

# A Simple Approximation for the Vibrational Partition Function of a Hindered Internal Rotation

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A simple formula is presented for calculating the approximate partition function of a hindered internal rotational mode of a polyatomic molecule. The formula gives useful accuracy over the whole range from harmonic oscillator to hindered rotator to free rotator.

## INTRODUCTION

With the improvement in our ability to estimate geometrical structures and harmonic vibrational frequencies from electronic structure calculations, it becomes straightforward to estimate equilibrium constants for chemical reactions using the harmonic oscillator-rigid rotator approximation<sup>1</sup> for vibrational-rotational partition functions. This approximation is also commonly used in quasiequilibrium rate calculations such as transition state theory<sup>2</sup> or generalized transition state theory.<sup>3</sup> In many cases the dominant error in such a treatment may be the failure of the harmonic approximation for one or more low-frequency vibrations that would be treated more appropriately as hindered internal rotations. Since there are no simple analytic solutions to the hindered rotation problem, special approximations must be introduced. The purpose of the present note is to present a simple general formula that will allow one to estimate an improved vibrational partition function for a hindered rotator without increasing the computational complexity over the harmonic oscillator approximation.

## THEORY

Consider a general polyatomic molecule described by mass-scaled Cartesian coordinates<sup>3</sup>

$$x_{i\gamma} = (m_i/\mu)^{1/2} R_{i\gamma} \quad (1)$$

where  $m_i$  is the mass of atom  $i$ ,  $\mu$  is an arbitrary mass, and  $R_{i\gamma}$  is a Cartesian coordinate for  $\gamma = x, y$ , or  $z$ . (Mass-weighted Cartesians<sup>4</sup> are obtained if  $\mu = 1$ .) The potential energy for displacement along

normal mode  $m$  may be written in the harmonic approximation as

$$V = V_o + \frac{1}{2} k_m Q_m^2 \quad (2)$$

where  $V_o$  is a constant energy,  $k_m$  is the force constant, and the normal mode coordinate is defined as usual as a linear combination of Cartesians:<sup>4</sup>

$$Q_m = \sum_{i\gamma} (x_{i\gamma} - x_{i\gamma,0}) L_{i\gamma m}. \quad (3)$$

The harmonic energy levels are<sup>4</sup>

$$E_m(v_m) = \left( v_m + \frac{1}{2} \right) \hbar \omega_m, \quad v_m = 0, 1, \dots, \quad (4)$$

where  $\hbar$  is Dirac's  $h$  and the frequency is

$$\omega_m = (k_m/\mu)^{1/2}. \quad (5)$$

The harmonic partition function at temperature  $T$  is<sup>1</sup>

$$Q_m^{\text{har}} = \frac{e^{-0.5u_m}}{1 - e^{-u_m}} \equiv 0.5 \operatorname{csch} 0.5u_m \quad (6)$$

where

$$u_m = \frac{\hbar \omega_m}{\tilde{k}T} \quad (7)$$

and  $\tilde{k}$  is the Boltzmann constant. We note that partition functions depend on the zero of energy, and in this article all partition functions correspond to  $V_o = 0$  [i.e., not to  $E_m(0) = 0$ ]; this is the most convenient choice for both equilibrium and rate calculations based on force fields.

If the vibrational mode under consideration corresponds physically to an internal rotation, a better approximation is to replace eq. (2) by<sup>5</sup>

$$V = V_o + \frac{1}{2} W_m (1 - \cos \sigma_m \phi) \quad (8)$$

where  $W_m$  is the barrier to internal rotation,  $\sigma_m$  is the symmetry number (e.g.,  $\sigma_m = 3$  for internal rotation about the C—O bond in methanol), and  $\phi$  is the twist angle. In order to match (8) to (2) for small vibrational amplitudes we equate

$$V \sim V_o + \frac{1}{4} W_m \sigma_m^2 \phi^2 + \dots \quad (9)$$

to

$$V \sim V_o + \frac{1}{2} k_m r_m^2 \phi^2 \quad (10)$$

where  $r_m$  is the effective moment arm of the internal rotation, which yields

$$W_m = 2k_m r_m^2 / \sigma_m^2. \quad (11)$$

The moment of inertia for the internal rotation is

$$I_m = \mu r_m^2, \quad (12)$$

and it will be discussed later in the article.

