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ON THE USE OF EXACT VIBRATIONAL STATE COUNTING METHODS IN RRKM --ETC(U)
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N00014-75-C-0690

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by S. E. Stein and B. S. Rabinovitch

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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1. REPORT NUMBER NR092-549-TR04 ✓	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) On the Use of Exact Vibrational State Counting Methods in RRKM Rate Calculations		5. TYPE OF REPORT & PERIOD COVERED Technical <i>rept.</i>
7. AUTHOR(s) S. E. Stein and B. S. Rabinovitch <i>Stephen</i>		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0690 NR 092-549
9. PERFORMING ORGANIZATION NAME AND ADDRESS Professor B. S. Rabinovitch Department of Chemistry BG-10 University of Washington Seattle, WA 98195		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research, Code 473 Department of the Navy 800 N. Quincy Arlington, VA 22217		12. REPORT DATE 15 Apr 77
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 13
		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release; its distribution is unlimited.		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Submitted to Chemical Physics Letters		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Computer algorithm Eigenstate densities RRKM theory Unimolecular reaction Vibrational levels		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) 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.		

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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 $1-5 \text{ cm}^{-1}$ 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 $(I-1)G$ in the available energy levels, where G is a chosen "grain" size. For present purposes, $P(E) \equiv P'(R(E/G) + 1)$, where the quantity $R(E/G)$ denotes the integer nearest to the value (E/G) . Thus, $P(E)$ is effectively the number of levels around energy E within an energy interval of length G . 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 G . 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, G 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 G . Errors in calculated $P(E)$ are negligible ($< 1\%$ error) for molecules of chemical interest with choice of a grain of $1-5 \text{ cm}^{-1}$ [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 G .

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_{uni} , may be numerically evaluated as [6]

$$k_{\text{uni}} = a \sum_{n=0}^{\infty} \left(\frac{\sum_{E^{\ddagger}=0}^{n\ell} P(E^{\ddagger}) \exp(-n\ell/kT)}{1 + b \left(\frac{\sum_{E^{\ddagger}=0}^{n\ell} P(E^{\ddagger})}{N(E_0 + n\ell)} \right)^p} \right) \ell \quad (1)$$

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^{\ddagger} is the active energy in the activated complex. For computations using direct counting, the term $\sum_{E=0}^{n\ell} P(E)$ is obtained by summing all P' (I) elements up to $I = (E/G) + 1$. The term $N(E_0 + n\ell)$ is evaluated by

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

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 ℓ/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 ℓ 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 ℓ . A choice of ℓ/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 ($10,000 \text{ cm}^{-1}$ and $20,000 \text{ cm}^{-1}$). 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 ℓ .

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, ν_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 ν_i to be exactly divisible by the value nG , where $n = 2, 3, 4, \dots$. 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 ν_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 $n\ell$, $n = 2, 3, \dots$, does not divide exactly into all ν_i . This rule, in practice, will always be satisfied when using frequencies that have not been arbitrarily pre-grained and $\ell/G \geq 1$. 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 , $i = 1, 2, \dots, i_m$, 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 :

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

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

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

$$H_i = H_i - 1.$$

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 is given sums and densities of states have been computed using the harmonic oscillator model of HH. Exact results are given in column A ($G/\text{cm}^{-1} = 100$). In model B, which uses $G/\text{cm}^{-1} = 200$, all frequencies were rounded downward or unchanged. This appears to be the method used by HH. Sums given by HH at $22,400 \text{ cm}^{-1}$ differ slightly from those in Table 2 because the former results were given as sums up to, but not including $24,400 \text{ cm}^{-1}$. 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 $\Sigma P(E)$ follow errors in $N(E)$ very closely, confirming the smooth behavior of the latter function.

