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Nonharmonic Degrees of Freedom: Densities of States and Thermodynamic Functions

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A universal algorithm for the calculation of the density-of-states, partition, and other thermodynamic functions of internal one-dimensional nonharmonic degrees of freedom is developed and analyzed. The algorithm is exact in the classical limit and results in analytical formulas for many types of potentials. Quantum effects are taken into account via the inverse Laplace transform of the classical partition function corrected for quantum effects by the method of Pitzer and Gwinn. Explicit formulas are reported for a variety of selected potential types (double-well inversion, quartic oscillator, etc.). An extension of the classical treatment to multidimensional potentials is described.

I. Introduction

Modeling of many classes of chemical reactions requires a knowledge of the density-of-states, sum-of-states, and partition functions of the involved molecules. The established approach is based on creating a model of the molecule consisting of a collection of harmonic oscillators and free one- and two-dimensional rotors. The density-of-states and sum-of-states functions of such an idealized molecule are easily calculated using, for example, the Beyer−Swinehart algorithm.[1,2] The presence of significantly nonharmonic degrees of freedom such as hindered rotations, inversions, quartic oscillators, etc. complicates the calculations. If all individual energy levels of a nonharmonic degree of freedom are known, they can be included via the Stein−Rabinovitch approach.[3] However, in spite of the existence of efficient algorithms,[4] determining individual energy levels for many types of potentials proves to be impractical since density-of-states functions are, generally, needed at very high energies (10^4−10^5 cm^{-1}) corresponding to large quantum numbers.

The problem of determining densities of states of nonharmonic degrees of freedom has been recently reviewed by Forst,[5] Troe,[6] and Ming et al.[7] Forst[5] developed an algorithm for computing sums of states for a collection of nonseparable anharmonic oscillators with known individual energy levels, as well as a fast approximate algorithm for determining densities of states via a numerical Laplace transform of the overall partition function. Algorithms were reported for estimating classical-limit anharmonic densities of states based on simplified models of several stretch potentials (Troe[6]) and on microcanonical sampling of the classical phase space (Ming et al.[7]). Quasi-classical expressions for density- and sum-of-states functions were derived for the Morse potential on the basis of the explicitly known vibrational energy levels (ref 6 and references therein). The specific case of the one-dimensional sinusoidally hindered rotor has received much attention (refs 8−12 and references therein). Knyazev et al.[11] developed analytical formulas for the density-of-states and sum-of-states functions that are exact in the classical approximation. Forst[9] reported an algorithm for calculating the density-of-states function of a system consisting of independent oscillators, free rotors, and one-dimensional hindered rotors via a numerical inversion of the overall partition function. In its quantum form, the algorithm uses the approximation of Truhlar[13] to the quantum partition function of a one-dimensional hindered rotor. Universal analytical formulas for sums and densities of states that included corrections for quantum effects based on an inverse Laplace transform (ILT) of the Pitzer−Gwinn approximation[14] to the quantum partition function were recently reported by Knyazev.[8]

In the current work, we report a universal algorithm for calculating densities and sums of states, as well as partition and thermodynamic functions, for any one-dimensional nonharmonic degree of freedom. The algorithm is exact in the classical limit and results in analytical formulas for many types of potentials. Corrections for quantum effects are introduced via the ILT of the Pitzer−Gwinn approximation. In section II, the algorithm is described for the general case of an arbitrary nonharmonic potential. In section III, several specific cases of nonharmonic potentials are examined and corresponding analytical formulas are derived. Implications for chemical kinetics modeling are discussed in section IV.

II. General Case

The partition function of any system can be considered as a Laplace transform of the corresponding density-of-states function $\rho(E)$ by definition

$$Q(\beta) = \int_0^\infty \rho(E) \exp(-\beta E)\, \mathrm{d}E = L[\rho(E)]$$

where $\beta = (k_B T)^{-1}$ is an inverse reduced temperature and E is the energy. Thus, provided that the dependence of the partition function on temperature is known, one can obtain the density-of-states function by inverse Laplace transform (ILT):

$$\rho(E) = L^{-1}[Q(\beta)]$$

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II.1. Classical Limit. *Densities and Sums of States.* In the classical limit, the partition function of a system with Hamiltonian $H(p, q)$ is obtained by an integral over phase space

$$Q_{\mathrm{CL}} = \frac{1}{h}\int_{-\infty}^{\infty} \mathrm{d}p \int_{q_1}^{q_2} \mathrm{d}p \exp(-\beta H(p, q)) \qquad \text{(II.1.1)}$$

where p is the momentum and q_1 and q_2 limit the range of coordinate q values. Describing the Hamiltonian of a one-dimensional degree of freedom as

$$H(p, q) = \frac{p^2}{2\mu} + V(q)$$

(μ is the reduced mass and $V(q)$ is the potential energy function) and evaluating the integral over momentum p, we obtain

$$Q_{\mathrm{CL}} = \frac{1}{h}\left[\frac{2\pi\mu}{\beta}\right]^{1/2} \int_{q_1}^{q_2} \mathrm{d}q \exp(-\beta V(q))$$

If an arbitrary "reference" value of $q = q_0$ is chosen, one can express potential energy as a function of the "reduced" coordinate $\xi = q/q_0$ and the expression for Q_{CL} acquires form

$$Q_{\mathrm{CL}} = \left[\frac{8\pi^3\mu q_0^2}{h^2\beta}\right]^{1/2} \frac{1}{2\pi}\int_{\xi_{\min}}^{\xi_{\max}} \mathrm{d}\xi \exp(-\beta V(\xi)) = \left[\frac{\pi}{B\beta}\right]^{1/2} \frac{1}{2\pi}\int_{\xi_{\min}}^{\xi_{\max}} \mathrm{d}\xi \exp(-\beta V(\xi)) = \tilde{Q}_{\mathrm{ROT}}(\beta)\, \tilde{Q}_{\mathrm{SH}}(\beta) \qquad \text{(II.1.2)}$$

where

$$B = \frac{h^2}{8\pi^2\mu q_0^2} \qquad \text{(II.1.3)}$$

is an "effective" rotational constant, $\tilde{Q}_{\mathrm{ROT}}(\beta) = [\pi/(B\beta)]^{1/2}$, and

$$\tilde{Q}_{\mathrm{SH}}(\beta) = \frac{1}{2\pi}\int_{\xi_{\min}}^{\xi_{\max}} \mathrm{d}\xi \exp(-\beta V(\xi)) \qquad \text{(II.1.4)}$$

Mathematically, this is equivalent to having two degrees of freedom, one pseudo-rotation with the partition function $\tilde{Q}_{\mathrm{ROT}}(\beta)$ and one "shape-related" degree of freedom with the partition function $\tilde{Q}_{\mathrm{SH}}(\beta)$, which is determined by the shape of the $V(\xi)$ potential.

The density-of-states function of pseudo-rotation is given by

$$\tilde{\rho}_{\mathrm{ROT}}(E) = \frac{1}{\sqrt{BE}} \qquad \text{(II.1.5)}$$

If the density-of-states function of the shape-related degree of freedom, $\tilde{\rho}_{\mathrm{SH}}(E) = L^{-1}[\tilde{Q}_{\mathrm{SH}}(\beta)]$, is known, the overall density-of-states function $\rho_{\mathrm{CL}}(E)$ can be obtained by a numerical or analytical convolution:

$$\rho_{\mathrm{CL}}(E) = \int_0^E \tilde{\rho}_{\mathrm{ROT}}(E - \epsilon)\, \tilde{\rho}_{\mathrm{SH}}(\epsilon)\, \mathrm{d}\epsilon = \frac{1}{\sqrt{B}}\int_0^E \frac{\tilde{\rho}_{\mathrm{SH}}(\epsilon)\, \mathrm{d}\epsilon}{\sqrt{E - \epsilon}} \qquad \text{(II.1.6)}$$

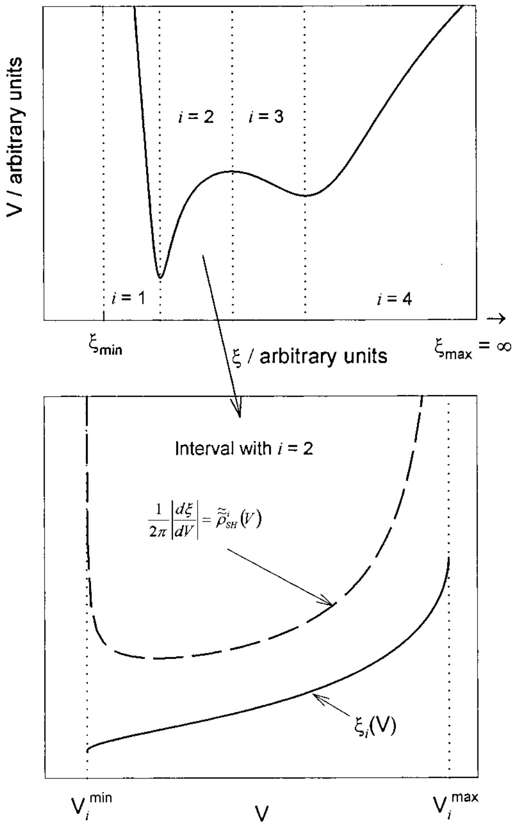

Figure 1. Upper plot: arbitrary $V(\xi)$ potential energy function. The ξ axis is divided into four segments (numbered by $i = 1-4$) with monotonic $V(\xi)$ dependencies. Lower plot (segment 2): corresponding inverse $\xi_i(V)$ function and resultant $\tilde{\tilde{\rho}}^{i}_{\mathrm{SH}}(V) = [1/(2\pi)]\cdot|\mathrm{d}\xi/\mathrm{d}V|$ dependence (a component of the overall $\tilde{\rho}_{\mathrm{SH}}(V)$ dependence, see text).

