-1}\\ y_- \end{pmatrix}$$

$$=\begin{pmatrix} y_+\frac{\cos\alpha}{\sqrt{N}}-\frac{1}{\sqrt{2}}y_1-\frac{1}{\sqrt{6}}y_2-\frac{1}{\sqrt{12}}y_3-\frac{1}{\sqrt{20}}y_4+\cdots-\frac{1}{\sqrt{N(N-1)}}y_{N-1}+y_-\frac{\sin\alpha}{\sqrt{N}}\\ y_+\frac{\cos\alpha}{\sqrt{N}}+\frac{1}{\sqrt{2}}y_1-\frac{1}{\sqrt{6}}y_2-\frac{1}{\sqrt{12}}y_3-\frac{1}{\sqrt{20}}y_4+\cdots-\frac{1}{\sqrt{N(N-1)}}y_{N-1}+y_-\frac{\sin\alpha}{\sqrt{N}}\\ y_+\frac{\cos\alpha}{\sqrt{N}}+\frac{2}{\sqrt{6}}y_2-\frac{1}{\sqrt{12}}y_3-\frac{1}{\sqrt{20}}y_4+\cdots-\frac{1}{\sqrt{N(N-1)}}y_{N-1}+y_-\frac{\sin\alpha}{\sqrt{N}}\\ y_+\frac{\cos\alpha}{\sqrt{N}}+\frac{3}{\sqrt{12}}y_3-\frac{1}{\sqrt{20}}y_4+\cdots-\frac{1}{\sqrt{N(N-1)}}y_{N-1}+y_-\frac{\sin\alpha}{\sqrt{N}}\\ y_+\frac{\cos\alpha}{\sqrt{N}}+\frac{4}{\sqrt{20}}y_4+\cdots-\frac{1}{\sqrt{N(N-1)}}y_{N-1}+y_-\frac{\sin\alpha}{\sqrt{N}}\\ \vdots\\ y_+\frac{\cos\alpha}{\sqrt{N}}+\sqrt{\frac{N-1}{N}}y_{N-1}+y_-\frac{\sin\alpha}{\sqrt{N}}\\ -y_+\sin\alpha+y_-\cos\alpha \end{pmatrix}. \tag{4.17}$$

C. Overlaps

Having worked out the normal mode transformation, it remains to show that all allowed overlaps are the same. As already noted, the allowed overlaps are those in which only one sign of q_0 changes. Therefore, without loss of generality, let us consider two configurations in which only the kth replica changes sign,

$$Q_1=\sum_{j=0}^{N-1}h_jq_j, \tag{4.18}$$

$$Q_2=\sum_{j=0}^{N-1}h_jq_j-2h_kq_k, \tag{4.19}$$

where $h_j=\pm1$. From Eq. (4.17), we have that

$$q_j=\sum_{l=0}^{N}Z_{jl}y_l, \tag{4.20}$$

and the elements Z_{jl} are those of the orthogonal normal mode transformation. For simplicity we used here the notation that $y_0=y_+$ and $y_N=y_-$. We may then rewrite

$$Q_1 = \sum_{l=0}^{N}\sum_{j=0}^{N-1} h_j q_j Z_{jl} y_l, \tag{4.21}$$

$$Q_2 = \sum_{l=0}^{N}\sum_{j=0}^{N-1} h_j q_j Z_{jl} y_l - 2h_k \sum_{l=0}^{N} Z_{kl} y_l. \tag{4.22}$$

The potential associated with the configuration Q_1 is

$$\begin{aligned} V(Q_1) &= \sum_{j=1}^{N-1} \frac{\omega_0^2 y_j^2}{2} + \frac{\lambda_0^2 y_0^2}{2} + \frac{\lambda_N^2 y_N^2}{2} - \omega_0^2 \sum_{j=0}^{N-1} h_j q_j q_0 + \frac{N}{2}\omega_0^2 q_0^2 \\ &= \sum_{j=1}^{N-1} \frac{\omega_0^2 y_j^2}{2} + \frac{\lambda_0^2 y_0^2}{2} + \frac{\lambda_N^2 y_N^2}{2} - \omega_0^2 q_0 \sum_{l=0}^{N} y_l \sum_{j=0}^{N-1} h_j Z_{jl} + \frac{N}{2}\omega_0^2 q_0^2. \end{aligned} \tag{4.23}$$

