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THE SYMMETRIC TOP

SPIN-ROTATIONAL PARTITION FUNCTION

by

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Thesis Director's signature:

[Signature]

Houston, Texas

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I. **INTRODUCTION**

Early in the study of statistical mechanics, one is introduced to the consequences of the Pauli exclusion principle as applied to the spin-rotational partition function of homonuclear diatomic molecules. After demonstrating how the partition function can be broken into a sum over even and a sum over odd rotational levels with proper spin weights, the example of ortho and para hydrogen is usually given. From a study of this system, inferences are drawn which help us to convince ourselves that we may obtain sufficiently accurate spin-rotational p.f. (partition functions) in most all instances by merely dividing the sum over all states by the so-called symmetry number associated with the molecule. In order to see how good this sort of corrected Boltzmann counting actually is, we deal with the analogous effects of the exclusion principle upon the symmetric top p.f. (A symmetric top molecule has at least two equal moments of inertia.)

Also, since a symmetric top is capable of possessing much symmetry, it presents a more general problem than that of the simple linear molecule which can have only two elements of rotational symmetry.

We have chosen the symmetric top as opposed to the more general asymmetric top because of the existence of a relatively simple general expression for the energy levels of the symmetric top, where-
as no such explicit expression exists for the asymmetric top. Although the asymmetric top can be treated, it is not easily amenable to revealing analytic manipulations which we shall find so important in characterizing the general behavior of the partition function.

The format is essentially this. First, a formalism is developed such that an expression for the sum over allowed states is readily set up from the cycle structures of the operations of the rotational symmetry group associated with the molecule under question. This turns out to be a series good for calculations at low temperatures. Secondly, high temperature forms are developed from which we are able to see how fast the corrections to the "symmetry number approximation" diminishes with increased temperature and/or size of the molecule. A number of physical interpretations are drawn which give qualitative information concerning the behavior of what we label as statistical effects.

The most important points of interest are:

1. We may regard the spin-rotational partition function as consisting of contributions from each element of the molecule's rotational group.

2. The contribution of the identity element increases with temperature like $T^{r}$. $\mathfrak{r}$ is 3/2 for all symmetric tops except for the limiting case of the linear molecule where it is 2/2.
3. Contributions from the other symmetry elements decrease with increase in temperature like $T^\mu e^{-\lambda T}$. $\mu$ is some small positive number and $\lambda$ is a function of the moment of inertia about the axis of rotation associated with each group element.

The contribution from the identity element dominates at high temperatures. It turns out to be the "corrected Boltzmann" partition function.

**Nomenclature.** A partition function involving identical particles can be divided into its corrected Boltzmann part plus corrections to this approximation. As will become clear in the development, we choose to call these two parts the direct p.f. ($Z_d$) and the exchange p.f. ($Z_{ex}$) respectively.

\[ Z = Z_d + Z_{ex} \quad (1.1) \]

\[ Z_d = \frac{1}{\hbar} \sum_n g_{n,s} e^{-\beta E_n} \quad (1.2) \]

\[ Z_{ex} = Z - Z_d \quad (1.3) \]

The symmetry number is denoted by $\hbar$. The sum is over all energy levels and $g_{n,s}$ is the degeneracy of the $n$th energy level including nuclear spin but disregarding the exclusion principle. Quite arbi-
trarily, we call non-zero $Z_{ex}$'s quantum statistical effects, and the difference between the classical p.f. and the direct p.f. we call quantum effects. $Z_{ex}$ originates from our inability to distinguish between identical particles. But, this indistinguishability is a consequence of the uncertainty principle, a quantum effect. 1
II. **FORMULATION OF THE LOW TEMPERATURE EXPANSIONS.**

The Exclusion Principle and Group Theory. In what follows, a well known relationship from group theory is used to set up the spin-rotational partition function. Wilson has described in detail the group theoretical machinery necessary for finding the true degeneracy of an energy level when the transformation properties of its set of degenerate eigenfunctions are known. He gives the weights of the rotational levels of various types of molecules. We employ his method to procure explicit expressions for the weights of symmetric top energy levels and use these weights to construct the spin-rotational p.f.

