Chemical Reviews

METHODS FOR CALCULATING ENERGY-LEVEL DENSITIES

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Contents

I. Introduction

A. PREFATORY REMARKS

In terms of the notation defined below in section B, $k(E)$, the microcanonical rate constant for unimolecular decomposition of a reactant species with internal energy E, is given in statistical theory by the remarkably simple expression[1]

$$k(E) = 0 \qquad (E < E_0)$$

$$k(E) = \frac{G^{\ddagger}(E - E_0)}{hN(E)} \qquad (E > E_0)$$

where E_0 is the energy threshold for reaction and h is Planck's constant. The function $N(E)$ in the denominator is the density of states of the reactant, whereas the function $G^{\ddagger}(E - E_0)$ is related to the density of states of the activated complex or transition state, as denoted by the superscript $\ddagger$. The unimolecular rate theory that leads to the above expression is associated with the names of Rice, Ramsperger, Kassel, Marcus, and Eyring, and is often referred to as the Rice–Marcus, RRKM, or quasi-equilibrium theory. It is in connection with unimolecular rate calculations using this theory that the need for reasonably accurate energy level densities arose for the first time; ever since, unimolecular rate theory has provided most of the impetus for the development of this slightly esoteric subject.

There are other areas of statistical physics where densities of states play an important role (nuclear processes, spectroscopy, among others) but, to the chemist, unimolecular rate theory is doubtless the most likely area where he will be confronted with the subject matter of this review. Therefore the present review is somewhat slanted toward aspects of the energy level density problem inherent in such rate calculations.

The first consideration to bear in mind is that $k(E)$, or functions related to it, are generally averaged over a distribution of energies between $E = E_0$ and $E = E'$, where E' is some

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(1) See, for example, O. K. Rice, "Statistical Mechanics, Thermodynamics and Kinetics," W. H. Freeman, San Francisco, Calif., 1967, p 560, eq (1.10).

more or less high value of E, in principle infinity if the distribution is thermal. This means that for the purpose of such averaging, which is normally done by numerical integration, $k(E)$ must be generated at a large number of equally spaced energy intervals. Therefore reasonable *speed* of computation is essential, and this means mainly the speed of calculating $N(E)$ and $G^{\ddagger}(E - E_0)$, since these functions are the most difficult part of the problem.

The second consideration concerns the difference in energies at which the numerator and denominator of $k(E)$ are evaluated. Near threshold ($E \rightarrow E_0$), the function $G^{\ddagger}(E - E_0)$ is evaluated at $E - E_0 \sim 0$, while the function $N(E)$ is evaluated at $E \sim E_0$. Since, as will be shown later in section VI.B, these two functions are basically the same, the method therefore must be *accurate* essentially at *all* energies, from zero onwards, a very difficult proposition.

The density $N(E)$, which appears in the denominator of $k(E)$, refers to energy levels of the reactant molecule among which the energy E is randomized. If a simplified molecular model is used, involving a collection of separable (*i.e.*, noninteracting) degrees of freedom, the problem then becomes one of calculating $N(E)$ for such a collection of separable degrees of freedom. This sort of simplification is necessary because, on the one hand, the energy level density problem was solvable until very recently only for the simplified molecular model; on the other hand, not enough is known about interactions among internal degrees of freedom in polyatomic molecules to make calculations of $N(E)$ for interacting degrees of freedom worthwhile at the present time. Similar considerations apply to $G^{\ddagger}(E - E_0)$ and the degrees of freedom involved in it.

The specification of the number and nature of the degrees of freedom (separable or otherwise) for which $N(E)$ or $G^{\ddagger}(E - E_0)$ is to be calculated is a problem proper to unimolecular rate theory and will not be discussed here. Suffice it to say that while such a specification can be accomplished without too much difficulty for the reactant molecule, *i.e.*, for the purpose of calculating $N(E)$, information about the transition state is usually scanty, and the assignment of degrees of freedom to be included in $G^{\ddagger}(E - E_0)$ is therefore on less firm grounds. For this reason methods of calculation giving a moderate error at low energies can be tolerated if the error does not exceed the probable error due to the uncertainty in the assignment of the degrees of freedom in the transition state.

With these provisos in mind, this review is concerned with general methods for calculating the functions $N(E)$ and $G(E)$ for degrees of freedom that are assumed to be separable, unless stated otherwise. The combinatorial nature of the problem is shown in sections II and VI. It is pointed out in section III that while the calculation of $N(E)$ and/or $G(E)$ does not present any difficulty in principle, the bookkeeping gets quite out of hand for all but the simplest systems and the lowest energies. Practical considerations therefore dictate the use of some suitable approximation, not afflicted with the bookkeeping disability. A general method for obtaining such an approximation can be based on the inversion of the partition function, as shown in section IV; all the various approximations considered in the subsequent sections are discussed from this point of view. Inversion of the classical partition function is discussed in section V for rotational states and in section VII for vibrational states; inversion of the quantum mechanical vibrational partition function is treated in section VIII. Refinements, notably anharmonicity, are dealt with in section IX. Finally section X discusses the pros and cons of the various approximations and gives some practical hints for those wishing to undertake such calculations.

It is tacitly assumed throughout this review[2] that the vibration–rotation states among which the energy E is randomized all belong to the same electronic state. Several electronic states might participate in reactions of charged species produced by photoionization or electron impact, for example, and, although state densities involving more than one electronic state could be computed in principle by the methods of section IX, there is as yet no such rate computation on record, most likely because very little is known about the spacing of electronic states in the reactants of interest.

B. TERMINOLOGY AND BASIC CONCEPTS

To avoid any confusion of symbols and meaning, define for *positive E:*

$N(E)$ = number of states *per unit energy*, *i.e.*, the density of states at energy E; units in energy^{-1}.

$W(E)$ = number of states *at* energy E, *i.e.*, the quantum mechanical degeneracy of state of energy E; this quantity is dimensionless. Note that

$$W(E) = N(E)\delta E \qquad (1)$$

(δE = allowance in E) so that $N(E)$ may be considered a smooth-function version of $W(E)$.

$G(E)$ = *total* number of states at energy E, *i.e.*, the number of states between 0 and E; this quantity is likewise dimensionless. Note that

$$G(E) = \sum_{E=0}^{E} W(E) \quad \text{or} \quad \int_0^{\infty} N(E)\mathrm{d}E \qquad (2)$$
$$N(E) = \mathrm{d}G(E)/\mathrm{d}E$$

It is useful to establish a connection between the density (or number) of states of a system and its partition function. If Q is the partition function for the specified system, we have, by definition

$$Q = \sum_E W(E)e^{-E/kT} \quad \text{or} \quad \int_0^{\infty} N(E)e^{-E/kT}\,\mathrm{d}E \qquad (3)$$

(quantum mechanically) (semiclassically)

E shall always be taken to mean energy in excess of zero-point energy, so that the first term of the quantum mechanical partition function will be unity, and the lower limit of the integral in the semiclassical expression for Q will be zero. Usually Q for bound states is desired, in which case the summation or integration should end at some large, but finite, value of E. However, it is preferable to keep the definition of Q as an integral with limits (0, ∞), with the understanding that above some large and finite E, when there are no more bound states, $N(E)$ is zero.

The absence of a subscript in the above definitions is to indicate that they apply to a collection of states belonging to any type of degree of freedom. A subscript v will be used for vibrational states, subscript r for rotational states, and subscript vr for vibrational–rotational[3] states; for example, $N_r(E)$,

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(2) A short and largely historical review has been given previously by H. M. Rosenstock, *Advan. Mass Spectrom.*, 4, 523 (1968).

(3) The term means that the available energy is shared between vibrational and rotational states, but does *not* imply that vibrational and rotational states are coupled, *i.e.*, that the expression for total energy has cross-terms involving both vibrations and rotations.

$W_r(E)$, and $G_{vr}(E)$ are, respectively, the density of rotational states, the number of vibrational states, and the total number of vibrational–rotational states, all at energy E. Similarly, Q_v, Q_r, and Q_{vr} represent, respectively, the vibrational, rotational, and vibrational–rotational partition function.

The subscripts are also meant to have a quantitative significance, in the sense that, unless assigned an explicit value ($r = 2$, $v = 3$, etc.), it is understood the formula in question refers to a total of r rotors (r as defined in eq 40) and v oscillators.

Quantum mechanically, only discrete values of E are allowed, so that $W(E)$ will be zero everywhere except at those values of E which are allowed. Consequently, $W(E)$ is, in principle, a string of δ functions, and $G(E) = \Sigma^{E}{}_{E=0}W(E)$ is a step function (see Figure 1). When E is sufficiently high and the number of degrees of freedom not too small, there will be an allowed state at almost every energy, so that $W(E)$ becomes practically a smooth function of E; under these conditions the density of states $N(E)$ is the more useful and convenient representation. $G(E) = \int_0^\infty N(E)\, dE$ is then obviously also a smooth function of E. Conversely, when the allowed values of E are widely spaced, as when E is low and the number of degrees of freedom small, $N(E)$ and $G(E) = \int_0^\infty N(E)\, dE$ will not be a useful representation.

It should be obvious that $N(E)$, $W(E)$, or $G(E)$ cannot be calculated unless the allowed energy levels of the system under consideration are known. The calculation of these levels is a purely quantum mechanical problem which is not dealt with here, because for separable degrees of freedom it is sufficient to consider only energy levels for a system of independent oscillators and/or rotors, and these can be found in any standard treatise on quantum mechanics.[4]

II. Direct Evaluation of W(E) and G(E) in Simple Systems

For the purpose of illustrating the general principles involved in the enumeration of vibrational states, it is useful to consider a few simple systems at low energies where $W_v(E)$ and $G_v(E)$ can be easily calculated by hand exactly. Generalization to more complex oscillator systems and higher energies should be obvious. The practical interest of these simple calculations is that, as we shall see, direct enumeration of states is the only accurate method for calculating $W_v(E)$ [or $N_v(E)$] and $G_v(E)$ at low energies.

Direct enumeration of $N_{vr}(E)$ and $G_{vr}(E)$ for vibrational–rotational systems will be considered in section VI.

A. INDEPENDENT HARMONIC OSCILLATORS

In the case of a single harmonic oscillator of frequency ν, the energy levels are nondegenerate and are given by

$$E = nh\nu \qquad n = 0, 1, 2, \ldots \tag{4}$$

where n is the vibrational quantum number and E is energy in excess of zero-point energy. Hence $W(E)$ is unity when $E = nh\nu$ and zero otherwise, $G(E) = \Sigma_n 1$, and $N(E) = 1/h\nu =$ constant. These relations are illustrated graphically in Figure 1.

When there are several independent oscillators, $W(E)$ is the number of ways a given total energy E can be distributed among the oscillators. The problem is particularly simple when the oscillators are all of the same frequency. Suppose their number is q; if the total energy E is regarded as n quanta ($E = nh\nu$), $W(E)$ will be the number of ways n quanta can be distributed among q oscillators, an elementary combinatorial problem which has the solution[5]

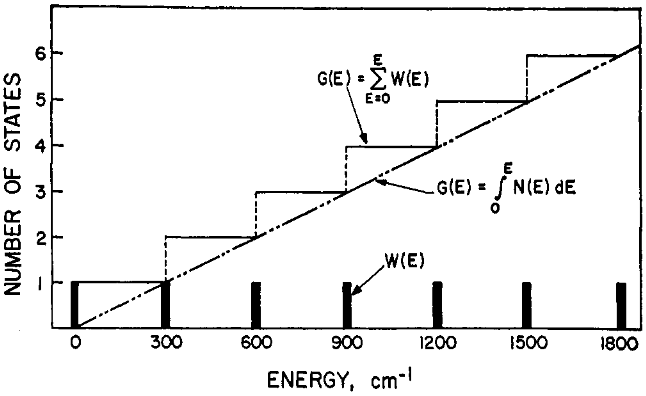

Figure 1. Number of states for one harmonic oscillator of frequency 300 cm^{-1}. Heavy vertical line is the quantum mechanical degeneracy $W(E)$. The step-function represents the quantum mechanical sum of states $G(E)$. The line ------ is the continuous-function approximation to $G(E)$. The density $N(E)$ is the slope of this line, which in the present instance is constant at 1/300 (cm^{-1})$^{-1}$. Quantum mechanically, $G(0) = 1$. The continuous-function approximation is drawn to give the classical result $G(0) = 0$. The thickness of the line for $W(E)$ represents δE, the allowance in E. Graphs of harmonic $G(E)$ *vs.* E for a number of polyatomic molecules can be found in G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 2466 (1963).

$$W_{v=q}(E) = \binom{n+q-1}{n} = \frac{(n+q-1)!}{n!(q-1)!} \tag{5}$$

and

$$G_{v=q}(E) = \sum_{n=0}^{n} \frac{(n+q-1)!}{n!(q-1)!} = \frac{(n+q)!}{n!q!} \tag{6}$$

It is convenient to regard the q oscillators, all of the same frequency ν, as *one* q-fold degenerate oscillator. If we now have a total of v oscillators belonging to s groups of frequencies, some oscillators will be degenerate if $v > s$; the problem then reduces to the equivalent, and somewhat simpler, problem of s oscillators, the ith being q_i-fold degenerate ($v = \Sigma^s{}_{i=1}q_i$). The total energy is $E = \Sigma^s{}_{i=1}n_ih\nu_i$, where n_i and ν_i are the total quantum number and frequency, respectively, of the ith oscillator. The number of ways of distributing $\Sigma^s{}_{i=1}n_i$ quanta among the s oscillators, with n_i quanta in the ith, is

$$\prod_{i=1}^{s} \frac{(n_i + q_i - 1)!}{n_i!(q_i - 1)!} \tag{7}$$

a simple product, since the oscillators are assumed to be independent. If some of the frequencies are commensurable, a given value of E can be realized by several sets of n_i's, so that in general

$$W_v(E) = \sum_{\Sigma n_i h\nu_i = E} \left[\prod_{i=1}^{s} \frac{(n_i + q_i - 1)!}{n_i!(q_i - 1)!} \right] \tag{8}$$

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[4] See, for example, H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," Wiley, New York, N. Y., 1944.

