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Optimal Diabatic Bases Via Thermodynamic Bounds

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Abstract

Describing kinetic processes within a perturbation theory approach such as Fermi's Golden Rule requires an understanding of the initial and final states of the system. A number of different methods have been proposed for obtaining these diabatic-like states, but a robust criterion for evaluating their accuracy has not been established. Here, we approach the problem of determining the most appropriate set of diabatic states for use in incoherent rate expressions. We develop a method that rotates an initial set of diabats into an optimized set beginning with a zeroth-order diabatic Hamiltonian and choosing the rotation that minimizes the effect of non-diabatic terms on the thermodynamic free energy. The Gibbs-Bogoliubov (GB) bound on the Helmholtz free energy is thus used as the diabatic criterion. We first derive the GB free energy for a two site system and then find an expression general for any electronic system Hamiltonian. Efficient numerical methods are used to perform the minimization subject to orthogonality constraints, and we examine the resulting diabats for system Hamiltonians in various parameter regimes. The transition from localized to delocalized states is clearly seen in these calculations, and some interesting features are discussed.

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I. INTRODUCTION

In either non-adiabatic electron transfer within Marcus theory,[1] or energy transfer in Förster or Dexter theories,[2, 3] the problem of defining diabatic states is one of significant importance.[4, 5] These theories share a common root in the Fermi’s Golden Rule result for the transition rate from initial to final state, W_{if} ($\hbar = 1$ throughout):

$$W_{if} = 2\pi\rho(E_f)|V_{if}|^2 \tag{1}$$

where ρ is the density of final states and V_{if} , the electronic coupling matrix element, is the perturbation which causes a transition to occur. The task of defining states appropriate for these types of rate expressions is the topic of this work.

Quantum chemical calculations of V_{if} are made complicated by several facts: 1) quantum chemistry within the Born-Oppenheimer approximation seeks to find eigenstates of the Hamiltonian at each set of nuclear coordinates, leading to adiabatic states which change character as the nuclear coordinates change, 2) strictly diabatic states (with derivative couplings zero everywhere) do not exist beyond one-dimension, and so there is no unique prescription for defining ‘exactly’ diabatic states,[6] and 3) any unitary rotation of a set of diabats is itself diabatic, and there is an infinite degree of arbitrariness. The first problem suggests an expansion of diabatic states in an adiabatic basis; the goal is then to determine the adiabatic-diabatic transformation matrix by imposing some criterion for diabatic states, leading to methods such as fragment charge difference,[7] fragment excitation difference,[8, 9] Generalized Mulliken-Hush,[10] and state localization.[4, 11, 12] Alternatively, diabatic states can be produced directly using either constraints on the electronic density[5, 13] or valence bond wavefunctions.[14] Both deductive and constructive strategies, however, rely on a somewhat arbitrary set of criteria for diabatization, based on chemical intuition. While these different methods generally lead to qualitatively similar electronic coupling values, significant quantitative differences can arise.[15, 16] We are thus interested in constructing a method that provides a more robust criterion for diabatic basis and V_{if} .

In the following, we develop a formal approach that avoids the arbitrariness of most diabatization schemes. Our method yields diabats that naturally transition between completely localized sites and delocalized states as system parameters such as the strength of the bath are varied. Consider the following scenario for transitions from initial to final states in a given system. At high temperature, thermal fluctuations (e.g. in the solvent or the

molecular backbone) strongly localize the electronic states, making localized diabatic states appropriate for the rate expression. At lower temperatures, the fluctuations are smaller, and the electronic wavefunction will gradually spread out, until at very low temperatures transitions between delocalized states will be observed. As the localized and delocalized states only differ by a fixed unitary rotation (i.e. independent of the nuclei), both form equally valid diabatic bases for describing kinetics. However, these bases are not equally appropriate for all problems: in some cases the localized limit is attained, while in others the delocalized picture is physically relevant. Hence, we require a method that is able to distinguish, from all possible unitary rotations of a given diabatic basis, which states are appropriate for a given physical system.

We begin by describing the Gibbs-Bogoliubov bound for the Helmholtz free energy and its use as a variational tool for identifying an optimal diabatic basis by partitioning the total Hamiltonian into zeroth-order and perturbative parts. We apply this idea to a spin-boson-like system and derive an expression for the free energy of the system as a function of variational parameter. Next, we treat the case of arbitrary system Hamiltonians and outline an efficient numerical scheme for minimizing the free energy that makes use of an analytic expression for the local gradient of the free energy with respect to the antisymmetric generator of an orthogonal matrix. We apply this scheme to explore optimal diabats for a number of model Hamiltonians and discuss our findings in terms of spatial ‘orbital-like’ plots, as well as participation ratios. Finally, we conclude by discussing the qualitative insights gleaned from our method and future steps towards more rigorous diabatization schemes.

II. GIBBS-BOGOLIUBOV FREE ENERGY MINIMIZATION

The Helmholtz free energy of a system is given by

$$A_H = -\beta^{-1} \ln \text{Tr} e^{-\beta H} \quad (2)$$

where $\beta = (k_B T)^{-1}$ is the inverse temperature and H the Hamiltonian. In the following sections, H is taken to be a matrix of operators which depend on the nuclei.

Based on the convexity of A_H , the Gibbs-Bogoliubov (GB) theorem states that an upper bound on the true free energy can be obtained by considering a trial Hamiltonian \overline{H}_0 : [17]

$$A_H \leq -\beta^{-1} \ln \text{Tr} e^{-\beta \overline{H}_0} + \langle H - \overline{H}_0 \rangle_{\overline{H}_0} \quad (3)$$

where the first term on the r.h.s. is the free energy of the trial Hamiltonian, and the second term is the difference between original and trial Hamiltonians, averaged over the trial Hamiltonian ensemble. If we further choose the trial Hamiltonian by partitioning into an exactly solvable (diagonal) part and a perturbation via a unitary (and orthogonal) transformation:

$$U^T H U = \bar{H} = \bar{H}_0 + \bar{V} \quad (4)$$

we have

$$A_H \leq -\beta^{-1} \ln \text{Tr} e^{-\beta \bar{H}_0} + \langle \bar{V} \rangle_{\bar{H}_0} \quad (5)$$

$$\leq -\beta^{-1} \ln \text{Tr} e^{-\beta \bar{H}_0} = A^0 \quad (6)$$

where the last term in Eqn. 5 vanishes because we have chosen \bar{V} to be entirely off-diagonal. For identifying diabatic states, we choose the perturbation to be the off-diagonal electronic coupling.

Our approach makes use of the GB bound in the following way: we begin with an original diabatic Hamiltonian, \bar{H}_0 , and diabatic coupling, \bar{V} . By rotating the diabatic states, we find different values of A^0 corresponding to different assignments of \bar{H}_0 . From the GB bound, the rotation which minimizes A^0 is the one for which \bar{H}_0 most closely approximates H , the true Hamiltonian, and thus produces, in some sense, the optimal set of diabatic states for describing a complex problem. This rotation yields our definition for the optimal diabatic basis. This use of thermodynamic bounds for finding optimal bases has been used before, for example in studying tunneling in the SB problem,[18] exciton[19, 20] and electron transfer,[21] and charge carrier mobility calculations.[22] Unlike most previous work, however, which treated the bath as the perturbation, we apply a partitioning between diagonal and off-diagonal electronic elements to obtain diabatic states. We are interested in the nature of the optimal diabats and their consequences on the calculation of electronic couplings.

