# Accurate evaluation of internal energy level sums and densities including anharmonic oscillators and hindered rotors*

Stephen E. Stein† and B. S. Rabinovitch

*Department of Chemistry, University of Washington, Seattle, Washington 98195*

(Received 27 September 1972)

The calculation of molecular energy level sums and densities is necessary for the treatment of many physical and chemical problems including reaction rates. An extension of Beyer and Swinehart's algorithm for directly computing harmonic oscillator eigenstate sums and densities is described. With this new algorithm it is possible to compute exact or near-exact energy level sums and densities for degrees of freedom such as free and hindered rotors and anharmonic oscillators so long as the energy levels for each degree of freedom can be specified. Computer calculation by this technique is practical even for large molecules up to all chemically interesting energies and error is confined to small rounding errors. Results by this algorithm are compared to values of energy level sums that have been given in the literature by various alternative approximate treatments and permit more rigorous testing of the latter and assessment of the approximations involved.

## INTRODUCTION

Since the advent of the statistical theory of unimolecular decomposition[1] there has been a persistent interest in an increasingly accurate calculation of the relevant internal molecular energy level densities and sums. Of course, these quantities are of considerable importance for other phenomena as well. If $E$ is the active energy in the molecule above the zero point energy, define $N(E)$ as the density of eigenstates of the molecule; $G(E)$ is the sum of states

$$\sum_0^{E_{max}} P(E),$$

where $P(E)$ is the degeneracy of the level, or number of complexions of the system at energy $E$. Several methods have been developed for practical computation of eigenstate densities and sums for fairly large molecules up to most chemically interesting energies. In all calculations it was assumed that the internal degrees of freedom were separable.

The simplest method used for the determination of harmonic energy level sums has been by direct count.[2,3] In this method frequencies are grouped together in as few degenerate groups as possible (six or seven groups have been a practical maximum). While this method can be precise, it works economically only up to moderate chemically interesting energies.

A semiempirical approximation method[4,5] has been given which takes explicit account of the dispersion of vibrational frequencies for the molecule in question. This method has proven both simple and convenient for vibrational and free rotational problems[6] and is widely used because of its reasonable accuracy and ease of calculation without benefit of machine computation.

All of the basic approximate techniques for calculating molecular energy level densities are based on approximating the inversion of the quantum mechanical partition function, $Q$,[7,8]

$$Q = \int_0^\infty N(E) \exp(-E/kT) dE = \mathcal{L}(N(E)),$$

where $\mathcal{L}(N(E))$ is the Laplace transform of $N(E)$. By inverting the Laplace transform $N(E)$ may be obtained,

$$N(E) = \mathcal{L}^{-1}(1/kT).$$

There have been three methods given for approximating $\mathcal{L}^{-1}(1/kT)$. The first method expresses the inversion integral in a series of Bernoulli polynomials[9–12] which lead to $N(E)$ by use of Cauchy's theorem. A truncated form of the complete expansion was obtained earlier by several authors[9,10] but is somewhat less accurate, especially at lower energies (down to about 3000 cm$^{-1}$).[13] This method has not been applied to degrees of freedom other than harmonic oscillators and free rotors.

A second technique uses the method of steepest descents.[14–16] This method works about as well as the first for harmonic oscillators and free rotors and has been applied with limited success to anharmonic oscillators, to which the direct method was first applied.[3]

A third and, in principle, more accurate procedure is based on the numerical approximation of the Laplace transform.[17] This method has not yet been used or tested adequately.

All of these inversion methods are computationally more or less complex and vary in the ease of programming. Moreover, they are not uniformly adequate or successful. Indeed, their degree of success and generality has not been properly tested because a sufficient range of exact results have not been known against which tests could be made.

To this time the practical situation is the following. The approximations to $\mathcal{L}^{-1}(1/kT)$ have been compared to harmonic oscillator molecules which consist of three to five degenerate vibrational groups. The

largest molecule considered, cyclopropane, with 21 modes was reduced to five degenerate frequency groups.

Since the expense of making exact counts increases with the number of vibrations and/or frequencies, the larger the molecule the lower the maximum energy up to which exact counts have been made. For larger molecules at higher energies, sums and densities of eigenstates from the various approximations have usually not been compared to exact counts, and their validity and characteristics have not been well assessed in this range. This situation is especially unfortunate because the reduced energy parameter, $E'$, defined in terms of the total zero point energy $E_z$ as $E' = E/E_z$, decreases with increasing size of the molecule for fixed $E$, and the largest value of $E'$ for which a general comparison has been made[14] with exact counts for even a molecule of moderate complexity such as $cyclo$-$C_3H_6$ is quite low ($0.6E_z = 30$ kcal mole$^{-1}$).