The canonical partition function is of the form:

\[ Z = \sum_n \omega_n e^{-\beta E_n} \]  

where the sum is over all energy levels of the system. \( E_n \) is the energy of the \( n \)th energy level and \( \omega_n \) is the number of linearly independent solutions of the proper symmetry satisfying Schrödingers equation:

\[ H \psi_n = E_n \psi_n \]
Since $H$, the Hamiltonian, is a linear differential operator, any linear combination of the degenerate $\psi_n$'s is also a solution. The number of such independent solutions corresponding to a given eigenvalue $E_n$ is the degeneracy of the eigenvalue. When we include the nuclear spin degeneracy, we call this number $g_{n,s}$. However, the Pauli exclusion principle states that only those combinations which are either symmetric or antisymmetric with respect to all pairwise interchanges of identical particles are acceptable. If a pairwise interchange involves Bose particles (those with integer spins), the wavefunction must be symmetric and if it involves Fermi particles (those with half-integer spins), it must be antisymmetric. Therefore, with this extra restriction, nature requires that $\omega_n \leq g_{n,s}$.

We now turn to obtaining an expression for $\omega_n$ in terms of the transformation properties of the set of $g_{n,s}$ degenerate eigenfunctions. Our model, a rigid rotor, will be any molecule which can be satisfactorily described by the wavefunction:

$$\psi = \psi_e \psi_v \psi_r \psi_s \psi_t$$

(2.2)

That is, the wavefunction is a product of electronic, vibrational, rotational, nuclear spin and translational wavefunctions. This is known to describe moderately well the behavior of many small polyatomic molecules. It is fairly straight forward to include free internal rotation,
but because this complicates the presentation without presenting anything essentially new, we omit this category of molecules.

Associated with a molecule is its rotational group. This is the group consisting of symmetry operations which are equivalent to rotations. This will usually be a subgroup of the full point group of the molecule.

A given eigenvalue will in general be degenerate. This set of degenerate eigenfunctions forms a basis for a reducible representation of the rotational group of the molecule. That is, they serve as a set of functions from which we may construct a matrix representation for each of the elements of our group. From group theory we know that the number of independent linear combinations we can form which are a basis for an irreducible representation, \( \lambda \), is given by:  

\[
\omega^{(\lambda)} = \frac{1}{\hbar} \sum_{\rho} h_{\rho} \chi_{\rho}^{(\lambda)} \phi_{\rho},
\]

(2.3)

where \( h \) is the order of the group, \( h_{\rho} \) is the number of elements in the \( \rho \)-th class, the \( \rho \)-sum is over all classes, \( \chi_{\rho}^{(\lambda)} \) is the character of the \( \rho \)-th class of the \( \lambda \)-th irreducible representation, and \( \phi_{\rho} \) is the trace of the matrix representation of the transformation properties of our set of degenerate eigenfunctions. So, without actually constructing the wavefunctions, equation (2.3) tells us the number of linearly independent eigenfunctions having a specified symmetry which
can be constructed by taking linear combinations of the unsymmetrized eigenfunctions. For our purposes \( \lambda \) will be either the symmetric or antisymmetric irreducible representation as is dictated by the exclusion principle.

Eigenfunctions in the form of equation (2.2) will be a basis for a direct product representation. Since the trace of a direct product representation is the product of the traces of the separate representations, we can write:

\[
\omega_n^{(a)} = \frac{1}{\hbar} \sum_\rho \hbar \rho \chi_\rho^{(a)} \phi_{\rho e} \phi_{\rho v} \phi_{\rho r} \phi_{\rho s} \phi_{\rho t}
\]

where \( e, v, r, s, \) and \( t \) have the same meaning as in (2.2). The subscript \( n \) is included to remind us that we shall now be interested in the number of times the irreducible representation \( \lambda \) occurs in the reducible representation provided by the degenerate eigenfunctions of the \( n \)th energy level.

Now, let us examine the implications of the Pauli exclusion principle. Our product wavefunction must be symmetric or antisymmetric with respect to the interchange of any pair of identical nuclei according to whether the pair consists of bosons or fermions respectively. This tells us that the matrix representing the transformation properties of the properly symmetrized set of degenerate eigenfunctions is one dimensional with a trace of either plus or minus one. That is, the exclusion
principle determines $\chi^{(n)}_\rho$ of equations (2.3) and (2.4). For a Bose system it is always +1. To find its value for a molecule which contains Fermi nuclei, we examine an operation of the $\rho$ th class. If the operation involves an even number of pairwise interchanges of Fermi particles, it equals +1, and if an odd number, it equals -1. In the next paragraph we shall describe a quick way to determine $\chi^{(n)}_\rho$.