III. TWO SITE MODEL

A. Formalism

We begin by examining a two electronic site system, with each site coupled linearly to a *different* set of harmonic baths. This model is relevant for studying electron or energy transfer in donor-acceptor systems, where the localizing effect of the bath is important. This approach is mathematically equivalent to the spin-boson problem when the two sites are coupled to their relevant baths with identical strength.[23] We express our Hamiltonian in an original crude diabatic basis of localized sites. Writing matrix quantities in bold, we have

$$\mathbf{H} = \mathbf{H}^{\mathbf{S}} + \mathbf{H}^{\mathbf{B}} + \mathbf{H}^{\mathbf{SB}} \quad (7)$$

with

$$\mathbf{H}^{\mathbf{S}} = \begin{pmatrix} \varepsilon & \Delta \\ \Delta & -\varepsilon \end{pmatrix} \quad (8)$$

$$\mathbf{H}^{\mathbf{B}} = \mathbf{I} \left(\sum_j \omega_{1j} (\hat{a}_{1j}^\dagger \hat{a}_{1j} + 1/2) + \sum_j \omega_{2j} (\hat{a}_{2j}^\dagger \hat{a}_{2j} + 1/2) \right) = \mathbf{I} \hat{h}_B \quad (9)$$

$$\mathbf{H}^{\mathbf{SB}} = \begin{pmatrix} \sum_j M_{1j} (\hat{a}_{1j} + \hat{a}_{1j}^\dagger) & 0 \\ 0 & \sum_j M_{2j} (\hat{a}_{2j} + \hat{a}_{2j}^\dagger) \end{pmatrix} = \begin{pmatrix} \hat{h}_{1SB} & 0 \\ 0 & \hat{h}_{2SB} \end{pmatrix} \quad (10)$$

so that

$$\mathbf{H} = \begin{pmatrix} \varepsilon + \hat{h}_B + \hat{h}_{1SB} & \Delta \\ \Delta & -\varepsilon + \hat{h}_B + \hat{h}_{2SB} \end{pmatrix} \quad (11)$$

In our notation, ε is half the energy gap, and Δ is the electronic coupling between the two sites in the original basis. $\omega_{Kj}, a_{Kj}, a_{Kj}^\dagger, M_{Kj}$ are the frequency, annihilation operator, creation operator, and electron-phonon coupling for the j^{th} vibrational mode coupled to the K^{th} electronic site.

We wish to determine the optimal diabatic basis which can be produced from the initial input states by: first applying an orthogonal transformation to the Hamiltonian, then calculating the Helmholtz free energy of the zeroth-order (diagonal) transformed Hamiltonian, and finally determining the optimal transformation by minimizing subject to the GB bound:

$$A_H \leq A^0(\mathbf{U}) = -\beta^{-1} \ln \text{Tr} e^{-\beta \overline{\mathbf{H}^0}(\mathbf{U})} \quad (12)$$

where

$$\bar{\mathbf{H}} = \mathbf{U}^T \mathbf{H} \mathbf{U} = \bar{\mathbf{H}}^0 + \bar{\mathbf{V}} \quad (13)$$

We seek to minimize $A^0(\mathbf{U})$ subject to \mathbf{U} being orthogonal. We thus only consider matrices in $\text{SO}(2)$:

$$\mathbf{U} = \begin{pmatrix} \cos(\theta) & -\sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{pmatrix} \quad (14)$$

The transformed Hamiltonian is given by

$$\bar{\mathbf{H}} = \begin{pmatrix} \bar{\varepsilon} + \hat{h}_B + \hat{h}_{1_{SB}} \cos^2 \theta + \hat{h}_{2_{SB}} \sin^2 \theta & \bar{\Delta} \\ \bar{\Delta} & -\bar{\varepsilon} + \hat{h}_B + \hat{h}_{1_{SB}} \sin^2 \theta + \hat{h}_{2_{SB}} \cos^2 \theta \end{pmatrix} \quad (15)$$

where

$$\bar{\varepsilon} = \varepsilon \cos 2\theta + \Delta \sin 2\theta \quad (16)$$

$$\bar{\Delta} = \Delta \cos 2\theta + \frac{\sin 2\theta}{2} \left(-2\varepsilon - \hat{h}_{1_{SB}} + \hat{h}_{2_{SB}} \right) \quad (17)$$

The diagonal part of Eqn. 15 is taken to be $\bar{\mathbf{H}}^0$. We calculate the Helmholtz free energy, taking system trace first:

$$A^0 = -\beta^{-1} \ln \text{Tr}_B \left[e^{-\beta(\bar{\varepsilon} + \hat{h}_B + \hat{h}_{1_{SB}} \cos^2 \theta + \hat{h}_{2_{SB}} \sin^2 \theta)} + e^{-\beta(-\bar{\varepsilon} + \hat{h}_B + \hat{h}_{1_{SB}} \sin^2 \theta + \hat{h}_{2_{SB}} \cos^2 \theta)} \right] \quad (18)$$

We apply small-polaron transformations to diagonalize the phonon degrees of freedom,[24] resulting in the following simplified expression for the free energy:

$$A^0 = -\beta^{-1} \ln \text{Tr}_B \left[e^{-\beta(\bar{\varepsilon} + \hat{h}_B - \frac{\eta_1}{2} \cos^4 \theta - \frac{\eta_2}{2} \sin^4 \theta)} + e^{-\beta(-\bar{\varepsilon} + \hat{h}_B - \frac{\eta_1}{2} \sin^4 \theta - \frac{\eta_2}{2} \cos^4 \theta)} \right] \quad (19)$$

where the spectral density of each bath

$$J_K(\omega) = \frac{\pi}{2} \sum_j \frac{M_{Kj}^2}{\omega_{Kj}} \delta(\omega - \omega_{Kj}) \quad (20)$$

is taken to be of Debye form (with critical frequency ω_{Kc})

$$J_K(\omega) = \eta_K \frac{\omega_{Kc} \omega}{\omega_{Kc}^2 + \omega^2} \quad (21)$$

and the coupling strength of the system-bath interaction is given by $\eta_K = 2 \sum_j M_{Kj}^2 / \omega_{Kj}$. Note that $\eta_K = 2\lambda_K$, where λ_K is the Marcus reorganization energy for the bath coupled

to site K . The bath trace now simply yields the partition functions, Z_K , for the two free harmonic-oscillator baths:

$$A^0 = -\beta^{-1} \ln \left[e^{-\beta(\bar{\varepsilon} - \frac{\eta_1}{2} \cos^4 \theta - \frac{\eta_2}{2} \sin^4 \theta)} + e^{-\beta(-\bar{\varepsilon} - \frac{\eta_1}{2} \sin^4 \theta - \frac{\eta_2}{2} \cos^4 \theta)} \right] - \beta^{-1} (\ln Z_1 + \ln Z_2) \quad (22)$$

As the partition functions have no θ dependence, they can be neglected in the minimization of A^0 . If, for the sake of simplicity, we make the additional assumption that both sets of baths have identical coupling strengths ($\eta_1 = \eta_2$), we obtain

$$A^0 = -\beta^{-1} \ln (\cosh \beta \bar{\varepsilon}) - \frac{\eta}{2} (\cos^4 \theta + \sin^4 \theta) \quad (23)$$

Eqn. 23 is very similar to the result for the SB problem where the same set of bath modes is coupled to each site:[21, 25]

$$A^0 = -\beta^{-1} \ln (\cosh \beta \bar{\varepsilon}) - \frac{\eta}{2} (\cos^2 2\theta) \quad (24)$$

We see that for large system-bath coupling (reorganization energy), A^0 is minimized by $\theta = 0$ and the states remain in the original site basis. Conversely when η is small, the first term dominates and leads to diagonalization of the electronic Hamiltonian and delocalized adiabatic-like states. In this two state case, it is simple to search numerically for the value of θ which minimizes A^0 . This value of θ determines an orthogonal matrix, \mathbf{U} , which rotates the original localized site basis into the best diabatic basis as determined by our thermodynamic criterion.

