On the Use of Exact Vibrational State Counting Methods in RRKM Rate Calculations

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Prepared for publication in Chemical Physics Letters

Technical Report No. NR092-549-TR04
Contract N00014-75-C-0690, NR092-549

April 15, 1977

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Computer algorithm
Eigenstate densities
RRKM theory
Unimolecular reaction
Vibrational levels
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ON THE USE OF EXACT STATE COUNTING
METHODS IN RRKM RATE CALCULATIONS

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ABSTRACT

The use of direct counts of molecular energy level degeneracies, $P(E)$, at internal energy, $E$, in RRKM unimolecular reaction rate calculations is clarified. Highly accurate densities of states for use in practical rate calculations can be obtained by utilizing an energy level "grain" size of 1-5 cm$^{-1}$ and by suitable averaging of $P(E)$ over small energy intervals. An easily programmed algorithm for rounding energy levels to multiples of this "grain" size is given and applied to sum and density calculations.
1. INTRODUCTION

The advent of highly efficient algorithms [1-3] for direct computation of energy level degeneracies, $P(E)$, and sums, $\Sigma P(E)$, now permit such computations to be performed with great accuracy over the entire energy range of chemical interest. In practical calculations, these algorithms typically require 5000-20,000 computer storage spaces and an execution time of 0.1-100 sec.

Using energy levels or fundamental harmonic oscillator frequencies of individual degrees of freedom as input, direct counting algorithms yield a linear array, $P'$, whose elements $P'(I)$ contain the number of different ways of arranging the energy $(I-1)\, \Delta$ in the available energy levels, where $\Delta$ is a chosen "grain" size. For present purposes, $P(E) = P'(R(E/\Delta) + 1)$, where the quantity $R(E/\Delta)$ denotes the integer nearest to the value $(E/\Delta)$. Thus, $P(E)$ is effectively the number of levels around energy $E$ within an energy interval of length $\Delta$. The only errors in $P(E)$ that may arise using this method result from the necessity of altering the input energy levels (or fundamental frequencies) to become integral multiples of $\Delta$. An algorithm proposed by Beyer and Swinehart [1] (BS), which has been compared to other schemes by Stein and Rabinovitch [2], computes $P(E)$ and $\Sigma P(E)$ for molecular degrees of freedom whose energy levels are evenly spaced (harmonic oscillators). For maximum accuracy, $\Delta$ is typically chosen to be between 1 cm$^{-1}$ and 5 cm$^{-1}$ which is generally within the known accuracy of fundamental vibrational frequencies.

A related algorithm by Stein and Rabinovitch (SR) computes $P(E)$ and $\Sigma P(E)$ for any degrees of freedom whose energy levels are known [3] (examples
are Morse anharmonic oscillators and symmetric hindered rotors). The SR algorithm computes exact $P(E)$ values for sets of energy levels, each level of which has been rounded to an integral multiple of $C$. Errors in calculated $P(E)$ are negligible (< 1% error) for molecules of chemical interest with choice of a grain of 1-5 cm$^{-1}$ [3]. For a computation involving both harmonic and non-harmonic degrees of freedom, it is straightforward to apply the BS algorithm for the harmonic degrees of freedom and then apply the SR algorithm or other [4] for the non-harmonic degrees of freedom.

Recently, Hayward and Henry (HH) [5] have questioned the stability of counting methods for accurately determining sums and densities of states as required for RRKM unimolecular rate calculations. They have alleged that such methods may be highly inaccurate partly because of the inherent non-linearity of sums and densities as a function of energy, but primarily on the grounds that that lack of smoothness of $P(E)$ versus $E$ can yield erroneous values for densities, $N(E)$. It will be shown that such objections are not valid for calculations using a small enough step size with realistic vibrational frequencies; for practical computations the use of $P(E)$, derived from direct counting methods, to obtain $N(E)$ is highly accurate.

In this paper we shall discuss the correct application of the output of these computations, $P(E)$, for evaluating densities and sums of states. Attention is also given to the method used for rounding energy levels and frequencies to multiples of $C$.