[5] J. E. Mayer and M. G. Mayer, "Statistical Mechanics," Wiley, New York, N. Y., 1940, Appendix VII.

where the summation is taken over all sets of positive, integral (zero included) values of n_i satisfying $\Sigma^s_{i=1} n_i h\nu_i = E$. Similarly

$$G_v(E) = \sum_{\Sigma n_i h\nu_i \leq E} \left[\prod_{i=1}^{s} \frac{(n_i + q_i - 1)!}{n_i!(q_i - 1)!} \right] \qquad (9)$$

where the summation is taken over all sets of n_i's such that all values of $\Sigma^s_{i=1} n_i h\nu_i$ between 0 and E are generated.

A simple example of seven oscillators with four different frequencies is worked out explicitly in Table I. In this case the overtones are partially commensurable, so that the energy of 1000 cm^{-1}, for example, is realized by four sets of n_i's.

Table I

$W_v(E)$ and $G_v(E)$ by Exact Enumeration of States for a System of Independent Oscillators at $E \leq 1000$ cm^{-1} [a,b]

n_i				Morse			Harmonic		
i =									
1	*2*	*3*	*4*	E	$W_v(E)$	$G_v(E)$	E	$W_v(E)$	$G_v(E)$
0	0	0	0	0	1	1	0	1	1
1	0	0	0	196	1	2	200	1	2
0	1	0	0	294	3	5	300	3	5
2	0	0	0	388	1	6	400	1	6
1	1	0	0	490	3	9	500	3	9
3	0	0	0	576	1	10	600	7	16
0	2	0	0	582	3	13			
0	2	0	0	588	3	16			
2	1	0	0	682	3	19	700	5	21
0	0	1	0	686	2	21			
4	0	0	0	760	1	22	800	7	28
1	2	0	0	778	3	25			
1	2	0	0	784	3	28			
0	3	0	0	864	3	31	900	15	43
3	1	0	0	870	3	34			
0	3	0	0	876	6	40			
0	3	0	0	882	1	43			
1	0	1	0		2				
5	0	0	0	940	1	44	1000	14	57
2	2	0	0	970	3	47			
2	2	0	0	976	3	50			
0	1	1	0	980	6	57			
0	0	0	1		1				

[a] The frequencies in cm^{-1} are (degeneracies in brackets): 200 (1), 300 (3), 700 (2), 1000 (1). If the oscillators are harmonic, total energy E in cm^{-1} is $E = 200n_1 + 300n_2 + 700n_3 + 1000n_4$. Here n_i (*cf.* eq 7) is the total quantum number of the ith q_i-fold degenerate oscillator, defined as $n_i = \Sigma^{q_i}_{j=1} n_j$, where the n_j's are the quantum numbers of the individual oscillators in the degenerate set. If the oscillators are Morse oscillators, the anharmonicity coefficient is assumed for simplicity to be $x = 0.01$ for all oscillators, and the total energy E in cm^{-1} is then $E = 200m_1 + 300m_2 + 700m_3 + 1000m_4$, where, since eq 7 no longer applies, $m_i = \Sigma(0.99n_j - 0.01n_j^2)$, the n_j's being the quantum numbers of the individual oscillators of the q_i-fold degenerate set, as above. The sum is taken over all sets of n_j's such that $\Sigma^{q_i}_{j=1} n_j = n_i$. [b] At values of E not listed, there are no states, so that $W_v(E)$ is zero and $G_v(E)$ is the same as for the next lower listed E.

B. INDEPENDENT ANHARMONIC OSCILLATORS

When the oscillators are independent and anharmonic, the procedure for determining $W_v(E)$ and $G_v(E)$ by direct counting is more tedious. A specific example is worked out in Table I for the case of Morse oscillators, whose individual energy levels are given by

$$E = h\nu[n(1 - x) - n^2x] \qquad (10)$$

where x is the anharmonicity constant. The basic frequency ν of each oscillator is assumed to be the same as that of its harmonic counterpart. Energy levels of an anharmonic oscillator are no longer integral multiples of the basic frequency, and therefore oscillators of the same basic frequency cannot be usefully combined into degenerate sets, since even if the total quantum number is the same, some combinations of levels have slightly different energies. For example, the oscillator with $\nu = 300$ cm^{-1} has energy levels at 0, 294, 582, ... cm^{-1}. This oscillator is triply degenerate; let us label the three members a, b, c. If the total quantum number $n_i = n_a + n_b + n_c = 2$, we can have, for example, $n_a = 2$, $n_b = 0$, $n_c = 0$, in which case the energy is 582 cm^{-1}; by permutation of the labels there are two other ways of realizing this energy, making this a total of three states at 582 cm^{-1}. We can also have $n_i = 2$ with $n_a = 1$, $n_b = 1$, $n_c = 0$, in which case the energy is $2 \times 294 = 588$ cm^{-1}, and by permutation of the labels are obtained two other states at this energy, for a total of three. In the harmonic case, all such states have energy 600 cm^{-1}, and their number (six) follows immediately from eq 5.

For the purpose of enumerating states by computer in more complex systems, the procedure indicated in Table I can be systematized.[6]

C. INDEPENDENT RIGID FREE ROTORS

The energy levels of a one-dimensional rigid free rotor are given by

$$E = m^2 \frac{\hbar^2}{2I} \qquad m = 0, 1, 2, \ldots \qquad (11)$$

where I is the moment of inertia and m the rotational quantum number. Except for the nondegenerate level at $m = 0$, all other levels are doubly degenerate. Therefore $W_{r=1}(E) = 2$, except that $W_{r=1}(0) = 1$, and $G_{r=1}(E) = 2m^* + 1$, where $m^* = (2IE/\hbar^2)^{1/2}$; *i.e.*, m^* is the quantum number corresponding to the (allowed) energy E at which $G(E)$ is to be calculated. If for reasons of symmetry[7] only each σ-th value of m is allowed, then $G_{r=1}(E) = 2(m^*/\sigma) + 1$.

The energy levels of a two-dimensional rigid free rotor are given by

$$E = J(J + 1)\frac{\hbar^2}{2I} \qquad J = 0, 1, 2, \ldots \qquad (12)$$

where I is again the moment of inertia and J the rotational quantum number. Every level is $(2J + 1)$-fold degenerate. Hence $W_{r=2}(E) = 2J^* + 1$, $G_{r=2}(E) = \Sigma_{J=0}^{J=J^*}(2J + 1) = (J^* + 1)^2$, where J^* is, as before, the rotational quantum number corresponding to the energy at which $G_{r=2}(E)$ is to be calculated. If for reasons of symmetry only every σ-th value of J is allowed, then $G_{r=2}(E) = [(J^*/\sigma) + 1](J^* + 1)$.

For a collection of independent rigid free rotors, $W_r(E)$ and $G_r(E)$ could be determined by a direct enumeration procedure similar to that used for oscillators in Table I. Such a tedious

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(6) R. E. Harrington, Ph.D. Thesis, University of Washington, 1960, Appendix I.

(7) Reference 5, p 174 ff.

process is not really necessary because an analytic function expression, sufficiently accurate for most applications, can be easily obtained for $G_r(E)$ and its derivative.

Observe that for a typical value of $I \sim 5 \times 10^{-40}$ g cm^2, the ratio $\hbar^2/2I \sim 5$ cm^{-1}. If $\sigma = 1$, the rotational energy corresponding to, say, $J = 10$, is $\sim$500 cm^{-1} and so $G_{r=2}(500) = 121$, *i.e.*, roughly one state every 5 cm^{-1} on the average. Contrast this with a (nondegenerate) harmonic oscillator having a frequency of 500 cm^{-1} (this is, in fact, a rather low frequency for a typical molecular oscillator); therefore, $G_{v=1}(500) = 1$, *i.e.*, one state every 500 cm^{-1}. Thus $G_r(E)$ for rotors is almost a continuous function of E, and $N_r(E)$, rather than $W_r(E)$, would be the more convenient representation.

III. Approximation to N(E) and G(E). General Considerations

A. NEED FOR AN APPROXIMATION

The fairly complex bookkeeping required even in the almost trivial examples of counting of states worked out explicitly in the previous section suggests that, at energies of chemical interest where 10^{10} states or more might be involved, direct enumeration of states is not a feasible procedure, except by computer, and even there machine time becomes quite appreciable at high energies.[8] A vast expenditure of machine time on exact sums or densities of states is quite unwarranted in the course of a unimolecular rate calculation since the number and nature of the approximations that have to be made in the theory is such that these densities or sums of states are substituted into expressions that are at best only approximate.

Ideally, we would like to replace the time-consuming enumeration of individual states by an analytical function expression for $G(E)$ [as a minimum, the function should at least have a first derivative so that $N(E)$ can be obtained], and in the process we would be willing to trade some accuracy for a significantly shortened machine time. As a reasonable compromise, one might wish to find an approximate expression for $G(E)$ giving 10% accuracy or so, in exchange for a reasonable machine time, *i.e.*, a few minutes for the 50 or 100 different energy values at which $G(E)$ or $N(E)$ might be required.

B. NUMBER OF STATES AS VOLUME IN PHASE SPACE

A closed-form approximation to $N(E)$ or $G(E)$ can be in principle obtained from statistical ensemble theory. In classical statistical mechanics, the density of states at energy E is the "volume" in phase space of the hypersurface E = constant of thickness dE, and is given by[9]

$$N(E)\mathrm{d}E = \int_{E \le H \le E+\mathrm{d}E} \cdots\cdots \int \prod_{i=1}^{k} \mathrm{d}p_i \mathrm{d}q_i \tag{13}$$

where q_i is the generalized coordinate, p_i is its conjugate momentum, and $H(p_i,q_i)$ is the Hamiltonian of the system under consideration, assumed to have k degrees of freedom. The total number of states $G(E)$ is the total volume of phase space enclosed by the hypersurface of constant energy E = constant, and is therefore given by

$$G(E) = \int_{0 \le H \le E} \cdots \int \prod_{i=1}^{k} \mathrm{d}p_i \mathrm{d}q_i \tag{14}$$

A statistical ensemble where E = constant is called the microcanonical ensemble, and $N(E)$ and $G(E)$ are therefore sometimes referred to as the microcanonical density and sum of states, respectively.

The evaluation of the multiple integrals in eq 13 and 14 is difficult and tedious; more convenient is the semiclassical equivalent of eq 14. Semiclassically, E is taken as a (continuous) function of the quantum numbers $n_1, n_2, \ldots, n_k$

$$E = \mathrm{f}(n_1, n_2, \ldots, n_k) \tag{15}$$

where n_i is the quantum number for the ith degree of freedom. If ω_i is the degeneracy (*i.e.*, the number of states) associated with n_i, then

$$G(E) = \int_{\mathrm{f}(n_1,n_2,\ldots,n_k) \le E} \cdots\cdots \int \omega_1 \mathrm{d}n_1\, \omega_2 \mathrm{d}n_2 \ldots \omega_k \mathrm{d}n_k \tag{16}$$

where the integration is over a range of quantum numbers such that the total energy does not exceed the specified value. The integral in (16) is difficult to evaluate for a general case, but if the degrees of freedom are separable (*i.e.*, independent), there are no cross-terms in the energy expression and the function f can often be written in the form of a sum

$$\mathrm{f}(n_1, n_2, \ldots, n_k) = \sum_{i=1}^{k} \left(\frac{n_i}{a_i}\right)^{b_i} \tag{17}$$

where a_i and b_i are constants. With this form of f, the integral (16) is known as Dirichlet's integral which has a simple solution.[10] $N(E)$ is then easily obtained by differentiation with respect to E.

As an example, $G_r(E)$ and $N_r(E)$ are calculated for a collection of k independent two-dimensional rigid free rotors ($r = 2k$). The total energy is clearly

$$E = \sum_{i=1}^{k} J_i(J_i + 1)\frac{\hbar^2}{2I_i} \tag{18}$$

where J_i and I_i are the quantum number and moment of inertia, respectively, of the ith rotor. Assuming that I_i is not too small, so that the rotors are sufficiently semiclassical and integration may be performed, it follows that

$$G_{r=2k}(E) = \int \cdots \int \prod_i (2J_i + 1)\frac{\mathrm{d}J_i}{\sigma_i} \tag{19}$$

subject to

$$\sum_{i=1}^{k} \frac{J_i(J_i + 1)\hbar^2}{2I_i} \le E$$

The result is

$$G_{r=2k}(E) = \prod_{i=1}^{k} \left(\frac{2I_i}{\hbar^2\sigma_i}\right) \frac{E^k}{\Gamma(k + 1)} \tag{20}$$

where σ_i is the symmetry number of the ith rotor and $\Gamma(k + 1) = k!$ Differentiation with respect to E yields

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[8] As a very rough guide, $G(E)$ in steps of 100 cm^{-1} by actual counting of states in a moderately complex molecular system, would require machine time (IBM 360) of the order of seconds up to 5000 cm^{-1}, of the order of minutes up to about 15,000 cm^{-1}, and of the order of hours above about 30,000 cm^{-1}.

[9] R. C. Tolman, "Principles of Statistical Mechanics," Oxford University Press, New York, N. Y., 1938, p 490 ff.

[10] See ref 9, Appendix II.

$$N_{r-2k}(E) = \prod_{i=1}^{k}\left(\frac{2I_i}{\hbar^2\sigma_i}\right)\frac{E^{k-1}}{\Gamma(k)} \tag{21}$$

Equations 20 and 21 represent, as shown in section III, a very good approximation to $N_r(E)$ and $G_r(E)$. Unfortunately, the classical approach described here is unsuitable for calculating the vibrational $N_v(E)$ and $G_v(E)$ with any decent accuracy because of the much larger quantization of vibrational states. Even though the resulting inaccurate expressions can be corrected empirically to yield quite accurate harmonic $N_v(E)$ and $G_v(E)$, there is another, much more general approach to the problem of calculating $N(E)$ and $G(E)$. It is based on the inversion of the partition function and has the virtue of being very simple mathematically and of yielding approximations of high accuracy; all the semiclassical-type expressions can be easily obtained in this context as a special case.