Determination of the $\tilde{\rho}_{SH}(E)$ Function. The potential energy profile is divided into several segments with monotonic $V(\xi)$ dependencies (Figure 1). These ξ-variable intervals of the segments are bound by $\xi_{\min}$, $\xi_{\max}$, and the extrema of the $V(\xi)$ function at several values of ξ. One can now represent the integral in (II.1.4) as a sum of integrals over the individual intervals (indexed by $1 \le i \le N$)

$$\tilde{Q}_{\mathrm{SH}}(\beta) = \frac{1}{2\pi}\sum_{i=1}^{N}\int \mathrm{d}\xi \exp(-\beta V(\xi)) = \frac{1}{2\pi}\sum_{i=1}^{N}\int_{V_i^{\min(\max)}}^{V_i^{\max(\min)}} \mathrm{d}V \left(\frac{\mathrm{d}\xi_i(V)}{\mathrm{d}V}\right) \exp(-\beta V) \qquad \text{(II.1.7)}$$

where $\xi_i(V)$ is an inverse $V(\xi)$ function in the ith interval. Again, the limits of integration over V are determined by the extrema of $V(\xi)$, $V_i^{\min}$ and $V_i^{\max}$.

For each interval i, we define the function

$$\tilde{\tilde{\rho}}^{i}_{\mathrm{SH}}(V) \equiv \tilde{\tilde{\rho}}^{i}_{\mathrm{SH}}(E) = \begin{cases} \dfrac{1}{2\pi}\left|\dfrac{\mathrm{d}\xi_{\mathrm{i}}}{\mathrm{d}V}\right|, & V_i^{\min} < V < V_i^{\max} \\ 0, & V \le V_i^{\min};\ V \ge V_i^{\max} \end{cases} \qquad \text{(II.1.8)}$$

Substituting (II.1.8) into (II.1.7), exchanging integration limits for intervals where $\mathrm{d}V(\xi)/\mathrm{d}\xi < 0$, and extending them from zero to infinity, we obtain

$$\tilde{Q}_{\mathrm{SH}}(\beta) = \sum_{i=1}^{N}\int_0^{\infty}\mathrm{d}V \tilde{\tilde{\rho}}^{i}_{\mathrm{SH}}(V) \exp(-\beta V) = \int_0^{\infty}\mathrm{d}V\Big[\sum_{i=1}^{N}\tilde{\tilde{\rho}}^{i}_{\mathrm{SH}}(V)\Big] \exp(-\beta V) \qquad \text{(II.1.9)}$$

which is equivalent to a Laplace transform of the $[\sum_{i=1}^{N}\tilde{\tilde{\rho}}^{i}_{\mathrm{SH}}(V)]$ function. Therefore, the density-of-states function $\tilde{\rho}_{\mathrm{SH}}(E) = L^{-1}[\tilde{Q}_{\mathrm{SH}}(\beta)]$ of the shape-related pseudo-degree of freedom is given by the sum of individual $\tilde{\tilde{\rho}}^i_{SH}(E)$ terms, which are, in turn, determined by the dξ/dV derivatives (formula II.1.8):

$$\tilde{\rho}_{SH}(E) = \sum_{i=1}^{N} \tilde{\tilde{\rho}}^i_{SH}(E) \qquad \text{(II.1.10)}$$

This (in many cases, *analytical*) $\tilde{\rho}_{SH}(E)$ dependence can thus be easily determined for any $V(\xi)$ potential. Then it can be analytically (preferred) or numerically convoluted (formula II.1.6) with the "pseudo-rotational" density-of-states function $\tilde{\rho}_{ROT}(E)$ to yield the overall classical $\rho_{CL}(E)$ density-of-states function.

It is interesting to note that for any potential energy well the $\tilde{\rho}_{SH}(E)$ function is determined by the energy dependence of the "width" (the distance between the left and right "walls") of the well. This can be shown by a variable transform: if ξ_i and ξ_{i+1} form the left and right walls of the well, by defining the width $w = \xi_{i+1} - \xi_i$ and "center" $c = {}^1/_2(\xi_{i+1} + \xi_i)$ one obtains for the shape-related density-of-states function

$$\tilde{\tilde{\rho}}_i(V) + \tilde{\tilde{\rho}}_{i+1}(V) = \frac{1}{2\pi}\frac{\mathrm{d}w}{\mathrm{d}V}$$

which is independent of c. The same holds for a complex potential consisting of multiple connected wells. Therefore, any "tilting" or other distortion of the potential that does not change the width vs energy dependence will not result in any change of the classical density-of-state function.

Thermodynamic and Partition Functions. The partition function $Q_{CL}(\beta)$ is given by the product of $\tilde{Q}_{ROT}(\beta)$ and $\tilde{Q}_{SH}(\beta)$. If the integral in (II.1.4) or (II.1.9) (which is the same) can be evaluated analytically, the problem of calculating $Q_{CL}(\beta)$ is solved. In this case, first and second derivatives of $\tilde{Q}_{SH}(\beta)$ can be determined analytically and thermodynamic functions of the shape-related pseudo-degree of freedom can now be evaluated via formulas

$$\text{internal energy} \qquad \tilde{U}_{SH} = -N_A \frac{\mathrm{d} \ln \tilde{Q}_{SH}(\beta)}{\mathrm{d}\beta} \qquad \text{(II.1.11)}$$

$$\text{heat capacity} \qquad \tilde{C}_{V,SH} = R\beta^2 \frac{\mathrm{d}^2 \ln \tilde{Q}_{SH}(\beta)}{\mathrm{d}\beta^2} \qquad \text{(II.1.12)}$$

$$\text{entropy} \qquad \tilde{S}_{SH} = R\left(\ln \tilde{Q}_{SH}(\beta) - \beta\frac{\mathrm{d} \ln \tilde{Q}_{SH}(\beta)}{\mathrm{d}\beta}\right) \qquad \text{(II.1.13)}$$

where N_A is Avogadro's number and R is the universal gas constant. They can now be combined with the thermodynamic functions of the "pseudo-rotation" calculated via standard methods to give the overall thermodynamic functions.

If analytical evaluation of $\tilde{Q}_{SH}(\beta)$ is impossible, the partition function and its first and second derivatives needed to calculate thermodynamic functions via II.1.11−13 can easily be obtained via numerical integration:

$$\begin{aligned} \tilde{Q}_{SH}(\beta) &= \int_0^\infty \tilde{\rho}_{SH}(E) \mathrm{e}^{-\beta E}\, \mathrm{d}E \\ \frac{\mathrm{d}\, \tilde{Q}_{SH}(\beta)}{\mathrm{d}\beta} &= -\int_0^\infty E\tilde{\rho}_{SH}(E)\, \mathrm{e}^{-\beta E}\, \mathrm{d}E \qquad \text{(II.1.14)} \\ \frac{\mathrm{d}^2\, \tilde{Q}_{SH}(\beta)}{\mathrm{d}\beta^2} &= \int_0^\infty E^2\tilde{\rho}_{SH}(E)\, \mathrm{e}^{-\beta E}\, \mathrm{d}E \end{aligned}$$

II.2. Correction for Quantum Effects. *Partition, Density-of-States, and Sum-of-States Functions.* Pitzer and Gwinn[14] suggested that the classical partition function can be corrected to account for quantum effects via a multiplication by the ratio of quantum (Q_Q^{HO}) to classical (Q_{CL}^{HO}) partition functions of a corresponding harmonic oscillator (i.e., an oscillator with a frequency derived from the curvature at the bottom of the nonharmonic potential):

$$Q_Q = Q_{CL}\frac{Q_Q^{HO}}{Q_{CL}^{HO}} \qquad \text{(II.2.1)}$$

Isaacson and Truhlar[15] have demonstrated that such a correction for quantum effects can be applied with good accuracy to a variety of potentials with different functional forms.

