<u>Supporting Information</u>

A Systematic Approach for Computing Zero-Point Energy, Quantum Partition Function, and Tunneling Effect Based on Kleinert's Variational Perturbation Theory

Kin-Yiu Wong[*] and Jiali Gao

Department of Chemistry and Digital Technology Center

University of Minnesota, Minneapolis, MN 55455

[*] Author to whom correspondence should be addressed. Current primary email: kiniu@umn.edu ; permanent email: kiniu@alumni.cuhk.net

This Supporting Information is organized as follows:

I. Computational details

A. Asymmetric double-well potential

To calculate the classical configuration integrals involving W:

$$Q_{QM} = \sqrt{\frac{Mk_BT}{2\pi\hbar^2}} \int_{-\infty}^{\infty} e^{-\beta W(x_0)} dx_0, \tag{S1}$$

we first interpolated W_1, W_2, and W_3 on a 0.01Å grid, which is mass-scaled in units of atomic mass unit (AMU), before carrying out the numerical integrations. The areas of the integrations were chosen such that their values are converged at least up to 3 significant figures. All the numerical integrations and interpolation were performed with Mathematica.[1] We also computed the eigenenergies of this asymmetric double-well potential by the Rayleigh-Ritz variational method (Section II), in which the Schrödinger equation was solved in a basis of 114 Gauss-Hermite polynomials. The partition functions calculated by summing over these eigenenergies with the Boltzmann factor are virtually identical to the quantum results reported in the Mielke-Truhlar paper.[2]

B. The Morse potential for bond vibration

The numerically exact bound eigenenergy states $E_{n'}$ for the Morse potential are:[3,4]

$$E_{n'} = \hbar\omega_0\left[\left(n'+\frac{1}{2}\right)-\frac{1}{\zeta}\left(n'+\frac{1}{2}\right)^2\right], \tag{S2}$$

where $\hbar$ is Planck's constant divided by 2π and $\zeta = \frac{2\gamma}{\hbar}\sqrt{2MD_e}$. The quantum number n' can be chosen from any non-negative integers as long as $E_{n'}$ are smaller than the dissociation energy D_e. Although the form in Eq. (S2) is only numerically exact, it has been validated for the most unfavorable internuclear case, i.e., a hydrogen molecule.[4] The quantum vibrational (bound) partition function is obtained by summing over all bound energy states $E_{n'} \leq D_e$ with the Boltzmann factor:

$$Q_{qm}(\text{bound}) = \sum_{n'=0}^{E_{n'}\leq D_e} e^{-E_{n'}/k_BT}, \tag{S3}$$

where $E_{n'}$ is the energy in Eq. (S2), k_B is Boltzmann's constant, and T is temperature. On the other hand, the classical vibrational (bound) partition function is given by

$$Q_{cl}(\text{bound}) = \frac{1}{h} \int_{r_1}^{\infty} dr \int_{-\sqrt{2M[D_e - V(r)]}}^{\sqrt{2M[D_e - V(r)]}} dp \exp\left\{-\beta\left[\frac{p^2}{2M} + V(r)\right]\right\}, \tag{S4}$$

where h is Planck's constant, r_1 is the point $V(r_1) = D_e$, p is the momentum associated with r. The limits of the above integral are used to ensure only the energy smaller than D_e is included in the partition function.

Special care has to be taken when we use the effective centroid potential W to calculate $Q_{qm}(\text{bound})$. Since the Morse potential is an unbound potential (i.e., $V(\infty) \neq \infty$), if we integrate over the whole phase-space with W, the quantum partition function we obtain is the Boltzmann's sum of both bound eigenenergy states and the unbound continuous energy states, i.e.,

$$\sqrt{\frac{Mk_BT}{2\pi\hbar^2}} \int_0^{\infty} e^{-\beta W(r)} dr = Q_{qm}(\text{bound}) + Q_{qm}(\text{unbound}), \tag{S5}$$

Similarly, if we integrate over the whole phase-space with V, the classical partition function we calculate is the Boltzmann's sum of both bound and unbound continuous energy states, i.e.,

$$\sqrt{\frac{Mk_BT}{2\pi\hbar^2}} \int_0^{\infty} e^{-\beta V(r)} dr = Q_{cl}(\text{bound}) + Q_{cl}(\text{unbound}), \tag{S6}$$