Because of the inherent simplicity of the method, further treatment and development of approximations to $N(E)$ and $G(E)$ will be based entirely on the inversion of the partition function.

IV. Inversion of the Partition Function

In this section are derived a few general relations which will be useful later.

A. PARTITION FUNCTION AS A LAPLACE TRANSFORM[11]

The partition function Q can be written, with $1/kT = s$, in the form

$$Q = \int_0^\infty N(E)e^{-Es}\,dE \tag{22}$$

This integral is a function of s, or symbolically

$$Q = l(s) = \mathcal{L}\{N(E)\} \tag{23}$$

where $\mathcal{L}\{\ \}$ denotes the operation to be performed on the function inside the compound bracket, *i.e.*, multiplication by $\exp(-Es)$ and integration with respect to E between 0 and ∞. $\mathcal{L}\{N(E)\}$ is called the Laplace transform of $N(E)$ and s is the transform parameter. The interest of this representation for our purpose is that there exist standard ways for reversing the operation, *i.e.*, $N(E)$ can be obtained from Q

$$N(E) = \mathcal{L}^{-1}\{l(s)\} \tag{24}$$

where $\mathcal{L}^{-1}\{\ \}$ denotes the inverse Laplace transform. The reciprocal correspondence between a function and its transform is the subject of operational calculus which has its own theorems and rules for operations on, and relations between, $N(E)$ and $l(s)$. These may be found in standard treatises[12] on the Laplace transformation; there are also extensive tables[13] of transform pairs, so that simple problems may be solved by merely finding the appropriate entry in the tables.

The integration theorem of the Laplace transformation, applied to eq 23, asserts that

$$\frac{l(s)}{s} = \mathcal{L}\left\{\int_0^E N(x)\mathrm{d}x\right\} = \mathcal{L}\{G(E)\} \tag{25}$$

since by eq 2 the integral of density is the sum of states. Inverting eq 25 gives $G(E) = \mathcal{L}^{-1}\{l(s)/s\}$, which can be combined with eq 24 in the more compact expression

$$\left.\begin{matrix} N(E) \\ (k=0) \\ G(E) \\ (k=1) \end{matrix}\right\} = \mathcal{L}^{-1}\left\{\frac{l(s)}{s^k}\right\} \tag{26}$$

Sections V, VI, and VII involve essentially trivial forms of $l(s)$, so that the inverse transform (26) may be found in tables and the result easily verified by very unsophisticated calculation. The actual evaluation of (26) for more complicated forms of $l(s)$ is given in sections VIII and IX.

B. CONVOLUTION

Suppose there are two independent systems (indexed 1 and 2), for which

$$l_1(s) = \mathcal{L}\{N_1(E)\} \qquad l_2(s) = \mathcal{L}\{N_2(E)\} \tag{27}$$

then according to the convolution theorem

$$\begin{aligned}\mathcal{L}^{-1}\{l_1(s)l_2(s)\} &= \int_0^E N_1(x)N_2(E-x)\,\mathrm{d}x \quad \text{or} \\ &= \int_0^E N_1(E-x)N_2(x)\,\mathrm{d}x\end{aligned} \tag{28}$$

Since by definition $l_1(s) \equiv Q_1$, $l_2(s) \equiv Q_2$, then

$$l_1(s)l_2(s) \equiv Q_1Q_2 = Q_{1,2} \equiv l_{1,2}(s) \tag{29}$$

where $Q_{1,2}$ is the partition function of the combined system, assumed to factorize into Q_1 and Q_2. The inverse transform of $Q_{1,2}$ is $N_{1,2}(E)$, the density of states of the combined system, and from eq 28 and 29 it follows immediately

$$\begin{aligned}N_{1,2}(E) &= \int_0^E N_1(E-x)N_2(x)\,\mathrm{d}x \quad \text{or} \\ &= \int_0^E N_1(x)N_2(E-x)\,\mathrm{d}x\end{aligned} \tag{30}$$

In other words, if the partition function factorizes into two factors, the densities of separated and combined systems are related by convolution.[14] The quantum mechanical analog of eq 30 is

$$N_{1,2}(E) = \sum_{x=0}^{E} N_1(E-x)N_2(x)\,\delta x = \sum_{x=0}^{E} N_1(E-x)W_2(x), \text{ etc.} \tag{31a}$$

or, after multiplying both sides by δE

$$W_{1,2}(E) = \sum_{x=0}^{E} W_1(E-x)W_2(x), \text{ etc.} \tag{31b}$$

where $W_1(E)$ and $W_2(E)$ are the number of states of constituent systems, and $W_{1,2}(E)$ is the number of states of the combined system.[15]

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[11] S. H. Bauer, *J. Chem. Phys.*, 6, 403 (1938); 7, 1097 (1939).

[12] See, for example, G. Doetsch, "Guide to the Applications of Laplace Transforms," Van Nostrand, New York, N. Y., 1961.

[13] For example, G. E. Roberts and H. Kaufman, "Tables of Laplace Transforms," W. B. Saunders, Philadelphia, Pa., 1966.

[14] R. Kubo, "Statistical Mechanics," North-Holland Publishing Co., Amsterdam, 1965, p 103.

[15] For two degenerate independent harmonic oscillators, $W_1(E)$ and $W_2(E)$ are each given by the appropriate form of eq 5; when these are substituted into eq 31b, eq 8 is recovered.

Writing $L(s) = l(s)/s$, there follows from eq 25 for a combined system consisting of parts 1 and 2

$$L_{1,2}(s) = \mathcal{L}\{G_{1,2}(E)\} = \frac{l_1(s)l_2(s)}{s} = L_1(s)l_2(s) \text{ or } l_1(s)L_2(s) \quad (32)$$

Applying the convolution theorem to the product $L(s)l(s)$

$$\begin{aligned} G_{1,2}(E) &= \mathcal{L}^{-1}\{L_1(s)l_2(s)\} = \int_0^E G_1(E - x)N_2(x)\,\mathrm{d}x \quad \text{or} \\ &\qquad \int_0^E G_1(x)N_2(E - x)\,\mathrm{d}x \\ &= \mathcal{L}^{-1}\{l_1(s)L_2(s)\} = \int_0^E N_1(x)G_2(E - x)\,\mathrm{d}x \quad \text{or} \\ &\qquad \int_0^E N_1(E - x)G_2(x)\,\mathrm{d}x \end{aligned} \quad (33)$$

The quantum mechanical equivalent of the above relations is

$$G_{1,2}(E) = \sum_{x=0}^{E} G_1(E - x)W_2(x), \text{ etc.} \quad (34)$$

Therefore the total sum of states of a combined system whose partition function factorizes into two factors is given by the convolution of the *density* (or number of states) of one part and the *sum of states* of the other part.

The result (33) or (34), like the previous results (30) or (31), depends on the factorizability of the partition function for the total system, $Q_{1,2}$, into two parts, Q_1 and Q_2. Such factorizability arises if there are no cross-terms in the total energy, *i.e.*, if the degrees of freedom involved in Q_1 are independent of, and therefore separable from, those in Q_2.

Therefore the general problem of calculating $N(E)$, $W(E)$, or $G(E)$ for a complex system of many degrees of freedom can be sometimes simplified by calculating these functions separately for each of two (or more) groups of degrees of freedom which are separable, and then by obtaining the density and related functions for the total system by convolution. Such two groups of degrees of freedom that can be usefully treated separately are the vibrational and rotational degrees of freedom because of their very different quantization.

V. Approximation to N(E) and G(E) for Rotational States

A good approximation to $N_r(E)$ and $G_r(E)$ can be obtained very easily and therefore will be considered first.

A. SEPARABILITY OF ROTATIONS

It shall be assumed that in *every* case the rotational degrees of freedom of a molecule can be represented as a collection of free independent one- and two-dimensional rigid rotors. The one-dimensional rotors (partition function $Q_{r=1}$), characterized by one axis of rotation and one moment of inertia, will be useful as a representation of internal rotations, and the two-dimensional rotor (partition function $Q_{r=2}$), characterized by two axes of rotation and two equal moments of inertia, will be useful as a representation of external (or overall) rotations. If the three external rotations of a symmetric top are involved, it shall be assumed that the rotation having the smallest (or largest) moment of inertia is separable from the other two, so that the partition function for the three rotations of a symmetric top ($Q_{r=3}$) can be written

$$Q_{r=3} = Q_{r=1}Q_{r=2} \quad (35)$$

Similarly, if the three external rotations of an asymmetric (or similar) top are involved, with three unequal moments of inertia, it shall be assumed that the total partition function $Q_{r=3}$ is the product of three one-rotor partition functions

$$Q_{r=3} = Q'_{r=1}Q''_{r=1}Q'''_{r=1} \quad (36)$$

where the primes denote that the moments of inertia are different. Hence it will suffice to consider only $Q_{r=1}$ and $Q_{r=2}$.

B. CLASSICAL ROTATIONAL PARTITION FUNCTION Q_r AND ITS INVERSION

The energy levels for a one-dimensional rotor are given by eq 11, and therefore the partition function is

$$Q_{r=1} = \frac{2}{\sigma}\int_0^\infty \exp[-m^2\hbar^2/2IkT]\,\mathrm{d}m = \frac{(8\pi^3IkT)^{1/2}}{h\sigma} \quad (37)$$

The energy levels of a two-dimensional rotor are given by eq 12, and hence

$$Q_{r=2} = \frac{1}{\sigma}\int_0^\infty (2J + 1) \times \exp[-J(J + 1)\hbar^2/2IkT]\,\mathrm{d}J = \frac{8\pi^2IkT}{h^2\sigma} \quad (38)$$

Division by σ has been performed in both cases to allow for symmetry considerations.

The results (37) and (38) assume that the rotations behave classically, *i.e.*, that the spacing between energy levels is small (moment of inertia I not too small, *i.e.*, larger than that for H_2 or D_2), and that integration is permissible (temperature above ~20 °K). These conditions are usually satisfied in systems of chemical interest.

In the general case when there are k_1 one-dimensional rotors and k_2 two-dimensional rotors, all separable, the total partition function is

$$Q_r = Q'_r(kT)^{r/2} \quad (39)$$

where

$$Q'_r = \left(\frac{8\pi^2}{h^2}\right)^{r/2}\pi^{k_1/2}\prod_{i=1}^{k_1}\left(\frac{I_i}{\sigma_i^2}\right)^{1/2}\prod_{j=1}^{k_2}\left(\frac{I_j}{\sigma_j}\right) \quad (40)$$

and $r = k_1 + 2k_2$. The exponent r may be considered to be the total number of rotations; note that a two-dimensional rotor counts for two rotations.

In Laplace transform notation

$$Q_r \equiv l_r(s) = Q'_r s^{-r/2} \qquad (s = 1/kT) \quad (41)$$

From tables of Laplace transforms

$$\begin{aligned} \mathcal{L}^{-1}\{s^{-r/2}\} &= \frac{E^{(r/2)-1}}{\Gamma(r/2)} \\ \mathcal{L}^{-1}\{s^{-(1+r/2)}\} &= \frac{E^{r/2}}{\Gamma(1 + r/2)} \end{aligned} \quad (42)$$

(Γ = gamma function) so that there follows immediately the result

$$N_r(E) = \frac{Q'_rE^{(r/2)-1}}{\Gamma(r/2)}, \quad G_r(E) = \frac{Q'_rE^{r/2}}{\Gamma(1 + r/2)} \quad (43)$$

With $r = 2k$, this is the same result obtained more laboriously from Dirichlet's integral in section III.B.

Table II

Comparison of Exact and Approximate $N(E)$ and $G(E)$ for One One-Dimensional Rigid Free Rotor[a]

m^*	*E, cm*$^{-1}$	*Exact G(E) (eq 46)*	*Approx G(E) (eq 45)*	*Error, %*	*Exact N(E) (eq 47)*	*Approx N(E) (eq 45)*	*Error, %*
0	0	1	0	−100	0.04444	∞	∞
3	45	3	2	−30	0.014815	0.02222	+49
9	405	7	6	−14	0.006349	0.007407	+17
12	720	9	8	−11	0.004938	0.005556	+13
21	2205	15	14	−7	0.002963	0.003175	+7
30	4500	21	20	−5	0.002116	0.002222	+5

[a] Rotor is assumed to have $\hbar^2/2I = 5$ cm^{-1}, $\sigma = 3$.