The sums of complexions for a model of grouped harmonic frequencies coupled with 2–12 rigid rotors have been compared to exact values for the various approximations.[13] These methods generally worked well in the energy region considered ($<20\,000$ cm$^{-1}$).

Energy level sums have been calculated for a few simple anharmonic oscillator (Morse) molecules, but an "exact" count has been made only for one very simple, four-frequency model.[16] Only for two of these model molecules have the sums of complexions by various approximations been intercompared.[14] The degree of validity of these approximations is very uncertain for larger molecules. All of them are unsatisfactory at low energy extremes and reversion to direct counting has been necessary.

There have been no published calculations of $N(E)$ or $G(E)$ for hindered rotor molecules.

Recently, Beyer and Swinehart[18] (BS) reported a startlingly simple computational algorithm which can be used to calculate $G(E)$ and $N(E)$ for harmonic oscillators, accurately and economically. This algorithm counts the sum directly, and does it very efficiently without frequency grouping. In general, the results are equally accurate at all energies.

We have developed an extension of the algorithm of BS which can be used to calculate energy level sums for any kind of degree of freedom, with accuracy equal to that obtained from the original algorithm. The extended algorithm has been used to calculate exact energy level sums for molecules containing harmonic oscillators, with and without a cutoff energy, anharmonic Morse oscillators (which automatically entail energy cutoffs), internal free rotors, "Pitzer" internal rotors (defined as a free rotor with zero energy at half the barrier height), hindered internal rotors, and over-all (free) rotors. The range of applications of this algorithm is limited only by a knowledge of the energy levels for the degrees of freedom concerned.

Although computationally more involved than the original algorithm, the extended method remains economically feasible for all chemically interesting energies and molecules, and is also equally accurate at low energies.

It thus appears probable that for most practical chemical problems there may no longer be much need for the use of the approximate computational methods mentioned earlier; nonetheless, useful physical insights can be gained in the future by the extended testing of certain of these approximations which is now possible.

## BEYER–SWINEHART ALGORITHM

This algorithm is implemented as follows[18]:

(1) Choose a suitable grain size, $\Delta E$ (discussed further below).

(2) Reduce each fundamental frequency, $\nu_i$, to an integer, $R_i$, such that $R_i \Delta E \cong \nu_i$. (A rounding error will be introduced here if $R_i \Delta E \neq \nu_i$.)

(3) Initialize an array, $T(I)$, $I = 1$ to $I = M$, such that $T(1) = 1$ and $T(2)$ to $T(M) = 0$.

(4) For each harmonic fundamental frequency, $\nu_i$, carry out the following sequence of additions:

$$T(R_i + 1) = T(1) + T(R_i + 1),$$

$$T(R_i + 2) = T(2) + T(R_i + 2),$$

$$T(I) = T(I - R_i) + T(I),$$

$$T(M) = T(M - R_i) + T(M).$$

(5) The $T$ array now contains $P(E_m)$ where $P(E_m) = T(R_m + 1)$, and where $R_m \Delta E = E_m$, the active vibrational energy. If $E_m$ is not an exact multiple of $\Delta E$ it is necessary to interpolate between two successive members of $T$ to find $P(E_m)$; also $N(E_m) = P(E_m)/\Delta E$. If

$$\sum_0^{E_{max}} P(E_m) \quad \text{or} \quad \int_0^{E_{max}} N(E)dE$$

is desired, simply set, for $I = 2$ to $I = M$,

$$T(I) = T(I) + T(I - 1),$$

and $\sum P(E_m)$ will be contained in $T(R_m + 1)$.