Using the notation

$$\eta_l = \sum_{j=0}^{N-1} h_j Z_{jl}, \tag{4.24}$$

$$\kappa_l = \sum_{j=0}^{N-1} h_j Z_{jl} - 2h_k Z_{kl}, \tag{4.25}$$

we may rewrite the two potentials as

$$\begin{aligned} V(Q_1) &= \sum_{j=1}^{N-1} \frac{\omega_0^2}{2}(y_j - \eta_j q_0)^2 + \frac{\lambda_0^2}{2}\left(y_0 - \frac{\omega_0^2}{\lambda_0^2}\eta_0 q_0\right)^2 \\ &\quad + \frac{\lambda_N^2}{2}\left(y_N - \frac{\omega_0^2}{\lambda_N^2}\eta_N q_0\right)^2 + \frac{\omega_0^2 q_0^2}{2}\left(N - \sum_{j=1}^{N-1}\eta_j^2 \right. \\ &\quad \left. - \frac{\omega_0^2}{\lambda_0^2}\eta_0^2 - \frac{\omega_0^2}{\lambda_N^2}\eta_N^2\right), \end{aligned} \tag{4.26}$$

$$\begin{aligned} V(Q_2) &= \sum_{j=1}^{N-1} \frac{\omega_0^2}{2}(y_j - \kappa_j q_0)^2 + \frac{\lambda_0^2}{2}\left(y_0 - \frac{\omega_0^2}{\lambda_0^2}\kappa_0 q_0\right)^2 \\ &\quad + \frac{\lambda_N^2}{2}\left(y_N - \frac{\omega_0^2}{\lambda_N^2}\kappa_N q_0\right)^2 + \frac{\omega_0^2 q_0^2}{2}\left(N - \sum_{j=1}^{N-1}\kappa_j^2 \right. \\ &\quad \left. - \frac{\omega_0^2}{\lambda_0^2}\kappa_0^2 - \frac{\omega_0^2}{\lambda_N^2}\kappa_N^2\right). \end{aligned} \tag{4.27}$$

We then evaluate the overlap of the ground state wave functions of the two Hamiltonians associated with Q_1 and Q_2. For the jth normal mode, $1 \le j \le N-1$, we find that

$$\langle \varphi_j(Q_1)|\varphi_j(Q_2)\rangle = \exp\left(-\frac{(\eta_j - \kappa_j)^2 \omega_0 q_0^2}{4\hbar}\right), \text{ j} = 1, \ldots, \text{N} - 1. \tag{4.28}$$

However, from Eqs. (4.24) and (4.26), we have that

$$\eta_j - \kappa_j = 2h_k Z_{kj}. \tag{4.29}$$

Considering that $h_k^2 = 1$ for all k, this implies that

$$\langle \varphi_j(Q_1)|\varphi_j(Q_2)\rangle = \exp\left(-\frac{\omega_0}{\hbar} Z_{kj}^2 q_0^2\right), \text{ j} = 1, \ldots, \text{N} - 1. \tag{4.30}$$

Similarly,

$$\langle \varphi_0(Q_1)|\varphi_0(Q_2)\rangle = \exp\left(-\frac{\lambda_0}{\hbar}\frac{\omega_0^4}{\lambda_0^4} Z_{k0}^2 q_0^2\right), \tag{4.31}$$

$$\langle \varphi_N(Q_1)|\varphi_N(Q_2)\rangle = \exp\left(-\frac{\lambda_N}{\hbar}\frac{\omega_0^4}{\lambda_N^4} Z_{kN}^2 q_0^2\right), \tag{4.32}$$