C. TEST OF THE APPROXIMATION

For a one-dimensional rotor, $r = 1$, and noting that $\Gamma(1/2) = \pi^{1/2}$, $\Gamma(3/2) = {}^1/_2\pi^{1/2}$, eq 43 yields

$$N_{r=1}(E) = \frac{(8\pi^2I)^{1/2}}{h\sigma}E^{-1/2}$$
$$G_{r=1}(E) = \frac{2(8\pi^2I)^{1/2}}{h\sigma}E^{1/2} \tag{44}$$

Since in terms of the notation used in section II, E in this case is equal to $E = (m^*)^2h^2/8\pi^2I$, eq 44 are equivalent to

$$N_{r=1}(E) = \left(\frac{8\pi^2I}{h^2}\right)\left(\frac{1}{m^*\sigma}\right)$$
$$G_{r=1}(E) = \frac{2m^*}{\sigma} \tag{45}$$

The exact result for $G_{r=1}(E)$ is, as seen in section II.C

$$(\text{exact})G_{r=1}(E) = \frac{2m^*}{\sigma} + 1 \tag{46}$$

while for the exact $N_{r=1}(E)$ it is

$$(\text{exact})N_{r=1}(E) = \frac{\Delta G_{r=1}(E)(\text{exact})}{\Delta E} =$$
$$\frac{2}{(h^2/8\pi^2I)[(m^* + \sigma)^2 - (m^*)^2]} = \frac{8\pi^2I}{h^2}\left[\frac{2}{2m^*\sigma + \sigma^2}\right] \tag{47}$$

Thus the approximation for $N_{r=1}(E)$ (eq 44 or 45) yields essentially the exact result when $\sigma = 1$; when $\sigma \neq 1$, the approximation gives a slightly high density at low m^*, and the result becomes exact when $2m^*\sigma \gg \sigma^2$. Compared with the exact result (46), the approximation for $G_{r=1}(E)$ (eq 44 or 45) gives a slightly low result, particularly when m^* is low and σ is high

A numerical comparison of exact and approximate values of $N_{r=1}(E)$ and $G_{r=1}(E)$ is shown in Table II for the specific example of the internal rotation of a methyl group which is a case that comes up often in practice. The exact value of the *reduced* moment of inertia of the methyl group, which is the value of I to be used in the formulas, depends on the molecular framework to which the CH_3 group is attached, but $I \sim 5 \times 10^{-40}$ g cm^2 is probably a reasonable value, and this gives $\hbar^2/2I = 5$ cm^{-1}. Because of the threefold symmetry of the methyl group, only every third value of m is allowed,[16] so that $\sigma = 3$. The table shows that the approximation formulas (eq 45) give tolerable results (10% accuracy or better) when the rotational energy is about 1000 cm^{-1} or higher. A nuisance is the approximate $N_{r=1}(E)$ which goes to infinity as $E \rightarrow 0$, and this must be taken into account in programming.

It may be noted that $N_{r=1}(E)$ and $G_{r=1}(E)$ as given by eq 44 can be rendered exact by making them conform to eq 47 and 46, respectively; in the latter case, this involves merely adding unity on the right-hand side of eq 44.

For two rotations, $r = 2$ and noting that $\Gamma(1) = \Gamma(2) = 1$, it follows from (43) that

$$N_{r=2}(E) = Q'_{r=2} \qquad G_{r=2}(E) = Q'_{r=2}E \tag{48}$$

Thus the approximate density of states for two rotations is a constant. Note that the constant $Q'_{r=2}$ is equal to $8\pi^3(I_1I_2)^{1/2}/h^2\sigma_1\sigma_2)$ if the two rotations consist of two (independent) one-dimensional rotors (indexed 1 and 2), and equal to $8\pi^2I/h^2\sigma$ if they consist of one two-dimensional rotor.

When dealing with one two-dimensional rotor, then, in terms of the notation of section II, $E = J^*(J^* + 1)h^2/8\pi^2I$, so that (48) is equivalent to

$$G_{r=2}(E) = \frac{J^*}{\sigma}(J^* + 1) \tag{49}$$

which may be compared with the exact result obtained previously in section II.C

$$(\text{exact})G_{r=2}(E) = \left(\frac{J^*}{\sigma} + 1\right)(J^* + 1) \tag{50}$$

The exact density of a two-dimensional rotor is given by

$$(\text{exact})N_{r=2}(E) = \frac{\Delta G_{r=2}(E)(\text{exact})}{\Delta E} =$$
$$\frac{\left(\frac{J^*}{\sigma} + 2\right)(J^* + 2) - \left(\frac{J^*}{\sigma} + 1\right)(J^* + 1)}{(h^2/8\pi^2I)[(J^* + \sigma)(J^* + \sigma + 1) - J^*(J^* + 1)]} =$$
$$\frac{8\pi^2I}{h^2}\left[\frac{(J^*/\sigma) + J^* + 3}{2\sigma J^* + \sigma + \sigma^2}\right] \tag{51}$$

so that the exact density decreases slightly as J^* increases.

In Table III is presented a numerical comparison of exact and approximate values of $N_{r=2}(E)$ and $G_{r=2}(E)$ in one specific case where $h^2/8\pi^2I = 5$ cm^{-1} and $\sigma = 1$. In general, the approximations give low results, which are within 10% of the exact value above 100 cm^{-1} for the density, and above 500 cm^{-1} for the sum of states. With a higher assumed σ, the agreement would be slightly worse.

In summary, then, the classical approximation to $N_r(E)$ and $G_r(E)$ is mathematically very simple and gives an acceptable accuracy at energies above about 500 cm^{-1}; for a chemi-

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(16) See ref 4, p 359.

Table III

Comparison of Exact and Approximate $N(E)$ and $G(E)$ for One Two-Dimensional Rigid Free Rotor[a]

J^*	E, cm^{-1}	Exact $G(E) = (J^* + 1)^2$	Approx $G(E) = J^*(J^* + 1)$	Error, %[b]	Exact $N(E)$[c]	Approx $N(E) = 2I/\hbar^2$	Error, %[b]
0	0	1	0	100	0.3	Density	−33
1	10	4	2	−50	0.25	constant	−25
2	30	9	6	−33	0.233	at	−15
3	60	16	12	−25	0.225	0.200	−10
4	100	25	20	−20	0.220	(cm^{-1})$^{-1}$	−10
5	150	36	30	−17	0.2166		−8
10	550	121	110	−9	0.2091		−4
30	4650	961	930	−3	0.2032		−2

[a] Rotor is assumed to have $\hbar^2/2I = 5$ cm^{-1}, $\sigma = 1$. [b] % error calculated relative to exact value. Units of $N(E)$ are (cm^{-1})$^{-1}$.

[c] $$\text{Exact } N(E) = \frac{\Delta G(E)(\text{exact})}{\Delta E} = \frac{(J^* + 2)^2 - (J^* + 1)^2}{[(J^* + 1)(J^* + 2) - J^*(J^* + 1)]5} = 0.2\left(\frac{2J^* + 3}{2J^* + 2}\right)(\text{cm}^{-1})^{-1}.$$

cal system, this is a quite low energy. Therefore the approximation is suitable for use at all energies in rate calculations where accurate behavior near reaction threshold is not desired, *e.g.*, when averaging over some distribution of energies is involved. Note, however, that rate calculations near threshold involve the lowest energy states of the transition state (but not of the molecule). Given the usual ambiguity about the structure of the transition state, the error introduced by the classical approximation in the rotational part of $G^{\pm}_{vr}(E)$ at low E is insignificant compared with the error in the vibrational part of $G^{\pm}_{vr}(E)$ arising from uncertain assignment of vibrational states of the transition state.

For the same reason, there is little advantage in considering a *restricted* internal rotor: the transition state is not known well enough to make worthwhile explicit consideration of energy levels inside the potential barrier hindering rotation, while in the molecule, if it has n degrees of freedom, the average excitation energy per degree of freedom is at least E_0/n, and this is usually larger than barrier height, so that the rotor is basically a free rotor for all practical purposes.

The good low-energy behavior of the classical approximation to $N_r(E)$ and $G_r(E)$ is consistent with the inverse relationship between energy and temperature involved in the Laplace transformation: if the partition function being inverted is valid down to low temperatures, $N(E)$ and $G(E)$ so obtained will be valid down to low energies.

VI. Direct Evaluation of $N_{vr}(E)$ and $G_{vr}(E)$ in Simple Systems

In the previous section is presented a very simple approximation to $N_r(E)$ and $G_r(E)$ which, with a certain proviso, is valid essentially at all energies. We now anticipate the result of the following sections, summarized in Table V, where it is shown that for vibrational states below about 3000 or 4000 cm^{-1} no sufficiently accurate approximation to $N_v(E)$ and $G_v(E)$ is available. Therefore $N_v(E)$ and $G_v(E)$ below these energies must be obtained by direct count, while this is not necessary for $N_r(E)$ and $G_r(E)$.

A. CONVOLUTION FOR VIBRATIONAL–ROTATIONAL STATES

To obtain $N_{vr}(E)$ and $G_{vr}(E)$ for vibrational–rotational states of a system where vibrations and rotations are independent and therefore separable, one may usefully put to profit relations 31 and 34 obtained by convolution. These general relations, applied to the specific problem on hand, show how to combine *exact* $N_v(E)$ with approximate (but very good) $N_r(E)$ [or $G_r(E)$] to yield an essentially exact $N_{vr}(E)$ and $G_{vr}(E)$. Because of the simple form of $N_r(E)$, the expenditure of mathematical labor (and of machine time) for $N_{vr}(E)$ and $G_{vr}(E)$ is thus no more than necessary for good accuracy. Direct and exact counting of vibrational–rotational states not involving an approximation for the rotational part is, of course, possible, but the much greater machine time does not make the modest increase in accuracy (mostly below 500 cm^{-1}) worthwhile.

Substituting (43) for $N_r(E)$ and $G_r(E)$, eq 31a yields

$$N_{vr}(E) = \frac{Q'_r}{\Gamma(r/2)} \sum_{x=0}^{E} W_v(x)(E - x)^{(r/2)-1} \qquad (52)$$

and eq 34 yields

$$G_{vr}(E) = \frac{Q'_r}{\Gamma(1 + r/2)} \sum_{x=0}^{E} W_v(x)(E - x)^{r/2} \qquad (53)$$

The quantum form of the convolution integral was deliberately chosen since eq 52 and 53 are meant to be used at low energies where vibrational states are widely spaced; for the same reason, expressions are used that involve $W_v(x)$ rather than the less appropriate $N_v(x)$. Note that x in (52) and (53) means vibrational energy, and to underline that fact E_v is sometimes written[17] for x.

B. DIRECT ENUMERATION OF VIBRATIONAL–ROTATIONAL STATES

The only nontrivial part of eq 52 and 53 is $W_v(x) \equiv W_v(E_v)$, and it is given by eq 8. Thus the direct[18] enumeration of vibrational–rotational states may be accomplished by a procedure similar to that shown in section II. The major difference is that, as a consequence of the smooth-function approximation to the rotational part, there is now a state or states at every value of E, and that all allowed values of $E - E_v$ must be generated and raised to the proper power. For purposes of

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(17) Equations 52 and 53 were first derived by R. A. Marcus (*J. Chem. Phys.*, 20, 359 (1952)) who used the notation $x \equiv E_v$, $W_v(x) = P(E_v)$.

(18) In the literature, eq 52 and 53 are usually represented as the "exact" enumeration of rotational–vibrational states, although they actually involve an approximation for the rotational part.

Table IV

$N'_{vr}(E)$ and $G'_{vr}(E)$ by Direct Enumeration of States[a]

$N'_{vr}(E) = \Sigma W_v(E_v)$ (*cf.* eq 52)
$G'_{vr}(E) = \Sigma\{W_v(E_v) \times (E - E_v)\}$ (cm^{-1}) (*cf.* eq 53)

E, cm^{-1}	$N'_{vr}(E)$	$G'_{vr}(E)$, *all terms of sum shown*
		Harmonic
0	1	0
100	1	$1 \times 100 = 100$
200	2	$1 \times 200 = 200$
300	5	$1 \times 300 + 1 \times (300 - 200) = 400$
400	6	$1 \times 400 + 1 \times (400 - 200) + 3 \times (400 - 300) = 900$
500	9	$1 \times 500 + 1 \times (500 - 200) + 3 \times (500 - 300) + 1 \times (500 - 400) = 1500$
		Anharmonic
0	1	0
100	1	$1 \times 100 = 100$
200	2	$1 \times 200 + 1 \times (200 - 196) = 204$
300	5	$1 \times 300 + 1 \times (300 - 196) + 3 \times (300 - 294) = 422$
400	6	$1 \times 400 + 1 \times (400 - 196) + 3 \times (400 - 294) + 1 \times (400 - 388) = 934$
500	9	$1 \times 500 + 1 \times (500 - 196) + 3 \times (500 - 294) + 1 \times (500 - 388) + 3 \times (500 - 490) = 1564$

[a] For a system consisting of two rigid free rotors and seven harmonic oscillators (same oscillators as those of Table I).

subsequent numerical integration, it is usually sufficient to generate $N_{vr}(E)$ or $G_{vr}(E)$ in 100-cm^{-1} intervals.

In Table IV is worked out the explicit calculation, at 100-cm^{-1} intervals, of the first few values of $N'_{vr}(E) = (Q'_r)^{-1} \cdot N_{vr}(E)$ and of $G'_{vr}(E) = (Q'_r)^{-1}G_{vr}(E)$ for a collection of seven oscillators, harmonic or anharmonic, and two rigid free rotors; the purpose of the division by Q'_r is to make the results independent of the properties of the individual rotors. This is a particularly simple case since the terms $(E - E_v)$ appear only to unit power in $G'_{vr}(E)$, and contribute merely a factor of one in $N'_{vr}(E)$. To render the calculation immediately verifiable, the collection of oscillators is the same as that used in Table I, so that E_v and $W_v(E_v)$ may be found there.

It may be noted that the numbers in the column under $N'_{vr}(E)$ in Table IV are the same as the numbers under $G_v(E)$ in Table I; *i.e.*, the so-called reduced density $N'_{vr}(E)$ for $r = 2$ (two rotors) is the same as $G_v(E)$ for the oscillators alone. This result may be easily generalized[19] as follows.

Write the convolution integral (28) for v vibrations and $r + 2$ rotations as

$$N'_{v(r+2)}(E) = \int_0^E N'_{vr}(x)N'_{r=2}(E - x)\,\mathrm{d}x \qquad (54)$$

Since by eq 48 $N'_{r=2}(E - x) = 1$, it follows that

$$N'_{v(r+2)}(E) = \int_0^E N'_{vr}(x)\,\mathrm{d}x = G'_{vr}(E) \qquad (55)$$

When $r = 0$, the reduced densities and sums of states become the densities and sums of states of pure vibrational states, $N_v(E)$ and $G_v(E)$, respectively, *i.e.*

$$[G'_{vr}(E)]_{r=0} = G_v(E), \quad [N'_{vr}(E)]_{r=0} = N_v(E) \qquad (56)$$

Equation 55 remains valid for $r = 0$, so that

$$[N'_{vr}(E)]_{r=2} = G_v(E) \qquad (57)$$

Relations 55–57 are useful for reducing the amount of computation since they show that, except for the definition of r, $N'_{vr}(E)$ and $G'_{vr}(E)$ are basically equivalent. This equivalence arises from the use of approximation 43 for the rotations, but does not otherwise depend on the use of any particular expression for the vibrations; in fact, relations 55–57 could also have been derived using the quantum form (31a) of the convolution integral.