Several important considerations enter in using this algorithm. The energy difference between any two consecutive members of the $T$ array is always the same and may be called the grain size, $\Delta E = $ [energy at $T(I)$ − energy at $T(I-1)$]. It should be understood that this algorithm works exactly for $\nu_i$ which are exact multiples of $\Delta E$. A decrease in $\Delta E$ will generally decrease the calculation error. Any error in the $N(E)$ or $G(E)$ is always due to this graining error, but with good judgment in frequency rounding the error is quite small (less than 1%) for most calculations. In many instances, $\Delta E$ may be as small as 1 cm$^{-1}$, and if

TABLE I. Percentage deviation due to graining of calculated level sums from exact value for harmonic molecules.

| $E$ kcal mole$^{-1}$ | Exact[a] | % Error | | | | Present paper[f] | Present paper[g] |
|---|---|---|---|---|---|---|---|
| | | BS[b] | BS[c] | BS[d] | BS[e] | | |
| A. NH$_3$[h] | | | | | | | |
| 10 | 14 | 14 | 0 | 0 | 0 | 0 | 0 |
| 20 | 94 | 94 | 0 | 0 | 0 | 0 | 0 |
| 30 | 375 | 375 | 0 | 0 | 0 | 0 | 0 |
| 40 | 1 135 | 1 135 | 0 | 0.18 | 0.088 | 0 | 0 |
| 50 | 2 916 | 2 916 | 0.034 | 0.17 | 0.10 | 0 | 0 |
| 70 | 13 518 | 13 518 | 0.059 | 0.24 | 0.18 | 0 | 0 |
| 100 | ⋯ | 77 418 | 0.068 | 0.14 | 0.075 | 0 | −0.020 |
| B. Cyclopropane[i] | | | | | | | |
| 10 | 802 | 802 | | 0 | | | 0 |
| 20 | 77 522 | 77 522 | | −0.22 | | | −0.090 |
| 30 | 2 680 083 | 2 680 083 | | −0.039 | | | +0.015 |
| 40 | ⋯ | 49 612 574 | | −0.050 | | | +0.10 |
| 50 | ⋯ | 6.1142800(8)[j] | | −0.18 | | | +0.087 |
| 70 | ⋯ | 4.0751802(10) | | −0.10 | | | +0.11 |
| 100 | | 5.8325046(12) | | −0.17 | | | +0.069 |

[a] M. R. Hoare, J. Chem. Phys. **52**, 5695 (1970).

[b] With grain of 1 cm$^{-1}$ and $N = 40\,000$.

[c] Uncorrected, grain of 2 cm$^{-1}$.

[d] Uncorrected, grain of 5 cm$^{-1}$.

[e] BS linearly corrected, grain of 5 cm$^{-1}$.

[f] Grain of 2 cm$^{-1}$.

[g] Grain of 5 cm$^{-1}$.

[h] Frequencies as in Footnote a (cm$^{-1}$): 3337, 950, 3414(2), 1628(2) cm$^{-1}$.

[i] Frequencies as rounded in Ref. 20 (cm$^{-1}$): 3221(6), 1478(3), 1118(7), 879(3), 750(2).

[j] $1.00(8) = 1.00 \times 10^8$. In subsequent tables, applies to all members of a row.

the $\nu_i$ are given only to this precision, then the calculation is exact.

By this method each level is calculated separately, and each degree of freedom of a degenerate vibration mode is considered separately.

The maximum energy $E_{max}$ for which the procedure applies is determined by $E_{max} = (M-1)\Delta E$. Since $T(1)$ represents the zero energy term, $T(I)$ represents the $T(I-1)\Delta E$ energy term. It is desirable in principle to have as large an $M$ as possible. The size of $M$ is limited by the storage space of the computer being used and the machine time limit. Values of $M = 10\,000$ for a 100-frequency molecule are not excessive.

## AN EXTENDED ALGORITHM

This algorithm is applied as follows:

(1) Determine suitable $\Delta E$ and $M$.

(2) Initialize two arrays, $T$ and $AT$, both of length $M$ such that $T(1) = AT(1) = 1$, and all other members of both arrays are zero.

(3) For each degree of freedom, $j$, carry out the following:

Enumerate all energy levels up to $E_{max}$; call the $k$th level $E_{jk}$.

Reduce each $E_{jk}$ to an integer, $R_{jk}$, such that $R_{jk}\Delta E \simeq E_{jk}$. Judicious rounding of the level will enhance the accuracy.

Perform the following sequence of additions for $k = 1$ to $k = k_{max}(E_{jk_{max}} \leq E_{max})$:

$$AT(R_{jk}+1) = AT(R_{jk}+1) + T(1),$$

$$AT(R_{jk}+I) = AT(R_{jk}+I) + T(I),$$

$$AT(M) = AT(M) + T(M-R_{jk}).$$

For $I = 1$ to $I = M$,

$$T(I) = AT(I).$$

(4) $P(E_m)$ is contained in $T(R_m+1)$. To get $\sum P(E_m)$, set $T(I) = T(I) + T(I-1)$, for $I = 2$ to $I = M$.