Please note that since the energy spectrum of both quantum and classical unbound states are continuous, we have the following identity:

$$Q_{qm}(\text{unbound}) = Q_{cl}(\text{unbound}). \tag{S7}$$

Thus, by combing Eq. (S5), (S6), and (S7), we can express $Q_{qm}(\text{bound})$ in terms of W as follows:

$$Q_{qm}(\text{bound}) - Q_{cl}(\text{bound}) = \left(\sqrt{\frac{Mk_BT}{2\pi\hbar^2}} \int_0^{\infty} e^{-\beta W(r)} dr - \sqrt{\frac{Mk_BT}{2\pi\hbar^2}} \int_0^{\infty} e^{-\beta V(r)} dr\right)$$

$$\Rightarrow Q_{qm}(\text{bound}) = \left(\sqrt{\frac{Mk_BT}{2\pi\hbar^2}} \int_0^{\infty} e^{-\beta W(r)} dr - \sqrt{\frac{Mk_BT}{2\pi\hbar^2}} \int_0^{\infty} e^{-\beta V(r)} dr\right) + Q_{cl}(\text{bound}) \tag{S8}$$

Eq. (S8) is an *exact* expression relating $Q_{qm}(\text{bound})$ to W, although it requires calculating three different integrals.

We should use Eq. (S8) to compute $Q_{qm}(\text{bound})$. However, the orders of magnitude of each of the three integrals in Eq. (S8) actually are quite different from that of $Q_{qm}(\text{bound})$ (e.g., at 200 K, $Q_{cl}(\text{bound}) = 3.44 \times 10^{-2}$ and $Q_{qm}(\text{bound}) = 5.45 \times 10^{-7}$), so a very high precision for each of these three integration is required to achieve an accurate value of $Q_{qm}(\text{bound})$, particularly at low temperature. Fortunately enough, at lower temperature, $Q_{qm}(\text{bound})$ is getting closer to the following estimates:

$$Q_{qm}(\text{bound}) \approx \sqrt{\frac{Mk_BT}{2\pi\hbar^2}} \left[\int_{r_0(1-\Delta r_0)}^{r_0(1+\Delta r_0)} e^{-\beta W(r)} dr \right]. \tag{S9}$$

Eq. (S9) provides a much simpler way to evaluate $Q_{qm}(\text{bound})$ at low temperature involving only one integral to compute. Because at lower temperature, more bound states are contributed by the vicinity of r_0, the equilibrium position. At the zero-temperature limit, there is only one bound state (the ground state or zero-point energy) located at the minimum point of W.[5-8]

We used Eq. (S8) for T = 200, 300, 400, 500, and 1000 K. The zero lower-limit and infinity upper-limit of the first two integrals in Eq. (S8) have been replaced by $0.3r_1$ (r_1 is the point where $V(r_1) = D_e$) and $3r_0$ respectively. These two limits are chosen for the accuracy up to 3 significant figures (sig. fig.) because identical results (in 3 sig. fig.) can be obtained with smaller regions to be integrated, i.e., integrating from r_1 to $1.5r_0$. For T = 50 and 100 K, we used Eq. (S9) to compute the partition functions. We justified the value of Δr_0 by changing it from 0.1 to 0.5 and comparing the result with the one obtained by Eq. (S8) at higher temperature 200 K. All values are identical at least up to 3 significant figures. All the numerical integrations and interpolations were performed using Mathematica.[1] To compute all integrals involving W numerically, we first interpolated 300 points of W_1 or W_2 between $0.3r_1$ and $3r_0$ before carrying out the numerical integrations.

C. Symmetric and asymmetric Eckart potentials

The Eckart potential may be defined as follows:[9]

$$V(x) = \frac{A\exp\left(\dfrac{2\pi x}{L}\right)}{1+\exp\left(\dfrac{2\pi x}{L}\right)} + \frac{B\exp\left(\dfrac{2\pi x}{L}\right)}{\left[1+\exp\left(\dfrac{2\pi x}{L}\right)\right]^2}, \qquad (S10)$$

where x is the reaction coordinate, L is a characteristic length, A and B are constants associated with the height and symmetry of the barrier. For general values of A and B (with $B>0$), the expression in Eq. (S10) has limiting values of $V \to 0$ as $x \to -\infty$ and $V \to A$ as $x \to +\infty$, so that A represents the endothermicity of the reaction or the reaction energy. When $B > A$, V shows a maximum value with