2. GENERAL DISCUSSION

In order to obtain an overall rate constant for an elementary reaction occurring over a range of energies, rate constant elements are individually
evaluated over small energy intervals, from \( E \) to \( E + \ell \), and then summed.

In particular, the RRKM unimolecular rate constant for thermally induced reactions, \( k_{\text{uni}} \), may be numerically evaluated as \[6\]

\[
    k_{\text{uni}} = a \sum_{n=0}^{\infty} \left( \frac{\ell \Sigma P(E^+)}{1 + b(\Sigma P(E^+))/N(E_0 + n\ell)p} \right) \tag{1}
\]

where \( a \) and \( b \) are constants which depend on the specific reaction type, \( p \) is the pressure, \( E_0 \) is the threshold energy for reaction and \( E^+ \) is the active energy in the activated complex. For computations using direct counting, the term \( \Sigma P(E) \) is obtained by summing all \( P' \) elements up to \( I = (E/G) + 1 \).

The term \( N(E_0 + n\ell) \) is evaluated by

\[
    N(E_0 + n\ell) = \frac{1}{\ell} \sum_{M=-R(\ell/2G)}^{R(\ell/2G)} P'(R(E_0 + n\ell)/G) + 1 + M \tag{2}
\]

This expression simply sums all \( P(E) \) elements in the energy range \( E_0 + (n - \frac{1}{2})\ell \) to \( E_0 + (n + \frac{1}{2})\ell \). This formula (2) is strictly correct only when \( \ell/G \) is not an integer in which case care must be taken to count each \( P' \) element only once.

For the sum, given by formula (1), to accurately approximate an integral quantity, the value \( \ell \) must be chosen small enough to ensure a linear variation of the integral quantity over the range of each summation. Thus, it is necessary for \( P(E) \), \( \Sigma P(E) \) and \( \exp(-E/kT) \) to be linear over each energy interval of length \( \ell \). A choice of \( \ell/cm^{-1} \) between 50 and 200 is small enough to ensure such behavior, even for large molecules. To illustrate, \( P(E) \) values derived for a 120 frequency harmonic oscillator are shown in Figure 1 near energies typical of unimolecular chemical reaction (10,000 cm\(^{-1}\) and 20,000 cm\(^{-1}\)). For
any calculation in which non-linearity of this type is suspected, it is straightforward to perform a second calculation with a reduced value of \( \lambda \).

To illustrate the roughness of \( P(E) \) versus \( E \) and the supposed dependence of \( N(E) \) on \( G \) due to this roughness, HH chose a harmonic oscillator model in which all frequencies, \( \nu_i \), were multiples of 100 cm\(^{-1}\). They reported that \( N(E) \) is dependent on \( G \) for \( G/\text{cm}^{-1} = 10, 50 \) and 100. They have chosen a pathological case which can only result by pre-gaining each \( \nu_i \) to be exactly divisible by the value \( nG \), where \( n = 2, 3, 4, \ldots \). In such cases, \((n-1)\) out of \( n \) members of the \( P' \) array will necessarily be equal to zero. For example, in any model, if the \( \nu_i \) are multiples of 100 cm\(^{-1}\), there is no way to completely distribute an energy which is an odd multiple of 50 cm\(^{-1}\). Therefore, for the \( G/\text{cm}^{-1} = 50 \) model, HH reported densities a factor of two greater than for the \( G/\text{cm}^{-1} = 100 \) and for the \( G/\text{cm}^{-1} = 10 \) model densities were reported to be higher by a factor of ten.

Such a situation will not arise if \( n\lambda, n = 2, 3, \ldots \), does not divide exactly into all \( \nu_i \). This rule, in practice, will always be satisfied when using frequencies that have not been arbitrarily pre-grained and \( \lambda/G > 1 \).