The sequence of additions performed for each frequency using the algorithm of BS is similar to the sequence of additions performed at each energy level in the extended algorithm. In the BS technique, members on the $T$ array are added on to other members of

TABLE II. Level sums for anharmonic molecules.

| $E$ kcal mole$^{-1}$ | This paper[a] | This paper[b] | SSV[c] | W[d] | HR[e] | HR[f] | TL[g] | This paper[h] |
|---|---|---|---|---|---|---|---|---|
| A. Cyclopropane[i] | | | | | | | | |
| 10 | 8.17(2) | 8.17 | $\cdots$ | 8.27 | 9.15 | 9.25 | 7.83 | 8.21 |
| 20 | 9.3016(4) | 9.2897 | 9.13 | 10.2 | 11.4 | 11.3 | 8.54 | 9.3850 |
| 30 | 3.4491(6) | 3.4527 | $\cdots$ | 4.12 | 4.70 | 4.53 | 3.15 | 3.5435 |
| 50 | 9.1962(8) | 9.1951 | 8.49 | 12.2 | 15.0 | 13.5 | 8.20 | 9.5350 |
| 100 | 1.2139(13) | 1.2138 | 1.08 | 1.78 | 3.40 | 2.19 | 1.05 | 1.2890 |
| 150 | $\cdots$ | 8.6582(15) | 7.40 | 12.8 | 43.2 | 11.8 | 7.59 | 9.5221 |
| 200 | $\cdots$ | 1.4543(18) | 1.19 | 2.06 | 11.6 | 3.35 | 1.47 | 1.6763 |

| $E$ kcal mole$^{-1}$ | This paper[k] | | SSV[c] | | | | | |
|---|---|---|---|---|---|---|---|---|
| B. CD$_4$[j] | | | | | | | | |
| 20 | 1414 | | 1372 | | | | | |
| 50 | 3.9728(5) | | 3.686 | | | | | |
| 100 | 9.3214(7) | | 9.481 | | | | | |
| 125 | 6.2919(8) | | 7.138 | | | | | |
| 150 | 3.0861(9) | | 3.692 | | | | | |
| 180 | 1.5575(10) | | 1.882 | | | | | |

[a] Extended algorithm with linear anharmonic correction and low grain of 2 cm$^{-1}$ (see the Appendix).

[b] Same as a, with low grain of 10 cm$^{-1}$.

[c] Reference 19.

[d] K. A. Wilde, J. Chem. Phys. 41, 448 (1964).

[e] Reference 14—Method 1.

[f] Reference 14—Method 2.

[g] Reference 16.

[h] Exact nonrounded frequencies and anharmonicity constants as given by S. J. Cyvin, Spectrochim. Acta 16, 1022 (1960) using linear (Footnote i) anharmonic correction with low grain of 10 cm$^{-1}$.

[i] Frequencies as rounded in Ref. 19 (cm$^{-1}$): 3321(6), 1478(3), 1118(7), 879(3), 750(2); anharmonicity constants: 0.024945, 0.00819, 0.00729, 0.00845, 0.00740, respectively.

[j] Frequencies as in Ref. 19 (cm$^{-1}$): 2336.8(3), 2143.2(1), 1109.4(2), 1026.8(3); anharmonicity constants=0.016585, 0.01365, 0.00775, 0.01962, respectively.

[k] Using anharmonic linear correction with low grain of 8 cm$^{-1}$.

TABLE III. Level sums for contrived anharmonic molecule.[a]

| $E$ kcal mole$^{-1}$ | TL[b] "exact" | This paper[c] | HR[d] | HR[e] | TL[f] | HP[g] |
|---|---|---|---|---|---|---|
| 2.31 | 1 | 1 | 1.17 | 1.20 | 0.89 | 0.90 |
| 11.53 | 13 | 13 | 11.3 | 11.6 | 10 | 14.92 |
| 23.06 | 61 | 61 | 61.5 | 63.8 | 52.5 | 62.20 |
| 46.12 | 533 | 535 | 526 | 542 | 419 | 534.1 |
| 92.24 | 7 191 | 7 353 | 8035 | 6 782 | 5830 | 6972 |
| 138.36 | 44 171 | 44 934 | 5.33(4) | 34 937 | 3.1(4) | $\cdots$ |
| 184.48 | 162 935 | 163 924 | 2.315(5) | 1.2(5) | 1.32(5) | $\cdots$ |

[a] Frequencies and anharmonicity constants given by Tou and Lin (Ref. 16) cm$^{-1}$: 3000(2), 2000, 1000; 0.025, 0.010, and 0.007, respectively.