VII. Approximations Based on Inversion of Classical Partition Function

We now follow essentially the historical development of the subject, even though the techniques originally used were somewhat different. Thus eq 60 were first obtained from Dirichlet's integral,[20] and eq 69 by convolution.[21]

A. VIBRATIONAL STATES

The classical vibrational partition function for one harmonic oscillator is $Q_{v=1} = kT/h\nu$, and for v independent oscillators is therefore $Q_v^{\text{class}} = (kT)^v/\Pi^v_{i=1}h\nu_i$, which in Laplace transform notation becomes

$$Q_v^{\text{class}} = \frac{1}{\prod_{i=1}^{v} h\nu_i}\left(\frac{1}{s^v}\right) \qquad (58)$$

where $s = 1/kT$. Since

$$\mathcal{L}^{-1}\left\{\frac{1}{s^v}\right\} = \frac{E^{v-1}}{\Gamma(v)}, \quad \mathcal{L}^{-1}\left\{\frac{1}{s^{v+1}}\right\} = \frac{E^v}{\Gamma(v + 1)} \qquad (59)$$

then the *classical* density and sum of states is, respectively

$$N_v(E) = \frac{E^{v-1}}{\Gamma(v)\prod_{i=1}^{v} h\nu_i}, \quad G_v(E) = \frac{E^v}{\Gamma(v + 1)\prod_{i=1}^{v} h\nu_i} \qquad (60)$$

As is well known, the true (quantum mechanical) vibrational partition function has the form (58) only at high temperature, which means that (60) will approach the true (quantum mechanical) count only at high energies, given the reciprocal relation between temperature and energy of the Laplace trans-

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(19) W. Forst and Z. Prášil, *J. Chem. Phys.*, **51**, 3006 (1969).

(20) Reference 9, p 492, eq 111.12.

(21) G. M. Wieder and R. A. Marcus, *J. Chem. Phys.*, 37, 1835 (1962).

formation. At low energies (60) will give results that are too low; *cf.* Table V.

One obvious source of error is the zero-point energy of the v oscillators, $E_z = {}^1/_2\Sigma^v{}_{i=1}h\nu_i$, which is of course ignored in the classical expression 60. E_z is fixed and only energy $E \geq E_z$ of the classical oscillators should be available for distribution among the oscillators. Since E in $N_v(E)$ and $G_v(E)$ should refer only to this distributable part of total energy (*cf.* definition of E in section I.B), we can expect that eq 60 will perform better if E on the right-hand side of eq 60 is not allowed to drop too much below E_z. Taking advantage of the fact that $N_v(E)$ and $G_v(E)$ are defined only for positive E, this can be accomplished by shifting the zero of energy to the vicinity of E_z, say aE_z ($a \lesssim 1$), so that energies below aE_z will be negative, and therefore excluded from $N_v(E)$. The result of such energy zero shift is that eq 60 become

$$N_v(E) = \frac{(E + aE_z)^{v-1}}{\Gamma(v)\prod_{i=1}^{v} h\nu_i} \tag{61}$$

$$G_v(E) = \frac{(E + aE_z)^{v}}{\Gamma(v + 1)\prod_{i=1}^{v} h\nu_i} \tag{62}$$

which for $a = 1$ is referred to as the semiclassical approximation and was used in that form for the first time by Marcus and Rice.[22]

The factor a appears in front of E_z in the expectation that appropriate manipulation of E_z may further improve the approximation.[23-25] In expression 62 for $G_v(E)$, Whitten and Rabinovitch[26a] have used with good results the empirical relations

$$\begin{gathered} a = 1 - \beta w \\ \log_{10} w = -1.0506(E/E_z)^{1/4} \qquad (E > E_z) \\ w^{-1} = 5E/E_z + 2.73(E/E_z)^{1/2} + 3.51 \qquad (E < E_z) \end{gathered} \tag{63}$$

where

$$\beta = \frac{v - 1}{v}\alpha_2 \tag{64}$$

and

$$\begin{gathered} \alpha_2 = \langle\nu^2\rangle/\langle\nu\rangle^2 \\ \langle\nu^2\rangle = \frac{1}{v}\sum_{i=1}^{v} \nu_i{}^2, \quad \langle\nu\rangle = \frac{1}{v}\sum_{i=1}^{v} \nu_i \end{gathered} \tag{65}$$

Since the relation between $G_v(E)$ and $N_v(E)$ should be that of a function and its derivative, note that $G_v(E)$ with an energy-dependent a does not yield upon differentiation $N_v(E)$ of the simple form given by eq 61.

B. VIBRATIONAL-ROTATIONAL STATES

The classical vibrational-rotational partition function for independent vibrations and rotations is, from (39) and (58)

$$Q_{vr}{}^{\text{class}} = \frac{Q'_r}{\prod_{i=1}^{v} h\nu_i}\left(\frac{1}{s^{v+r/2}}\right) \tag{66}$$

which, apart from a constant factor and different exponent, is identical with (58), so that it follows immediately

$$N_{vr}(E) = \frac{Q'_r E^{v-1+r/2}}{\Gamma(v + r/2)\prod_{i=1}^{v} h\nu_i}, \quad G_{vr}(E) = \frac{Q'_r E^{v+r/2}}{\Gamma(v + 1 + r/2)\prod_{i=1}^{v} h\nu_i} \tag{67}$$

The problem with vibrational zero-point energy persists, of course, and we may therefore correct, as in the case of pure vibrational states, by writing

$$\left.\begin{matrix} N_{vr}(E) \\ (k = 0) \\ G_{vr}(E) \\ (k = 1) \end{matrix}\right\} = \frac{Q'_r(E + a_k E_z)^{v-1+k+r/2}}{\Gamma(v + k + r/2)\prod_{i=1}^{v} h\nu_i} \tag{68}$$

where $a_k = 1 - \beta_k w$. The w of eq 63 may still be used,[26] but β needs to be redefined. A definition which was found[19] to give very good results is

$$\beta_k = \frac{(v - 1)(v - 1 + k + r/2)}{v^2}\alpha_2 \tag{69}$$

where α_2 is the same as in eq 65. This definition, while slightly different from the one proposed[26b] originally, has the virtue that it preserves the rule of eq 55, whereby $G_{vr}(E)$ can be obtained from the formula for $N_{vr}(E)$ by replacing everywhere r with $r + 2$, and whereby one and the same formula yields $G_v(E)$ ($k = 1$) and $N_v(E)$ ($k = 0$) by letting $r = 0$ (note that with $r = 0$, $k = 1$, eq 69 reduces to eq 64).

The performance of the classical approximation to $N_{vr}(E)$, as well as of the two semiclassical approximations, one with $a = 1$ and the other with energy-dependent a, is compared in Table V. The classical approximation is seen to give a gross underestimate, and the semiclassical approximation with $a = 1$ a gross overestimate that improves at higher energies, just what one would expect. As always when there is an energy-dependent factor in front of E_z, differentiation of $G_{vr}(E)$ (eq 68, $k = 1$) with respect to E gives $N_{vr}(E)$ of a form that is different from that given by eq 68 with $k = 0$; nevertheless, $N_{vr}(E)$ or $G_{vr}(E)$ of eq 68 represents a very good approximation, as may be seen from Table V.

VIII. Approximations Based on the Inversion of Quantum Mechanical Partition Function

The quantum mechanical vibrational partition function, unlike its classical counterpart, is valid at all temperatures, so that it may be expected that its inversion will yield a smooth-function approximation to $N_{vr}(E)$ or $G_{vr}(E)$ valid to much lower energies than was the case with the inversion of the classical Q_{vr} (eq 67). A complicating factor, however, is that the quantum Q_v is no longer simply proportional to a power of s, the transform parameter. Thus instead of (66), we will have $Q_{vr} = l(s)$, where $l(s)$ is now sufficiently complicated to require the actual evaluation of the inverse transform (26).

By the Fourier–Mellin integration theorem, we have quite generally for any $l(s)$

$$\mathfrak{L}^{-1}\left\{\frac{l(s)}{s^k}\right\} = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}\frac{l(s)e^{sE}}{s^k}\,\mathrm{d}s = I \tag{70}$$

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(22) R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, **55**, 894 (1951).

(23) B. S. Rabinovitch and R. W. Diesen, *J. Chem. Phys.*, **30**, 735 (1959).

(24) B. S. Rabinovitch and J. H. Current, *ibid.*, **35**, 2250 (1961).

(25) C. Lifshitz and M. Wolfsberg, *ibid.*, **41**, 1879 (1964).

(26) (a) G. Z. Whitten and B. S. Rabinovitch, *ibid.*, **38**, 2466 (1963); (b) *ibid.*, **41**, 1883 (1964).

The integral I involves s as the complex variable $s = x + iy$, and the path of integration is along a straight line parallel to the imaginary axis with abscissa c. There are essentially two[26c] methods that have been used for the approximate evaluation of I: the method of residues, which yields a polynomial related to the generalized Bernoulli polynomial, and the method of steepest descents. They will both be discussed in turn.

We shall assume familiarity with standard procedures of integration in the complex plane and therefore will mention them, when necessary, only in the barest outline.

A. EVALUATION OF INVERSION INTEGRAL BY CAUCHY'S RESIDUE THEOREM

The path of integration in (70) can be closed (Jordan's Lemma), and then by Cauchy's theorem the value of the integral I is given by the sum of residues at poles. A residue at pole of order $(n + 1)$, located at $s = a$, is the coefficient of s^n in Taylor series expansion of (s^{n+1} × integrand) about $s = a$. Thus the first, and major, part of the problem is to find a suitable expansion for the integrand of I.

For one harmonic oscillator of frequency ν, the quantum partition function is

$$Q_{v=1} = \frac{1}{(1 - e^{-h\nu/kT})} = \frac{e^{h\nu/2kT}}{2 \sinh (h\nu/2kT)} \tag{71}$$

if the ground vibrational level is taken as the zero of energy. We know therefore that for a system comprising a collection of v quantum harmonic oscillators, the vibrational part of the function $l(s)$ in I (eq 70) will involve a factor of the form

$$l_v(s) = \frac{1}{2^v}\prod_{j=1}^{v} \frac{e^{h\nu_j s/2}}{\sinh (h\nu_j s/2)} \tag{72}$$

and this product of hyperbolic sines must now be expanded in powers of s. This is the difficult part of the expansion of the total integrand, since the rotational part contributes only $s^{-r/2}$ (eq 41).

A ready-made expansion, useful for the present purpose, may be obtained from relations involving generalized Bernoulli polynomials[27,28a]

$$\prod_{j=1}^{n} \frac{(\alpha_j z)}{\sinh (\alpha_j z)} = \sum_{\substack{i=0 \\ (\text{even } i)}}^{\infty} D_i^{(n)}(\alpha_1, \ldots, \alpha_n)\frac{z^i}{i!} \tag{73}$$

which is interesting in that it consists of even powers of z only; $D_i^{(n)}(\alpha_1, \ldots, \alpha_n)$ is a coefficient which will be discussed further below. Comparing the left-hand side of (73) with (72), note that the product $\Pi^v{}_{j=1}e^{h\nu_j s/2} = e^{1/2\Sigma_j h\nu_j s}$ spoils the identity. However $1/2\Sigma^v{}_{j=1}h\nu_j$ is E_z, the zero-point energy of the v oscillators, which suggests that $l_v(s)$ of eq 72 would have the right form if we used instead a quantum vibrational partition function with energy zero at the potential minimum. With this energy zero, the partition function for one oscillator is obtained by multiplying (71) by $e^{-h\nu/2kT}$; for v oscillators the factor which multiplies (72) is therefore $\Pi^v{}_{j=1}e^{-h\nu_j s/2}$. Hence the complete partition function for r rotations and v vibrations, with vibrational energy zero at the potential minimum, is in Laplace transform notation

$$l_{vr}(s) = \frac{Q'_r}{2^v s^{r/2} \prod\limits_{\substack{j=1 \\ (\text{even } i)}}^{v} \sinh (h\nu_j s/2)} \tag{74}$$

The assumption implicit in (74) is that vibrations and rotations are independent, and that rotations behave classically as discussed in section V. The integrand of I is therefore

$$\text{integrand} = \frac{Q'_r e^{s\epsilon}}{2^v s^{k+r/2} \prod\limits_{j=1}^{v} \sinh (h\nu_j s/2)} = \frac{Q'_r e^{s\epsilon}}{s^{v+k+r/2}\prod\limits_j h\nu_j} \prod_{j=1}^{v} \frac{(h\nu_j s/2)}{\sinh (h\nu_j s/2)} \tag{75}$$

To underline the fact that total energy now includes vibrational energy referred to vibrational potential minimum as zero, we write ϵ for E in (75). Then $\epsilon = E + E_z$. From (73) it follows that

$$\text{integrand} = \frac{Q'_r e^{s\epsilon}}{s^{v+k+r/2}\prod\limits_j h\nu_j} \sum_{\substack{i=0 \\ (\text{even } i)}}^{\infty} D_i^{(v)}\left(\frac{h\nu_1}{2}, \ldots, \frac{h\nu_v}{2}\right)\frac{s^i}{i!} \tag{76}$$

The coefficient $D_i^{(v)}[(h\nu_1/2), \ldots, (h\nu_v/2)]$ is defined by[28b,29]

$$D_i^{(v)}\left(\frac{h\nu_1}{2}, \ldots, \frac{h\nu_v}{2}\right) = \sum\left\{\frac{i!}{m_1!m_2!\ldots m_v!}\left[\left(\frac{h\nu_1}{2}\right)^{m_1} \cdots \left(\frac{h\nu_v}{2}\right)^{m_v}\right]D_{m_1}\ldots D_{m_v}\right\} \tag{77}$$

where the sum is taken over all positive even values (zero included) of $m_1, m_2, \ldots, m_v$ such that

$$m_1 + m_2 + \ldots + m_v = i \tag{78}$$

D_m is related to Bernoulli numbers B_m through

$$D_{2m} = 2(-1)^m(2^{2m-1} - 1)B_m \qquad (m > 1) \tag{79}$$

$$D_0 = 1$$

The first three values of $D_i^{(v)}$ {this shortened notation will be used henceforth for $D_i^{(v)}[(h\nu_1/2), \ldots, (h\nu_v/2)]$} are[28c,29]

$$D_0^{(v)} = 1 \tag{80}$$

$$D_2^{(v)} = -\frac{1}{3}\sum_j\left(\frac{1}{2}h\nu_j\right)^2 \tag{81}$$

$$D_4^{(v)} = \frac{1}{3}\left[\sum_j\left(\frac{1}{2}h\nu_j\right)^2\right]^2 + \frac{2}{15}\sum_j\left(\frac{1}{2}h\nu_j\right)^4 \tag{82}$$

Since both the expansion of $e^{s\epsilon}$ and of $l_v(s)$ have unity as the leading term [$D_0^{(v)} = 1$], we see immediately from (76) that the integrand has a pole of order $(v + k + r/2)$ at $s = 0$. There are lower order poles on the imaginary axis, but the approximation is now made that only the residue at the pole at origin ($s = 0$) is significant, the other poles merely contributing oscillating terms which are assumed to approximately cancel out. Now

$$(s^{v+k+r/2} \times \text{integrand}) = \frac{Q'_r}{\prod\limits_j h\nu_j}\left\{e^{s\epsilon} \sum_{\substack{i=0 \\ (\text{even } i)}}^{\infty} D_i^{(v)}\frac{s^i}{i!}\right\} \tag{83}$$

(26c) NOTE ADDED IN PROOF. Since this review was submitted, a third method has been described by M. R. Hoare and P. Pal, *Mol. Phys.*, **20**, 695 (1971), involving *numerical* inversion of the Laplace transform, claimed to be the "ultimate" method.