B. Results

As we initially begin in the site basis, the columns of \mathbf{U} correspond to the best diabatic basis expanded in a linear combination of localized sites. We plot these wavefunctions as well as two additional properties. First, we calculate the thermodynamic probability for each optimized state

$$P_i = \frac{\text{Tr}_B e^{-\beta \bar{H}_{ii}}}{\sum_i \text{Tr}_B e^{-\beta \bar{H}_{ii}}} \quad (25)$$

This gives us a natural ordering for the diabatic states that emerge from the optimization procedure, and we will refer to the highest probability state as the diabatic ground state. In addition, we can calculate a localization measure for each state - the participation number

defined as

$$\gamma_i = \left(\sum_K U_{Ki}^4 \right)^{-1} \quad (26)$$

where γ_i can range from 1 (totally localized) to N (totally delocalized) for each system.

For the two site system, we can vary four parameters and examine the nature of the diabatic states: ε , half the energy gap between sites, Δ , the electronic coupling between sites, η , the system-bath coupling, assumed identical for each site-bath, and β , the inverse temperature. To aid in visualization, we take $\varepsilon = 0$ and at discrete temperatures examine color contour plots of the participation number of the diabatic ground state, γ_1 , as a function of Δ and η . Here, a value of $\gamma_1 = 1$ indicates the optimized diabats have remained totally localized ($\mathbf{U} = \mathbf{I}$), while $\gamma_1 = 2$ indicates the optimized diabats are totally delocalized (corresponding to an adiabatic basis in the electronic representation). The results are shown in Fig. 1.

We comment on a few interesting properties in these plots. First, generally we see that increasing system-bath coupling leads to more localization, while increasing the electronic coupling between sites leads to more delocalization; both observations are in accord with physical intuition. We also find increased temperature leads to greater localization - this is also a reasonable result, as higher temperature will enhance the system-bath coupling. More surprising, however, is that the transition between localized and delocalized states becomes sharper as temperature rises.

To examine this feature more closely, in Fig. 2 we plot A^0 and γ_1 as a function of inter-site coupling. At room temperature, we see a fairly smooth transition in γ_1 from localized to delocalized as Δ increases. At higher temperature (3000 K), the transition shifts to higher values of Δ (corresponding to a stronger localizing bath to be counteracted), and the transition in γ_1 sharpens - concomitant with increased slope in the free energy. The standard spin-boson model (Eqn. 24) displays qualitatively similar results. We examine these features further for a different system Hamiltonian in the next section. Thus we see that the simple prescription of choosing diabatic states that minimize the free energy leads to diabatic states that can adapt to a variety of physical circumstances.

IV. GENERAL SYSTEM HAMILTONIAN

A. Formalism

For more complicated systems, with multiple donor or acceptor sites, a more general treatment is necessary. To generalize to a system with N sites, we allow for any form of electronic system Hamiltonian while retaining the same form of system-bath coupling (different sets of baths coupled linearly to each site). Throughout the following we use lower case letters for bath mode indices and capital letters for electronic sites. We have

$$\mathbf{H} = \mathbf{H}^{\mathbf{S}} + \mathbf{H}^{\mathbf{B}} + \mathbf{H}^{\mathbf{SB}} \quad (27)$$

$$\mathbf{H}^{\mathbf{B}} = \mathbf{I} \sum_K \sum_j \omega_{Kj} \left(\hat{a}_{Kj}^\dagger \hat{a}_{Kj} + 1/2 \right) = \mathbf{I} \hat{h}_B \quad (28)$$

$$\mathbf{H}^{\mathbf{SB}} = \sum_K \mathbf{T}^K \sum_j M_{Kj} \left(\hat{a}_{Kj} + \hat{a}_{Kj}^\dagger \right) = \sum_K \mathbf{T}^K \hat{h}_{KSB} \quad (29)$$

where \mathbf{T}^K is the matrix with zeros everywhere except for the K^{th} diagonal element which is unity:

$$T_{MN}^K = \delta_{MK} \delta_{NK} \quad (30)$$

We proceed as before by applying an orthogonal transformation, determined by minimizing the Helmholtz free energy:

$$\bar{\mathbf{H}} = \mathbf{U}^T \mathbf{H} \mathbf{U} = \bar{\mathbf{H}}^0 + \bar{\mathbf{V}} \quad (31)$$

$$\bar{\mathbf{H}}^0 = \sum_K \mathbf{T}^K \mathbf{U}^T \mathbf{H} \mathbf{U} \mathbf{T}^K \quad (32)$$

$$A \leq A^0(\mathbf{U}) = -\beta^{-1} \ln \text{Tr} e^{-\beta \bar{\mathbf{H}}^0(\mathbf{U})} \quad (33)$$

Once again, we take the system trace first:

$$A^0 = -\beta^{-1} \ln \text{Tr}_B \sum_J e^{-\beta \bar{H}_{JJ}} \quad (34)$$

where the diagonal part of the transformed Hamiltonian is given by

$$\bar{H}_{JJ} = [\mathbf{U}^T \mathbf{H} \mathbf{U}]_{JJ} = \bar{\varepsilon}_J + \sum_K U_{KJ}^2 \left(\hat{h}_B + \hat{h}_{KSB} \right) \quad (35)$$

$$\bar{\varepsilon}_J = [\mathbf{U}^T \mathbf{H}^{\mathbf{S}} \mathbf{U}]_{JJ} \quad (36)$$

For an orthogonal matrix $\sum_K U_{KJ}^2 = 1$, so we can write

$$A^0 = -\beta^{-1} \ln \left[\sum_J e^{-\beta \bar{\epsilon}_J} \text{Tr}_B \exp \left(-\beta \left(\hat{h}_B + \sum_K U_{KJ}^2 \hat{h}_{K_{SB}} \right) \right) \right] \quad (37)$$

To evaluate the bath trace, we once again apply the small-polaron transformation. The result is (dropping the bath partition functions as before)

$$A^0 = -\beta^{-1} \ln \left[\sum_J \exp \left(-\beta \left(\bar{\epsilon}_J - \sum_K \frac{U_{KJ}^4}{2} \eta_K \right) \right) \right] \quad (38)$$

As in the two state case, minimizing A^0 yields an orthogonal matrix, \mathbf{U} , the columns of which are the best set of diabatic states according to our thermodynamic criterion.

To obtain a numerical scheme that minimizes A^0 subject to orthogonality constraints, the method of Lagrange multipliers could be applied, resulting in a generalized eigenvalue equation to be solved self-consistently. However, we find that this route leads to convergence difficulties in higher dimensions. A better approach is to make use of the antisymmetric generators of $\text{SO}(N)$.