$$V_{\max} = \frac{(A+B)^2}{4B}, \qquad (S11)$$

at the value of x equals

$$x_{\max} = \frac{L}{2\pi}\ln\left(\frac{B+A}{B-A}\right). \qquad (S12)$$

$V_{\max}$ is the height of the energy barrier for motion from the negative infinity of x to the positive infinity. When $A=0$, the potential reduces to be symmetric and $V(x)$ can be conveniently written in terms of a hyperbolic cosine function:

$$\begin{aligned} V(x) &= \frac{B}{\left[\exp\left(\dfrac{\pi x}{L}\right)+\exp\left(\dfrac{-\pi x}{L}\right)\right]^2} \\ &= \frac{V_{\max}}{\cosh^2\left(\dfrac{\pi x}{L}\right)}, \end{aligned} \qquad (S13)$$

where $V_{\max} = \dfrac{B}{4}$ (with $A=0$).

The exact probability of tunneling transmission over Eckart barrier is[9]

$$\Upsilon(E) = \begin{cases} 1 - \dfrac{\cosh\left\{2\pi\left[a_\gamma(E)-b_\gamma(E)\right]\right\}+\cosh\left[2\pi d_\gamma(E)\right]}{\cosh\left\{2\pi\left[a_\gamma(E)+b_\gamma(E)\right]\right\}+\cosh\left[2\pi d_\gamma(E)\right]} & \text{when } E > A \\ 0 & \text{when } E \leq A \end{cases}, \qquad (S14)$$

where E is the total energy of the incident particle with mass M,

$$a_\gamma(E) = \frac{1}{2}\sqrt{\frac{E}{\frac{1}{2M}\left(\frac{h}{2L}\right)^2}}, \quad (S15)$$

$$b_\gamma(E) = \frac{1}{2}\sqrt{\frac{E-A}{\frac{1}{2M}\left(\frac{h}{2L}\right)^2}}, \quad (S16)$$

$$d_\gamma(E) = \frac{1}{2}\sqrt{\frac{B}{\frac{1}{2M}\left(\frac{h}{2L}\right)^2} - 1}, \quad (S17)$$

and h is Planck's constant.

In Johnston's textbook,[10,11] a_γ, b_γ, and d_γ are expressed in terms of α_1 and α_2. α_1 is related to the height of the barrier from left to right, V_1, while α_2 is related to the height of the barrier from right to left, V_2:

$$V_1 = \alpha_1 \frac{\hbar\omega^*}{2\pi}, \quad (S18)$$

$$V_2 = \alpha_2 \frac{\hbar\omega^*}{2\pi}, \quad (S19)$$

where

$$V_1 = \frac{(A+B)^2}{4B}, \quad (S20)$$

$$V_2 = \frac{(A-B)^2}{4B}, \quad (S21)$$

and $i\omega^*$ is the imaginary angular frequency at the top of the barrier:

$$i\omega^* = i\sqrt{\frac{1}{M}\frac{\pi^2}{2L^2}\frac{(A^2-B^2)^2}{B^3}}. \quad (S22)$$

For a symmetric Eckart barrier (i.e., $A=0$), the probability of tunneling transmission over the barrier is simplified as follows:[12]

$$\Upsilon(E) = \frac{\cosh\{4\pi[a_\gamma(E)]\} - 1}{\cosh\{4\pi[a_\gamma(E)]\} + \cosh[2\pi d_\gamma(E)]}, \qquad (S23)$$

with

$$a_\gamma(E) = \frac{L}{h}\sqrt{2ME}, \qquad (S24)$$

$$d_\gamma(E) = \frac{L}{h}\sqrt{8MV_{max} - \frac{h^2}{4L^2}}. \qquad (S25)$$

The quantum rate constant of a chemical reaction over the Eckart barrier is[10]

$$k_{qm} = \frac{1}{h}\frac{1}{Q_R}\int_0^\infty \Upsilon(E)\exp(-E/k_BT)dE, \qquad (S26)$$

where Q_R is the partition function for the reactant. Since the potential is flatten out at negative infinity of x, the reactant in this model is essentially a free particle. Q_R for a free particle in classical mechanics is the same as that in quantum mechanics. But $\Upsilon(E)$ for a classical particle is zero for $E < V_{max}$, and unity for $E > V_{max}$. As a result, the ratio of the quantum to classical rate constants for the Eckart potential is given as follows:

$$\kappa = \frac{k_{qm}}{k_{cl}} = \frac{\exp(V_{max}/k_BT)}{k_BT}\int_0^\infty \Upsilon(E)\exp(-E/k_BT)dE. \qquad (S27)$$

In other words, this κ is the quantum tunneling correction factor to the classical rate constant for the Eckart barrier, which may also be called as transmission coefficient. Since $\Upsilon(E) = 0$ when $E \leq A$ [Eq. (S14)], κ is the same for both forward and backward chemical reactions.

