

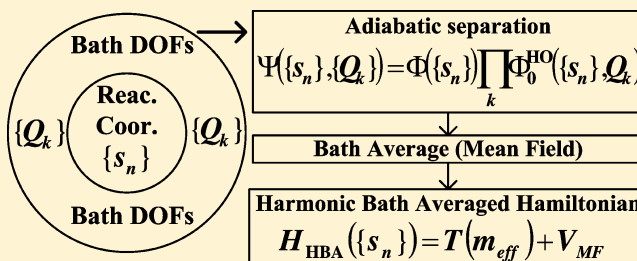
Harmonic Bath Averaged Hamiltonian: An efficient Tool To Capture Quantum Effects of Large Systems

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ABSTRACT: Starting from a reaction path Hamiltonian, a suitably reduced harmonic bath averaged Hamiltonian is derived by averaging over all the normal mode coordinates. Generalization of the harmonic bath averaged Hamiltonian to any dimensions are performed and the feasibility to use a linear reaction path/surface are investigated and discussed. By use of a harmonic bath averaged Hamiltonian, the tunneling splitting and proton transfer dynamics of malonaldehyde is briefly discussed and shows that the harmonic bath averaged Hamiltonian is an efficient tool to capture quantum effects in larger systems.



INTRODUCTION

The fundamental prerequisite of theoretical simulations of molecular reaction dynamics is a suitable molecular Hamiltonian. For very small systems this can be done by direct ab initio calculations of the potential energy surfaces (PES)^{1–3} and analytical derivations of kinetic energy operators.^{4–7} However, such an approach is no longer feasible for even slightly larger systems due to the exponential scaling of the computational effort for explicit calculation of a high dimensional PES and nuclear quantum dynamics simulations. Approximate Hamiltonians using normal mode coordinates are also widely adopted, which go back to contributions by Eckart,⁸ Wilson,⁹ and Watson.¹⁰ For example, the MULTIMODE program of Bowman et al.¹¹ based on the Watson Hamiltonian¹⁰ has been successfully applied to many systems. Another good alternative is the well established reaction path/surface Hamiltonian method, which divides the total coordinates into a few large amplitude reaction coordinates and many orthogonal harmonic motions.^{12–19} In general, the reaction surface Hamiltonian of a fairly large system can still be obtained because the direct ab initio calculations only involve a few large amplitude reaction coordinates.

To predict quantum effects, quantum dynamics are normally adopted after a molecular Hamiltonian has been obtained.^{20–22} Although the reaction path/surface Hamiltonian of a fairly large system can be obtained, the full dimensional quantum dynamics is still restricted to small systems even with efficient propagation programs such as the multiconfiguration time-dependent Hartree approach (MCTDH)²³ which has been widely used for high dimensional quantum dynamics.^{21,22,24} On the other hand, molecular dynamics methods have the capability to simulate large systems but fail to predict quantum effects. To meet the challenge of exploring quantum effects in

large systems, two standard types of methods are generally considered: QM/MM methods²⁵ that focus on quantum description of electrons and the reduced dimensional quantum dynamics methods^{26–29} that focus on nuclear quantum effects. In ref 28 a suitably reduced harmonic bath averaged (HBA) Hamiltonian has been reported and has shown to well reproduce experimentally observed quantum tunneling splittings of malonaldehyde and its deuterated isotopomer. This potentially paves the way for applications of the HBA Hamiltonian to larger molecular systems. In the present work the HBA method will be investigated in more detail which includes a concise theoretical derivation and interpretation of the approximations involved, the nontrivial generalization to the multidimensional case and a simplified form for linear reaction path/surface.

The present work is organized as follows. First a detailed derivation of the HBA Hamiltonian will be given and discussed. Then the generalization of the one-dimensional HBA Hamiltonian to the multidimensional case is investigated. After the general description, a special case of the HBA Hamiltonian for linear reaction path/surface is derived and its advantages and disadvantages are discussed. Following the entire description of the theory of the HBA Hamiltonian method brief discussions about its applications are provided. Finally the present work is summarized in the last section.

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THEORY

Derivation of Harmonic Bath Averaged Hamiltonian.