[b] "Exact" sums as given in Ref. 16.

[c] Extended algorithm with grain of 2 cm$^{-1}$ below 100 kcal, grain of 4 cm$^{-1}$ above 100 kcal.

[d] Reference 14, Method 1.

[e] Reference 14, Method 2.

[f] Reference 16.

[g] Reference 17.

TABLE IV. Level sums for ethane[a] for several different internal rotor models.

| $E$ cm$^{-1}$ | Hindered rotor[b] | "Pitzer" rotor[c] | Free rotor[d] | Harmonic librator[e] |
|---|---|---|---|---|
| 500 | 2 | 2.3 | 4.3 | 2 |
| 1 000 | 8 | 5 | 12.7 | 7 |
| 2 000 | 55.7 | 51.6 | 88 | 51 |
| 4 000 | 1187 | 1042 | 1728 | 1081 |
| 6 000 | 1.3111(4)[f] | 1.2264 | 1.8211 | 1.223 |
| 8 000 | 9.8719(4) | 9.3943 | 13.071 | 9.336 |
| 10 000 | 5.7428(5) | 5.5023 | 7.1416 | 5.537 |
| 20 000 | 4.2130(8) | 4.1413 | 5.0222 | 4.465 |
| 30 000 | 4.4204(10) | 4.3772 | 5.0613 | 5.087 |
| 40 000 | 1.66923(12) | 1.65849 | 1.86446 | 2.064 |

[a] Frequencies (cm$^{-1}$): 7915(2), 1388, 995, 1370, 2974(2), 1460(2), 822(2), 2950(2), 1469(2), 1190(2). Rotational constant is 10.705 cm$^{-1}$; barrier height $V_0 = 1024$ cm$^{-1}$.

[b] Extended algorithm using exact levels (Ref. 20) below several times the barrier height and Pitzer levels above.

[c] Zero energy taken at 361 cm$^{-1}$ (i.e., $\frac{1}{2}V_0$ minus 151 cm$^{-1}$, the lowest hindered rotor level).

[d] Zero energy assumed to be at bottom of the potential well.

[e] Frequency taken as 285 cm$^{-1}$.

[f] Multiplication factors apply to all members of the row.

the $T$ array. In the extended technique, members of the $T$ array, which is set equal to the $AT$ array after each degree of freedom is calculated, are added on to members of the $AT$ array.

This algorithm can now be used to find $N(E)$ or $\sum P(E)$ for a molecule containing any type of degree of freedom for which the energy levels can be enumerated. Graining errors are generally less important in this technique because the exact energy levels are rounded at each level, which eliminates a cumulative error due to graining. However, since $G(E)$ increases in rather irregular jumps at low $E$, at each grain one must be especially cautious in rounding $E$ to $R$.

The BS algorithm may be used in conjunction with the extended algorithm to save machine time for molecules containing harmonic oscillators as well as other degrees of freedom with nonevenly spaced energy levels. Harmonic degrees of freedom are first calculated using the BS technique, after which both the $T$ and $AT$ arrays of the extended algorithm are set equal to the BS $T$ array. The extended algorithm is then applied to the remaining degrees of freedom.

Since two arrays of equal length are necessary for the present algorithm, then if all of the computer storage space were used $\Delta E$ would be twice as large as the $\Delta E$ using the BS technique. However, the loss of accuracy which might result from increased $\Delta E$ is compensated by the gain in accuracy due to rounding at each level. Several refinements for further improving accuracy at larger values of $\Delta E$ are described in the Appendix. Again, if vibration frequencies were specified only to the nearest wavenumber and if the grain size could be taken to be 1 cm$^{-1}$ (quite practical for many calculations) then no rounding or graining errors would arise at any energy.

## APPLICATIONS AND RESULTS

### Harmonic Oscillators

The BS algorithm should always be used in calculating harmonic oscillator sums if the grain size used is smaller than the accuracy of the fundamental frequencies. On a CDC 6400 computer, for example, $\Delta E$ may be made as low as 1 cm$^{-1}$ for an energy of 40 000 cm$^{-1}$; thus any set of frequencies specified to 1 cm$^{-1}$ may be calculated without error up to this energy (see Table I).