(27) A. Erdelyi, W. Magnus, F. Oberhettinger, and F. G. Tricomi, "Higher Transcendental Functions," Vol. I, McGraw-Hill, New York, N. Y., 1953, p 40, eq (38).

(28) (a) N. E. Nörlund, *Acta Math.*, 43, 184 (1922); (b) *ibid.*, 43, 166 (1922); (c) *ibid.*, 43, 167 (1922).

(29) E. Thiele, *J. Chem. Phys.*, 39, 3258 (1963).

To obtain the residue at $s = 0$, we need the coefficient of $s^{v+k-1+r/2}$ in (83). Expanding $e^{s\epsilon}$ in powers of s, and multiplying together the two series inside the compound bracket of (83), it is found that the coefficient of s^n is

$$\sum_{\substack{i=0\\ (\text{even } i)}}^{n \text{ or } n-1} \frac{D_i^{(v)}\epsilon^{n-i}}{(n-1)!i!}$$

where the summation is taken to $i = n$ if n is even, and to $i = n - 1$ if n is odd; therefore the series (84) has $[(n/2) + 1]$ terms for n even, and $(n + 1)/2$ terms for n odd. Writing $\epsilon = E + E_z$, there finally follows the result

$$\left.\begin{array}{l} N_{vr}(E) \\ (k = 0) \\ G_{vr}(E) \\ (k = 1) \end{array}\right\} \cong (\text{residue at } s = 0) = \frac{Q'_r}{\prod_j h\nu_j} \sum_{\substack{i=0\\ (\text{even } i)}}^{n \text{ or } n-1} \frac{D_i^{(v)}(E + E_z)^{n-i}}{(n-i)!i!} \tag{84}$$

where $n = v + k - 1 + r/2$.

Equation 84 was first derived for $k = 1, r = 0$ by Thiele,[29] and in essentially the above general form by Forst, Prášil, and St. Laurent.[30] A truncated form of (84) was obtained by Haarhoff[31] and also by Schlag and Sandsmark.[32] Equation 84 was extensively tested[19,30] against direct count (section VI) and found to represent an excellent approximation to harmonic $N_{vr}(E)$ and $G_{vr}(E)$, valid to very low energies ($<$3000 cm^{-1}) (Table V).

It will be noted that the leading term of (84) is the semiclassical approximation 61 or 62 with $a = 1$, so that (84) may be considered a generalization of the semiclassical approximation. The importance of terms beyond the first increases as the energy decreases (the terms are alternately positive and negative), so that at low energies (below $\sim$5000 cm^{-1}) all the $(n/2) + 1$ or $(n + 1)/2$ terms, as the case may be, must be computed for good accuracy, whereas at high energies the first few terms are usually sufficient. For this reason, the truncated expression of Haarhoff[31] is also quite adequate at higher energies. Since his formula is relatively easy to program, it is quite useful for some purposes and is therefore given below, transcribed into our notation

$$\left.\begin{array}{l} N_{vr}(E) \\ (k = 0) \\ G_{vr}(E) \\ (k = 1) \end{array}\right\} = Q'_r \left\{\left(\frac{2}{\pi v}\right)^{1/2}\left(\frac{v}{n+1}\right)^{n+1/2}\left(1 - \frac{1}{12(n+1)}\right) \times \frac{\lambda(h\langle\nu\rangle^{n-v})}{1+\eta}\right\}\left[\left(1+\frac{\eta}{2}\right)\left(1+\frac{2}{\eta}\right)^{\eta/2}\right]^{n+1}\left(1 - \frac{1}{(1+\eta)^2}\right)^{\beta_{\text{H}}} \tag{85}$$

where $n = v + k - 1 + r/2$, $\beta_{\text{H}} = [n(n - 1)\alpha_2 - v(n + 1)]/6v$, $\eta = E/E_z$, $1/\lambda = \Pi_i(\nu_i/\langle\nu\rangle)$, and α_2 is given by eq 65. The above β_{H} should not be confused with β of eq 64 or β_k of eq 69.

The performance of eq 84 and 85 is compared in Table V at various energies and various values of r. Both perform quite well, but at higher values of r eq 84 is better.

B. EVALUATION OF INVERSION INTEGRAL BY THE METHOD OF STEEPEST DESCENTS

The method of steepest descents[33] is based on the proposition that at some value of s, say $s = s^*$, the integrand will have a saddle point, *i.e.*, a minimum with respect to the real plane, and a steep maximum with respect to the imaginary plane; the maximum is assumed to be so steep that contributions to the integral from values of s other than $s = s^*$ can be neglected. The accuracy of the approximation to I so obtained depends on the steepness of the maximum.

It is convenient to define[14,19] a function $\phi(s)$

$$\phi(s) = \ln [I(s)] - k \ln s + sE \tag{86}$$

Then the integrand of I is simply $\exp[\phi(s)]$. The integrand will have a saddle point at $s = s^*$ so that $\phi'(s^*) = 0$, *i.e.*, s^* is the solution of

$$\frac{1}{I(s^*)}\left[\frac{\mathrm{d}I(s)}{\mathrm{d}s}\right]_{s=s^*} - \frac{k}{s^*} + E = 0 \tag{87}$$

The existence of a saddle point at s^* suggests that the path of integration in (70) be so chosen that $c = s^*$; then

$$I = \frac{1}{2\pi i}\int_{s^*-i\infty}^{s^*+i\infty} \exp[\phi(s)]\,\mathrm{d}s = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \exp[\phi(s^* + iy)]\,\mathrm{d}y \tag{88}$$

Expanding $\phi(s)$ around s^* [and keeping in mind that $\phi'(s^*) = 0$] yields

$$\phi(s) = \phi(s^*) + {}^1/_2(s - s^*)^2\,\phi''(s^*) + \ldots \tag{89}$$

if the series is cut off after the second derivative;[34] then, since $s - s^* = iy$, the integral (88) becomes simply

$$I = \frac{\exp[\phi(s^*)]}{2\pi}\int_{-\infty}^{+\infty} \exp\left[-\frac{1}{2}\phi''(s^*)y^2\right]\mathrm{d}y = \frac{\exp[\phi(s^*)]}{[2\pi\phi''(s^*)]^{1/2}} \tag{90}$$

To avoid the nuisance of handling exponentials, put $e^{-s} = z$. Then $I(s)$ becomes a function of z, $I(z)$, which we will write $Q(z)$ to underline the fact that $I(s)$ or $I(z)$ is actually the partition function Q in disguise. The function $\phi(s)$ then becomes

$$\phi(z) = \ln [Q(z)] - k \ln [\ln z^{-1}] - E \ln z \tag{91}$$

The saddle point of this function is now at $\theta = e^{-s^*}$, where θ is the solution of $\phi'(s^*) = -\theta\phi'(\theta) = 0$

$$\theta\left(\frac{\mathrm{d} \ln Q(z)}{\mathrm{d}z}\right)_{z=\theta} + \frac{k}{\ln \theta^{-1}} - E = 0 \tag{92}$$

Thus eq 87, which is a transcendental equation in s^*, becomes an algebraic equation in θ. Since $\phi''(s^*) = \theta^2\phi''(\theta)$, eq 70 and 90 become

$$\left.\begin{array}{l} N(E) \\ (k = 0) \\ G(E) \\ (k = 1) \end{array}\right\} = \frac{Q(\theta)}{[\ln \theta^{-1}]^k\theta^E[2\pi\theta^2\phi''(\theta)]^{1/2}} \tag{93}$$

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[30] W. Forst, Z. Prášil, and P. St. Laurent, *J. Chem. Phys.*, **46**, 3736 (1967); **48**, 1431 (1968); see also D. C. Tardy, B. S. Rabinovitch, and G. Z. Whitten, *ibid.*, **48**, 1427 (1968).

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

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

[33] H. Jeffreys and B. S. Jeffreys, "Methods of Mathematical Physics," Cambridge University Press, New York, N. Y., 1956, p 503.

[34] For an account of the "full" steepest descent method which includes higher derivatives, see M. R. Hoare, *J. Chem. Phys.*, **52**, 5695 (1970). Inclusion of the third derivative improves the approximation slightly; higher derivatives have no effect.

Table V

Comparative Test of Various Approximations for $N'_{vr}(E)$ at Several Energies[19] [a]

r	E, cm^{-1}	Approximation/direct count[c]					
		Method[b]					
		(a)	(b)	(c)	(d)	(e)	(f)
2	1,000	2.6×10^{-17}	27.43	0.536	0.596	0.573	0.660
	2,000	2.1×10^{-13}	17.13	0.715	0.760	0.756	0.808
	3,000	2.7×10^{-11}	11.59	0.810	0.844	0.845	0.883
	4,000	6.8×10^{-10}	8.90	0.910	0.936	0.940	0.972
	5,000	6.4×10^{-9}	6.41	0.880	0.898	0.902	0.927
	10,000	3.6×10^{-6}	3.12	0.989	0.995	0.998	1.014
	20,000	4.1×10^{-4}	1.73	1.005	1.003	1.003	1.013
3	1,000	1.9×10^{-17}	80.27	1.177	1.203	1.181	1.324
	2,000	1.3×10^{-13}	30.17	1.003	1.016	1.025	1.076
	3,000	1.6×10^{-11}	16.96	0.981	0.990	1.002	1.034
	4,000	4.0×10^{-10}	11.45	0.997	1.003	1.014	1.039
	5,000	4.2×10^{-9}	8.30	0.990	0.994	1.003	1.025
	10,000	2.5×10^{-6}	3.41	0.999	0.998	1.002	1.016
	20,000	3.2×10^{-4}	1.79	1.005	1.00005	1.001	1.011
4	1,000	7.7×10^{-18}	127.60	1.388	1.279	1.304	1.400
	2,000	6.1×10^{-14}	41.33	1.084	1.038	1.071	1.094
	3,000	8.6×10^{-12}	22.05	1.048	1.019	1.046	1.062
	4,000	2.3×10^{-10}	14.04	1.034	1.013	1.035	1.049
	5,000	2.5×10^{-9}	9.87	1.019	1.003	1.020	1.034
	10,000	1.7×10^{-6}	3.73	1.007	0.9997	1.006	1.018
	20,000	2.5×10^{-4}	1.86	1.007	0.99998	1.001	1.010
12	1,000	8.4×10^{-21}	8985.50	5.744	1.052	2.986	0.997
	2,000	2.4×10^{-16}	831.00	2.344	0.996	1.708	1.030
	3,000	6.8×10^{-14}	223.20	1.686	1.0001	1.386	1.025
	4,000	3.0×10^{-12}	92.11	1.428	1.0001	1.244	1.021
	5,000	4.9×10^{-11}	48.18	1.297	0.99998	1.168	1.019
	10,000	1.0×10^{-7}	8.66	1.094	1.000000	1.045	1.015
	20,000	4.0×10^{-5}	2.72	1.035	0.9999995	1.009	1.009

[a] Expressed as fractional deviation of reduced density $N'_{vr}(E)$ from direct count. (Note that $N'_{v(r-2)}(E) = G'_{vr}(E)$, $N_{v(r-3)}(E) = G'_{v(r-1)}(E)$, etc.) Molecular model consists of 15 harmonic oscillators with frequencies (in cm^{-1}, degeneracies in brackets): 983 (4), 1415 (4), 2000, 3034 (6); plus 2, 3, 4, or 12 rigid free rotors. [b] Approximation method: (a) classical (eq 67); (b) semiclassical (eq 68) with $a_k = 1$; (c) semiclassical (eq 68) with a_k given by eq 68, β_k by eq 69; (d) Bernoulli polynomials (eq 84); (e) Haarhoff (eq 85); (f) steepest descents (eq 95). [c] Direct count as in section VI.