1. Minimization Over the Antisymmetric Generators of $\text{SO}(N)$

We can construct a robust convergence strategy by making use of the generator of the $\text{SO}(N)$ group: $\mathbf{U} = e^{\mathbf{\Delta}}$, for $\mathbf{\Delta}$ antisymmetric ($\mathbf{\Delta}^T = -\mathbf{\Delta}$). Specifically, we follow this iterative procedure:

1. We begin with the initial guess $\mathbf{U}_0 = \mathbf{I}$.^[26]
2. We take our next guess to be of the form: $\mathbf{U}_{n+1} = \mathbf{U}_n e^{\mathbf{\Delta}}$, with $\mathbf{\Delta}$ an antisymmetric matrix.
3. We calculate the local gradient of $A^0(\mathbf{U}_n)$: $\mathbf{C}_n = \left. \frac{dA^0}{d\mathbf{\Delta}} \right|_{\mathbf{\Delta}=\mathbf{0}}$. \mathbf{C} depends on the current value of \mathbf{U} and is derived in the Appendix.
4. We perform Fletcher-Reeves conjugate-gradient optimization and line search (using Brent's algorithm) over positive scalar λ to find our next step:

$$\min_{\lambda} A^0(\lambda) = \min_{\lambda} A^0 \left(\mathbf{U}_n e^{-\lambda \left(\mathbf{C}_n + \frac{\|\mathbf{C}_n\|}{\|\mathbf{C}_{n-1}\|} \mathbf{C}_{n-1} \right)} \right) \longrightarrow \lambda_{\text{opt}} \quad (39)$$

where $\|\mathbf{X}\|$ is the Frobenius norm of matrix \mathbf{X} .

5. We form our new (still orthogonal) best guess: $\mathbf{U}_{\mathbf{n}+1} = \mathbf{U}_{\mathbf{n}} e^{-\lambda_{\text{opt}} \left(\mathbf{C}_{\mathbf{n}} + \frac{\|\mathbf{C}_{\mathbf{n}}\|}{\|\mathbf{C}_{\mathbf{n}-1}\|} \mathbf{C}_{\mathbf{n}-1} \right)}$ and repeat steps 2-5 until convergence.

This iterative procedure, which combines our knowledge of the analytic gradient of the free-energy as a function of the rotation matrix with a conjugate-gradient optimization, is a robust and efficient computational path towards determining diabatic states for general electronic Hamiltonians.

B. Results

We now turn to a larger electronic system Hamiltonian to see if the trends in Section III B apply in general. For simplicity, we consider all system-bath couplings to be equal, $\eta_K = \eta$, although our method is not at all restricted to this assumption. We examine four sites arranged in a square where, as diagrammed in Fig. 3, each site is coupled to its nearest neighbors. For simplicity, we once again choose the sites to be isoenergetic, and the inter-site couplings as well as the system-bath couplings to be identical ($\varepsilon_K = 0$, $\Delta_{KL} = \Delta$, $\eta_K = \eta$).[27]

In Fig. 4 we plot the resulting diabatic states for a given set of parameters. As we vary Δ , holding η and temperature constant, we move from completely localized states (with equal probability P_i) to delocalized states (with a well separated ground state) when inter-site electronic coupling is strong enough to overwhelm the system-bath localization effect. In a parameter range between these extremes, states emerge with some degree of localization. Unlike the two site case, however, the width of this parameter regime is extremely narrow at all temperatures. In Fig. 5, we have plotted the participation ratio of the ground state, γ_1 , as a function of Δ and η at a number of temperatures. We find somewhat similar results as in Fig. 1, except the intermediate regime between $\gamma_1 = 1$ and $\gamma_1 = 4$ has nearly vanished, even at low temperatures.

The sharpness of the transition can also be seen in Fig. 6, where both the Helmholtz free energy and participation ratio are plotted. Even at room temperature, and in contrast to the two site result in Fig. 2, we see that after a gradual increase in the participation ratio from $\gamma_1 = 1.0$ to 1.3, there is a sharp rise to the delocalized $\gamma_1 = 4.0$ solution. To ensure that this result is not an artifact of the 2x2 model, we have also examined 3x3 and

4x4 systems and found similarly sharp transitions (see Fig. 7 for an example of the states in the 4x4 case). However, we find that the transition between localized and delocalized states can be smoothed by breaking the symmetry of the system through three possible means: 1) the site energies: $\varepsilon_K \neq \varepsilon_L$, 2) the inter-site couplings: $\Delta_{KL} \neq \Delta_{MN}$, or 3) the system-bath coupling: $\eta_K \neq \eta_L$. As an example, allowing the site energies to differ slightly results in a significantly broader transition, as seen in Fig. 8. The impact of symmetry on the transition between localized and delocalized diabats may be an interesting topic for future research and presents an opportunity for experimental study.

V. CONCLUSIONS

In this work we have applied the GB bound to the problem of identifying the most appropriate diabatic states. Diabatic states are an important ingredient in calculating electronic coupling matrix elements for rate expressions, but their construction is made difficult by the ambiguity arising from unitary transformations of diabatic states. The GB bound allows us to remove the arbitrariness in rotating different diabatic bases. Specifically, we applied a variational procedure to solve a generalized spin-boson problem, yielding an improved set of states which are consistent with the chosen form of the system-bath interaction. We derived an expression for the Helmholtz free energy of the trial Hamiltonian, A^0 , in both the two site case as well as for a general electronic system Hamiltonian. We then constructed an efficient computational procedure for minimizing A^0 using the antisymmetric generators of orthogonal matrices and conjugate-gradient optimization.

Examining the results of our method for specific electronic Hamiltonians, we studied the transition from localized to delocalized states as a function of the various parameters in the system. We saw that the GB procedure predicts a sharp localized/delocalized transition for systems with a high degree of symmetry (in electronic and system-bath components), while breaking this symmetry results in a smoother transition. The primary strength of the GB method is that the system-bath Hamiltonian dictates the optimal diabats (via the free energy) rather than forcing localization by chemical intuition and constraining an arbitrary operator such as the atomic charges or dipole moment. In comparison to previous methods that define diabats for kinetic problems such as energy and electron transfer, the thermodynamic criterion has the advantage of being more general - for example, in General-

ized Mulliken-Hush,[10] a specific operator is introduced for obtaining charge-transfer states appropriate for electron transfer rates. An alternative prescription,[11] using localization criteria, provides states appropriate for energy-transfer. The thermodynamic criteria can be used in both electron and energy transfer regimes by modifying the system-bath interaction.

While the applications in this paper have been toward model systems, we are interested in applying the GB bound to real experimentally-relevant systems. Our method can be extended by inputting a given set of electronic couplings and diabatic state energies. This information can be combined with estimates of the system-bath coupling (Marcus reorganization energy) through simulation of bath fluctuations or vibrational mode analysis. The thermodynamic minimization procedure will then yield a new set of optimized diabatic states, from which electronic couplings and other information can be extracted. We will examine the results of such calculations in the future.

Another future direction involves choosing a different criterion for diabatization, kinetic rather than thermodynamic. In this work, we have chosen to minimize free energy as the criterion for best diabatic states - i.e. the most thermodynamically probable states. We could also find diabats subject to minimizing the transition rate as calculated within Fermi's Golden Rule. We can apply a similar transformation to the system which will result in bath operators entering into the off-diagonal matrix elements, necessitating a non-Condon rate to be calculated. We are interested in comparing the resulting diabatic states with the GB states. New insights into the most appropriate diabatization procedure for quantum chemical calculations of energy and charge transfer rates should be gained by exploring both the thermodynamic and kinetic criteria.