The BS algorithm also yields ideal results if a grain size can be chosen which divides exactly into the fundamental frequencies.

If the rounded frequencies do not fall within the uncertainties in the true frequencies, a graining error will result. The relative difference between the true and rounded frequency remains constant while the magnitude of this difference increases with increasing energy. This tends to increase the absolute graining error in $\sum P(E_v)$ with increasing energy. If all of the relative changes in the rounding of frequencies are added, a small linear correction may be made in $G(E_v)$ (see the Appendix).

If it is desired to have greater accuracy than can be given by the BS algorithm, the extended algorithm may be used. With sufficient storage space and a little care in the rounding of energy levels to make sure that no systematic rounding error occurs, an accuracy of 0.1% in $G(E_v)$ usually may be obtained for any set of levels. Also, in the extended algorithm, selected energy levels which are above some dissociation limit may be excluded from the calculation (see the Appendix).

## Over-All Rotation

Free rotor levels are straightforwardly incorporated into the sum of complexions using the present algorithm. Energy levels of a one-dimensional rigid rotor are given by

$$E = Bn^2, \qquad n = 0, 1, 2\cdots,$$

and are nondegenerate for $n=0$ and are doubly degenerate for $n>0$; $B$ is the rotational constant. Tou and Lin[16] calculated the exact sum of complexions for a model consisting of five harmonic vibrations with one free rotor ($B=5.9506$ cm$^{-1}$) to four significant figures. Calculations using the present algorithm agree exactly with their values.

## Anharmonic Oscillators

Values have been reported in the literature for the sums of complexions for two anharmonic oscillator molecules[19] (Table II). A Morse potential was assumed. The energy levels of a Morse oscillator are $E = h\nu n[1 - x(1+n)]$, where $n$ is an integer which varies between 0 and $(1/x-1)$; $x$ is the anharmonicity constant. This set of levels ends at the dissociation energy. The only direct computer count of the sum of complexions for an anharmonic model up to interesting energies has been made by Tou and Lin.[16] They used a simple four-frequency model molecule (Table III) which was later employed[14] to compare various approximations. Although a discrepancy between our count and Tou and Lin's was less than the error of any of the other methods compared over the full energy range, this lack of agreement was disturbing. We have carefully examined this discrepancy and believe that the error may lie in Tou and Lin's enumeration of the energy levels.

Cyclopropane has been the most widely intercompared anharmonic molecule (Table II.A), although exact values had previously not been available. Schlag et al.[19] and Tou and Lin yield the best results, with the former slightly more accurate at lower energies and the latter more accurate at very high energies, when compared with the present values. Both of Hoare and Ruijgrok techniques[14] fail rather badly in the middle energy range.

As a matter of interest, the results of an exact calculation for cyclopropane, with the best detailed values of molecular parameters, are given in the last column of Table II.A. A brief comparison is also given for CD$_4$ in Table II.B.

## Internal Rotors

When density-of-states calculations are made which include internal rotational degrees of freedom, one of three common approximations is generally used. At low energy, the internal rotor is assumed to behave like a harmonic librator. For this approximation to work, the average energy in this mode must be well below barrier height. If not, either a free rotor, or a "Pitzer" free rotor may be used to approximate the true rotor. The harmonic oscillator approximation fails badly at high energies and the Pitzer rotor approximation is poor at low energies. The free rotor approximation is best at very high energies, but even there it can be inaccurate. There has been no approximation which works for both high and low energies. This range of accuracy is necessary if the average energy of the internal rotor is anywhere near the barrier height and good accuracy is desired. If the precise lower energy levels (up to say $1\frac{1}{2}$ times the barrier height) may be directly computed and the higher energy levels approximated by the Pitzer rotor, then the sum of complexions will be more accurate than any of the above-mentioned approximations at all energies, especially at energies up to several times the barrier height.

Exact energy levels (using Koehler and Dennison's method of continued fractions[20]) were computed for ethane-hindered rotation up to 3 times the barrier height. Pitzer rotor levels were used for higher energy levels. Table IV compares $G(E_v)$ for harmonic ethane containing a hindered rotor to a model containing a Pitzer rotor and one containing a free rotor. As expected, the Pitzer rotor fails somewhat just above the barrier, while it is in good agreement at higher energies. However, the free rotor fails badly at all energies, especially lower ones. Error remains high ($>20\%$) at even very high energies.