The starting point for the derivation of HBA Hamiltonian is the classical reaction path Hamiltonian for zero total angular momentum obtained by Miller and co-workers^{12,14}

$$H(p_s, s, \{P_k, Q_k\}) = \sum_{k=2}^{3N-6} \left(\frac{1}{2} P_k^2 + \frac{1}{2} \omega_k^2(s) Q_k^2 \right) + V_0(s) + \frac{1}{2} \frac{[p_s - \sum_{k,l=2}^{3N-6} Q_k P_{k,l}(s)]^2}{[1 + \sum_{k=2}^{3N-6} Q_k B_{k,1}(s)]^2} \quad (1)$$

where s is the mass weighted reaction coordinate and $\{Q_k\}$ are the normal modes orthogonal to s with corresponding conjugate momenta p_s and $\{P_k\}$, respectively. The zeroth-order potential $V_0(s)$ can be obtained from constrained optimizations with fixed s and the normal-mode frequencies $\{\omega_k(s)\}$ from diagonalizing the projected Hessian matrix of the optimized structure, which is just the standard procedures of generating a reaction path Hamiltonian. Along the reaction path each normal mode vector $L_k(s)$ varies, which leads to couplings between each pair of coordinates with coupling parameters in eq 1 defined as¹²

$$B_{k,l}(s) = \frac{\partial L_k(s)}{\partial s} \cdot L_l(s) \quad k = 2, \dots, 3N-6; \quad l = 1, \dots, 3N-6 \quad (2)$$

Here, $\{L_k(s)\}$ ($k = 2, \dots, 3N-6$) are the $3N-7$ normal mode vectors and $L_1(s)$ is the unit vector for the reaction path coordinate s .

According to a recent study on quantum kinetic energy operators⁷ the quantum Hamiltonian can be obtained from eq 1 by replacing each P_k^2 by $\hat{P}_k^\dagger \hat{P}_k$ and the last term $([p_s - \dots]^2/[1 + \dots]^2)$ by $([p_s - \dots]^\dagger [1 + \dots]^{-2} [p_s - \dots])$. In the following the simplified notations P_k^2 and $([p_s - \dots]^2/[1 + \dots]^2)$ are still used to denote $\hat{P}_k^\dagger \hat{P}_k$ and $[p_s - \dots]^\dagger [1 + \dots]^{-2} [p_s - \dots]$, respectively. In this way the quantum Hamiltonian has the same form as eq

1 and eq 1 will be referred to as the quantum Hamiltonian in the following. According to ref 7 each $\hat{P}_k^\dagger = \hat{P}_k$ is Hermitian whereas p_s is non-Hermitian. For a fairly large system such a $3N-6$ dimensional reaction path Hamiltonian is still not feasible for full quantum dynamics. Consequently, suitably reduced dimensional models which capture the essential elements of the nuclear dynamics and the couplings between the various degrees of freedom are more practical alternatives.

The formal development of the HBA Hamiltonian is based on the following ansatz for the ground state wave function of eq 1:

$$\Psi(s, \{Q_k\}) = \Phi(s) \prod_{k=2}^{3N-6} \Phi_0^{\text{HO}}(s, Q_k) \quad (3)$$

where $\Phi_0^{\text{HO}}(s, Q_k)$ is the ground state wave function of the corresponding harmonic oscillator (HO) which parametrically depends on s , namely

$$\left(\frac{1}{2} P_k^2 + \frac{1}{2} \omega_k^2(s) Q_k^2 \right) \Phi_0^{\text{HO}}(s, Q_k) = \frac{1}{2} \omega_k(s) \Phi_0^{\text{HO}}(s, Q_k)$$

It should be noted that compared to methods based on standard time-dependent self-consistent field (TDSCF) and multiconfiguration TDSCF (MC-TDSCF) approximations^{30,31} in which the wave function is expressed in terms of Hartree products $\Phi(s) \prod_{k=2}^{3N-6} \Phi_0^{\text{HO}}(Q_k)$, the present method corresponds to the limit of MC-TDSCF with *all* configurations because the bath wave function $\Phi_0^{\text{HO}}(s, Q_k)$ in eq 3 is s -dependent. Consequently, the HBA Hamiltonian method is expected to be a powerful method for nuclear quantum dynamics. In general, the bath wave function $\Phi_0^{\text{HO}}(s, Q_k)$ is a slowly varying function of s . Calculating the absolute squares of both sides of eq 3 and integrating out $\{Q_k\}$ one finds that $|\Phi(s)|^2$ is the one-dimensional reduced density along the reaction coordinate s . Averaging eq 1 over all the bath coordinates $\{Q_k\}$ yields the following one-dimensional HBA Hamiltonian H^{HBA}