In terms of path-integral quantum transition state theory (PI-QTST),[13-17] k_{qm} is approximated as follows (with no correction for re-crossings):

$$k_{qm} \approx k_{PI-QTST} = \frac{k_BT}{h}\frac{1}{Q_R}\exp(-W_{max}/k_BT), \qquad (S28)$$

where W_{max} is the maximum point or the saddle point of the effective centroid potential. Note that W_{max} is not necessarily located at the x_{max} in Eq. (S12).

For the symmetric Eckart potential, the parameters we used are: $M = 1836$ electronic mass, $\omega^* = 1047.2$ cm^{-1}, and $\alpha_1 = \alpha_2 = 12$. This set of parameters has been extensively used to

test the tunneling effects for PIMC simulations.[10,13,18] But for modeling the kinetic isotope effects on the protium/deuterium transfers over the symmetric Eckart barrier, we used the following parameters,[19] which are close to the ones used above: $M = 1.0078250$ and 2.0141018 AMU (atomic mass units), $V_{max} = 5.7307$ kcal/mol, and $L = 1.0967$ Å.

For the asymmetric Eckart potential, we used this set of parameters:[16] $A = -\dfrac{18}{\pi}$ kcal/mol,

$B = \dfrac{54}{\pi}$ kcal/mol, $L = \dfrac{8}{\sqrt{3\pi}}$ Å, and $M = 1836$ electronic mass.

II. Eigenenergies of the asymmetric double-well potential

Quantum state	Eigenenergy (hartree)
1	4.20895E-03
2	1.17045E-02
3	1.32405E-02
4	1.69572E-02
5	1.98854E-02
6	2.39617E-02
7	2.84721E-02
8	3.34363E-02
9	3.87813E-02
10	4.44689E-02
11	5.04686E-02
12	5.67559E-02
13	6.33117E-02

III. Instructions to obtain analytical closed forms of KP1/P20, KP2/P20, KP3/P6 at the zero-Ω limit in the formats of Mathematic notebook and FORTRAN

The nth-order Kleinert variational perturbation (KPn) approximation, $W_n^{\Omega}(x_0)$, can be written in terms of ordinary integrations:[5]

$$W_n^{\Omega}(x_0) = -k_B T \ln Q_{\Omega}^{x_0} + \frac{k_B T}{\hbar} \int_0^{\beta\hbar} d\tau \left\langle V_{\text{int}}^{x_0}\left[x(\tau_1)\right]\right\rangle_{\Omega}^{x_0}$$

$$-\frac{k_B T}{2!\hbar^2} \int_0^{\beta\hbar} d\tau_1 \int_0^{\beta\hbar} d\tau_2 \left\langle V_{\text{int}}^{x_0}\left[x(\tau_1)\right]V_{\text{int}}^{x_0}\left[x(\tau_2)\right]\right\rangle_{\Omega,c}^{x_0} + \cdots + k_B T \frac{(-1)^{n+1}}{n!\hbar^n}\left\{\prod_{j=1}^{n}\int_0^{\beta\hbar} d\tau_j\right\}\left\langle \prod_{k=1}^{n} V_{\text{int}}^{x_0}\left[x(\tau_k)\right]\right\rangle_{\Omega,c}^{x_0}$$

$$\text{(S29)}$$

where $V_{\text{int}}^{x_0}\left[x(\tau)\right] = V\left[x(\tau)\right] - \frac{1}{2}M\Omega^2\left[x(\tau) - x_0\right]^2$. If the potential energy function V is an mth-order polynomial, i.e.,

$$V(x) = b_0 + b_1 x + b_2 x^2 + \cdots + b_m x^m = \sum_{i=0}^{m} b_i x^i, \qquad \text{(S30)}$$