In the limit of a small barrier ( $W_m \approx 0$ ), the internal rotation may be treated as free, in which case the partition function is well approximated by the standard classical result<sup>1</sup>

$$Q_m^{\text{fr}} = \hbar^{-1} (2\pi \bar{I}_m \bar{k} T)^{1/2} \quad (13)$$

where we have introduced the convenient definition

$$\bar{I}_m = I_m / \sigma_m^2 \quad (14)$$

which may be called the reduced moment of inertia. It will also be convenient to define

$$\bar{r}_m = r_m / \sigma_m \quad (15)$$

so

$$\bar{I}_m = \mu \bar{r}_m^2. \quad (16)$$

In the limit as  $\omega_m$  becomes small, eq. (6) may be replaced by its classical limit

$$Q_m^{\text{har}} \approx u_m^{-1} \equiv \ell_m / \Lambda \quad (17)$$

where  $\ell_m$  is the Boltzmann average of the vibrational amplitude given by<sup>6</sup>

$$\ell_m = (2\pi \bar{k} T / k_m)^{1/2} \quad (18)$$

and  $\Lambda$  is the Boltzmann average deBroglie wavelength given by<sup>1,6</sup>

$$\Lambda = \hbar (2\pi / \mu \bar{k} T)^{1/2} \quad (19)$$

For comparison we then write (13) as

$$Q_m^{\text{fr}} = 2\pi \bar{r}_m / \Lambda. \quad (20)$$

Johnston<sup>6</sup> has used the suggestive form of eqs. (17) and (20) to discuss the hindered rotator transition in clear physical terms. Consider changing the Hamiltonian such that  $\omega_m$  and  $W_m$  decrease. Then the harmonic oscillator turns into a hindered rotator and eventually a free rotator. Then, at fixed temperature,  $\ell_m$  and hence  $Q_m^{\text{har}}$  increase as  $k_m^{-1/2} \sim \omega_m^{-1}$ . Eventually

then  $Q_m^{\text{har}}$  must exceed the physical limit of a totally free internal rotation. Physically the maximum distance over which an internal rotation may range is  $2\pi \bar{r}_m$ , and when  $\ell_m$  exceeds this, the harmonic approximation leads to unbounded systematic overestimates. It has been pointed out that this kind of failure of the harmonic approximation for low-frequency bending partition functions may lead to spurious high-temperature results for atom-diatom rate calculations,<sup>7</sup> and the effects may be even more serious for polyatomic reactions which may have low-frequency modes. The objective of this article is to suggest a simple fix for eq. (6) that avoids these spurious results. We accomplish this by obtaining a smooth interpolating function between eqs. (17) and (20). Applying this to eq. (6) provides a smooth interpolation between (6) for high  $\omega_m$  and eq. (20) for low  $\omega_m$ .

Of course one can always solve numerically for the energy levels of a system described by eqs. (8) and (12) and calculate the partition function by summing Boltzmann factors for the resulting energy levels.<sup>8</sup> Although this is easily affordable on modern computers, the effort is not always justified, especially considering that the replacement of the true internal rotation problem by a single uncoupled mode with the potential of eq. (8) is itself only an approximation to the true situation.