Formula II.2.1 can be used to obtain the density-of-states function via the ILT of $Q_Q(T)$. Such an approach to determining the density-of-states function, however, should be used with caution, since the approximation of (II.2.1), while describing the temperature dependence of the quantum partition function with reasonable accuracy for a variety of systems, is not derived from any fundamental principles and, therefore, does not have a physical meaning. It is only a phenomenological expression providing for a smooth transition from the low-temperature region on one side, where the ratio Q_{CL}/Q_{CL}^{HO} is equal to 1 and the partition function of a system can be described by Q_Q^{HO}, and the high-temperature region on the other side, where Q_Q^{HO} approaches Q_{CL}^{HO} and the partition function is well approximated by Q_{CL}. Agreement between the exact partition function and that given by (II.2.1) can be improved if the exact energies of the zeroth and first vibrational levels are known. In this case, Q_Q^{HO} can be calculated using a vibrational frequency corresponding to the actual 0 → 1 transition, and values of the partition function relative to the classical potential minimum can be obtained with higher accuracy by using the exact energy of the zeroth level.[15]

For a nonharmonic degree of freedom, three components of (II.2.1) are obtained as follows: Q_{CL} is given by (II.1.2),

$$Q_{CL}^{HO} = (h\nu\beta)^{-1}, \quad \text{and} \qquad Q_Q^{HO} = \exp(-{}^1/_2 h\nu\beta)(1 - \exp(-h\nu\beta))^{-1} \qquad \text{(II.2.2)}$$

where h is Planck's constant and ν is the frequency of the corresponding harmonic oscillator. Here, the bottom of the classical potential is taken as an energy reference point for all partition functions. The density-of-states function $\rho_Q(E)$ is given by the ILT of $Q_Q(\beta)$:

$$\rho_Q(E) = L^{-1}\left[Q_{CL}(\beta)\frac{Q_Q^{HO}(\beta)}{Q_{CL}^{HO}(\beta)}\right] = h\nu L^{-1}[\beta Q_{CL}(\beta)\; Q_Q^{HO}(\beta)] \qquad \text{(II.2.3)}$$

The sum-of-states function $W_Q(E)$ is given by the expression[16]

$$W_Q(E) = \int_0^E \rho_Q(\epsilon)\, \mathrm{d}\epsilon = L^{-1}\left[\frac{Q_Q(\beta)}{\beta}\right] = h\nu L^{-1}[Q_{CL}(\beta)\; Q_Q^{HO}(\beta)] \qquad \text{(II.2.4)}$$

Since the quantum density-of-states function of a harmonic oscillator

$$\rho_{\mathrm{Q}}^{\mathrm{HO}}(E) = L^{-1}[Q_{\mathrm{Q}}^{\mathrm{HO}}(\beta)] = \sum_{i=0}^{N(E)} \delta(E - h\nu(i + {}^1/_2)) \qquad (\mathrm{II.2.5})$$

where $N(E) = \mathrm{int}([E/(h\nu)] - (1/2))$ (int(x) means integer part), we can obtain via the convolution formula

$$W_{\mathrm{Q}}(E) = h\nu \int_0^E \rho_{\mathrm{CL}}(E - x) \sum_{i=0}^{N(x)} \delta(x - h\nu(i + {}^1/_2))\, \mathrm{d}x = h\nu \sum_{i=0}^{N(E)} \rho_{\mathrm{CL}}(E - h\nu(i + {}^1/_2)) \qquad (\mathrm{II.2.6})$$

For any function $F(\beta)$ the ILT of $\beta F(\beta)$ is given by[16,17]

$$L^{-1}[\beta F(\beta)] = f'(E) + f(0)\,\delta(E), \quad \text{where } f(E) = L^{-1}[F(\beta)]$$

as can be checked via integration by parts. Using this, (II.2.5) for $\rho_{\mathrm{Q}}^{\mathrm{HO}}(E)$, and the convolution formula, we can obtain for the quantum density-of-states function

$$\rho_{\mathrm{Q}}(E) = h\nu \int_0^E [\rho'_{\mathrm{CL}}(E - x) + \delta(E - x)\, \rho_{\mathrm{CL}}(0)] \times \sum_{i=0}^{N(x)} \delta(x - h\nu(i + {}^1/_2))\, \mathrm{d}x = h\nu \sum_{i=0}^{N(E)} [\rho'_{\mathrm{CL}}(E - h\nu(i + {}^1/_2)) + \rho_{\mathrm{CL}}(0)\, \delta(E - h\nu(i + {}^1/_2))] \qquad (\mathrm{II.2.7})$$

where $\rho'_{\mathrm{CL}}(E)$ is the first derivative of the $\rho_{\mathrm{CL}}(E)$ function.

In most practical applications, in calculating densities of states and performing numerical manipulations of related functions (e.g., solving master equation[18] for unimolecular reactions), the energy scale is divided into an array of energy bins of small size, and continuous functions are replaced with arrays. In such cases, to avoid problems associated with singularities of $\rho_{\mathrm{CL}}(E)$ and δ-functions in (II.2.7), it is advisable to calculate the value of the density-of-states function for each energy bin as an increment of the $W(E)$ function between the upper and lower borders of the bin divided by the bin width:

$$\rho_{\mathrm{Q}}(E) = \frac{\delta W_{\mathrm{Q}}(E)}{\delta E} \qquad (\mathrm{II.2.8})$$

Since the classical partition function is given by $Q_{\mathrm{CL}}(\beta) = \tilde{Q}_{\mathrm{ROT}}(\beta)\, \tilde{Q}_{\mathrm{SH}}(\beta)$, one may choose to apply the above "quantum correction" formalism to the shape-related pseudo-degree of freedom first and then include the pseudo-rotational $\tilde{Q}_{\mathrm{ROT}}(\beta)$ and $\tilde{\rho}_{\mathrm{ROT}}(E)$ functions.

For some forms of potential, $\rho_{\mathrm{CL}}(E)$ may decrease with energy. This will result in nonmonotonic behavior of $W_{\mathrm{Q}}(E)$ obtained from (II.2.6). Such nonmonotonic behavior corresponds to negative values of the density-of-states function $\rho_{\mathrm{Q}}(E)$, which is physically meaningless. Fortunately, these negative values (an artifact caused by applying ILT to the Pitzer–Gwinn approximation) are usually eliminated from the overall density-of-states function of a molecule if rotational degrees of freedom are included by a convolution. If such rotational degrees of freedom are not present, one needs to correct the $W_{\mathrm{Q}}(E)$ dependence by smoothing or "straightening" the sections of $W_{\mathrm{Q}}(E)$ with negative $\rho_{\mathrm{Q}}(E)$ (see ref 8 for an example of using classical expression for smoothing at high energies). One can note that the general large-scale behavior of classical ($W_{\mathrm{CL}}(E)$) and quantum ($W_{\mathrm{Q}}(E)$) sum-of-states functions are very similar since calculating the sum in (III.2.6) is almost identical to integrating the classical density of states with a very large step size (step size equal to $h\nu$).

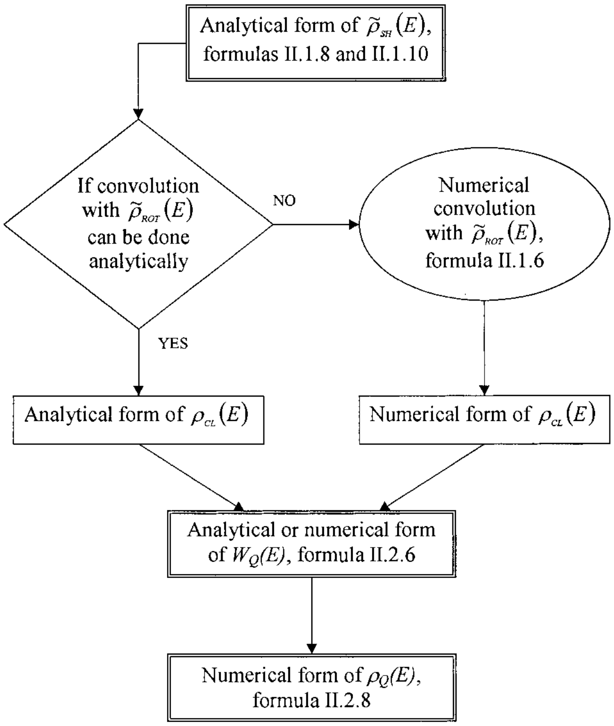

Figure 2. Schematic algorithm for calculating a density-of-states function (section II).

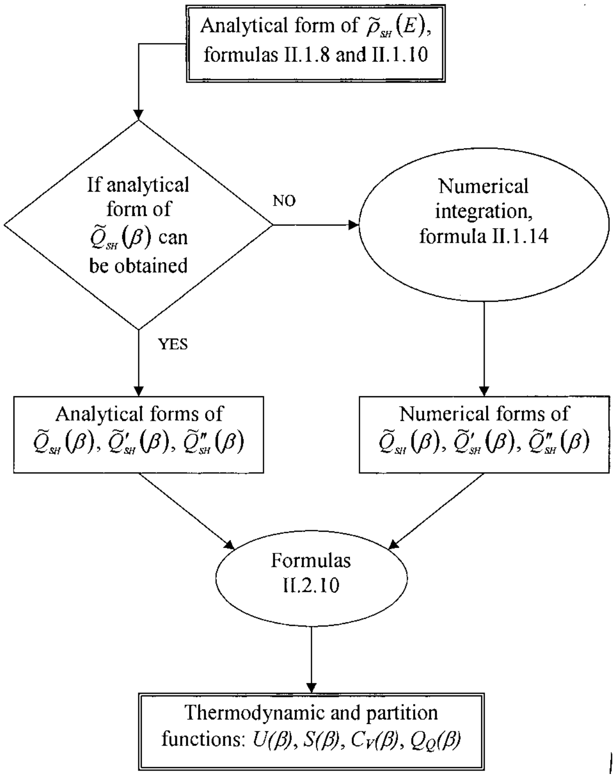

Figure 3. Schematic algorithm for calculating partition and thermodynamic functions (section II).

The above overall algorithm for obtaining the density-of-states and sum-of-states function is presented in Figure 2 in a schematic form. The algorithm for calculating the partition function is shown in Figure 3.