$$\begin{aligned} H^{\text{HBA}}(p_s, s) &= \left\langle \prod_{k=2}^{3N-6} \Phi_0^{\text{HO}}(s, Q_k) \middle| H(p_s, s, \{P_k, Q_k\}) \middle| \prod_{k=2}^{3N-6} \Phi_0^{\text{HO}}(s, Q_k) \right\rangle \\ &\approx \left\langle \prod_{k=2}^{3N-6} \Phi_0^{\text{HO}}(s, Q_k) \middle| \sum_{k=2}^{3N-6} \left(\frac{1}{2} P_k^2 + \frac{1}{2} \omega_k^2(s) Q_k^2 \right) \middle| \prod_{k=2}^{3N-6} \Phi_0^{\text{HO}}(s, Q_k) \right\rangle + V_0(s) \\ &\quad + \frac{1}{2} \frac{\langle \prod_{k=2}^{3N-6} \Phi_0^{\text{HO}}(s, Q_k) | [p_s - \sum_{k,l=2}^{3N-6} Q_k P_{k,l}(s)]^2 | \prod_{k=2}^{3N-6} \Phi_0^{\text{HO}}(s, Q_k) \rangle}{\langle \prod_{k=2}^{3N-6} \Phi_0^{\text{HO}}(s, Q_k) | [1 + \sum_{k=2}^{3N-6} Q_k B_{k,1}(s)]^2 | \prod_{k=2}^{3N-6} \Phi_0^{\text{HO}}(s, Q_k) \rangle} \\ &= \frac{1}{2} \frac{[p_s - iC(s)]^2}{1 + \Delta_1(s)} + V_0(s) + \sum_{k=2}^{3N-6} \frac{\omega_k(s)}{2} (1 + \Delta_k(s)) \end{aligned} \quad (4)$$

where each $\Delta_k(s) = \sum_{l=2}^{3N-6} |B_{l,k}(s)|^2 / 2\omega_l(s)$ ($k = 1, \dots, 3N-6$) and the sum excluding $l = k$ is a non-negative function and $C(s) = \sum_k B_{k,k}(s)/2$. Note the average has been truncated up to the second order of the coupling parameters $\{B_{k,l}(s)\}$; otherwise the average of the last term in eq 1 will contain higher-order terms of $\{B_{k,l}(s)\}$. After a gauge transformation, the function $C(s)$ can be eliminated and the HBA Hamiltonian can be rewritten as

$$H^{\text{HBA}}(p_s, s) = \frac{1}{2} \frac{p_s^2}{1 + \Delta_1} + V_0(s) + \sum_{k=2}^{3N-6} \frac{\omega_k(s)}{2} (1 + \Delta_k(s)) \quad (5)$$

The term $p_s^2/(1 + \Delta_1)$ actually should be evaluated as $p_s^\dagger (1 + \Delta_1)^{-1} p_s$, as mentioned above. Thus, $H^{\text{HBA}}(p_s, s)$ is a well-defined operator without singularity or large curvature problems

irrespective of whether it is one-dimensional or multidimensional¹⁴ compared to other reduced models based on reaction path/surface Hamiltonians.

As can be readily seen from eq 5, the HBA Hamiltonian manifestly includes the effects of all the bath modes and is thus expected to more realistically describe the dynamics of a multidimensional system. A closer inspection of $H^{\text{HBA}}(p, s)$ reveals that it contains two modifications compared to H_0 , which can be conveniently expressed as

$$m^{\text{HBA}}(s) = 1 + \Delta_1(s) \quad (6)$$

which plays the role of an effective mass instead of 1 due to the curvature of the reaction path, and an effective potential

$$V^{\text{HBA}}(s) = V_0(s) + \sum_{k=2}^{3N-6} \frac{\omega_k(s)}{2} (1 + \Delta_k(s)) \quad (7)$$

which includes the zero point vibration of each mode and the coupling between each pair of modes. Finally, it should be noted that the average in eq 4 corresponds to a mean-field approximation. Different from conventional mean field approximations, which normally lead to mean field potentials only, the present average provides both a mean field potential, which is the effective potential in eq 7, and the mean field kinetic coupling term $\Delta_1(s)$, which leads to the effective mass in eq 6.