To illustrate this point, shown in Table 1, we have computed \( P(E) \) for \( G/\text{cm}^{-1} = 60 \) and 50, with harmonic oscillator model of HH. Note that the variation in \( P(E) \) for the former case is very smooth, whereas for \( G/\text{cm}^{-1} = 50 \) (\( n = 2 \)), alternate \( P(E) \) quantities are equal to zero.

Use of the SR algorithm, which rounds-off each energy level, is even less prone to large fluctuations in \( P' \) than the BS algorithm.

Another point of concern in using these algorithms for \( N(E) \) or \( \Sigma P(E) \) evaluation is the method used for rounding fundamental frequencies or energy levels. For example, if all levels are rounded to a lower value, sums and
densities will be somewhat overcounted. More careful rounding can substantially reduce such errors. Of course, if a small enough $G$ is used, the absolute error will be negligible no matter what rounding method is used. A useful rounding scheme is as follows: Consider a set of $i_m$ energy levels (or fundamental frequencies) $E_i$, $i = 1, 2, \ldots, i_m$, a linear array $H_i$ (with $H_0 \equiv 0$) and a grain size $G$. Let $L(X)$ denote the greatest integer less than or equal to $X$ and let $E_{ir}$ represent the energy to which the $i$-th energy level (or fundamental frequency) is rounded. Then, for $i = 1$ to $i_m$:

$$H_i = H_{i-1} + E_i/G - L(E_i/G);$$

if $H_i < \frac{1}{2}$, $E_{ir} = GL(E_i/G)$

if $H_i \geq \frac{1}{2}$, $E_{ir} = G(L(E_i/G) + 1)$ and,

$$H_i = H_i - 1.$$

This scheme makes rounding decisions for each level based on rounding of previous levels.

To illustrate the effectiveness of this rounding scheme, in Table 2 are given sums and densities of states have been computed using the harmonic oscillator model of HH. Exact results are given in column A ($G/cm^{-1} = 100$). In model B, which uses $G/cm^{-1} = 200$, all frequencies were rounded downward or unchanged. This appears to be the method used by HH. Sums given by HH at 22,400 cm$^{-1}$ differ slightly from those in Table 2 because the former results were given as sums up to, but not including 24,400 cm$^{-1}$. In this present paper sums are evaluated up to and including the stated energies, using linear interpolation, if necessary. Model C utilizes the rounding scheme given earlier in this paper and is somewhat more accurate than the scheme of model B. This model is used here for illustrative purposes only, since for actual rate calculations $G$ will be much smaller than the values used here, and resulting errors will always be very considerably smaller (< 1% error).
Note, also, that errors in \( \mathcal{P}(E) \) follow errors in \( N(E) \) very closely, confirming the smooth behavior of the latter function.

In Table 3 are given \( \mathcal{P}(E) \) values using \( G/cm^{-1} = 10 \) for three anharmonic models given by HH, along with deviations in \( \mathcal{P}(E) \) resulting from the use of \( G/cm^{-1} = 20, 50, \) and 100. Here, again, these are larger \( G \) values than used in practice and are employed for illustrative purposes only. The rounding scheme given earlier is used in these computations. Note that errors in \( \mathcal{P}(E) \) are uniformly small for even the larger \( G \) values. In addition, we find that \( N(E) \) values, not given here, are smooth functions of energy and changes of \( N(E) \) with varying \( G \) follow changes of \( \mathcal{P}(E) \) very closely as for the harmonic oscillator model (Table 1). Spurious behavior of \( \mathcal{P}(E) \) and \( N(E) \) as a function of energy, as reported by HH, is not apparent; the peculiar results that they obtain must be due to errors in their computational technique and/or their faulty rounding scheme.

In summary, direct counting algorithms can be used to supply accurate densities and sums for RRKM rate calculations as long as grain sizes are small (1–5 \( cm^{-1} \)), integration intervals are \( \geq G \) and \( \lesssim 200 \ cm^{-1} \), and realistic vibrational parameters are employed.