In Table 3 are given $\Sigma P(E)$ values using $G/\text{cm}^{-1} = 10$ for three anharmonic models given by HH, along with deviations in $\Sigma P(E)$ resulting from the use of $G/\text{cm}^{-1} = 20, 50, \text{ and } 100$. 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 $\Sigma P(E)$ 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 $\Sigma P(E)$ very closely as for the harmonic oscillator model (Table 1). Spurious behavior of $\Sigma P(E)$ 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 ($1-5 \text{ cm}^{-1}$), integration intervals are $\geq G$ and $\lesssim 200 \text{ cm}^{-1}$, 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^a

$G/\text{cm}^{-1} = 60^b$ (present paper)		$G/\text{cm}^{-1} = 50$ (HH)	
E/cm^{-1}	$P(E)/10^5$	E/cm^{-1}	$P(E)/10^5$
9960	0.2087	9950	0.0
10020	0.2151	10000	0.3720
10080	0.2243	10050	0.0
10140	0.2363	10100	0.3694
10200	0.2499	10150	0.0
		10200	0.4415
19980	37.38	19950	0.0
20040	38.32	20000	66.03
20100	39.28	20050	0.0
20220	41.29	20100	68.05
20280	42.30	20150	0.0
		20200	72.96

^aFundamental frequencies/ cm^{-1} (degeneracies): 3000(2), 1500(2), 1000(2), 900(2), 500(2), 400(1).

^bFrequencies/ cm^{-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		
Exact Frequencies (cm^{-1}) ^a	Frequencies (cm^{-1}) After Rounding	
	$G/\text{cm}^{-1} = 200$	
<u>A</u>	<u>B</u> ^b	<u>C</u> ^c
3000(2)	3000(2)	3000(2)
1500(3)	1400(3)	1600(2), 1400(1)
1000(2)	1000(2)	1000(2)
900(2)	800(2)	1000(1), 800(1)
500(2)	400(2)	600(1), 400(1)
400(1)	400(1)	400(1)

Sums of States			
$E/10^3 \text{ cm}^{-1}$	Exact Sums	Percentage Deviation ^d	
		<u>B</u>	<u>C</u>
10	5.394×10^5	99.9	5.8
15	1.286×10^6	108.9	4.4
20	1.529×10^6	114.9	3.5
24.4	9.363×10^6	118.3	2.9

Densities of States			
$E/10^3 \text{ cm}^{-1}$	Exact Densities	Percentage Deviation ^d	
		<u>B</u>	<u>C</u>
10	372.0	102.2	5.0
15	6.808×10^3	109.9	3.3
20	6.603×10^4	114.9	2.5
24.4	3.523×10^5	115.6	0.5

^aSame as given by HH.

^bAll frequencies rounded downward or unchanged.

^cRounding scheme as given in text.

^dIt 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 3

Percentage Deviations in Sums of States for Three
Anharmonic Oscillator Models as a Function of Grain Size

$E/10^3 \text{ cm}^{-1}$	$\Sigma P(E)$ $G/\text{cm}^{-1} = 10$	Percentage Deviation from $G/\text{cm}^{-1} = 10$ Model			
		$G/\text{cm}^{-1} = 20$	$G/\text{cm}^{-1} = 50$	$G/\text{cm}^{-1} = 100$	
<u>Model F</u>					
5	6155	0.47	1.8	7.05	
10	6.032×10^5	0.66	1.92	5.95	
15	1.556×10^7	0.45	1.29	4.05	
20	1.985×10^8	0.35	1.06	3.07	
24.4	1.291×10^9	0.23	0.93	2.48	
<u>Model G</u>					
5	6068	0.00	0.00	0.13	
10	5.484×10^5	0.00	0.29	1.26	
15	1.331×10^7	0.00	0.60	1.65	
20	1.613×10^8	0.00	0.62	1.61	
24.4	1.003×10^9	0.00	0.60	1.60	
<u>Model H</u>					
5	6068	0.00	0.00	1.45	
10	5.503×10^5	0.09	0.71	3.71	
15	1.349×10^7	0.15	0.89	3.41	
20	1.651×10^8	0.12	0.85	2.79	
24.4	1.036×10^9	0.10	0.68	2.32	

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).

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- [6] See, for example P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," Wiley-Interscience, London, 1972 or W. Forst, "Theory of Unimolecular Reactions," Academic Press, New York, 1973.

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 $G = 100 \text{ cm}^{-1}$. Since all frequencies are exact multiples of G , results are exact. Points denote $P(E)$ values, lines are drawn for clarity only.