## CONCLUSIONS

The BS algorithm for computing harmonic oscillator sums is a very accurate and inexpensive technique. By an extension of this algorithm, the same (or better) accuracy as was possible for harmonic oscillators may be obtained for any type of degree of freedom for which the energy levels are known. One may be confident of the accuracy of this technique because it directly counts the number of complexions of the system at each energy.

Application is presently being made to the evaluation of the physical approximations that have been used in the past[2,4,16] to treat energy level sums for molecules having hindered rotor degrees of freedom. Both model systems and the practical problem of the calculation of the rates of decomposition for a homologous series of chemically activated long chain alkyl radicals are being examined.

TABLE V. Comparison of anharmonic $C_3H_6$[a] level sums and computation times for different techniques and grain sizes with the extended algorithm.

| Grain size (cm$^{-1}$) | Energy (kcal/mole) | | | | | | Computation time (sec)[b] |
|---|---|---|---|---|---|---|---|
| | 10 | 20 | 50 | 100 | 150 | 200 | |
| Method A: each energy level rounded to a grain multiple | | | | | | | |
| 4 | 8.17(2)[c] | 9.304(4) | 9.213(8) | 1.215(13) | 8.664(15) | 1.455(18) | 315 |
| 10 | 8.17 | 9.300 | 9.228 | 1.216 | 8.671 | 1.455 | 145 |
| 40 | 8.24 | 9.362 | 9.331 | 1.225 | 8.723 | 1.462 | 40 |
| 100 | 8.97 | 10.182 | 9.851 | 1.266 | 8.916 | 1.476 | 11 |
| Method B: each energy level weighted at nearest upper and lower grain multiple (see the Appendix) | | | | | | | |
| 2 | 8.17 | 9.302 | 9.203 | 1.214 | ... | ... | 353 |
| 5 | 8.17 | 9.300 | 9.213 | 1.215 | ... | ... | 141 |
| 10 | 8.17 | 9.297 | 9.230 | 1.217 | 8.673 | 1.456 | 231 |
| 40 | 8.28 | 9.388 | 9.337 | 1.225 | 8.717 | 1.462 | 62 |
| 100 | 9.12 | 10.198 | 9.804 | 1.262 | 8.911 | 1.488 | 17 |
| Method C: linear extrapolated correction of the Appendix | | | | | | | |
| Low grain (cm$^{-1}$) | | | | | | | |
| 10 | 8.17 | 9.290 | 9.195 | 1.214 | 8.658 | 1.454 | 350 |
| 40 | 8.10 | 9.136 | 9.191 | 1.213 | 8.655 | 1.454 | 94 |
| 80 | 7.82 | 9.083 | 9.163 | 1.211 | 8.648 | 1.453 | 49 |

[a] Frequencies and anharmonicity constants given in Footnote i of Table II.
[b] For a CDC 6400 computer.
[c] Multiplication factor applies to whole column.

## APPENDIX

A simple illustration of the extended algorithm is given. Calculate the densities of a system consisting of two degrees of freedom (whose levels are known) up to a maximum of 1000 cm$^{-1}$. Use a grain of 100 cm$^{-1}$ and begin by initializing the arrays $T$ and $AT$

| $I$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $T(I)$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $AT(I)$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0. |

Let one set of energy levels be 205, 206, 420, 650 cm$^{-1}$. Round these frequencies to 2, 2, 4, 7 units, respectively (1 unit = 100 cm$^{-1}$) and apply the algorithm

| $I$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $T(I)$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $AT(I+2)$ | | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $AT(I+2)$ | | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $AT(I+4)$ | | | | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $AT(I+7)$ | | | | | | | 1 | 0 | 0 | 0 | 0. |
| $T(I)$ | 1 | 0 | 2 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 |
| $AT(I)$ | 1 | 0 | 2 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 |

Let the second set of levels be 1, 20, 175, 510 cm$^{-1}$. Round the levels to 0, 0, 2, 5 units, respectively, and apply the algorithm

| $I$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $T(I)$ | 1 | 0 | 2 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 |
| $AT(I+0)$ | 1 | 0 | 2 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 |
| $AT(I+0)$ | 1 | 0 | 2 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 |
| $AT(I+2)$ | | 1 | 0 | 2 | 0 | 1 | 0 | 0 | 1 | 0 | |
| $AT(I+5)$ | | | | | 1 | 0 | 2 | 0 | 1 | 0. | |
| $T(I)$ | 3 | 0 | 7 | 0 | 5 | 1 | 1 | 5 | 0 | 2 | 0 |

To add degrees of freedom first set $AT=T$ and proceed as before.