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Appendix: Derivation of Local Gradient \mathbf{C}

Here we calculate the local gradient of the free energy with respect to an antisymmetric matrix. To account for the antisymmetric constraint, we take

$$\mathbf{C} = \frac{1}{2} (\mathbf{D} - \mathbf{D}^T) \quad (\text{A1})$$

where

$$\mathbf{D} = \left. \frac{d}{d\Delta} A^0 \right|_{\Delta=\emptyset} \quad (\text{A2})$$

with

$$A^0 = -\beta^{-1} \ln \sum_J^N e^{-x_J} \quad (\text{A3})$$

$$x_J = \beta \left([e^{-\Delta} \mathbf{U}^T \mathbf{H}^S \mathbf{U} e^{\Delta}]_{JJ} - \sum_K^N \frac{[\mathbf{U} e^{\Delta}]_{KJ}^4}{2} \eta_K \right) \quad (\text{A4})$$

We take the matrix derivative element by element and apply the chain rule:

$$D_{ST} = \frac{\sum_J^N e^{-y_J} \left. \frac{d}{d\Delta_{ST}} \left([e^{-\Delta} \mathbf{U}^T \mathbf{H}^S \mathbf{U} e^{\Delta}]_{JJ} - \sum_K^N \frac{[\mathbf{U} e^{\Delta}]_{KJ}^4}{2} \eta_K \right) \right|_{\Delta_{ST}=0}}{\sum_J^N e^{-y_J}} \quad (\text{A5})$$

where

$$y_J = \beta \left([\mathbf{U}^T \mathbf{H}^S \mathbf{U}]_{JJ} - \sum_K^N \frac{U_{KJ}^4}{2} \eta_K \right) \quad (\text{A6})$$

The two derivatives in the numerator yield:

$$\left. \frac{d}{d\Delta_{ST}} [e^{-\Delta} \mathbf{U}^T \mathbf{H}^S \mathbf{U} e^{\Delta}]_{JJ} \right|_{\Delta_{ST}=0} = [\mathbf{U}^T \mathbf{H}^S \mathbf{U}]_{JS} \delta_{TJ} - [\mathbf{U}^T \mathbf{H}^S \mathbf{U}]_{TJ} \delta_{SJ} \quad (\text{A7})$$

$$\left. \frac{d}{d\Delta_{ST}} [\mathbf{U} e^{\Delta}]_{KJ}^4 \right|_{\Delta_{ST}=0} = 4U_{KJ}^3 U_{KS} \delta_{TJ} \quad (\text{A8})$$

Combining, we find

$$D_{ST} = \frac{(e^{-y_T} - e^{-y_S}) [\mathbf{U}^T \mathbf{H}^S \mathbf{U}]_{TS} - 2e^{-y_T} \sum_K^N \eta_K U_{KT}^3 U_{KS}}{\sum_J^N e^{-y_J}} \quad (\text{A9})$$

$$C_{ST} = \left(\sum_J^N e^{-y_J} \right)^{-1} \left((e^{-y_T} - e^{-y_S}) [\mathbf{U}^T \mathbf{H}^S \mathbf{U}]_{ST} + \sum_K^N \eta_K U_{KS} U_{KT} (e^{-y_S} U_{KS}^2 - e^{-y_T} U_{KT}^2) \right) \quad (\text{A10})$$

This result, combined with a conjugate-gradient minimization and Brent's algorithm line search, yield a robust and efficient optimization method for minimizing $A^0(\mathbf{U})$.

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- [25] The definition of η is slightly different in the two cases; in the usual SB problem η arises from

the *difference* in electron-phonon couplings of the same bath to different electronic states, whereas for our problem η exists even if the electronic states have same electron-phonon couplings to *different* sets of bath modes.

[26] If the identity matrix corresponds to a local maximum, this initial guess is undesirable; therefore, in practice we usually begin with an orthogonal matrix generated from a random anti-symmetric matrix.

[27] To avoid issues with the high degree of symmetry in this system, we added small ($\approx .005$ eV) random perturbations to the site energies and inter-site couplings (while maintaining Hermiticity).

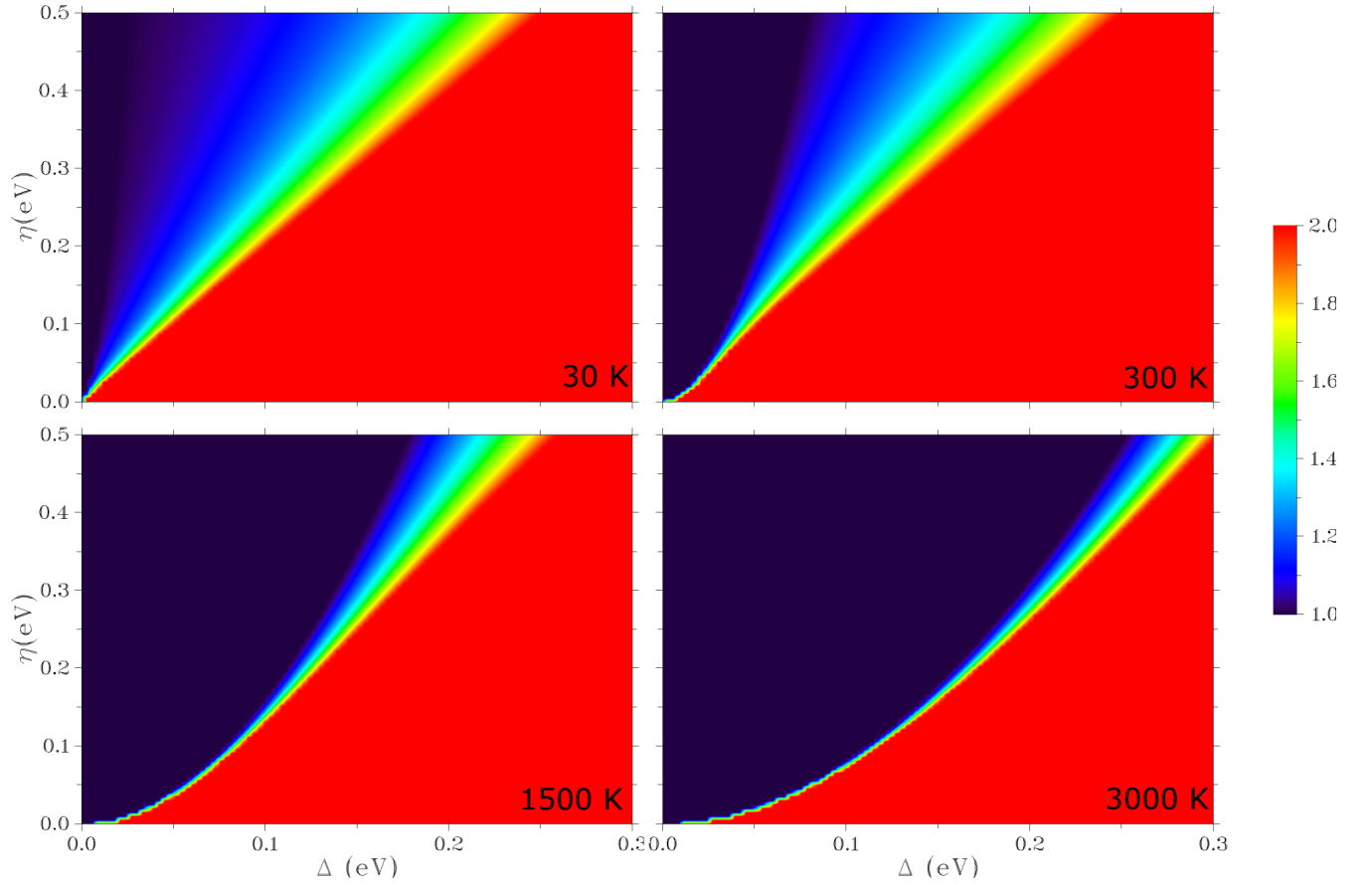


FIG. 1: For the two site model, the participation ratio for the diabatic ground state, γ_1 , is plotted as a function of the inter-site coupling, Δ , and the system-bath coupling, η , taken the same for both sites. $\varepsilon = 0$ in all cases. Purple indicates $\gamma_1 = 1$ (totally localized diabats), while red indicates $\gamma_1 = 2$ (totally delocalized diabats). The result is shown at four temperatures.