Thermodynamic Functions. The partition function corrected for quantum effects is given (II.2.1) by

$$Q_{\mathrm{Q}}(\beta) = Q_{\mathrm{CL}}(\beta)\frac{Q_{\mathrm{Q}}^{\mathrm{HO}}(\beta)}{Q_{\mathrm{CL}}^{\mathrm{HO}}(\beta)} = h\nu\beta\tilde{Q}_{\mathrm{SH}}(\beta)\,\tilde{Q}_{\mathrm{ROT}}(\beta)\,Q_{\mathrm{Q}}^{\mathrm{HO}}(\beta) \qquad \text{(II.2.9)}$$

In this formula the choice of reference energy conforms to that made in calculating $Q_{\mathrm{Q}}^{\mathrm{HO}}(\beta)$. Using the additivity property that follows from formula II.2.9, thermodynamic functions can be calculated by combining those of (1) a harmonic oscillator with partition function $Q_{\mathrm{Q}}^{\mathrm{HO}}(\beta)$, (2) a pseudo-rotation with partition function $\tilde{Q}_{\mathrm{ROT}}(\beta)$, and (3) another pseudo-degree of freedom described by the “partition function” $[h\nu\beta\tilde{Q}_{\mathrm{SH}}(\beta)]$. Thermodynamic functions of the harmonic oscillator ($U^{\mathrm{HO}}(\beta)$, $S^{\mathrm{HO}}(\beta)$, $C_{\mathrm{v}}^{\mathrm{HO}}(\beta)$) and pseudo-rotation ($\tilde{U}_{\mathrm{ROT}}(\beta)$, $\tilde{S}_{\mathrm{ROT}}(\beta)$, $\tilde{C}_{\mathrm{V,ROT}}(\beta)$) can be obtained by standard methods.[19] Noting that

$$\frac{\mathrm{d}}{\mathrm{d}\beta}(\ln[h\nu\beta\tilde{Q}_{\mathrm{SH}}(\beta)]) = \frac{1}{\beta} + \frac{\tilde{Q}'_{\mathrm{SH}}(\beta)}{\tilde{Q}_{\mathrm{SH}}(\beta)}$$

$$\frac{\mathrm{d}^2}{\mathrm{d}\beta^2}(\ln[h\nu\beta\tilde{Q}_{\mathrm{SH}}(\beta)]) = \frac{\tilde{Q}''_{\mathrm{SH}}(\beta)}{\tilde{Q}_{\mathrm{SH}}(\beta)} - \left(\frac{\tilde{Q}'_{\mathrm{SH}}(\beta)}{\tilde{Q}_{\mathrm{SH}}(\beta)}\right)^2 - \frac{1}{\beta^2}$$

and expressing thermodynamic functions via the partition function derivatives (see formulas II.1.11−13), we obtain for the one-dimensional degree of freedom under consideration

internal energy

$$U(\beta) = \tilde{U}_{\mathrm{ROT}}(\beta) + U^{\mathrm{HO}}(\beta) - N_{\mathrm{A}}\left\{\frac{1}{\beta} + \frac{\tilde{Q}'_{\mathrm{SH}}(\beta)}{\tilde{Q}_{\mathrm{SH}}(\beta)}\right\}$$

entropy

$$S(\beta) = \tilde{S}_{\mathrm{ROT}}(\beta) + S^{\mathrm{HO}}(\beta) + R\left\{\ln[h\nu\beta\tilde{Q}_{\mathrm{SH}}(\beta)] - 1 - \beta\frac{\tilde{Q}'_{\mathrm{SH}}(\beta)}{\tilde{Q}_{\mathrm{SH}}(\beta)}\right\} \qquad \text{(II.2.10)}$$

heat capacity

$$C_{\mathrm{V}}(\beta) = \tilde{C}_{\mathrm{V,ROT}}(\beta) + C_{\mathrm{V}}^{\mathrm{HO}}(\beta) + R\left\{\beta^2\frac{\tilde{Q}''_{\mathrm{SH}}(\beta)}{\tilde{Q}_{\mathrm{SH}}(\beta)} - \beta^2\left(\frac{\tilde{Q}'_{\mathrm{SH}}(\beta)}{\tilde{Q}_{\mathrm{SH}}(\beta)}\right)^2 - 1\right\}$$

The shape-related partition function $\tilde{Q}_{\mathrm{SH}}(\beta)$ and its first and second derivatives, $\tilde{Q}'_{\mathrm{SH}}(\beta)$ and $\tilde{Q}''_{\mathrm{SH}}(\beta)$, can be obtained either analytically or numerically (II.1.14).

This algorithm for calculating thermodynamic functions is presented in Figure 3 in a schematic form.

II.3. Extension of Classical Treatment to the Multidimensional Case. Let us consider an N-dimensional system described by a Hamiltonian with separable kinetic energy part

$$\mathrm{H}(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^{N}\frac{p_i^2}{2\mu_i} + \mathrm{V}(\mathbf{q}) \qquad \text{(II.3.1)}$$

where $\mathrm{V}(\mathbf{q})$ is an infinitely bound potential such that $\lim_{|\mathbf{q}|\to\infty}\mathrm{V}(\mathbf{q}) = \infty$ ($\mathbf{p}$ and $\mathbf{q}$ are multidimensional generalized momentum and coordinate). By choosing arbitrary “reference” vector $\mathbf{q}_0$, defining the reduced coordinate $\tilde{\mathbf{q}}$ ($\tilde{q}_i = q_i/q_{0i}$, $V(\tilde{\mathbf{q}}) = \mathrm{V}(\mathbf{q})$), and performing an integration over momenta in a way similar to that used in section II.1, we obtain for the multidimensional classical partition function

$$Q_{\mathrm{CL}}(\beta) = \frac{1}{h^{\mathrm{N}}}\int \mathrm{d}\mathbf{p}\,\mathrm{d}\mathbf{q}\,\exp(-\beta\,\mathrm{H}(\mathbf{p}, \mathbf{q})) = \prod_{i=1}^{N}\left[\frac{\pi}{B_i\beta}\right]^{1/2}\frac{1}{2\pi}\int \mathrm{d}\tilde{\mathbf{q}}\,\exp(-\beta V(\tilde{\mathbf{q}})) = \tilde{Q}_{\mathrm{ROT}}(\beta)\,\tilde{Q}_{\mathrm{SH}}(\beta) \qquad \text{(II.3.2)}$$

where $\tilde{Q}_{\mathrm{ROT}}(\beta)$ is a rotational partition function of a collection of N one-dimensional pseudo-rotors with rotational constants B_i given by (II.1.3), and shape-related partition function $\tilde{Q}_{\mathrm{SH}}(\beta)$ is given by

$$\tilde{Q}_{\mathrm{SH}}(\beta) = \frac{1}{2\pi}\int \mathrm{d}\tilde{\mathbf{q}}\,\exp(-\beta V(\tilde{\mathbf{q}})) \qquad \text{(II.3.3)}$$

We now define a generalized energy-dependent width of the potential energy function $V(\tilde{\mathbf{q}})$

$$w(E) = \int H(E - V(\tilde{\mathbf{q}}))\,\mathrm{d}\tilde{\mathbf{q}} \qquad \text{(II.3.4)}$$

where integration is performed from $-\infty$ to $+\infty$ in all dimensions and $H(x)$ is a Heaviside step function. This $w(E)$ function can also be described as an area of the reduced coordinate space contained inside the potential well at a particular energy E. The first derivative of the $w(E)$ function is given by

$$\frac{\mathrm{d}w(E)}{\mathrm{d}E} = \int \delta(E - V(\tilde{\mathbf{q}}))\,\mathrm{d}\tilde{\mathbf{q}} \qquad \text{(II.3.5)}$$

Defining

$$\tilde{\rho}_{\mathrm{SH}}(E) = \frac{1}{2\pi}\frac{\mathrm{d}w(E)}{\mathrm{d}E} \qquad \text{(II.3.6)}$$

and using (II.3.5), we see that

$$\int_0^E \tilde{\rho}_{\mathrm{SH}}(\epsilon)\exp(-\beta\epsilon)\,\mathrm{d}\epsilon = \frac{1}{2\pi}\int_0^E \frac{\mathrm{d}w(\epsilon)}{\mathrm{d}\epsilon}\exp(-\beta\epsilon)\,\mathrm{d}\epsilon = \frac{1}{2\pi}\int_0^E \mathrm{d}\epsilon\int \mathrm{d}\tilde{\mathbf{q}}\,\delta(\epsilon - V(\tilde{\mathbf{q}}))\exp(-\beta\epsilon) = \frac{1}{2\pi}\int \mathrm{d}\tilde{\mathbf{q}}\,\exp(-\beta V(\tilde{\mathbf{q}})) = \tilde{Q}_{\mathrm{SH}}(\beta) \qquad \text{(II.3.7)}$$

Therefore, the function $\tilde{\rho}_{\mathrm{SH}}(E)$ of (II.3.6) determined by the dependence of the generalized width of potential (i.e., the coordinate area bound by the potential energy well at a particular energy) on energy has the meaning of the density-of-states function of the shape-related pseudo-degree of freedom, i.e., the same as in the one-dimensional case (section II.1).