so that the full overlap is

$$\begin{aligned} \langle \Psi(Q_1)|\Psi(Q_2)\rangle = \exp\bigg[&-\frac{\lambda_0}{\hbar}\frac{\omega_0^4}{\lambda_0^4} Z_{k0}^2 q_0^2 - \frac{\lambda_N}{\hbar}\frac{\omega_0^4}{\lambda_N^4} Z_{kN}^2 q_0^2 \\ &- \frac{\omega_0}{\hbar}\sum_{j=1}^{N-1} Z_{kj}^2 q_0^2 \bigg], \end{aligned} \tag{4.33}$$

where Z is an orthogonal matrix so that

$$\sum_{j=1}^{N-1} Z_{kj}^2 = 1 - Z_{kN}^2 - Z_{k0}^2. \tag{4.34}$$

Moreover, for all k from 0 to $N-1$, we have from Eq. (4.17)

$$Z_{k0} = \frac{\cos\alpha}{\sqrt{N}}, Z_{kN} = \frac{\sin\alpha}{\sqrt{N}}, \tag{4.35}$$

so that

$$\begin{aligned} \langle \Psi(Q_1)|\Psi(Q_2)\rangle &= \exp\bigg[-\frac{\lambda_0}{\hbar}\frac{\omega_0^4}{\lambda_0^4}\frac{\cos^2\alpha}{N} q_0^2 - \frac{\lambda_N}{\hbar}\frac{\omega_0^4}{\lambda_N^4}\frac{\sin^2\alpha}{N} q_0^2 \\ &\quad - \frac{\omega_0 q_0^2}{\hbar} + \frac{\omega_0 q_0^2}{\hbar N} \bigg] \\ &= \exp\left[-\frac{\omega_0}{N\hbar} q_0^2 \left(N - 1 + \frac{(\omega_0 + \omega_c + Ng^2\omega_c)}{\sqrt{(\omega_0+\omega_c)^2 + Ng^2\omega_c^2}} \right) \right], \end{aligned} \tag{4.36}$$

and this is precisely what we conjectured in Eq. (3.54).

The mean energy has already been given in Eq. (3.56). The difference between the mean energy with and without coupling to the cavity is then

$$\begin{aligned} \Delta E &= \frac{\hbar}{2}\sqrt{(\omega_0+\omega_c)^2 + N\omega_c^2 g^2} + \frac{N-1}{2}\hbar\omega_0 - \left(\frac{N}{2}\hbar\omega_0 + \frac{\hbar}{2}\omega_c\right) \\ &= \frac{\hbar}{2}\sqrt{(\omega_0+\omega_c)^2 + N\omega_c^2 g^2} - \frac{\hbar}{2}(\omega_0 + \omega_c) \\ &= \frac{\hbar N \omega_c^2 g^2}{4(\omega_0+\omega_c)} + O(N^2 g^4), \end{aligned} \tag{4.37}$$

and this difference does not vanish, since $\sqrt{N} g \omega_c$ is the [approximate, cf. Eq. (4.13)] Rabi frequency.

V. DISCUSSION

The central results of this study are that (a) the vibrational strong coupling (VSC) to the cavity does not change the energy splitting of the ground states of a large ensemble of non-interacting molecules in the thermodynamic limit, and (b) the VSC does change the mean energy of the ground state. These conclusions result from a generalization of the two-state approximation used for a single replica to the N-replica case. The validity condition of the two-state approximation in the single-replica case is that the nonadiabatic coupling V is significantly smaller than the energy difference $\hbar\omega_0$ between successive energy levels of the diabatic oscillator.[24] In the case of N replicas, the width of the ground state "band" is NVS_N. Since S_N is exponentially small, the product NS_N remains small, so that energy levels of the ground-state manifold will not reach the average energy of the first excited states, and one may expect the approximation to be valid.

One may well ask what the physics underlying the fact that the coupling of N replicas to the vacuum field of the cavity does not induce a noticeable effect on the tunneling splitting is. We believe that the answer lies in the nature of the coupling. As is well understood, and as one sees from the normal modes of the replicas coupled to the cavity, one has $N - 1$ dark modes whose frequencies and coordinate shifts remain unchanged. In the limit of many replicas, this effect dominates the tunneling splitting. Does this imply that, in general, even in the presence of $N \gg 1$ replicas, one should not expect the coupling to the cavity to be interesting? Not necessarily; we have studied here only one aspect, and a limited one at that. We considered only symmetric systems and only tunneling splittings; this is insufficient for more general conclusions. Yet, the result does imply the importance of the "dark states" when considering cavity-induced dynamics.