Another way to proceed is to interpolate the tabulated thermodynamic functions of Pitzer and Gwinn.<sup>8,9</sup> These authors introduced two reduced variables, given in our notation by

$$\bar{W} = W_m / \bar{k} T \quad (21)$$

and

$$\bar{\Lambda} = 1 / Q_m^{\text{fr}}. \quad (22)$$

As a function of these variables they tabulated  $(G - G^{\text{fr}})/T$ , where  $G$  is the free energy for a system described by eq. (8) and  $G^{\text{fr}}$  is the free energy for the corresponding free rotator. Interpolating these tabulated values to obtain  $(G - G^{\text{fr}})/T$  for the  $\bar{W}$  and  $\bar{\Lambda}$  of interest, and using the harmonic approximation for the zero point energy, one may calculate the hindered rotator partition function by

$$Q_m^{\text{hin}} \approx \bar{\Lambda}^{-1} e^{-u_m/2 + (G - G^{\text{fr}})/\bar{k} T}. \quad (23)$$

(In using this formula, one should use the same value for  $\bar{k}$  as used in setting up the tables,  $\bar{k} = 8.616 \times 10^{-5}$  eV molecule<sup>-1</sup> K<sup>-1</sup>.) As for numerical solution of the Schroedinger equation as discussed in the previous paragraph, this two-dimensional interpolation is inconvenient and the effort may be unjustified in many cases. (In addition one is restricted to the range of values of the reduced parameters covered by the available tables.)

Instead we seek an approximation of the form

$$Q_m^{\text{hin}} \approx Q_m^{\text{har}} f_m \quad (24)$$

where  $Q_m^{\text{har}}$  is given by eq. (6), and  $f_m$  is an interpolating function. We place three restrictions on  $f_m$ , namely

$$f_m \xrightarrow{u_m \rightarrow \infty} 1 \quad (25)$$

$$f_m \xrightarrow{u_m \rightarrow 0} 2\pi\bar{r}_m/\ell_m \equiv Q_m^{\text{fr}}u_m \quad (26)$$

and

$$f_m \underset{u_m \rightarrow 0}{\sim} Q_m^{\text{fr}}u_m + O(u_m^3). \quad (27)$$

Equations (25) and (26) result from the requirement that eq. (24) accurately interpolate between the known accurate results (6) and (13) in the limits of high and low  $u_m$ . Equation (27) states that at small  $u_m$  the interpolating function should deviate quadratically (not linearly) from its limiting form. Equation (27) was enforced because the numerical values of  $(G - G^{\text{fr}})/T$  vary linearly with  $\bar{W}$  and hence, by eqs. (21), (11), and (5), quadratically with  $u_m$  at small  $\bar{\Lambda}$ .

The simplest function that satisfies eqs. (25)–(27) is

$$f_m = \tanh(Q_m^{\text{fr}}u_m) \quad (28)$$

Encouragingly the form of (28) is similar to that of eq. (6).

Thus the new method proposed here consists of using (24) and (28) together.

## RESULTS

We tested the new formula against the tables of Pitzer and Gwinn.<sup>8,9</sup> In terms of the reduced variables  $\bar{W}$  and  $\bar{\Lambda}$  used in eq. (22) (recall that  $(G - G_{\text{fr}})/T$  is tabulated as a function of  $\bar{W}$  and  $\bar{\Lambda}$ ) we have

$$u_m = (\pi\bar{W})^{1/2}\bar{\Lambda} \quad (29)$$

and

$$Q_m^{\text{hin}} = \frac{\tanh(\pi\bar{W})^{1/2}}{2 \sinh 0.5u_m}. \quad (30)$$

We compared the results obtained by this formula, which is equivalent to (6), (24), and (28), to those obtained from the tables. For example, for  $\bar{\Lambda} = 0.50$  and  $\bar{W} = 0.2$ , we obtain  $Q_m^{\text{hin}}$  equals 1.63 from the tables and 1.65 from eq. (30), as compared to  $Q_m^{\text{har}} = 2.51$  and  $Q_m^{\text{fr}} = 2.00$  for these parameters. The error in the new method is only 1.3%. Clearly the present result, based on correcting the vibrator limit, and the result from the tables, based on correcting the free rotator limit, are in excellent agreement in this case.