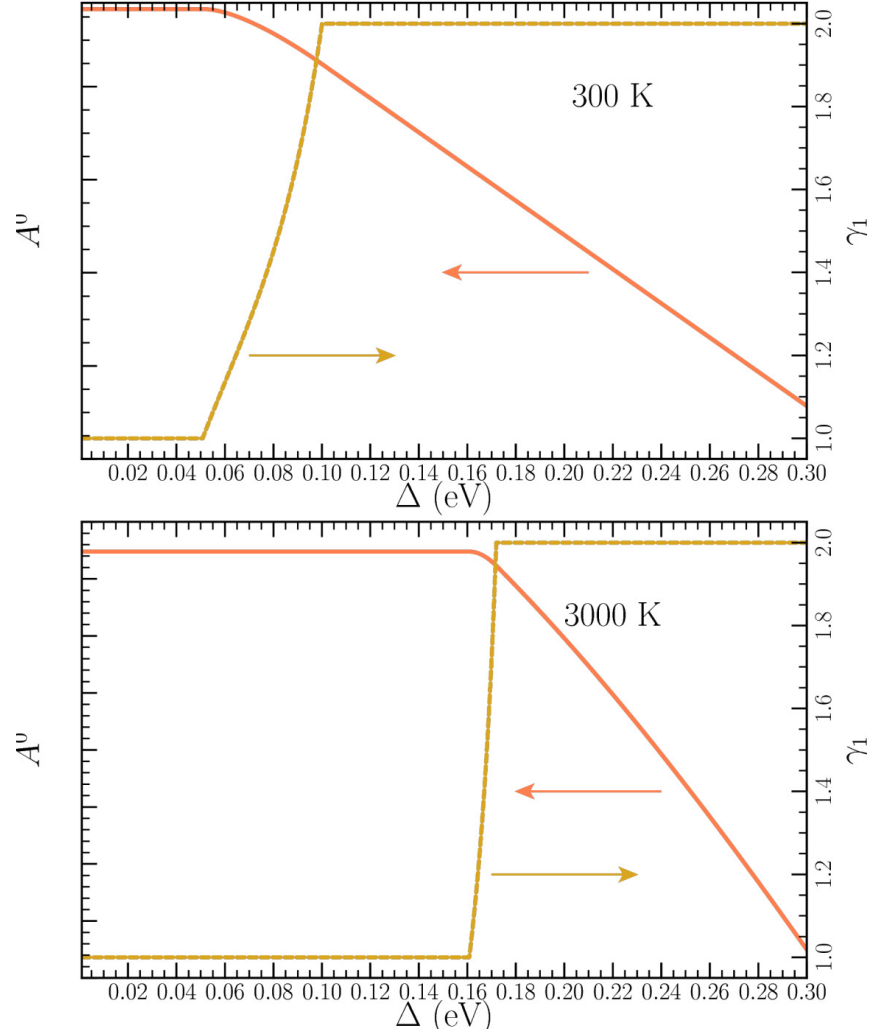


FIG. 2: For the two site model, the Helmholtz free energy, A^0 , and the participation ratio for the ground state, γ_1 , are plotted as a function of inter-site coupling, Δ , at two temperatures. As temperature increases, the slope of the free energy becomes larger, and the transition from localized to delocalized states becomes sharper. In both plots, $\varepsilon = 0$ and $\eta = .2$ eV.

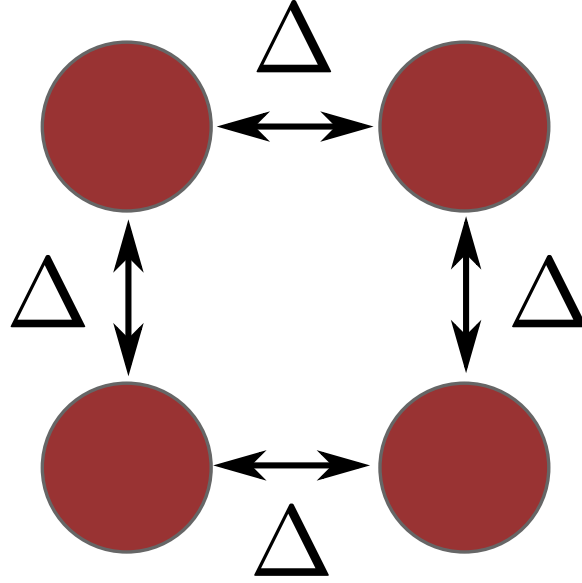


FIG. 3: A diagram of the four site model. The sites (red) are isoenergetic and coupled to each of their nearest neighbors with identical couplings Δ . Each site is also coupled to a set of harmonic baths with system-bath coupling η .

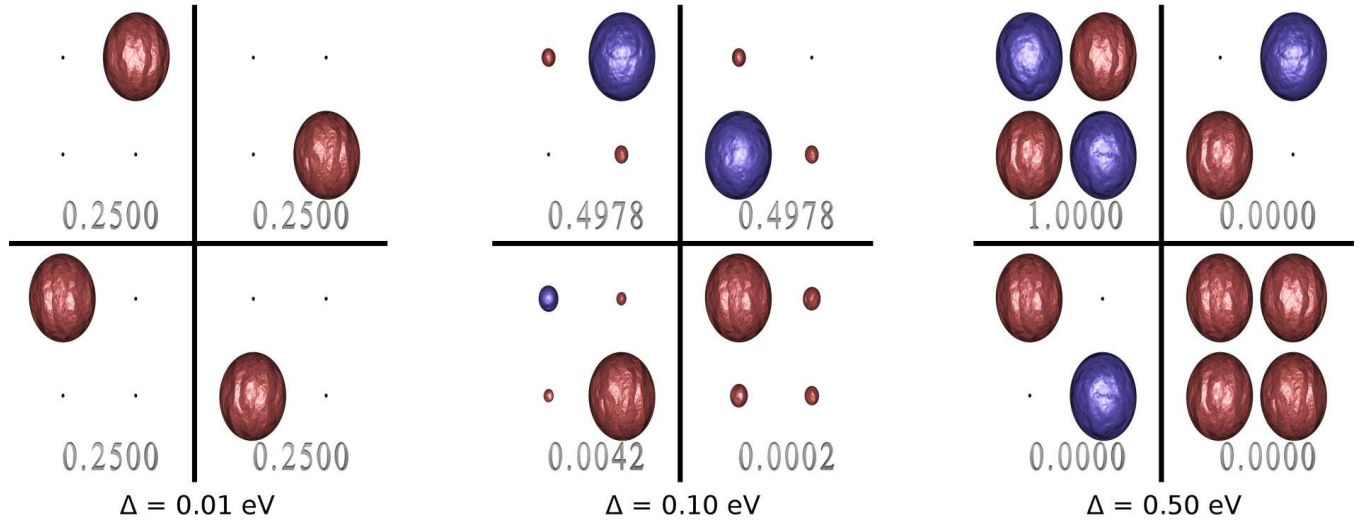


FIG. 4: The optimized diabatic states for the four site model are plotted at different values of inter-site coupling. At each value of Δ , the four diabatic states are plotted and the thermodynamic probability from Eqn. 25 for each state is shown underneath. Red and blue colors indicate the sign of the state at each site, and the radius of each circle is proportional to the magnitude of the coefficient. $\eta = .4$ eV and $T = 300$ K.