**Acknowledgement**

One of us (B. S. R.) acknowledges the support of the Office of Naval Research and of the National Science Foundation.
TABLE 1
P(E) for Harmonic Oscillator Model\textsuperscript{a}

<table>
<thead>
<tr>
<th>E/cm\textsuperscript{-1}</th>
<th>P(E)/10\textsuperscript{5}</th>
<th>E/cm\textsuperscript{-1}</th>
<th>P(E)/10\textsuperscript{5}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G/cm\textsuperscript{-1} = 60\textsuperscript{b} (present paper)</td>
<td></td>
</tr>
<tr>
<td>9960</td>
<td>0.2087</td>
<td>9950</td>
<td>0.0</td>
</tr>
<tr>
<td>10020</td>
<td>0.2151</td>
<td>10000</td>
<td>0.3720</td>
</tr>
<tr>
<td>10080</td>
<td>0.2243</td>
<td>10050</td>
<td>0.0</td>
</tr>
<tr>
<td>10140</td>
<td>0.2363</td>
<td>10100</td>
<td>0.3694</td>
</tr>
<tr>
<td>10200</td>
<td>0.2499</td>
<td>10150</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10200</td>
<td>0.4415</td>
</tr>
<tr>
<td>19980</td>
<td>37.38</td>
<td>19950</td>
<td>0.0</td>
</tr>
<tr>
<td>20040</td>
<td>38.32</td>
<td>20000</td>
<td>66.03</td>
</tr>
<tr>
<td>20100</td>
<td>39.28</td>
<td>20050</td>
<td>0.0</td>
</tr>
<tr>
<td>20220</td>
<td>41.29</td>
<td>20100</td>
<td>68.05</td>
</tr>
<tr>
<td>20280</td>
<td>42.30</td>
<td>20150</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20200</td>
<td>72.96</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Fundamental frequencies/cm\textsuperscript{-1} (degeneracies): 3000(2), 1500(2), 1000(2), 900(2), 500(2), 400(1).

\textsuperscript{b}Frequencies/cm\textsuperscript{-1} after graining: 3000(2), 1500(3), 1020(1), 960(1), 900(2), 540(1), 480(1), 420(1).
TABLE 2
Errors in \( \Sigma P(E) \) and \( N(E) \) for Different Grain Sizes and Rounding Methods

Vibrational Frequency Models

<table>
<thead>
<tr>
<th>Exact Frequencies (cm(^{-1}))(^{a})</th>
<th>Frequencies (cm(^{-1})) After Rounding ( G/cm^2 = 200 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( A )</td>
</tr>
<tr>
<td>3000(2)</td>
<td>3000(2)</td>
</tr>
<tr>
<td>1500(3)</td>
<td>1400(3)</td>
</tr>
<tr>
<td>1000(2)</td>
<td>1000(2)</td>
</tr>
<tr>
<td>900(2)</td>
<td>800(2)</td>
</tr>
<tr>
<td>500(2)</td>
<td>400(2)</td>
</tr>
<tr>
<td>400(1)</td>
<td>400(1)</td>
</tr>
</tbody>
</table>

Sums of States

<table>
<thead>
<tr>
<th>( E/10^3 ) cm(^{-1} )</th>
<th>Exact Sums</th>
<th>Percentage Deviation(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5.394 ( \times 10^5 )</td>
<td>99.9, 5.8</td>
</tr>
<tr>
<td>15</td>
<td>1.286 ( \times 10^6 )</td>
<td>108.9, 4.4</td>
</tr>
<tr>
<td>20</td>
<td>1.529 ( \times 10^8 )</td>
<td>114.9, 3.5</td>
</tr>
<tr>
<td>24.4</td>
<td>9.363 ( \times 10^8 )</td>
<td>118.3, 2.9</td>
</tr>
</tbody>
</table>

Densities of States

<table>
<thead>
<tr>
<th>( E/10^3 ) cm(^{-1} )</th>
<th>Exact Densities</th>
<th>Percentage Deviation(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>372.0</td>
<td>102.2, 5.0</td>
</tr>
<tr>
<td>15</td>
<td>6.808 ( \times 10^3 )</td>
<td>109.9, 3.3</td>
</tr>
<tr>
<td>20</td>
<td>6.603 ( \times 10^4 )</td>
<td>114.9, 2.5</td>
</tr>
<tr>
<td>24.4</td>
<td>3.523 ( \times 10^5 )</td>
<td>115.6, 0.5</td>
</tr>
</tbody>
</table>

\(^{a}\)Same as given by HH.