The current calculation is rigorous for an idealized model Hamiltonian; possible generalizations can be considered in connection with the realistic settings of optical cavities, which are discussed as follows:

1. The analysis presented here is only for the ground state manifold of N replicas; however, we expect no significant changes when considering the first few vibrational states of the single replica diabatic Hamiltonian, provided that the width of the cluster remains smaller than the energy difference between the mean energy of vibrational states.
2. The present paper has been limited to harmonic diabatic Hamiltonians; it should be possible to use perturbation theory to extend the analysis to anharmonic diabatic potentials.
3. The energy splitting is generally related to non-adiabatic processes, such as electron transfer, Förster resonance energy transfer, energy relaxation, and conical intersections. The rate calculations of these processes involve both the tunneling constant and the Frank–Condon factor. While the cavity effects are examined for the Frank–Condon factor, the tunneling constant is assumed to be constant, unperturbed by the cavity field. This paper not only confirms this assumption in the thermodynamic limit but also provides an N-dependent correction for the finite ensemble. Therefore, it would be interesting to consider the finite-size effect on these rate processes under VSC.
4. The reported study applies to the leading order of the coupling constant V between two diabatic potential surfaces. As the magnitude of V increases, higher-order terms in V become relevant, and the transition from diabatic to adiabatic tunneling is expected. In terms of the reactive rate, this is the transition from curve-crossing to barrier crossing and can be analyzed in the framework of a non-adiabatic instanton solution.[26] Previous TST (i.e., transition state theory) calculations of cavity-modified barrier crossing make several predictions, including changes on the single-molecule level, exponential dependence on g^2, and the lack of cooperativity and resonance.[11,23] These TST predictions for adiabatic barrier crossing are consistent with our new results for non-adiabatic quantum tunneling.
5. Optical cavities support a distribution of photon modes, which are essentially the eigen-solutions to the Maxwell equation in a confined or partially confined geometry. The multi-mode description has been well developed for electronic transitions and is now also adapted for the VSC setup.[27,28] The theoretical treatment of multi-mode cavities can be incorporated into the normal-mode analysis presented in this paper, such that the key predictions of our single-mode calculation are expected to remain valid. For example, on the basis of the analytical structure of Eq. (4.36), the multi-mode collective VSC effect will also vanish in the thermodynamic limit as in our single-mode analysis. Another relevant consideration is the finite coherence length due to the presence of static disorder or dynamical noise in a molecular sample.[29] The multi-mode description naturally introduces a spatial scale, which leads to the long-range coherence under VSC. However, the spatial localization of the polariton wave function will limit the extent of the collective VSC in the multi-mode description and thus reduce the cooperative effect in the thermodynamic limit.
6. The typical experiment measuring the effect of the cavity field on the molecular dynamics is implemented when the molecule is immersed in a liquid.[2] In principle, the surrounding liquid may be modeled in terms of bilinear coupling of the system to a harmonic bath[30] for which the normal mode transformation when coupled to a single oscillator has been worked out.[31,32] Although not trivial, this formalism may also be applied to the present problem; yet, it is probably less interesting, since the coupling to the liquid will typically further reduce the exponentially small tunneling splitting.
7. The solvent effect considered earlier becomes more interesting when applied to non-adiabatic rate processes. In the context of electron transfer, solvent fluctuations lead to diffusion-controlled electron transfer in the non-adiabatic limit. The quantum treatment of solute–solvent interactions can, in principle, explain the cooperativity and resonance in the VSC phenomena.[17]

These generalizations are beyond the scope of this paper and will be considered in future studies.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Eli Pollak: Investigation (equal). **Jianshu Cao**: Investigation (equal).

DATA AVAILABILITY

All data needed are included in the paper. The authors welcome any questions.

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