Multidimensional Harmonic Bath Averaged Hamiltonian. The multidimensional HBA Hamiltonian can be obtained following the same idea introduced in previous section. The starting point will be a reaction surface Hamiltonian. According to refs 12 and 14 the classical form of the reaction surface Hamiltonian for zero total angular momentum reads

$$\begin{aligned} H(\{p_n, s_n\}, \{P_k, Q_k\}) \\ = \sum_{k=D+1}^{3N-6} \left(\frac{1}{2} P_k^2 + \frac{1}{2} \omega_k^2 Q_k^2 \right) + V_0 \\ + \frac{1}{2} \sum_{nm=1}^D \tilde{p}_n [(1 + \mathbf{b})^{-2}]_{nm} \tilde{p}_m \end{aligned} \quad (8)$$

with

$$\begin{aligned} \tilde{p}_n &= (p_n - \sum_{k,l=D+1}^{3N-6} Q_k P_l B_{k,l,n}) \\ b_{nm} &= \sum_{k=D+1}^{3N-6} Q_k B_{k,n,m} \end{aligned}$$

where $\{s_n\}$ ($n = 1, \dots, D$) are the mass weighted reaction coordinates with total dimension D and $\{Q_k\}$ ($k = D + 1, \dots, 3N - 6$) are the normal modes orthogonal to $\{s_n\}$ with corresponding conjugate momenta $\{p_n\}$ and $\{P_k\}$. The corresponding coupling parameters $\{B_{k,l,n}\}$ are defined as

$$\begin{aligned} B_{k,l,n}(\{s_n\}) &= \frac{\partial L_k}{\partial s_n} \cdot L_l \\ k, l &= 1, \dots, 3N - 6; \quad n = 1, \dots, D \end{aligned} \quad (9)$$

where $\{L_k\}$ are the $3N - 6 - D$ dimensional normal mode coordinates ($k = D + 1, \dots, 3N - 6$) and D -dimensional reaction coordinates ($k = 1, \dots, D$). To avoid introducing too many

symbols, here the first two indexes includes both the reaction coordinates and bath coordinates and the last index only refers to the reaction coordinates. The matrix \mathbf{b} is the curvature matrix for the reaction surface.

Similarly, according to ref 7, the quantum Hamiltonian can be obtained from eq 8 by replacing each P_k^2 by $P_k^\dagger P_k$ and the last term $\frac{1}{2} \sum_{nm} (\dots) ([\dots]^{-2})_{nm} (\dots)$ by $\frac{1}{2} \sum_{nm} (\dots)^\dagger (([\dots]^\dagger [\dots])^{-1})_{nm} (\dots)$. As in the previous section, the simplified notations are still used in the following. Consequently, eq 8 will be referred to as the quantum Hamiltonian. A similar ansatz for an eigenfunction of eq 8 reads

$$\Psi(\{s_n\}, \{Q_k\}) = \Phi(\{s_n\}) \prod_{k=D+1}^{3N-6} \Phi_0^{\text{HO}}(\{s_n\}, Q_k) \quad (10)$$

with $\Phi_0^{\text{HO}}(\{s_n\}, Q_k)$ being the ground state eigenfunction of the corresponding harmonic oscillator that parametrically depends on $\{s_n\}$. Averaging eq 8 over $\{Q_k\}$ and ignoring third- and higher-order terms of $\{B_{k,l,n}\}$, the following multidimensional HBA Hamiltonian H^{HBA} is obtained

$$\begin{aligned} H^{\text{HBA}}(\{p_n, s_n\}) \\ = \langle \prod_{k=D+1}^{3N-6} \Phi_0^{\text{HO}}(Q_k) | H(\{p_n, s_n\}, \{P_k, Q_k\}) | \prod_{k=D+1}^{3N-6} \Phi_0^{\text{HO}}(Q_k) \rangle \\ \approx \frac{1}{2} \sum_{nm=1}^D (p_n^\dagger - (iC_n)^*) ([1 + \Delta_{:,n}]^{-1})_{nm} (p_m - iC_m) \\ + V_0(\{s_n\}) + \sum_{k=D+1}^{3N-6} \frac{\omega_k}{2} (1 + \Delta_k) \end{aligned} \quad (11)$$