\(^{b}\)All frequencies rounded downward or unchanged.

\(^{c}\)Rounding scheme as given in text.

\(^{d}\)It is important to realize that these "errors" are entirely due to the use of frequencies rounded to multiples of a grain size that is much larger than as would be used for accurate computations.
<table>
<thead>
<tr>
<th>$E/10^3 \text{ cm}^{-1}$</th>
<th>$\Sigma P(E)$</th>
<th>Percentage Deviation from $G/\text{cm}^{-1} = 10$ Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$G/\text{cm}^{-1} = 10$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Model F</td>
</tr>
<tr>
<td>5</td>
<td>6155</td>
<td>0.47</td>
</tr>
<tr>
<td>10</td>
<td>$6.032 \times 10^5$</td>
<td>0.66</td>
</tr>
<tr>
<td>15</td>
<td>$1.556 \times 10^7$</td>
<td>0.45</td>
</tr>
<tr>
<td>20</td>
<td>$1.985 \times 10^8$</td>
<td>0.35</td>
</tr>
<tr>
<td>24.4</td>
<td>$1.291 \times 10^9$</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Model G</td>
</tr>
<tr>
<td>5</td>
<td>6068</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>$5.484 \times 10^7$</td>
<td>0.00</td>
</tr>
<tr>
<td>15</td>
<td>$1.331 \times 10^8$</td>
<td>0.00</td>
</tr>
<tr>
<td>20</td>
<td>$1.613 \times 10^9$</td>
<td>0.00</td>
</tr>
<tr>
<td>24.4</td>
<td>$1.003 \times 10^9$</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Model H</td>
</tr>
<tr>
<td>5</td>
<td>6068</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>$5.503 \times 10^8$</td>
<td>0.09</td>
</tr>
<tr>
<td>15</td>
<td>$1.349 \times 10^9$</td>
<td>0.15</td>
</tr>
<tr>
<td>20</td>
<td>$1.651 \times 10^9$</td>
<td>0.12</td>
</tr>
<tr>
<td>24.4</td>
<td>$1.036 \times 10^9$</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Models F, G, and H correspond to models given in Reference [4] as 7, 9, and 10, respectively. These models use the same six fundamental frequencies given in Table 1, with diagonal anharmonicity constants (cm$^{-1}$) of

- Model F = $(-80, -12, -8, -7, 0, 0)$
- Model G = $(-50, -5, 0, 0, 0, 0)$
- Model H = $(-80, -5, 0, 0, 0, 0)$. 

Models F, G, and H correspond to models given in Reference [4] as 7, 9, and 10, respectively. These models use the same six fundamental frequencies given in Table 1, with diagonal anharmonicity constants (cm$^{-1}$) of

- Model F = $(-80, -12, -8, -7, 0, 0)$
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- Model H = $(-80, -5, 0, 0, 0, 0)$. 

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- Model G = $(-50, -5, 0, 0, 0, 0)$
- Model H = $(-80, -5, 0, 0, 0, 0)$. 

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- Model F = $(-80, -12, -8, -7, 0, 0)$
- Model G = $(-50, -5, 0, 0, 0, 0)$
- Model H = $(-80, -5, 0, 0, 0, 0)$.
REFERENCES


FIGURES 1a and 1b

Plots of $P(E)$ Versus $E$ for 120 Frequency Harmonic Oscillator Model

Fundamental frequencies in cm$^{-1}$ (degeneracies) = 3000(20), 1500(30), 1000(20), 900(20), 500(20), 400(10) with $G = 100$ cm$^{-1}$. Since all frequencies are exact multiples of $G$, results are exact. Points denote $P(E)$ values, lines are drawn for clarity only.