Thus, in a multidimensional case, the classical density-of-states function can be determined by a method that follows the same general algorithm described in section II.1. First, one determines (in many cases, this can be done analytically) the $\tilde{\rho}_{\mathrm{SH}}(E)$ function via the derivative of the $w(E)$ dependence. Second, to obtain the overall classical density of states, the $\tilde{\rho}_{\mathrm{SH}}(E)$ function is convoluted (analytically or numerically, first part of formula II.1.6) with the density-of-states function of pseudo-rotations $\tilde{\rho}_{\mathrm{ROT}}(E)$, which can be found using standard formulas (see, for example, ref 18).

III. Specific Cases of Individual Nonharmonic Potentials

In this section, analytical formulas for $\tilde{\rho}_{\mathrm{SH}}(E)$, $\rho_{\mathrm{CL}}(E)$, and $\tilde{Q}_{\mathrm{SH}}(\beta)$ are derived for several types of nonharmonic potentials.

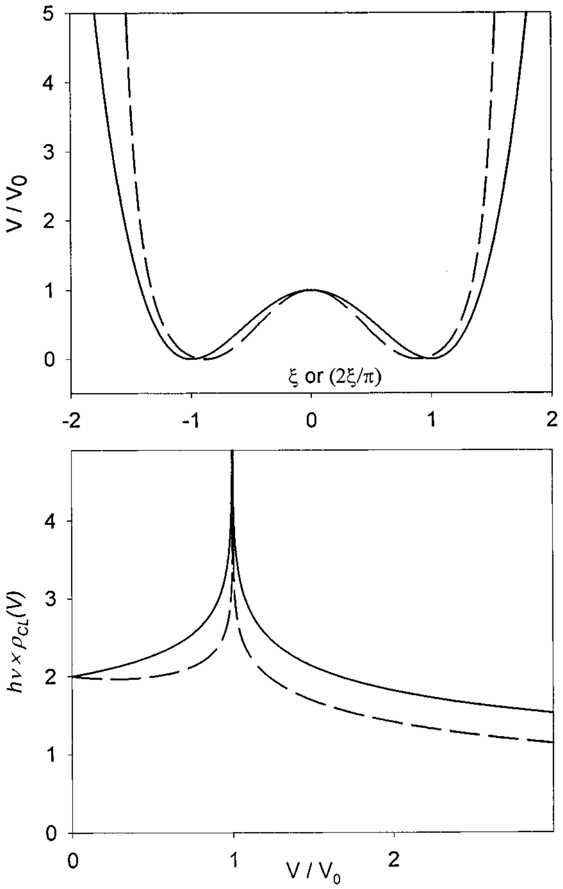

Figure 4. Upper plot: quartic−quadratic (formula III.1.1, solid line) and cos−tan^2 (formula III.2.1, $\gamma = 1$, dashed line) potentials. *X*-axis: ξ for quartic−quadratic and $2\xi/\pi$ for cos−tan^2 potentials (different scales are chosen to yield the same curvature at the potential bottom). Lower plot: Classical density-of-states functions relative to that of a corresponding single harmonic oscillator. Lines are the same as in the upper plot.

In most cases, these formulas involve special functions that can be easily computed using available numerical methods (e.g., ref 20).

III.1. Quartic−Quadratic Double-Well Potential. A potential energy function of the type $V(q) = aq^4 - bq^2$ ($a, b > 0$) is frequently used in spectroscopy to describe inversion and ring-puckering.[21] Expressed via parameters V_0 (the barrier between two connected wells) and q_0 (coordinate of energy minimum), the potential energy function acquires the form (Figure 4)

$$V = V_0(\xi^2 - 1)^2, \quad \xi = \frac{q}{q_0} \qquad \text{(III.1.1)}$$

Since the potential is symmetric, only the $\xi > 0$ region will be considered and the obtained derivatives will be multiplied by 2 to calculate $\tilde\rho^{i}_{SH}(E)$. Two branches of $\xi(V)$ and the corresponding $V(\xi)$ dependencies need to be considered:

1. $i = 1. \quad 0 < \xi < 1, \quad \xi_1(V) = \sqrt{1 - \sqrt{\dfrac{V}{V_0}}}, \quad 0 < V(\xi) < V_0$

2. $i = 2. \quad \xi > 1, \quad \xi_2(V) = \sqrt{1 + \sqrt{\dfrac{V}{V_0}}}, \quad 0 < V(\xi)$

Taking the derivatives, we obtain for the $\tilde\rho_{SH}(E)$ function

$$\tilde\rho_{SH}(E) = \tilde\rho^1_{SH}(E) + \tilde\rho^2_{SH}(E) = \frac{1}{4\pi V_0}\left\{\frac{1}{\sqrt{\epsilon(1+\sqrt{\epsilon})}} + \frac{H(1-\epsilon)}{\sqrt{\epsilon(1-\sqrt{\epsilon})}}\right\}, \quad \epsilon = \frac{E}{V_0} \qquad \text{(III.1.2)}$$

where $H(x)$ is a Heaviside step function. If the energy scale is divided into an array of energy bins, for each energy bin $\tilde\rho_{SH}(E)$ is best calculated (see formula II.2.8) as a increment of the corresponding sum-of-states function

$$\tilde W_{SH}(E) = \int_0^E \tilde\rho_{SH}(x)\,\mathrm{d}x = \frac{1}{\pi}\left[\sqrt{1+\sqrt{\epsilon}} - H(1-\epsilon)\sqrt{1-\sqrt{\epsilon}}\right]$$

The overall classical density-of-states function can be calculated via an analytical convolution (formula II.1.6)

$$\rho_{CL}(E) = \int_0^E \frac{\tilde\rho_{SH}(x)\,\mathrm{d}x}{\sqrt{B(E-x)}}$$

where the rotational constant B of the pseudo-rotation (formula II.1.3) is related to V_0 and the harmonic frequency ν derived from the curvature at the bottom of the potential via the expression

$$\sqrt{BV_0} = \frac{h\nu}{4}$$

Using (III.1.2) and substitutions $t = (x/V_0)^{1/2}$, $\varphi = (\epsilon)^{1/2} = (E/V_0)^{1/2}$, one can obtain for the $\rho_{CL}(E)$ function

$$\rho_{CL}(E) = \frac{1}{2\pi\sqrt{BV_0}}\left[\int_0^{\varphi} \frac{\mathrm{d}t}{\sqrt{(\varphi - t)(\varphi + t)(1 + t)}} + \int_0^{\varphi} \frac{H(1-t)\,\mathrm{d}t}{\sqrt{(\varphi - t)(\varphi + t)(1 - t)}}\right]$$

These integrals can be evaluated separately for $\varphi < 1$ and $\varphi > 1$ regions giving (Gradshteyn and Ryzhik,[22] eq 3.131)

$$\rho_{CL}(E) = \begin{cases} \dfrac{1}{\pi\sqrt{BV_0}\sqrt{1+\varphi}}\left[F\left(\dfrac{\pi}{4}, \sqrt{\dfrac{2\varphi}{1+\varphi}}\right) + F\left(\arcsin\sqrt{\dfrac{1+\varphi}{2}}, \sqrt{\dfrac{2\varphi}{1+\varphi}}\right)\right], & \varphi < 1 \\ \dfrac{1}{\pi\sqrt{BV_0}\sqrt{2\varphi}}\left[F\left(\arcsin\sqrt{\dfrac{\varphi}{1+\varphi}}, \sqrt{\dfrac{1+\varphi}{2\varphi}}\right) + F\left(\arcsin\sqrt{\dfrac{2}{1+\varphi}}, \sqrt{\dfrac{1+\varphi}{2\varphi}}\right)\right], & \varphi > 1 \end{cases}$$

where $F(x, y)$ is an elliptic integral of the first kind (as defined in ref 22). This functional form of the classical density-of-states function is illustrated in Figure 4.

Unfortunately, an analytical formula for $\tilde Q_{SH}(\beta)$ cannot be derived. Therefore, one needs to use numerical integration (formula II.1.14) to obtain the partition function derivatives and thermodynamic functions.

The first 16 exact energy levels of the quartic−quadratic double-well potential have been tabulated by Laane[23] for a wide variety of potential parameters. These tabulated values are used

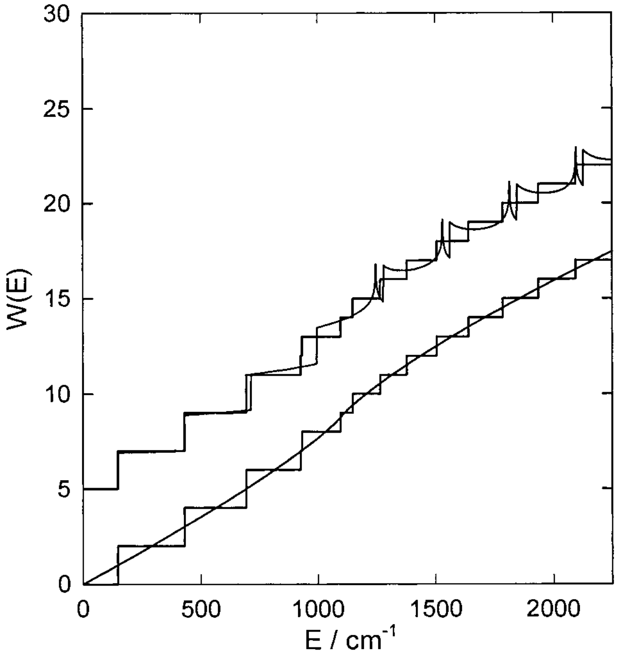

Figure 5. Plot of the sum-of-states functions for the quartic−quadratic potential obtained at different levels of approximation. The classical approximation ($W_{CL}(E)$, smooth curve, lower line) and classical corrected for quantum effects via the ILT of Pitzer−Gwinn approximation ($W_Q(E)$, complex nonmonotonic dependence, upper line) are compared with the exact $W(E)$ dependence obtained from the tabulated energy levels reported by Laane[23] (stepwise lines superimposed over both upper and lower lines). The values of $W_Q(E)$ and the corresponding exact $W(E)$ function are shifted upward by 5 units to avoid plot congestion. Parameters of the quartic−quadratic oscillator used: $V_0 = 1102$ cm^{-1}, $q_0 = 1$ Å, $\mu = 3.3$ amu. The value of $h\nu = 283.1$ cm^{-1} used to calculate $W_Q(E)$ via (II.2.6) was obtained from the tabulation of Laane[23] (energy of the 0 → 1 transition).