then the non-cumulant integrals associated with $\left\langle V_{\text{int}}^{x_0}\left[x(\tau_1)\right]\right\rangle_{\Omega}^{x_0}$, $\left\langle V_{\text{int}}^{x_0}\left[x(\tau_1)\right]V_{\text{int}}^{x_0}\left[x(\tau_2)\right]\right\rangle_{\Omega}^{x_0}$, and $\left\langle V_{\text{int}}^{x_0}\left[x(\tau_1)\right]V_{\text{int}}^{x_0}\left[x(\tau_2)\right]V_{\text{int}}^{x_0}\left[x(\tau_3)\right]\right\rangle_{\Omega}^{x_0}$ can be written in closed-form expressions:

$$\int_0^{\beta\hbar} d\tau_1 \left\langle V_{\text{int}}^{x_0}\left[x(\tau_1)\right]\right\rangle_{\Omega}^{x_0} = \sum_{i=0}^{m} c_i \text{FK1term}(i), \qquad \text{(S31)}$$

$$\int_0^{\beta\hbar} d\tau_1 \int_0^{\beta\hbar} d\tau_2 \left\langle V_{\text{int}}^{x_0}\left[x(\tau_1)\right]V_{\text{int}}^{x_0}\left[x(\tau_2)\right]\right\rangle_{\Omega}^{x_0} = \sum_{i,j=0}^{m} c_i c_j \text{FK2term}(i,j), \qquad \text{(S32)}$$

$$\int_0^{\beta\hbar} d\tau_1 \int_0^{\beta\hbar} d\tau_2 \int_0^{\beta\hbar} d\tau_3 \left\langle V_{\text{int}}^{x_0}\left[x(\tau_1)\right]V_{\text{int}}^{x_0}\left[x(\tau_2)\right]V_{\text{int}}^{x_0}\left[x(\tau_3)\right]\right\rangle_{\Omega}^{x_0}$$

$$\text{(S33)}$$

$$= \sum_{i,j,k=0}^{m} c_i c_j c_k \text{FK3term}(i,j,k),$$

where $c_0 = b_0 - \frac{1}{2}M\Omega^2 x_0^2$, $c_1 = b_1 + M\Omega^2 x_0$, $c_2 = b_2 - \frac{1}{2}M\Omega^2$, and $c_i = b_i$ for the rest of i.

$\text{FK1term}(i)$, $\text{FK2term}(i,j)$, and $\text{FK3term}(i,j,k)$ are lengthy functions in terms of $a(\Omega)$, $aij(\Omega)$, and $aijk(\Omega)$.

These FK terms are the same as the ones published in the previous study,[20] though the zero-Ω limit results of $a(\Omega=0)$, $aij(\Omega=0)$, and $aijk(\Omega=0)$ are now (as part of this Supporting Information) available in the formats of Mathematica notebook (i.e., "aijk_aij_aLimitOmegaZeroPublicDL.nb") and FORTRAN (i.e., "FK1_aLimitOmegaZeroFortran.txt", "FK2_aij40LimitOmegaZeroFortran.txt", and "FK3_a222to666_aijkLimitOmegaZeroFortran.txt").

IV. Instructions to obtain analytical closed forms of KP1/P20, KP2/P20, KP3/P6 at the zero-temperature limit in the formats of Mathematic notebook and FORTRAN

At the limit of zero-temperature, the FK terms in Eq. (S31), (S32), and (S33) becomes FK1termLimitTemperatureZero(i), FK2termLimitTemperatureZero(i, j), and FK3termLimitTemperatureZero(i, j, k), respectively. All are available (as part of this Supporting Information) in both formats of Mathematica notebook (i.e., "FK1FK2FK3termLimitTemperatureZeroPublicDL.nb") and FORTRAN (i.e., "FK1term0to20LimitTemperatureZeroFortran.txt", "FK2term00to2020LimitTemperatureZeroFortran.txt", and "FK3term000to666LimitTemperatureZeroFortran.txt").

The associated aLimitTemperatureZero(Ω), aijLimitTemperatureZero(Ω), and $aijk$LimitTemperatureZero(Ω) are available in both Mathematica notebook format (i.e., "aijk_aij_aLimitTemperatureZeroPublicDL.nb") and FORTRAN format (i.e., "FK1_aLimitTemperatureZeroFortran.txt", "FK2_aij40LimitTemperatureZeroFortran.txt", and "FK3_a222to666_aijkLimitTemperatureZeroFortran.txt") as well.

NOTE: All current analytical zero-temperature results are valid only when Ω is positive, though all results in principle should be even functions of Ω.

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