$Q(\theta)$ and θ^E are dimensionless, and the units of $\ln \theta^{-1}$ are (energy)$^{-1}$, and those of $\theta^2\phi''(\theta)$ are (energy)^2. Equation 93 was first derived by Forst and Prášil,[19] and in a slightly different form by Hoare and Ruijgrok.[35] In the case of v independent harmonic oscillators and r classical rigid free rotors

$$Q_{vr}(z) = Q_v(z)Q_r(z)$$

$$Q_v(z) = \prod_{i=1}^{v}(1 - z^{\alpha_i})^{-1} \tag{94}$$

$$Q_r(z) = Q'_r(\ln z^{-1})^{-r/2}$$

(α_i = wavenumber of ith oscillator) and hence[19]

$$\left.\begin{matrix} N_{vr}(E) \\ (k = 0) \\ G_{vr}(E) \\ (k = 1) \end{matrix}\right\} = \frac{Q'_r\prod_{i=1}^{v}(1 - \theta^{\alpha_i})^{-1}}{\theta^E(\ln \theta^{-1})^{k+r/2}[2\pi\theta^2\phi''(\theta)]^{1/2}} \tag{95}$$

where

$$\theta^2\phi''(\theta) = \sum_{i=1}^{v}\frac{\alpha_i{}^2\theta^{\alpha_i}}{(1 - \theta^{\alpha_i})^2} + \frac{k + r/2}{(\ln \theta^{-1})^2} \tag{96}$$

and θ is the solution of

$$\sum_{i=1}^{v}\frac{\alpha_i\theta^{\alpha_i}}{1 - \theta^{\alpha_i}} + \frac{k + r/2}{\ln \theta^{-1}} - E = 0 \tag{97}$$

Note that because k and $r/2$ always appear together, eq 95 satisfies relations 55 to 57. Equation 95 is tested against the direct count in Table V; it gives an excellent approximation, though not quite as good as the formula 85 based on Bernoulli polynomials. For earlier attempts at the application of the method of steepest descents to harmonic oscillator state densities, see ref 36 and 37. Thermodynamic implications of the steepest-descent method are discussed in ref 35.

IX. Approximation to $N_{vr}(E)$ and $G_{vr}(E)$ for More Realistic Systems

Methods shown in sections VII and VIII give $N_{vr}(E)$ and $G_{vr}(E)$ for a system comprising a collection of independent harmonic oscillators. The limitation of such a $N_{vr}(E)$ or $G_{vr}(E)$, no matter how accurately determined, is that it neglects several important features of real molecular vibrations.

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(35) M. R. Hoare and T. W. Ruijgrok, *J. Chem. Phys.*, **52**, 113 (1970). Equation 6.5 of this reference contains two errors.

(36) S. H. Lin and H. Eyring, *ibid.*, **39**, 1577 (1963); **43**, 2153 (1965).

(37) J. C. Tou and S. H. Lin, *ibid.*, **49**, 4187 (1968).

Foremost among these is vibrational anharmonicity. In the present context, the important consequences of anharmonicity are twofold: (1) Vibrational level spacing of an anharmonic oscillator decreases as vibrational energy increases, while for the harmonic oscillator it remains constant (section II); hence compared with the anharmonic case at a given E, the harmonic $G_v(E)$ is smaller. (2) As a consequence of (1), the anharmonic oscillator eventually dissociates when E is sufficiently high, while the harmonic oscillator does not, no matter how large the supplied energy may be. This means that at high E the harmonic $G_v(E)$ includes socalled "virtual states," *i.e.*, states that would be dissociated in a real molecule, and therefore should be excluded; consequently this effect tends to make the harmonic $G_{vr}(E)$ larger than it should be. Effects 1 and 2 both become appreciable at higher energies, and since they work in opposite directions, we may expect they will somewhat neutralize each other, although the extent to which this happens cannot be accurately predicted in the absence of an actual calculation.

Another feature of molecular vibrations (and rotations) that has been neglected is the coupling among the vibrations, and among vibrations and rotations. For the moment, the state of the art is such that this sort of coupling in polyatomic molecules is not well known and is difficult to describe, but eventually the assumption of total separability among all the internal degrees of freedom of a molecule may have to be abandoned if it turns out that the effect is important.

Finally, the third feature, though not really due to molecular vibrations or rotations themselves, is nevertheless important in the context of unimolecular rate theory. It concerns certain states that must be excluded from the density or sum of states on account of conservation requirements, *e.g.*, certain rotational states that are disallowed on account of conservation of angular momentum.

Each of the three complicating features mentioned can be easily taken into account when states are enumerated directly at low energies; in fact, we have considered direct evaluation of anharmonic $W_v(E)$ and $G_v(E)$ in section II, and of anharmonic $N_{vr}(E)$ and $G_{vr}(E)$ in section VI. However, the same sort of high-energy bookkeeping problem mentioned previously makes it imperative to find a smooth-function approximation incorporating some or all of the complicating features mentioned, particularly since their importance is likely to increase with energy.

A. THE GENERALIZED METHOD OF STEEPEST DESCENTS

A method in which all the various complicating features can be easily accommodated is the method of steepest descents. Note that in the derivation that leads to eq 93 no assumptions were made as to the form of $I(s)$ or $Q(z)$, and therefore we are in no way confined to considering $N_{vr}(E)$ or $G_{vr}(E)$ for harmonic oscillators only. It is not even necessary that the various degrees of freedom be separable, since it was not assumed that the partition function factorizes; in fact, all that is required is that we should be able to write down the partition function for the system in question.

It turns out,[38] however, that when $Q(z)$ is a polynomial (rather than an infinite series), eq 92 does not have a solution for all E when $k = 0$, but always has one when $k = 1$. A more general formulation of (93) is therefore

$$G(E) = \frac{Q(\theta)}{(\ln \theta^{-1})\theta^{E}[2\pi\theta^2\phi''(\theta)]^{1/2}} \tag{98}$$

$$N(E) = \frac{\mathrm{d}G(E)}{\mathrm{d}\theta}\frac{\mathrm{d}\theta}{\mathrm{d}E} = G(E)\left\{\ln \theta^{-1} - \frac{1}{\theta^2\phi''(\theta)} - \frac{\theta^3\phi'''(\theta)}{2[\theta^2\phi''(\theta)]^2}\right\} \tag{99}$$

Define the various logarithmic derivatives of $Q(z)$ as

$$F = \theta\left(\frac{\mathrm{d}\ln Q(z)}{\mathrm{d}z}\right)_{z=\theta}$$

$$S = \theta^2\left(\frac{\mathrm{d}^2\ln Q(z)}{\mathrm{d}z^2}\right)_{z=\theta} \tag{100}$$

$$T = \theta^3\left(\frac{\mathrm{d}^3\ln Q(z)}{\mathrm{d}z^3}\right)_{z=\theta}$$

also let

$$C^{-1} = \ln \theta^{-1}$$

then the various derivatives of the function $\phi(\theta)$ to be used in conjunction with (98) and (99) are

$$\theta\phi'(\theta) = F + C - E = 0 \text{ (this defines } \theta) \tag{101a}$$

$$\theta^2\phi''(\theta) = S + F + C^2 \tag{101b}$$

$$\theta^3\phi'''(\theta) = T + S - F + 2(C^3 - C^2) \tag{101c}$$

Very recently, Forst and Prášil[38] have used eq 98 and 99 to calculate $N_{vr}(E)$ and $G_{vr}(E)$ in various systems, harmonic and anharmonic, involving the exclusion of disallowed states. However, the following shall be limited to considerations of anharmonicity in a system of separable degrees of freedom which is of more immediate interest. The model used is the Morse oscillator which has been used by all workers in the field. It is certainly quite adequate for the purpose on hand.

B. CORRECTION FOR ANHARMONICITY IN A SYSTEM OF CLASSICAL MORSE OSCILLATORS

We might start with one of the approximations obtained for the harmonic case and attempt to modify it so as to include anharmonicity. This has been done by Haarhoff[31] who has so modified the semiclassical expression 62. Below is an outline of his argument.

The energy levels of a classical Morse oscillator, with energy referred to potential minimum as zero, are given by

$$\epsilon = \left(n + \frac{1}{2}\right)h\nu - \left(n + \frac{1}{2}\right)^2\frac{(h\nu)^2}{4D} \tag{102}$$

where D is the dissociation energy of the oscillator and $\epsilon = E + E_z$. Solving for the quantum number n

$$\left(n + \frac{1}{2}\right) = \frac{2D}{h\nu}\left\{1 - \sqrt{1 - \frac{\epsilon}{D}}\right\} \tag{103}$$

so that the density of levels at E is

$$\frac{\mathrm{d}n}{\mathrm{d}E} = \frac{1}{h\nu(1 - \epsilon/D)^{1/2}} = \frac{1}{h\nu}\left[1 + \frac{\epsilon}{2D} + \frac{3}{8}\left(\frac{\epsilon}{D}\right)^2 + \ldots\right] \tag{104}$$

The Laplace transform of $\mathrm{d}n/\mathrm{d}E$ gives an expansion for $I(s)$, the corresponding classical partition function for the Morse

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[38] W. Forst and Z. Prášil, *J. Chem. Phys.*, 53, 3065 (1970).

oscillator. Suppose the oscillator is the *i*th; then

$$\mathcal{L}\left\{\frac{\mathrm{d}n}{\mathrm{d}E}\right\} = \frac{1}{h\nu_i}\left[\frac{1}{s} + \frac{1}{2D_is^2} + \frac{3}{4D_i^2s^3} + \frac{15}{8D_i^3s^4}\right] = l_i(s) \quad (105)$$

For a collection of v such oscillators

$$l_v(s) = \prod_{i=1}^{v} l_i(s) \quad (106)$$

and then

$$N_v(E) = \mathcal{L}^{-1}\{l_v(s)\} = \mathcal{L}^{-1}\left\{\prod_{i=1}^{v} l_i(s)\right\} \quad (107)$$

Straightforward multiplication in (106) and term by term inversion in (107) yields

$$N_v(E) = \frac{\epsilon^{v-1}}{\Gamma(v)\prod_i h\nu_i}\left[1 + \frac{\epsilon}{v}\sum_i\frac{1}{2D_i} + \frac{\epsilon^2}{v(v+1)}\left\{\frac{5}{2}\sum_i\left(\frac{1}{2D_i}\right)^2 + \frac{1}{2}\left(\sum\frac{1}{2D_i}\right)^2\right\} + \ldots\right] \quad (108)$$

Since $\epsilon = E + E_z$, we recognize the factor in front of the square bracket as the semiclassical approximation (62). Hence the series inside the square brackets may be considered as a correction factor for anharmonicity, which we shall write as $C_0(E)$, to emphasize that it depends on E; subscript 0 anticipates eq 109. Equation 108 can be easily generalized to include r rotations by writing $v + r/2$ for v, and the corresponding correction factor for $G_{vr}(E)$ can be obtained by writing $r + 2$ for r (*cf.* eq 55). By various manipulations Haarhoff truncated the series in (108) to obtain the more compact formula (in our notation)

$$\left.\begin{array}{ll} (k = 0) & \dfrac{N_{vr}(E)\ (\text{Morse})}{N_{vr}(E)\ (\text{harm})} \\[2ex] (k = 1) & \dfrac{G_{vr}(E)\ (\text{Morse})}{G_{vr}(E)\ (\text{harm})} \end{array}\right\} = C_k(E) \quad (109)$$

$$C_k(E) = \left\{\left(1 + \frac{2}{\eta}\right)^{(\eta/2)(1+\eta/2)} \exp\left[-\frac{(\alpha_2 - 1)}{3(1+\eta)}\right]^{vE_z/(n+1)D}\right\} \times \exp\left[M_2(1+\eta)^2\left(\frac{E_z}{D}\right)^2 + M_3(1+\eta)^3\left(\frac{E_z}{D}\right)^3\right] \quad (110)$$

where D is the harmonic mean defined by $D^{-1} = \langle D_i^{-1}\rangle$

$$M_2 = v[4v + {}^5/_2(r + 2k)]/8(n+1)^2(n+2)$$

$$M_3 = v[24v^2 + {}^{59}/_2v(r + 2k) + {}^{37}/_4(r + 2k)^2]/24(n+1)^3(n+2)(n+3)$$

and the other symbols have the same significance as in eq 85, *viz.* $n = v + k - 1 + r/2$, $\eta = E/E_z$, $\alpha_2 = \langle\nu^2\rangle/\langle\nu\rangle^2$.

When tested[38], formula 110 has been found to perform very well in the case of a large molecule (cyclopropane, $v = 21$) up to 7 × 10^4 cm^{-1}, but in the case of a small molecule ($v = 5$) it has failed[39] above ~3 × 10^4 cm^{-1}. It turns out that (110) is unreliable at energies which represent an appreciable fraction of E_d, the energy required to dissociate the entire molecule ($E_d = \Sigma^v_{i=1}D_i - E_z$). Therefore the usefulness of formula 110 is limited to roughly $E < 0.1E_d$, which in a small molecule represents a rather narrow range of energies[40] since obviously a small molecule will have a low E_d.

For a different, but less useful, approach to $C(E)$ see ref 32, 41, and 42.

C. ANHARMONIC $N_{vr}(E)$ AND $G_{vr}(E)$ BY THE GENERALIZED METHOD OF STEEPEST DESCENTS

One might expect that a better result for the anharmonic correction factor $C(E)$ would be obtained by a suitable modification of an expression for density (or sum) of states which is based on the inversion of the quantum partition function. However, expression 84, excellent though it is, depends in a unique way on the expansion of a product of hyperbolic sines and cannot be usefully modified. The generalized method of steepest descents, on the other hand, offers a relatively easy way of calculating the anharmonic $N_{vr}(E)$ or $G_{vr}(E)$ directly. To this end, the partition function must be obtained first.