here to compare the results of the current approach with the exact $W(E)$ dependence (Figure 5). The sum-of-states function, $W(E)$, is chosen for the comparison because the density-of-states function ($\rho(E)$) is discrete in the exact quantum case (a sequence of δ-functions), is continuous in the classical approximation, and has both discrete and continuous components in the classical approximation corrected for quantum effects via the ILT of the Pitzer−Gwinn approximation (section II.2, eq II.2.7). At the same time, $W(E)$ is always continuous, which simplifies the comparison. As can be seen from Figure 5, both the classical ($W_{CL}(E)$) and classical corrected for quantum effects ($W_Q(E)$) functions follow the general large-scale $W(E)$ dependence obtained from exact energy levels. $W_Q(E)$ provides a better (almost exact) stepwise representation at low energies but displays nonphysical behavior (nonmonotonic growth) at higher energies. Methods of correcting such nonphysical $W_Q(E)$ dependencies are discussed in section II.2 and ref 8.

III.2. cos−tan^2 Double-Well Potential. We propose here another formula to describe a potential energy function of a double-well system

$$V(\xi) = \begin{cases} \dfrac{V_0}{2}(1 + \cos(\pi\xi)), & 0 \leq |\xi| \leq 1 \\ V_0\gamma^2 \tan^2\left(\dfrac{\pi}{2\gamma}(\xi - 1)\right), & 1 < |\xi| < \gamma + 1 \end{cases} \qquad \text{(III.2.1)}$$

where $\xi = q/q_0$ and q_0 is the coordinate of the potential energy minimum. The potential described by (III.2.1) (Figure 4) depends on three parameters (V_0, q_0, and γ) and thus is more flexible than the quartic−quadratic potential of (III.1.1). Also, its range of reduced coordinate ξ is confined to the interval $|\xi| < \gamma + 1$, which is more realistic than an unrestricted potential since such degrees of freedom as inversion and ring-puckering are necessarily restricted in coordinate.

Following the same general path of derivation as in the case of quartic−quadratic potential

$$\xi_1(V) = \frac{1}{\pi}\arccos\left(\frac{2V}{V_0} - 1\right), \quad 0 \leq |\xi_1| \leq 1, \quad 0 \leq V \leq V_0$$

$$\xi_2(V) = \frac{2\gamma}{\pi}\arctan\left(\sqrt{\frac{V}{V_0\gamma^2}}\right) + 1, \quad 1 \leq |\xi_2| \leq \gamma + 1, \quad V \geq 0$$

Taking the derivatives, we obtain for the $\tilde{\rho}_{SH}(E)$ function

$$\tilde{\rho}_{SH}(E) = \tilde{\rho}^1_{SH}(E) + \tilde{\rho}^2_{SH}(E) = \frac{H(V_0 - E)}{\pi^2\sqrt{E(V_0 - E)}} + \frac{\gamma^2}{\pi^2(E + V_0\gamma^2)}\sqrt{\frac{V_0}{E}} \qquad \text{(III.2.2)}$$

where $H(x)$ is a Heaviside step function. For the classical density-of-states function we can obtain (ref 22, eqs 3.131 and 3.147)

$$\rho_{CL}(E) = \int_0^E \frac{\tilde{\rho}_{SH}(x)\,dx}{\sqrt{B(E - x)}} = \int_0^E \frac{H(V_0 - x)\,dx}{\pi^2\sqrt{Bx(V_0 - x)(E - x)}} + \int_0^E \frac{\gamma^2\sqrt{V_0}\,dx}{\pi^2(V_0\gamma^2 + x)\sqrt{Bx(E - x)}} = \frac{\gamma}{\pi\sqrt{B(E + V_0\gamma^2)}} + \begin{cases} \dfrac{2\boldsymbol{K}\left(\sqrt{\dfrac{E}{V_0}}\right)}{\pi^2\sqrt{BV_0}}, & E < V_0 \\ \dfrac{2\boldsymbol{K}\left(\sqrt{\dfrac{V_0}{E}}\right)}{\pi^2\sqrt{BE}}, & E > V_0 \end{cases} \qquad \text{(III.2.3)}$$

where the rotational constant B of the pseudo-rotation (II.1.3) is related to V_0 and the harmonic frequency ν derived from the curvature at the bottom of the potential via the expression $(BV_0)^{1/2} = (h\nu)/\pi$.

The corresponding classical sum-of-states function is given by

$$W_{CL}(E) = \frac{2\gamma}{\pi\sqrt{B}}\left(\sqrt{E + V_0\gamma^2} - \sqrt{V_0\gamma^2}\right) + \begin{cases} \dfrac{4}{\pi^2}\sqrt{\dfrac{V_0}{B}}\left[\boldsymbol{E}\left(\sqrt{\dfrac{E}{V_0}}\right) - \left(1 - \dfrac{E}{V_0}\right)\boldsymbol{K}\left(\sqrt{\dfrac{E}{V_0}}\right)\right], & E < V_0 \\ \dfrac{4}{\pi^2}\sqrt{\dfrac{E}{B}}\boldsymbol{E}\left(\sqrt{\dfrac{V_0}{E}}\right), & E > V_0 \end{cases}$$

Here $\boldsymbol{K}(x)$ and $\boldsymbol{E}(x)$ are complete elliptic integrals of the first and second kind, respectively (as defined in ref 22). This functional form of the classical density-of-states function (III.2.3) is shown in Figure 4 together with that obtained for the quartic−quadratic potential.

An expression for the partition function (and its derivatives) of the shape-related pseudo-degree of freedom can be derived analytically by taking integrals in (II.1.14) (ref 22, eqs 3.364.1 and 3.466.1)

$$\tilde{Q}_{\mathrm{SH}}(\beta) = \frac{1}{\pi}\exp\left(-\frac{\beta V_0}{2}\right)\mathbf{I}_0\left(\frac{\beta V_0}{2}\right) + \frac{\gamma}{\pi}\exp(\beta V_0\gamma^2)\,\mathrm{erfc}(\gamma\sqrt{\beta V_0})$$

$$\tilde{Q}'_{\mathrm{SH}}(\beta) = \frac{V_0}{2\pi}\exp\left(-\frac{\beta V_0}{2}\right)\left[\mathbf{I}_1\left(\frac{\beta V_0}{2}\right) - \mathbf{I}_0\left(\frac{\beta V_0}{2}\right)\right] + \frac{\gamma^3 V_0}{\pi}\exp(\beta V_0\gamma^2)\,\mathrm{erfc}(\gamma\sqrt{\beta V_0}) - \frac{\gamma^2}{\pi}\sqrt{\frac{V_0}{\beta\pi}}$$

$$\tilde{Q}''_{\mathrm{SH}}(\beta) = \frac{{V_0}^2}{4\pi}\exp\left(-\frac{\beta V_0}{2}\right)\left[\mathbf{I}_0\left(\frac{\beta V_0}{2}\right) - \mathbf{I}_1\left(\frac{\beta V_0}{2}\right)\left(1 + \frac{2}{\beta V_0}\right)\right] + \frac{\gamma^5 {V_0}^2}{\pi}\exp(\beta V_0\gamma^2)\,\mathrm{erfc}(\gamma\sqrt{\beta V_0}) + \frac{\gamma^4 V_0}{\pi}\sqrt{\frac{V_0}{\beta\pi}} + \frac{\gamma^2}{\beta\pi}\sqrt{\frac{V_0}{\beta\pi}}$$

where $\mathbf{I}_0(x)$ and $\mathbf{I}_1(x)$ are modified Bessel functions and erfc(x) is the complementary error function.

The overall classical partition function can thus be expressed as

$$Q_{\mathrm{CL}}(\beta) = \frac{1}{\sqrt{\pi\beta B}}\left[\exp\left(-\frac{\beta V_0}{2}\right)\mathbf{I}_0\left(\frac{\beta V_0}{2}\right) + \gamma\exp(\beta V_0\gamma^2)\,\mathrm{erfc}(\gamma\sqrt{\beta V_0})\right]$$

III.3. Single-Well Quadratic−Quartic Potential.