If any energy level is $m$-fold degenerate (as in over-all rotation) this procedure may be simplified by first multiplying the $AT$ array by $m$ before adding to the $T$ array.

This extended algorithm has been modified so that the rounding of each level is unnecessary. Assume that the energy associated with the grain just below an energy level $(l_i)$ is equal to $E_i$. The energy level is divided into two levels, one at $E_i$, the other at $E_i+\Delta E$

($\Delta E$ is the grain size), with the weight of the upper $= (l_i - E_i)/\Delta E$ and the weight of the lower $= [1 - (l_i - E_i)]/\Delta E$. This procedure results in an increase in computation time but a proportionally greater decrease in graining error for large grain sizes. As a result, in order to compute $G(E_v)$ to moderate accuracy (several percent) the grain size using this modification may be about 5–10 times as large as used in the unmodified technique. Using this modification, the graining error has been found to increase rather linearly with the grain size. Therefore a linear correction may also be made if the computation is made at two different grain sizes. Finally, the contribution to the level sums due to any single specified set of levels may be calculated with zero error. This program first computes any harmonic energy level sums by using a modified BS method and then switches to the extended algorithm for other degrees of freedom, such as harmonic oscillators with a cutoff, over-all rotors, Pitzer internal rotors, free internal rotors, or exact hindered rotors using lower energy level input.

A comparison of results obtained by the various procedures just outlined, for several grain sizes, is presented in Table V. Method C is intrinsically the most accurate. Method A is very adequate, and less time consuming, for all grains of 40 cm$^{-1}$ and below, for this case. A program is available from us which efficiently computes $\sum P(E)$ or $P(E)$ using this method.

[1] R. A. Marcus and O. K. Rice, J. Phys. Colloid Chem. 58, 894 (1951); R. A. Marcus, J. Chem. Phys., 20, 359 (1952).

[2] R. E. Harrington, B. S. Rabinovitch, and R. W. Diesen, J. Chem. Phys. 1960; J. H. Current and B. S. Rabinovitch, J. Chem. Phys. 38, 783 (1963).

[3] F. W. Schneider and B. S. Rabinovitch, J. Am. Chem. Soc. 84, 4215 (1962).

[4] B. S. Rabinovitch and R. W. Diesen, J. Chem. Phys. 30, 735 (1959); B. S. Rabinovitch and J. H. Current, J. Chem. Phys. 35, 2250 (1961).

[5] G. Z. Whitten and B. S. Rabinovitch, J. Chem. Phys. 38, 2466 (1963); 41, 1883 (1964).

[6] D. C. Tardy, B. S. Rabinovitch, and G. Z. Whitten, J. Chem. Phys. 48, 1427 (1968).

[7] S. H. Bauer, J. Chem. Phys. 1, 1097 (1939).

[8] J. L. Magee and W. Hamill, J. Chem. Phys. 31, 1380 (1959).

[9] P. C. Haarhoff, Mol. Phys. 7, 101 (1963).

[10] E. W. Schlag and R. A. Sandsmark, J. Chem. Phys. 37, 168 (1962).

[11] E. Thiele, J. Chem. Phys. 39, 3258 (1963).

[12] W. Forst, Z. Prasil, and P. St. Laurent, J. Chem. Phys. 40, 3736 (1967).

[13] W. Forst, Chem. Rev. 71, 339 (1971).

[14] M. R. Hoare and T. W. Ruijgrok, J. Chem. Phys. 52, 113 (1970).

[15] S. H. Lin and H. Eyring, J. Chem. Phys. 39, 1577 (1963); 43, 2153 (1965).

[16] J. C. Tou and S. H. Lin, J. Chem. Phys. 49, 4187 (1968).

[17] M. R. Hoare and P. Pal, Mol. Phys. 20, 695 (1971).

[18] T. Beyer and D. F. Swinehart, Commun. Assoc. Comput. Machin. (to be published).

[19] E. W. Schlag, R. A. Sandsmark, and W. G. Valance, J. Chem. Phys. 40, 1461 (1964).

[20] J. S. Koehler and D. M. Dennison, Phys. Rev. 57, 1006 (1940).