where $\Delta_k = \sum_{l=D+1}^{3N-6} \sum_{n=1}^D (|B_{l,k,n}|^2 / 2\omega_l)$ ($k = D + 1, \dots, 3N - 6$ and the sum excluding $l = k$) and $C_n = \sum_k B_{k,n,n} / 2$. The difference from reaction path case is that the mass correction Δ_1 becomes a matrix $\Delta_{:,n}$ with elements

$$\Delta_{n,m} = \sum_{l=D+1}^{3N-6} \sum_{n'=1}^D \frac{B_{l,n,n'}^* B_{l,m,n'}}{2\omega_l} \quad (12)$$

After a gauge transformation, the function C_n can be eliminated and the HBA Hamiltonian can be rewritten as

$$\begin{aligned} H^{\text{HBA}}(\{p_n, s_n\}) &= \frac{1}{2} \sum_{nm=1}^D p_n^\dagger ([1 + \Delta_{:,n}]^{-1})_{nm} p_m + V_0(\{s_n\}) \\ &+ \sum_{k=D+1}^{3N-6} \frac{\omega_k}{2} (1 + \Delta_k) \end{aligned} \quad (13)$$

Because the coupling parameters $\{B_{k,l,n}\}$ are first-order small quantities the matrix inversion in eq 13 can be easily obtained as

$$([1 + \Delta_{:,n}]^{-1})_{nm} \approx 1 - \Delta_{n,m} \quad (14)$$

It should be mentioned that more eigenstates with excited harmonic bath can be solved by HBA Hamiltonian provided the eigenfunction can be approximated as

$$\Psi(\{s_n\}, \{Q_k\}) = \Phi(\{s_n\}) \prod_{k=D+1}^{3N-6} \Phi_{n_k}^{\text{HO}}(\{s_n\}, Q_k) \quad (15)$$

In this case the HBA Hamiltonian is almost the same as eq 13 except that $\omega_k/2$ should be replaced by $(n_k + 1/2)\omega_k$ and the new corrections

$$\Delta_k = \sum_{l=D+1}^{3N-6} \sum_{n=1}^D \frac{(2n_l + 1) |B_{l,k,n}|^2}{2\omega_l}$$

$$\Delta_{n,m} = \sum_{l=D+1}^{3N-6} \sum_{n'=1}^D \frac{(2n_l + 1) B_{l,n,n'}^* B_{l,m,n'}}{2\omega_l}$$

Harmonic Bath Averaged Hamiltonian for Linear Reaction Path/Surface. The linear reaction path/surface Hamiltonian is also widely used due to its formal simplification of the kinetic energy operator of the general reaction path/surface.^{15,19} The convenient parts include that the momenta associated with the linear reaction coordinates are Hermitian and the reaction path/surface can be easily defined without requirements of ab initio optimizations. Because the reaction path/surface is not optimized, the force on each orthogonal oscillator is no longer zero. From the formulations the only difference between linear reaction path/surface Hamiltonian and the above-discussed general reaction path/surface Hamiltonian is the potential part.¹⁹ The total potential energy of a reaction surface Hamiltonian reads

$$V(\{s_n\}, \{Q_k\}) = V_0 - \sum_{k=D+1}^{3N-6} f_k Q_k + \frac{1}{2} \sum_{k=D+1}^{3N-6} \omega_k^2 Q_k^2 \quad (16)$$

The linear reaction surface is defined by D constant unit vectors L_1, \dots, L_D without geometry optimization. Consequently, the orthogonal oscillators are not at their equilibrium positions. By shifting each normal mode to its equilibrium position, we can rewrite eq 16 as

$$V(\{s_n\}, \{Q_k\}) = V_0 - \frac{f_k^2}{2\omega_k^2} + \frac{1}{2} \sum_{k=D+1}^{3N-6} \omega_k^2 \left(Q_k - \frac{f_k}{\omega_k^2} \right)^2 \quad (17)$$