To judge the method more generally we compared it to the numerical results for a cross section of cases spanning the numerical table, in particular  $\bar{\Lambda} = 0.05$ ,

0.25, and 0.50 and  $\bar{W} = 0.2, 0.4, 0.8, 1, 3, 5, 10$ , and 20. The average absolute value of the relative deviation, i.e.,  $\langle |Q_m^{\text{hin}}(24) - Q_m^{\text{hin}}(23)/Q_m^{\text{hin}}(23)| \rangle$ , for these 24 cases is 6.9%. This magnitude of discrepancy is acceptable for practical applications, and we conclude that further refinements of the interpolation function are not needed.

## DISCUSSION

One important application of the new formula presented above is for reaction rate calculations on polyatomic molecules. Although the discussion above is cast in the language of stationary points and normal modes, all considerations pass smoothly to the case of reaction-path calculations<sup>3,10–15</sup> which involve generalized normal modes at nonstationary points as, e.g., in variational transition state theory.<sup>3,11,13</sup> In such calculations the mode characters, as well as their frequencies, are functions of a reaction coordinate  $s$ . The generalized transition state partition functions are typically calculated for many values of  $s$ , and it greatly facilitates the calculations to treat each mode by the same method all along the reaction path. The situation with previous separable approximations is clearly summarized in a recent review<sup>13b</sup> with special emphasis on transitional modes, i.e., those modes whose frequencies go to zero in an asymptotic limit: "Care must be exercised in using these simplifications, since it is unusual for a particular transitional mode to remain a vibration, free rotation, or hindered rotation over the whole range of reaction coordinate values. A hindered rotor treatment of a bending mode goes to the correct asymptotic limit of free rotation as the reaction coordinates is increased but does not go to the proper vibrator limit for small values of the reaction coordinate; the situation is reversed for a vibrator treatment of a transition bending mode." The present approximation can be applied over the whole range of mode characters from quantal harmonic vibration to quantal hindered internal rotation to classical free internal rotation, and so it may be applied very conveniently to both transitional and nontransitional modes even when the mode character changes with  $s$ . Furthermore the computational effort is negligible, and so it does not increase the computation time significantly even when many modes and many  $s$  values are involved. Of course since we have approximated the partition function directly, the method is directly applicable to canonical variational theory<sup>3</sup> but not to microcanonical variational theory.

The present approximation will also be useful for equilibrium and thermodynamic function<sup>16</sup> computations or reaction rate computations involving a small number of  $s$  values or a small number of modes, because the 7% average deviation from the more complicated numerical procedure will usually

be small compared to other approximations in the calculations.

We note here that bending motions of linear molecules may involve strong vibration-rotation coupling which effectively converts vibrations into a third overall rotation rather than an internal rotation, and this requires special treatment. The present calculations also neglect vibration-vibration mode coupling effects, which are important in many cases, but our goal has been to present a simple method for treating a single (one-dimensional) hindered rotation, not a completely general solution to the anharmonicity problem. Thus the treatment of special effects which may be present in two-dimensional hindered rotational motions such as occur in loose collision complexes<sup>17-19</sup> is also beyond our scope. The treatment of such motions as two uncoupled one-dimensional hindered rotators may sometimes be reasonable.

The hindered rotator partition function presented above is a function of the vibrational frequency  $\omega_m$ , the temperature  $T$ , and the reduced moment of inertia  $\bar{I}_m$  given in terms of the effective moment of inertia  $I_m$  by eq. (14). The frequency of the vibrational mode is assumed to be available from a normal mode analysis, and general methods<sup>9,20</sup> are available to estimate the moment of inertia for high-symmetry internal rotations in which the motion may be considered to consist of two rigid subgroups rotating around a fixed central bond (as in  $\text{H}_3\text{C}-\text{CH}_3$ <sup>21</sup>). In general, though, all atoms move in the vibration, and bond lengths and bond angles do change during the process. One cannot give a completely general prescription for the best internal rotation coordinate, and hence the value to be used for  $I_m$ , for an arbitrary molecule, but one can give a simple general scheme for calculating a reasonable physical value for  $I_m$  for a general internal rotation, and I conclude by suggesting one such scheme. (See Burkhard and Irvin<sup>22</sup> for a careful treatment of the internal rotation of two rigid but asymmetric tops, Lin and Swalen<sup>5</sup> for a review of methods for rigid internal rotators of which at least one is symmetric, and Herschbach et al.<sup>23</sup> for another approximate approach.)