A potential energy function of the type $V(q) = aq^4 + bq^2$ ($a, b > 0$) is used in spectroscopy to describe anharmonicity of vibrational modes. This $V(q)$ dependence can also be written in the following forms

$$V(q) = \frac{kq^2}{2} + \frac{\kappa q^4}{4} = \frac{kq^2}{2}\left(1 + \alpha\frac{kq^2}{2}\right) \qquad \text{(III.3.1)}$$

where $\kappa = \alpha k^2$. Defining $q_0 = [2/(\alpha k)]^{1/2} = [(2k)/\kappa]^{1/2}$ and $\xi = q/q_0$ we obtain

$$V(\xi) = \frac{\xi^2}{\alpha}(1 + \xi^2) \qquad \text{(III.3.2)}$$

Inverting this formula we obtain (only $\xi > 0$ needs to be considered since the potential is symmetric)

$$\xi(V) = \frac{1}{\sqrt{2}}\sqrt{\sqrt{1 + 4\alpha V} - 1}$$

$$\tilde{\rho}_{\mathrm{SH}}(E) = \frac{\alpha}{\pi\sqrt{2(1 + 4\alpha E)(\sqrt{1 + 4\alpha E} - 1)}} \qquad \text{(III.3.3)}$$

The overall classical density-of-states function is given by (see convolution formula II.1.6)

$$\rho_{\mathrm{CL}}(E) = \frac{\alpha}{\pi\sqrt{2B}}\int_0^E \frac{\mathrm{d}x}{\sqrt{(E - x)(1 + 4\alpha x)(\sqrt{1 + 4\alpha x} - 1)}}$$

The integral can be evaluated (ref 22, eq 3.131.5) by using the substitution $t = (1 + 4\alpha x)^{1/2}$ to obtain

$$\rho_{\mathrm{CL}}(E) = \frac{1}{\pi}\sqrt{\frac{\alpha}{B}}\,\frac{\boldsymbol{K}\left(\sqrt{\frac{\sqrt{1 + 4\alpha E} - 1}{2\sqrt{1 + 4\alpha E}}}\right)}{(1 + 4\alpha E)^{1/4}} \qquad \text{(III.3.4)}$$

where the rotational constant B of the pseudo-rotation (II.1.3) is related to α and the harmonic frequency derived from the curvature at the bottom of the potential ν via the expression $B = [\alpha(h\nu)^2]/4$.

An expression for the overall partition function and that of the shape-related pseudo-degree of freedom can be derived analytically by taking the integral in (II.1.4) (see ref 22, eq 3.469.1)

$$\tilde{Q}_{\mathrm{SH}}(\beta) = \frac{\exp\left(\frac{\beta}{8\alpha}\right)}{4\pi}\mathbf{K}_{1/4}\left(\frac{\beta}{8\alpha}\right) \qquad \text{(III.3.5)}$$

$$Q_{\mathrm{CL}}(\beta) = \frac{\exp\left(\frac{\beta}{8\alpha}\right)}{4\sqrt{\pi\beta B}}\mathbf{K}_{1/4}\left(\frac{\beta}{8\alpha}\right) = \frac{\exp\left(\frac{\beta}{8\alpha}\right)}{2h\nu\sqrt{\pi\alpha\beta}}\mathbf{K}_{1/4}\left(\frac{\beta}{8\alpha}\right) \qquad \text{(III.3.6)}$$

In the limiting cases of low energies, low temperatures, and small α, (III.3.4−III.3.6) reduce to the classical density-of-states and partition functions of a harmonic oscillator

$$\lim_{E\to 0}\rho_{\mathrm{CL}}(E) = \lim_{\alpha\to 0}\rho_{\mathrm{CL}}(E) = \frac{1}{h\nu}$$

$$\lim_{\beta\to\infty}Q_{\mathrm{CL}}(\beta) = \lim_{\alpha\to 0}Q_{\mathrm{CL}}(\beta) = \frac{1}{h\nu\beta}$$

III.4. Quartic Oscillator.

The potential energy function of a quartic oscillator (Figure 6) is given by

$$V = bq^4 = V_0\xi^4 \qquad \text{(III.4.1)}$$

where the dimensionless coordinate $\xi = q/q_0$ (q_0 is chosen arbitrarily). One thus obtains

$$\tilde{\rho}_{\mathrm{SH}}(E) = \frac{1}{4\pi V_0^{1/4}E^{3/4}} \qquad \text{(III.4.2)}$$

$$\rho_{\mathrm{CL}}(E) = \frac{1}{4\pi V_0^{1/4}\sqrt{B}}\int_0^E \frac{\mathrm{d}x}{x^{3/4}\sqrt{E - x}} = \frac{\boldsymbol{K}\left(\frac{1}{\sqrt{2}}\right)}{\pi\sqrt{2B}(V_0 E)^{1/4}} = \frac{2}{h}\sqrt[4]{\frac{\mu^2}{bE}}\boldsymbol{K}\left(\frac{1}{\sqrt{2}}\right) \qquad \text{(III.4.3)}$$

(ref 22, eq 3.152.3) where B is given by (II.1.3), μ is the reduced mass, and $\boldsymbol{K}(x)$ is complete elliptic integral of the first kind (as defined in ref 22). This energy dependence of the classical density-of-states function is illustrated in Figure 6. The sum-of-states function equals

$$W_{\mathrm{CL}}(E) = \frac{8}{3h}\sqrt[4]{\frac{\mu^2 E^3}{b}}\boldsymbol{K}\left(\frac{1}{\sqrt{2}}\right) \qquad \text{(III.4.4)}$$

Partition functions are obtained by Laplace transform of (III.4.2) and multiplication by $\tilde{Q}_{\mathrm{ROT}}(\beta)$

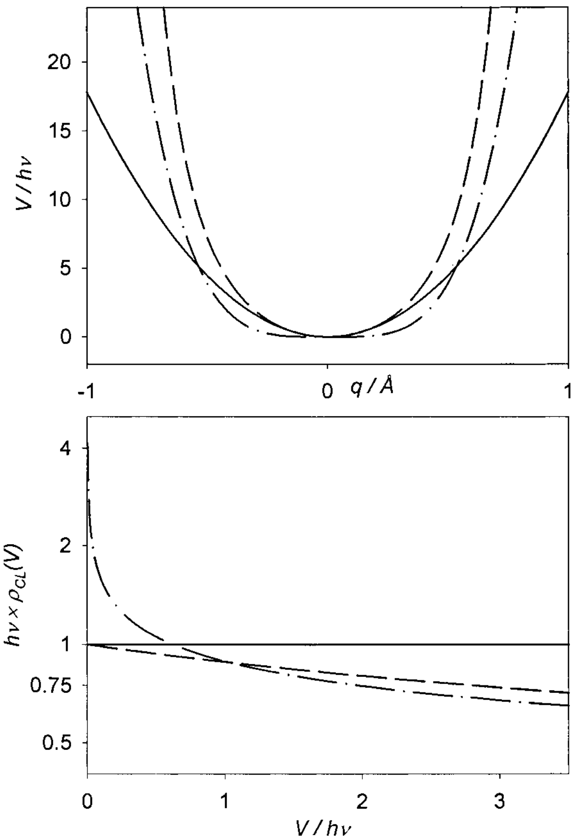

Figure 6. Upper plot: harmonic (solid line), tan^2 (formula III.5.1, dashed line), and quartic (formula III.4.1, dashed-and-dotted line) potentials. Parameters of individual potentials are selected to yield the same frequency (ν = 300 cm^{-1}) derived from the curvature at the potential bottom ($\nu_{0\to1}$ = 300 cm^{-1} for the quartic potential). For the tan^2 potential, $q_0 = 1$. Lower plot: Classical density-of-states functions relative to that of a corresponding harmonic oscillator. Lines are the same as in the upper plot.

$$\tilde{Q}_{\mathrm{SH}}(\beta) = \frac{\Gamma\left(\frac{1}{4}\right)}{4\pi(V_0\beta)^{1/4}} \qquad \text{(III.4.5)}$$

$$Q_{\mathrm{CL}}(\beta) = \frac{\Gamma\left(\frac{1}{4}\right)}{4V_0^{1/4}\beta^{3/4}\sqrt{\pi B}} = \sqrt[4]{\frac{\pi^2\mu^2}{4b\beta^3}}\,\frac{\Gamma\left(\frac{1}{4}\right)}{h} \qquad \text{(III.4.6)}$$

The parameters in formulas III.4.3-6 can be expressed via the frequency $\nu_{0\to1}$ of the 0 → 1 transition (which, for a particular molecule, may be known from spectroscopic data) using the parametrized energy levels calculated by Laane[23] ($\Delta E_{0\to1} = 2.7393 b^{1/3}\hbar^{4/3}(2\mu)^{-2/3}$)

$$\rho_{\mathrm{CL}}(E) = \frac{0.8885}{E^{1/4}(h\nu_{0\to1})^{3/4}}$$

$$W_{\mathrm{CL}}(E) = 1.1847\left(\frac{E}{h\nu_{0\to1}}\right)^{3/4}$$

$$Q_{\mathrm{CL}}(\beta) = \frac{1.0889}{(h\nu_{0\to1}\beta)^{3/4}}$$

III.5. tan^2 Oscillator. The one-dimensional potential energy function of the form (Figure 6)

$$V = \frac{2kq_0^2}{\pi^2}\tan^2\left(\frac{\pi q}{2q_0}\right) = V_0\tan^2\left(\frac{\pi}{2}\xi\right) \qquad \text{(III.5.1)}$$

where $V_0 = (2kq_0^2)/\pi^2$ and $\xi = q/q_0$ reduces to a harmonic oscillator with potential $V(q) = (kq^2)/2$ at low values of q (and, correspondingly, low energies). However, unlike that of a purely harmonic potential, the function of (III.5.1) is restricted in the q coordinate ($q < q_0$, $\xi < 1$), which results in more sparsely placed energy levels at high energies. Such potential may be suitable for describing certain types of bending vibrations, which, being almost harmonic at low energies, are restricted in coordinate owing to steric hindrances.