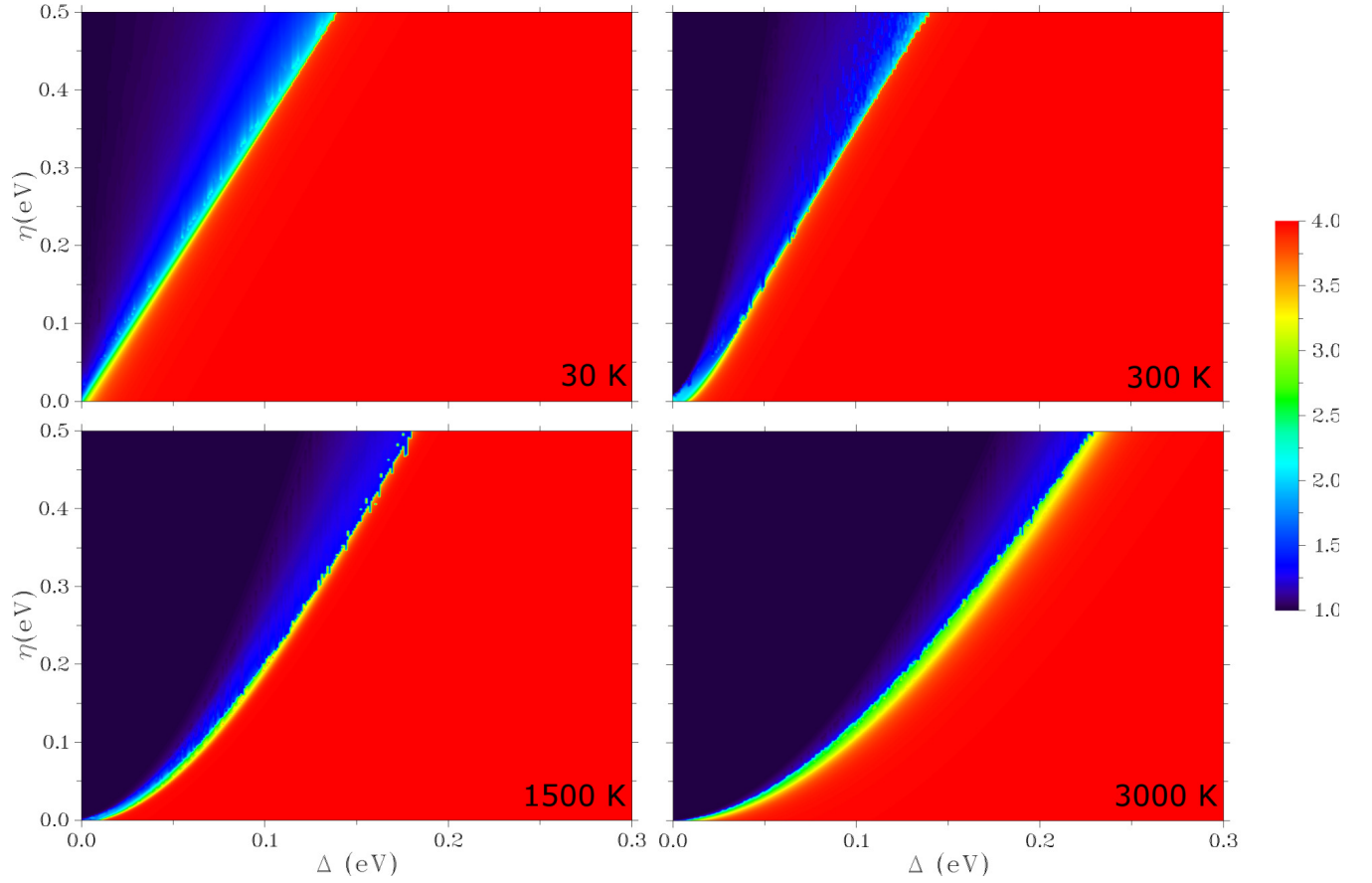


FIG. 5: For the four site model, the participation ratio for the diabatic ground state, γ_1 , is plotted as a function of the inter-site coupling, Δ , and the system-bath coupling, η , taken the same for all four sites. $\varepsilon = 0$ in all cases. Purple indicates $\gamma_1 = 1$ (totally localized diabats), while red indicates $\gamma_1 = 4$ (totally delocalized diabats). The result is shown at four temperatures.

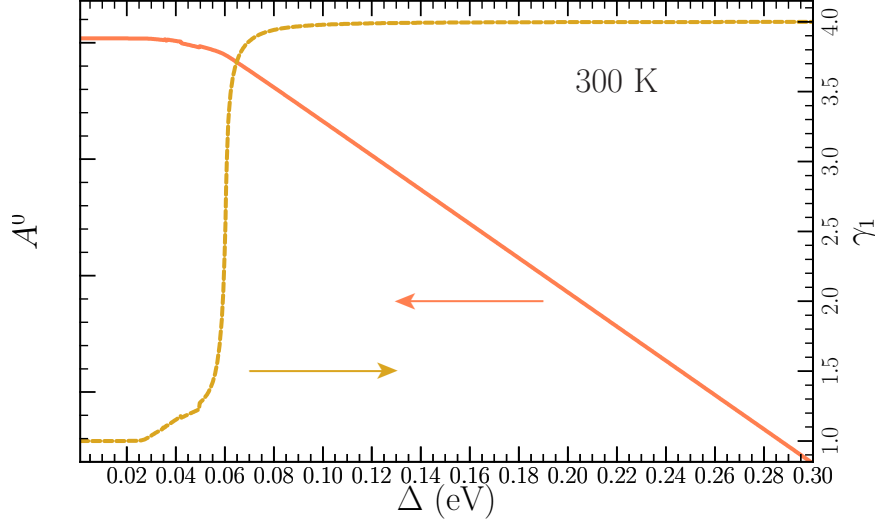


FIG. 6: For the four site model, the Helmholtz free energy, A^0 , and the participation ratio for the ground state, γ_1 , are plotted as a function of inter-site coupling, Δ , at $T = 300$ K. $\varepsilon = 0$ and $\eta = .2$ eV.