First perform a normal mode (or generalized normal mode) analysis by conventional techniques. Identify that mode or those modes for which the hindered rotator correction  $f_m$  will be applied. For each such mode  $m$ , defined two groups, to be called  $R_1$  and  $R_2$ , which are to be considered to be rotating with respect to one another with symmetry number  $\sigma_m$ . (This must be done on physical grounds based on general knowledge of the potential energy for wide-amplitude motions; in particular the harmonic mode itself does not contain this information. However, once  $R_1$  and  $R_2$  are identified, the rest of the scheme involves no choices.) In general every atom of the molecule should be included in one or another of the two subgroups. For each subgroup calculate

the reduced angular momentum by

$$\mathbf{J}_{R_1} = \sum_{i \in R_1} \mathbf{L}_{im} \times \mathbf{x}_{i,0} \quad (31)$$

where  $\in$  denotes "belongs to,"  $\mathbf{L}_{im} = (L_{ixm}, L_{iym}, L_{izm})$ , and  $\mathbf{x}_{i,0} = (x_{ix,0}, x_{iy,0}, x_{iz,0})$ , with a similar formula for  $\mathbf{J}_{R_2}$ . It is assumed here that the center of mass of the system is at the origin, i.e.,

$$\sum_i m_i^{1/2} x_{iy,0} = 0, \quad \gamma = x, y, z \quad (32)$$

Since a normal mode or generalized normal mode vibration as a whole carries no angular momentum, one will find  $\mathbf{J}_{R_1} = -\mathbf{J}_{R_2}$ . The axis through the center of mass of the molecule that is parallel to  $\mathbf{J}_{R_1}$  and  $\mathbf{J}_{R_2}$  is the axis of internal rotation for subgroups  $R_1$  with respect to subgroups  $R_2$ . Call this axis  $z'$  and its direction  $\hat{z}'$ , a unit vector. Define the  $x'$  and the  $y'$  axes to be perpendicular to  $\hat{z}'$ , and rotate the geometry  $\mathbf{x}_{i,0}$  to the new  $x'y'z'$  coordinate system. Now twist group  $R_1$  by  $\phi$  radians about the  $z'$  axis and equate  $I_{R_1} \dot{\phi}$  where an overdot denotes a time derivative, to the angular momentum. This yields

$$I_{R_1} = \mu \lim_{\phi \rightarrow 0} \frac{\left| \hat{z}' \cdot \sum_{i \in R_1} \Delta \mathbf{x}_i(\phi) \times \mathbf{x}_{i,0} \right|}{\phi} \quad (33)$$

where  $\Delta \mathbf{x}_i(\phi) = (\Delta x_{ix'}, \Delta x_{iy'}, 0)$ ,

$$\Delta x_{ix'} = x_{ix',0}(\cos \phi - 1) + x_{iy',0}(\sin \phi) \quad (34)$$

and

$$\Delta x_{iy'} = -x_{ix',0} \sin \phi + x_{iy',0}(\cos \phi - 1). \quad (35)$$

The moment of inertia  $I_{R_2}$  for the second subgroup is calculated similarly, and the effective moment of inertia for the internal rotation is approximated by<sup>8</sup>

$$I_m = \frac{I_{R_1} I_{R_2}}{(I_{R_1} + I_{R_2})}. \quad (36)$$

By assigning a  $\phi$ -independent effective value for  $I_m$  I have effectively assumed that internal rotation over the thermally accessible range with the internal rotors rigid does not appreciably alter the principal moments of inertia for overall rotation. If it does, a more general procedure should be devised to include the effects of vibration-rotation coupling.

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