The vibrational levels of a Morse oscillator, referred to ground state, are

$$E = h\nu[n(1 - x) - n^2x]$$

The maximum value of n ($n_{\max} = m$) is

$$m = \frac{1}{2}\left(\frac{1}{x} - 1\right) \quad (111)$$

so that the vibrational partition function for one Morse oscillator is

$$Q(z) = \sum_{n=0}^{m} z^{[n(1-x)-n^2x]h\nu} \quad (112)$$

Note that because the summation is taken only to $n_{\max} = m$, only levels below the dissociation limit are included, and (112) represents $Q(z)$ for bound vibrational states as, of course, it should. For v such oscillators

$$Q_v(z) = \prod_{i=1}^{v}\sum_{n_i=0}^{m_i} z^{w_i} \quad (113)$$

where $w_i = [n_i(1 - x_i) - n_i^2x_i]h\nu_i$; n_i is the vibrational quantum number of the *i*th oscillator ($n_{i(\max)} = m_i$) and ν_i is its frequency. Then the various logarithmic derivatives are

$$\left.\begin{aligned} F &= \sum_{i=0}^{v} F_i; \quad F_i = y_i^{-1}\sum_{n_i=0}^{m_i} w_i\theta^{w_i}; \quad y_i = \sum_{n_i=0}^{m_i}\theta^{w_i} \\ S + F &= \sum_{i=1}^{v}(S_i + F_i) \\ S_i + F_i &= y_i^{-1}\sum_{n_i=0}^{m_i} w_i^2\theta^{w_i} - (F_i)^2 \\ T + 3S + F &= \sum_{i=1}^{v}(T_i + 3S_i + F_i) \\ T_i + 3S_i + F_i &= y_i^{-1}\sum_{n_i=0}^{m_i} w_i^3\theta^{w_i} - 3F_iy_i^{-1}\sum_{n_i=0}^{m_i} w_i^2\theta^{w_i} + 2(F_i)^3 \\ T + S - F &= T + 3S + F - 2(S + F) \end{aligned}\right. \quad (114)$$

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(39) L.-K. Huy, W. Forst, and Z. Prášil, *Chem. Phys. Lett.*, in press.

(40) Note that in the case of cyclopropane, 7 × 10^4 cm^{-1} ~ $0.1E_d$, while in the cited case of the "small" molecule (patterned on hydrogen peroxide), 3 × 10^4 cm^{-1} ~ $0.25E_d$.

(41) E. W. Schlag, R. A. Sandsmark, and W. G. Valance, *J. Chem. Phys.*, **40**, 1461 (1964).

(42) K. A. Wilde, *ibid.*, **41**, 448 (1964).

Note that in all these formulas the polynomials in n_i must be summed term by term since there is no longer a simple formula for the sum as in the case of the harmonic oscillator, so that the computation is more complicated. θ is obtained by solving (101a) using (114); $G_v(E)$ and $N_v(E)$ then follow from (98) and (99), respectively. If separable rotations are also to be included, the partition function (113) can be easily modified by including the appropriate $Q_r(z)$ as a factor, which results in a trivial modification of the other equations. $G_v(E)$ calculated by means of eq 114 has been checked in the case of cyclopropane[38] and hydrogen peroxide[39] and found to give excellent results.

A somewhat different formulation of the Morse oscillator problem has been given by Hoare and Ruijgrok.[35] They avoid the tedious polynomials in n_i of eq 114 by writing the single-oscillator partition function (eq 112) in the form

$$Q(u) = \sum_n \exp[-u\{n(1-x) - n^2x\}] = \sum_n (e^{-un}e^{nux - n^2ux}) \quad (115)$$

where $u = h\nu/kT$. If the exponential in x is expanded to first order

$$e^{nux-n^2ux} \approx 1 + nux - n^2ux \quad (116)$$

eq 115 becomes

$$Q(u) = \sum_n e^{-un}[1 + n(n+1)ux] \quad (117)$$

and even if the summation over n is now extended to infinity, the effect is to make eq 117 roughly equivalent to eq 115 truncated at $n_{\max}$. After some manipulation, eq 117 summed from $n = 0$ to $n = \infty$ becomes (our notation)

$$Q(z) = \frac{1}{1-z^\alpha}\left\{1 - \frac{2xz^\alpha \ln z^\alpha}{(1-z^\alpha)^2}\right\} \quad (118)$$

($\alpha = h\nu$) which is in essence the harmonic partition function multiplied by a correction term (*cf.* eq 94). They further simplify the logarithm of eq 118 by the approximation $\ln\{1 - y\} \approx -y$, so that

$$\ln Q(z) \approx -\ln(1-z^\alpha) - \frac{2xz^\alpha \ln z^\alpha}{(1-z^\alpha)^2} \quad (119)$$

For several oscillators, eq 119 is then summed over the individual oscillators to get the logarithm of the total partition function, and the logarithmic derivatives (*cf.* eq 110) are then used in the usual way in eq 101 to obtain θ and the derivatives of $\phi(\theta)$, from which $G(E)$ follows *via* eq 98.

Compared with the method of eq 114, the method of Hoare and Ruijgrok gave, in the one case tested,[35] results that were somewhat worse at low energies and somewhat better at high energies. Elimination of the summations over n_i offers the possibility of saving some machine time, and therefore their method looks attractive if further tests can substantiate the validity of the approximations that lead to eq 119.

Figure 2 shows the energy dependence of $G_{vr}(E)$ for a system of five oscillators and two rigid free rotors.[38] The oscillators are assumed to be Morse, or harmonic, or harmonic with a cut-off such that each oscillator has the same dissociation energy as the corresponding Morse oscillator. Figure 2 gives a good idea how $G_{vr}(E)$ is decreased when "virtual" states of the harmonic oscillator are eliminated by application of the cut-off, and how $G_{vr}(E)$ rises again when vibrational level spacing is allowed to diminish with energy, as in the Morse oscillator.

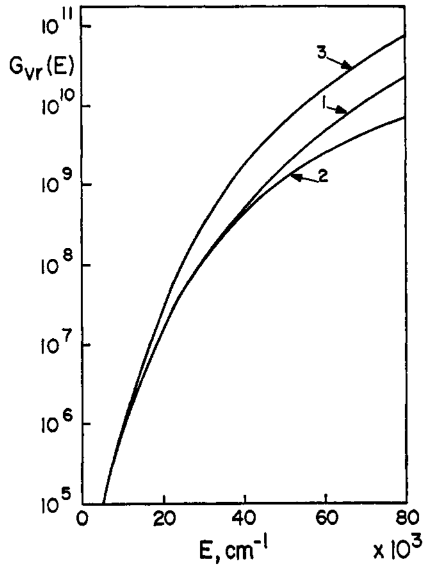

Figure 2. Energy dependence of $G_{vr}(E)$: (1) collection of harmonic oscillators, (2) collection of harmonic oscillators with cut-off, (3) collection of Morse oscillators (coupled with one two-dimensional rigid free rotor in all three cases). The collection consists of nondegenerate oscillators with frequencies ω_i (in cm^{-1}) and anharmonicity coefficients x_i:

ω_i	880	1296	1440	3774	3788
x_i	0.013	0.0226	0.0208	0.0232	0.0238

Each oscillator has the same dissociation energy (determined by x_i) in both the harmonic-with-cut-off and Morse oscillator representation. The moment of inertia of the rotor is $I = 3.157 \times 10^{-39}$ g cm^2. Frequencies, anharmonicity coefficients, and moment of inertia are patterned on hydrogen peroxide.

D. ANHARMONIC PARAMETERS IN MOLECULAR SYSTEMS

The application of a Morse oscillator representation to an actual molecular system requires the assignment of x_i or D_i to each oscillator. Either parameter will do since they are related[4] by

$$D_i = h\omega_i/4x_i \quad (120)$$

The parameter x_i is related to the spectroscopic normal frequency ω_i and the fundamental frequency ν_i by

$$x_i = \frac{\omega_i - \nu_i}{\omega_i} \quad (121)$$

The difference $\omega_i - \nu_i$ is usually a small difference between two large numbers, and unless both ω_i and ν_i are known very accurately, (121) will yield a very unreliable x_i, and hence also a poor D_i. However, even if the ω_i's and ν_i's are very accurate, there is a problem.[43] Spectroscopists usually calculate the ω_i's of a polyatomic molecule by the method of Dennison[44] which involves a more sophisticated relation between ω_i and x_i than eq 121, which is strictly valid only for a diatomic molecule. Using such ω_i's in (121) really amounts to adjusting each x_i to the somewhat artificial concept of an independent Morse

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(43) W. Forst and P. St. Laurent, *Can. J. Chem.*, **45**, 3169 (1967).

(44) D. M. Dennison, *Rev. Mod. Phys.*, **12**, 175 (1940).

oscillator, all this, of course, in addition to the assumption that the Morse function is an adequate representation for the vibration in question, which may not always be too evident.

If the vibration is a simple stretching vibration, D_i may also be calculated from the quadratic (f_{2i}) and cubic (f_{3i}) force constant, since in a Morse oscillator they are related by

$$D_i = (f_{2i})^3/2(f_{3i})^2 \tag{122}$$

The two force constants can be obtained from Badger's rule as modified by Herschbach and Laurie[45]

$$(-1)^m f_m = 10^{-(r_e - a_{xy})/b_{xy}} \tag{123}$$

where r_e is the equilibrium bond length between atoms of rows x and y in the periodic table, and a_{xy} and b_{xy} are tabulated semiempirical constants. If the dissociation energy of a stretching vibration is known from thermochemical data or other information, D_i may be obtained immediately. In such cases, eq 122 and 123 usually give much the same value for D_i, whereas it sometimes disagrees with D_i calculated from (120) and (121). In such a case, D_i calculated from (122) is likely to be more reliable.

Since eq 122 and 123 cannot be used for vibrations other than simple bond-stretching vibrations, *e.g.*, for skeleton bending vibrations or deformation vibrations, there is no alternative method for determining D_i in these cases if there is reason to believe that the ω_i's and ν_i's, if available, are not sufficiently accurate. This is a rather unfortunate limitation, but it turns out that the anharmonic $N_{vr}(E)$ or $G_{vr}(E)$ is not overly sensitive to any particular D_i, at least when E is not too high, so that the limitation is not serious in thermal systems where the range of pertinent energies is not large.[43,46-48]

X. Conclusions

The immediate conclusion, which even a casual glance at Table V will reveal, is that no one approximation method gives sufficiently accurate results below about 3000 cm^{-1}. A closer look will reveal that, in general, approximations given by eq 84 and 95 get better at low energies as r increases, while the other approximations generally get worse. Therefore the lowest energy at which results are still within, say, 10% of the direct count depends on the approximation formula being used and on the complexity of the molecular system for which the number of states is being evaluated.

In any event, whatever the approximation formula used, and whatever the notion of an "acceptable" accuracy, $N_{vr}(E)$ and $G_{vr}(E)$ have to be enumerated directly at low energies, which is why direct enumeration has been considered in some detail in sections II and VI. This requirement is not a serious handicap and the two sections should help the interested investigator do the work easily by hand up to 3000 or 4000 cm^{-1}, at which point an approximation formula can usually take over.

COMPUTER CALCULATIONS

Insofar as the approximation formulas are concerned, the computational effort required of the computer is least for the semiclassical methods, in particular eq 68 with β_k given by eq 69, which gives best accuracy for least expenditure of computer time. Programming of the formula is also very easy. Equations 84 and 85 require somewhat more machine time, but while programming of eq 85 is easy, that of eq 84 is more difficult mainly because of the complicated coefficient $D_i^{(v)}$ (eq 77). However, since the machine need calculate a given set of D_i's only once, which are then usable at all energies, machine time for a given range of energies by formula 84 is nevertheless quite comparable to that for formula 85.

Equations 95 or 98 and 99 are very easy to program, but machine time is higher than for the previously mentioned formulas because a new θ must be calculated for every energy at which $N(E)$ and $G(E)$ is desired;[49] *i.e.*, eq 97 or 101a must be solved repeatedly for every E. Another factor that tends to increase machine time is that since θ is a number generally between 0.9999 and unity, it must be calculated to a precision of about 10^{-10} to obtain $G(E)$ and $N(E)$ with good accuracy. The Newton–Raphson method[50] may be used to good advantage here; it takes about 15 iterations to find θ at the lowest (first) energy, and then using this θ as the input for iterations at the next higher E, etc., only 4 to 7 iterations are usually sufficient at all other energies.

These remarks apply to the calculation of $N(E)$ or $G(E)$ for a collection of harmonic oscillators. With anharmonic oscillators, machine time for eq 93 or 98 and 99 is higher again because of all the various summations that must be performed in eq 114. The correction factor $C_k(E)$ (eq 110), on the other hand, requires much less machine time.

We have not considered an approximation formula due to Vestal, *et al.*,[51-54] which was found[19] to give inferior results to all the other formulas at a much larger expenditure of computer time. Not discussed for the same reason is a rather complicated method for anharmonic $G_v(E)$ due to Wilde.[42]

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(45) D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **35**, 458 (1961).

(46) F. W. Schneider and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **84**, 4215 (1962).

(47) W. Forst and P. St. Laurent, *Can. J. Chem.*, **43**, 3052 (1965).

(48) W. Forst and P. St. Laurent, *J. Chim. Phys.*, **67**, 1018 (1970).

(49) Note that using eq 98 and 99, $G(E)$ and $N(E)$ are both calculated with the same θ, whereas eq 95 requires a θ for $N(E)$ and another θ for $G(E)$, *i.e.*, eq 97 must be solved twice at every E, once with $k = 0$ and then again with $k = 1$. In unimolecular rate calculations this is not much of a handicap because $N(E)$ is calculated for the molecule and $G(E)$ is calculated for the transition state at $E - E_0$, so that not only are the energies different, but the collection of oscillators and rotors for which the density and sum of states are calculated are also different, so that in any event two different θ's are required.

(50) A. Ralston, "A First Course in Numerical Analysis," McGraw-Hill, New York, N. Y., 1965, p 332.

(51) M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, U. S. Air Force Report ARL 62-426, 1962.

(52) M. L. Vestal, *J. Chem. Phys.*, **43**, 1356 (1965).

(53) M. Vestal and G. Lerner, U. S. Air Force Report ARL 67-0114, 1967.

(54) J. C. Tou and A. L. Wahrhaftig, *J. Phys. Chem.*, **72**, 3034 (1968).