Defining shifted normal mode coordinates $\tilde{Q}_k = Q_k - (f_k/\omega_k^2)$ and reorganized potential $\tilde{V}_0(\{s_n\}) = V_0 - (f_k^2/2\omega_k^2)$ the linear reaction surface Hamiltonian will have exactly the same form as the above-discussed general reaction surface Hamiltonian except that Q_k and V_0 are replaced by \tilde{Q}_k and \tilde{V}_0 , respectively. Following the same procedures detailed for general reaction surface Hamiltonian the HBA Hamiltonian for linear reaction surface can be obtained as

$$H^{\text{HBA}}(\{p_n, s_n\}) = \frac{1}{2} \sum_{nm=1}^D p_n^\dagger ([1 + \Delta_{:,n}]^{-1})_{nm} p_m + V_0(\{s_n\}) - \frac{f_k^2}{2\omega_k^2} + \sum_{k=D+1}^{3N-6} \frac{\omega_k}{2} (1 + \Delta_k) \quad (18)$$

From eq 12 Δ_{nm} are contributed by $B_{knn'}$ with $k \neq n$ because $k = D + 1, \dots, 3N$ while $n = 1, \dots, D$. For linear reaction surface $\{L_n\}$ ($n = 1, \dots, D$) are constants consequently

$$B_{knn'} = \frac{\partial L_k}{\partial s_{n'}} \cdot L_n = \frac{\partial L_k \cdot L_n}{\partial s_{n'}} - L_k \cdot \frac{\partial L_n}{\partial s_{n'}} = 0 - 0 = 0 \quad (19)$$

This means a linear reaction surface Hamiltonian has a much more simple form than eq 8 due to the fact that a linear reaction surface has no curvature. Because for a linear reaction surface the curvature matrix $\mathbf{b} = 0$, the last kinetic energy term in eq 8 is simplified to a diagonal sum $1/2 \sum_n \tilde{p}_n^2$. And the HBA Hamiltonian for linear reaction surface is simplified as

$$H^{\text{HBA}}(\{p_n, s_n\}) = \frac{1}{2} \sum_{n=1}^D p_n^2 + V_0(\{s_n\}) - \frac{f_k^2}{2\omega_k^2} + \sum_{k=D+1}^{3N-6} \frac{\omega_k}{2} (1 + \Delta_k) \quad (20)$$

which directly leads to the HBA Hamiltonian for a linear reaction path by setting $D = 1$.

Note that by working with linear reaction path/surface the couplings between different normal modes B_{kln} ($k, l = D + 1, \dots, 3N$) do not necessarily need to be small because all the couplings are transformed to the couplings between different normal modes which finally reflects in the function Δ_k of eq 20. And eq 20 is the exact average of the starting linear reaction surface Hamiltonian without truncation of any terms because the curvature matrix \mathbf{b} vanishes. In general, to decrease artificial (large) couplings between normal modes, one may need to use a linear reaction surface instead of a linear reaction path unless for the system with an optimized curvature reaction path quite close to a linear reaction path.

APPLICATIONS AND DISCUSSIONS

In this section a brief discussion on the applications of HBA Hamiltonian to proton transfer dynamics and tunneling splitting in malonaldehyde (MA) and acetylacetone (AcAc) will be given. The structures of MA and its methyl derivative AcAc are shown in Figure 1. They both have a fairly strong

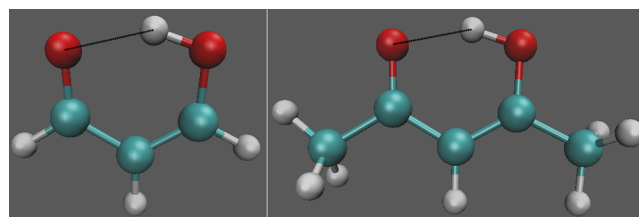


Figure 1. Structures of MA (left) and AcAc (right) with the intramolecular hydrogen bonds shown in dotted lines.

intramolecular hydrogen bond $\text{O}-\text{H}\cdots\text{O}$ with the shared proton transferring in between leading to quantum tunneling splitting of the lowest pair of vibrational eigenstates.