Following the route of derivations described in section II (and noting that formulas are very similar to those used for the second part of the cos−tan^2 potential, section III.2), we obtain

$$\tilde{\rho}_{\mathrm{SH}}(E) = \frac{1}{\pi^2}\sqrt{\frac{V_0}{E}}\,\frac{1}{E + V_0} \qquad \text{(III.5.2)}$$

$$\rho_{\mathrm{CL}}(E) = \frac{1}{\pi\sqrt{B(E + V_0)}} \quad \text{where} \quad B = \frac{(h\nu)^2}{\pi^2 V_0} \qquad \text{(III.5.3)}$$

(ν is the frequency derived from the curvature at the bottom of the potential), or

$$\rho_{\mathrm{CL}}(E) = \frac{1}{h\nu}\sqrt{\frac{V_0}{E + V_0}} \qquad \text{(III.5.4)}$$

$$\tilde{Q}_{\mathrm{SH}}(\beta) = \frac{1}{\pi}\exp(\beta V_0)\,\mathrm{erfc}(\sqrt{\beta V_0}) \qquad \text{(III.5.5)}$$

$$Q_{\mathrm{CL}}(\beta) = \sqrt{\frac{1}{\pi\beta B}}\exp(\beta V_0)\,\mathrm{erfc}(\sqrt{\beta V_0}) = \frac{1}{h\nu}\sqrt{\frac{\pi V_0}{\beta}}\exp(\beta V_0)\,\mathrm{erfc}(\sqrt{\beta V_0}) \qquad \text{(III.5.6)}$$

$$\tilde{Q}'_{\mathrm{SH}}(\beta) = \frac{V_0}{\pi}\left[\exp(\beta V_0)\,\mathrm{erfc}(\sqrt{\beta V_0}) - \frac{1}{\sqrt{\pi\beta V_0}}\right] \qquad \text{(III.5.7)}$$

$$\tilde{Q}''_{\mathrm{SH}}(\beta) = \frac{V_0^2}{\pi}\left[\exp(\beta V_0)\,\mathrm{erfc}(\sqrt{\beta V_0}) + \frac{1}{\sqrt{\pi\beta V_0}} + \frac{1}{\beta V_0\sqrt{\pi\beta V_0}}\right] \qquad \text{(III.5.8)}$$

The $\rho_{\mathrm{CL}}(E)$ dependence is illustrated in Figure 6.

III.6. Sinusoidally Hindered Rotor. Formulas for the partition, density-of-states, and sum-of-states functions of a one-dimensional rotor hindered by a sinusoidal potential

$$V = \frac{V_0}{2}(1 - \cos(nq)) \qquad \text{(III.6.1)}$$

have been reported before.[8,11,14] For completeness, we present here expressions for $\tilde{Q}_{\mathrm{SH}}(\beta)$, $\tilde{Q}'_{\mathrm{SH}}(\beta)$, and $\tilde{Q}''_{\mathrm{SH}}(\beta)$, needed to calculate thermodynamic functions:

$$\tilde{Q}_{\mathrm{SH}}(\beta) = \mathbf{I}_0({}^1\!/_2\beta V_0)\exp(-{}^1\!/_2\beta V_0) \qquad \text{(III.6.2)}$$

$$\tilde{Q}'_{\mathrm{SH}}(\beta) = {}^1\!/_2 V_0\exp(-{}^1\!/_2\beta V_0)[\mathbf{I}_1({}^1\!/_2\beta V_0) - \mathbf{I}_0({}^1\!/_2\beta V_0)] \qquad \text{(III.6.3)}$$

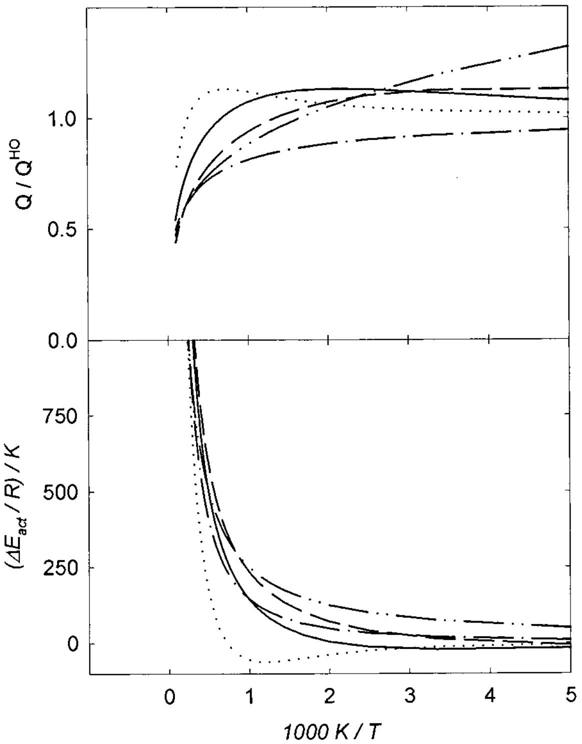

Figure 7. Temperature dependencies of partition functions (upper plot, relative to corresponding harmonic oscillators) and resultant changes in activation energy (lower plot, see text). Solid lines, quartic−quadratic double-well potential, $V_0 = 500$ cm^{-1}; dashed lines, quartic−quadratic double-well potential, $V_0 = 1500$ cm^{-1}; dotted lines, quartic-quadratic double-well potential, $V_0 = 250$ cm^{-1}; dashed-and-dotted lines, tan^2 potential (with $\nu = 300$ cm^{-1}, $\mu = 2$ amu, and $q_0 = 1$ Å); dashed-and-double-dotted lines, quartic potential (with $\nu_{0\rightarrow 1} = 300$ cm^{-1}).

$$\tilde{Q}''_{\mathrm{SH}}(\beta) = {}^1/_2 V_0^2 \exp(-{}^1/_2\beta V_0)\left[\mathbf{I}_0({}^1/_2\beta V_0) - \left(1 + \frac{1}{\beta V_0}\right)\mathbf{I}_1({}^1/_2\beta V_0)\right] \quad \text{(III.6.4)}$$

Here, $\mathbf{I}_0(x)$ and $\mathbf{I}_1(x)$ are modified Bessel functions. Expressions for thermodynamic functions resulting from substituting (III.6.2−4) into (II.2.10) are very similar to those reported recently by McClurg et al.[24] These authors applied the Pitzer−Gwinn approximation[14] of (II.2.1) with a correction to the energy of the zeroth vibrational level to obtain explicit formulas for thermodynamic functions of a hindered rotor. One should note, however, that the expression for internal energy given by McClurg et al. (formula 35 of ref 24) contains a mistake—the sign between the two terms in the figure brackets must be minus instead of plus. The Pitzer−Gwinn approximation, apparently, was derived by McClurg et al. independently (although ref 14 is among those cited in ref 24, it is not mentioned as the original source of the approximating formula).

IV. Discussion

The algorithm described solves the problem of calculating densities and sums of states exactly in the classical approximation. The critical step of the algorithm is obtaining the $\tilde{\rho}_{\mathrm{SH}}(E)$ function. In most cases, this can be done analytically (e.g., see section III). Even if an analytical expression cannot be derived, $\tilde{\rho}_{\mathrm{SH}}(E)$ can be easily obtained as a numerical array by solving the transcendental equation $V = V(\xi)$ to obtain the $\xi(V)$ dependence and $\mathrm{d}\xi/\mathrm{d}V = [\mathrm{d}V(\xi)/\mathrm{d}\xi]^{-1}$ function (the derivative can be taken analytically) for each of the intervals with monotonic $V(\xi)$ dependence, as described in section II.

One obvious immediate application of the described algorithm and the resulting formulas for specific potentials is in calculating densities of states and partition functions of molecules with such degrees of freedom as inversions (double-well) and sterically restricted vibrations. Currently, these degrees of freedom are represented in models by harmonic oscillators. The main drawback of such simplifications is the inadequate description of the temperature dependencies of partition functions ($Q(T)$). If, for example, the reactant molecule has an inversion degree of freedom and the transition state does not, this results in a temperature-dependent error in the ratio of partition functions and, hence, in the rate constant, which, in turn, yields incorrect activation energies. Figure 7 illustrates such temperature-dependent deviations in partition functions and resultant errors in activation energies for a variety of potentials.

Another potential application of the described algorithm is in calculating sums of states $W(E)$ and partition functions $Q(T)$ of transitional modes in variational transition-state theory (e.g., see ref 18). A number of methods to evaluate $W(E)$ and $Q(T)$ as functions of the reaction coordinate have been reported. These methods are based on knowledge of the potential energy surface (ref 25 and references therein) or on the use of switching functions (see ref 26 and references therein). The current algorithm provides a simple and easily automated method of treating transitional modes applicable if (1) the potential energy surface is known and (2) degrees of freedom can be assumed to be separable.

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