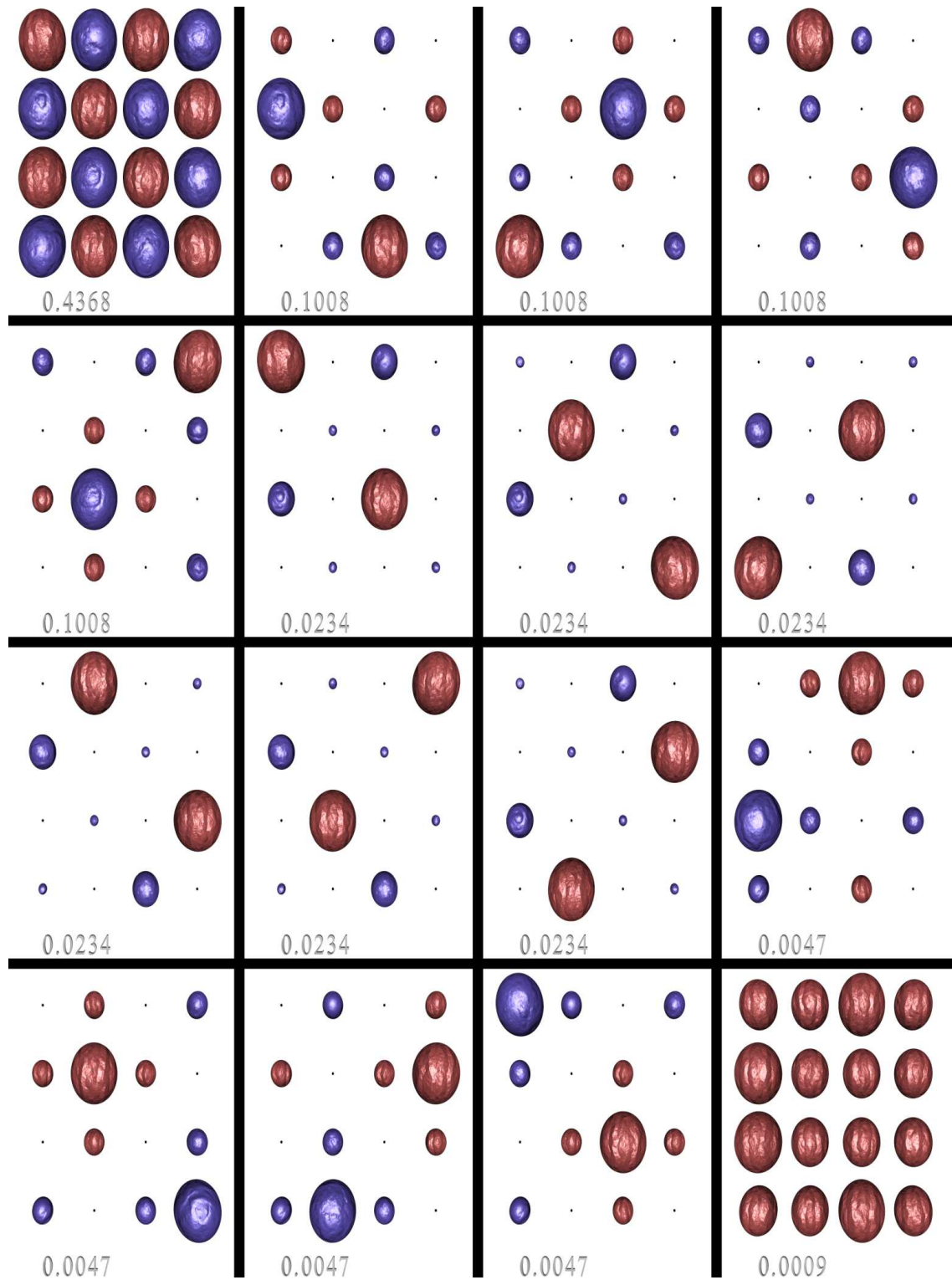


FIG. 7: The optimized diabatic states for a 16 site (4x4) model with periodic boundary conditions are plotted. The sixteen diabatic states are plotted and the thermodynamic probability from Eqn. 25 for each state is shown underneath. For each calculation, all sites are isoenergetic, $\eta = .4$ eV, $\Delta = .2$ eV, and $T = 3000$ K.

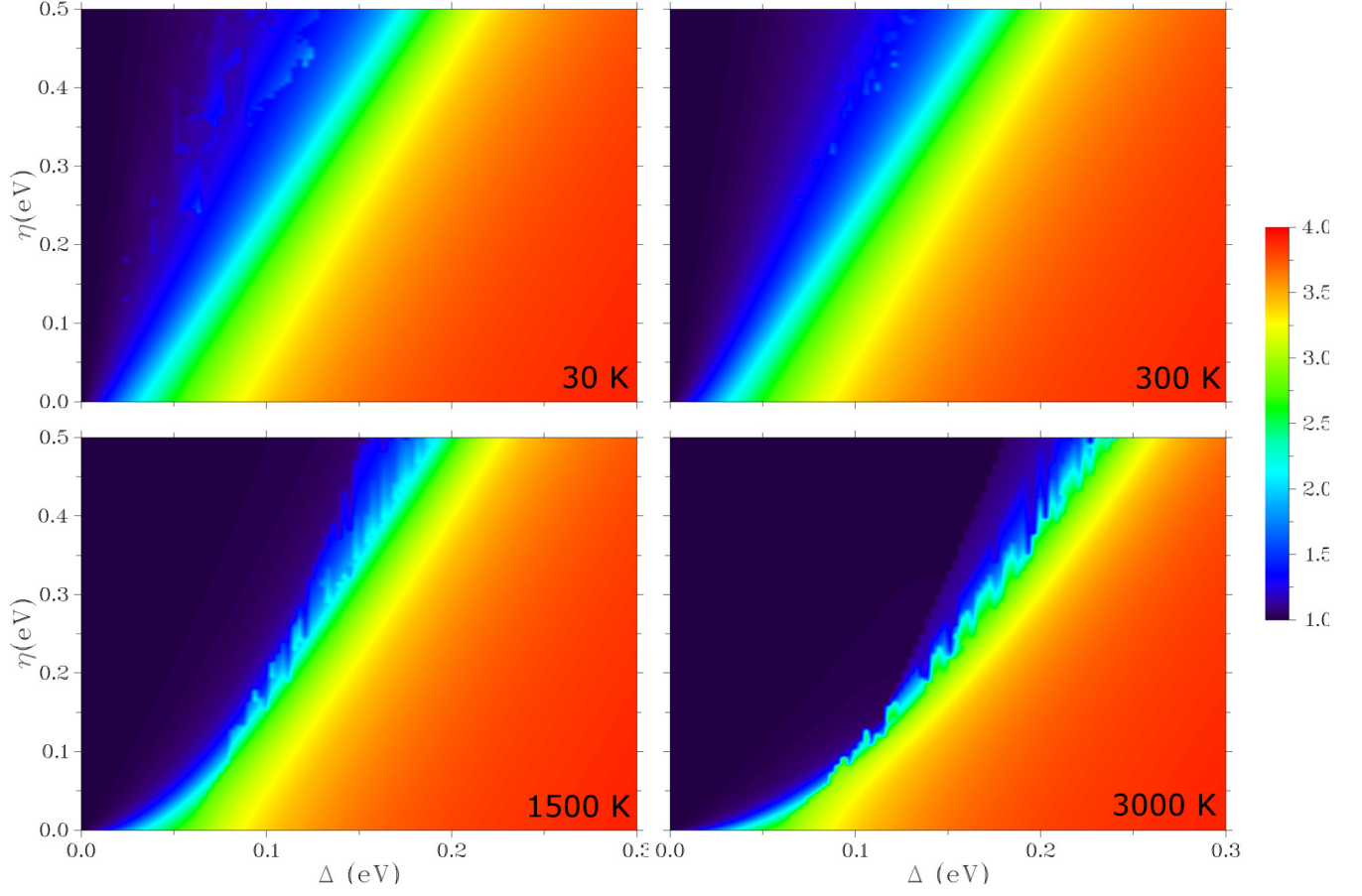


FIG. 8: For the four site model, the participation ratio for the diabatic ground state, γ_1 , is plotted as a function of the inter-site coupling, Δ , and the system-bath coupling, η , taken the same for all four sites. $\varepsilon = .02, .05, .09, .15$ eV for the different sites. Purple indicates $\gamma_1 = 1$ (totally localized diabats), while red indicates $\gamma_1 = 4$ (totally delocalized diabats). The result is shown at four temperatures.