The ground state splitting of MA is an interesting quantity that has been observed experimentally with very high accuracy.^{32,33} Apart from full dimensional quantum dynamics,³ which is extremely time-consuming, the tunneling splitting can also be obtained by the HBA Hamiltonian method detailed in the present work very efficiently.²⁸ To establish HBA Hamiltonian, the first step is the definition of the reaction path. In ref 28 the reaction coordinate is defined as $s = m_{\text{H}}^{1/2}(r_1 - r_2)/2$ with r_1 and r_2 being the two OH distances of the intramolecular hydrogen bond $\text{O}-\text{H}\cdots\text{O}$ of MA. The required data for the HBA Hamiltonian have been calculated at the MP2/6-311++G** level of theory with further improvement for zeroth-order potential $V_0(s)$ at CCSD(T)/6-311++G** level. Diagonalization of the zeroth-order one-dimensional model $H_0(p,s) = 1/2 p_s^2 + V_0(s)$ by ignoring all couplings between the reaction coordinate s and the bath modes $\{Q_k\}$ leads to a splitting of 72.1 cm^{-1} , which overestimates the experimentally observed splitting of 21.583 cm^{-1} by a factor of ~ 4 . Exploiting the HBA Hamiltonian in eq 5 will considerably improve the results. Using a constant mass correction $\Delta_1 =$

0.234 for the HBA Hamiltonian, the calculated tunneling splittings in ref 28 are 21.6 cm^{-1} for normal MA and 2.8 cm^{-1} for deuterated MA, which agree with the experimentally observed values of 21.583 and 2.915 cm^{-1} , respectively.^{32–34} In addition, the proton transfer fundamental frequency of MA at zero temperature is around 1600 cm^{-1} by the HBA Hamiltonian method, which also agree with recently reported results in ref 35, suggesting previous assignments of proton transfer mode around 3000 cm^{-1} may be incorrect. As a symmetric double methyl derivative of MA, AcAc is also expected to have a tunneling splitting in a symmetric double well potential. However, contrary to MA where measurements yielded a large ground state splitting accurately, experimental tunneling splitting of AcAc has not been obtained so far.³⁶ Theoretically, it is still quite challenging due to its multidimensional nature. Even with the present efficient HBA Hamiltonian method one would at least need to solve a 3D HBA Hamiltonian because the torsional motions of the two methyl groups are highly anharmonic which should be treated explicitly as reaction coordinates.

The work on MA uses a simple effective mass correction Δ_1 , which already leads to fairly good results. It should be noted that by using directly calculated mass function $\Delta_1(s)$ or a higher dimensional HBA Hamiltonian, the reported results can be further improved. The simple parameter Δ_1 can be considered as the quantum mechanical mean value of $\Delta_1(s)$ provided $\Delta_1(s)$ is slowly varying. Alternatively, it can be calculated from $\langle p_s^2 \rangle / (1 + \Delta_1) = \langle p_s^2 / (1 + \Delta_1(s)) \rangle$. The starting point for the HBA Hamiltonian is the reaction path/surface Hamiltonian. Once a suitable reaction path/surface Hamiltonian is generated, it is straightforward to calculate all the required functions for the HBA Hamiltonian. For the time being, the HBA Hamiltonian can be applied to systems varying from a few atoms to about 100 atoms depending on different levels of preferred ab initio calculations. And it can be further applied to systems of several thousand atoms using an empirical force field instead of ab initio calculations. For better performance of the HBA Hamiltonian, all the bath modes either should be nearly harmonic or have negligible effects on the properties of interest, which is also the general requirement of the reaction path/surface Hamiltonian method. The HBA Hamiltonian only explicitly includes a few degrees of freedom with large amplitude motions; consequently, the computational cost is quite small. However, as already mentioned, the HBA Hamiltonian contains all couplings $B_{k,l,n}(\{s_n\})$ between any pair of coordinates, which makes it feasible to capture the essence of quantum effects of the studied system. Thus the HBA Hamiltonian is an efficient tool expected to capture the quantum effects of fairly large systems.

SUMMARY

Detailed derivation of the harmonic bath averaged Hamiltonian from one dimension to multidimensions are performed. The physical meanings of the terms in the HBA Hamiltonian and the advantages of the HBA Hamiltonian are discussed. The simplification from general HBA Hamiltonian to the HBA Hamiltonian of a linear reaction path/surface are investigated with discussions on its advantages and disadvantages. The application to MA with a simplified HBA Hamiltonian already gives results in favorable agreement with experiments. Based on the detailed theoretical derivations and discussions and the good performance of the application, the HBA Hamiltonian

method is expected to be an efficient method to capture quantum effects of fairly large systems.

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Notes

The authors declare no competing financial interest.

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