A single pairwise interchange is called a transposition. Any permutation can be achieved by a series of transpositions. Though the number of transpositions one can use to realize a given permutation is not unique, it can be demonstrated that the parity of this number is always the same. This is necessary if the exclusion principle is to be unambiguous. Suppose we have N identical particles and we permute these particles by applying the permutation operator $\hat{P}$ as is partially specified by its cycle structure:

$$\hat{P} = \prod_{i=1}^N a_i \cdots a_N = t_1 a_1 t_2 a_2 \cdots t_N a_N$$

That is, the permutation involves $a_1$ independent cycles of length 1, $a_2$ of length 2, etc. The first expression is standard notation for cycle structures. The second is an alternate notation in which we have introduced the quantity $t$ to denote the type of nuclei involved in the cycle. One can readily show that the parity of this permutation is even if $N - \sum a_i$ is even and it is odd if $N - \sum a_i$ is odd. Hereafter, we shall
refer to $\sum q_i$ as $C(\rho)$. It is the total number of cycles involved in a permutation and is a characteristic of each class. Now, we can write for the properly symmetrized eigenfunctions,

$$\hat{P} \psi_n (i, a, b, \ldots N) = (-1)^{N_f - C(\rho, f)} \psi_n (i, a, b, \ldots N)$$

where $C(\rho, f)$ is the total number of cycles of the Fermi particles and $N_f$ is the total number of Fermi particles. Therefore,

$$\chi^{(\lambda)} = (-1)^{N_f - C(\rho, f)} .$$

This formula is independent of the presence of Bose particles because interchanges involving these must always be symmetric.

__Transformation Properties of the Sets of Degenerate Eigenfunctions.__

We now look for the traces of the various terms of our product representation as is required by equation (2.4).

A. **Spin Functions.** Turning first to the spin functions, we note that the trace is the number of functions which remain invariant under a given permutation of the labels of the particles. There are $(2s_A + 1)^{N_A}$ degenerate spin functions for a collection of $N_A$ nuclei of type A with spin $s_A$. We now demonstrate that the trace for a class $\rho$ with cycle structure $A_1^{a_1} A_2^{a_2} \ldots A_n^{a_n}$ of this $(2s_A + 1)^{N_A}$
dimensional reducible representation is given by

\[ \mathcal{O}_{\mathcal{O}_S} = (2s + 1)^{C(\mathcal{O}_S)} \]

(2.7)

\(C(\mathcal{O}_S)\), which we mentioned previously, is the total number of cycles involved in any one permutation of the \(\mathcal{O}\) th class. Another way of looking at \(C(\mathcal{O}_S)\) is that it is the number of parts of the partitioning induced by any of the permutations of the class when it operates on the particles. Reasoning as follows, one can see why relation (2.7) is true. If a spin function is to remain invariant under a permutation, each particle involved in a cycle must have the same spin function. Since there is a choice of \((2s + 1)\) functions for each cycle, the total number of possible choices of invariant functions is \((2s + 1)^{\text{power}}\) of the number of independent cycles. Therefore, the trace of spin function transformation matrix is given by the above relation.

The development so far applies only to spin functions of molecules with one set of identical nuclei. When there is more than one set, we have

\[ \psi_s = \psi_{s,A} \psi_{s,B} \cdots \]
where $\psi_{s, A}$ is the spin function of nuclei of type A and so on. In carrying through the analysis, we would use the direct product of the various spin functions. Therefore, we see that the only change in our previous result is that we now use a product over all types of nuclei:

$$\phi_{\rho, S} = \prod_i (2s_i + 1) C^{\rho, i}$$  \hspace{1cm} (2.8)

As an example, $\phi_{\rho, S}$ for a permutation of the structure:

$$A \xrightarrow{B} A$$

$$B \xrightarrow{C} B$$

$$C \xrightarrow{C} C$$

is $(2s_A + 1)^1 (2s_B + 1)^2 (2s_C + 1)^1$.

In our model the permutations of the nuclei are those induced by rotations.

B. **Rigid Rotor Eigenfunctions and Eigenvalues.** We now outline some quantum mechanical results concerning the rotation of certain rigid rotors. First, the rotational eigenvalues are given, then their degeneracies, after which, the traces of the matrix representation provided by the degenerate eigenfunctions are listed. For a discussion of the quantum mechanical rigid rotor we refer
our readers to references (2) and (4).

a. Linear Molecules

\[ E_\ell = \frac{\hbar^2}{2I} (\ell+1) \ell \quad \ell = 0,1,2,\ldots \]
\[ \beta E_\ell = \sigma (\ell+1) \ell \quad \sigma = \frac{\hbar^2}{2I} \kappa T \]

\( \beta = \frac{1}{\kappa T} \), \( \hbar \) is Planck's constant divided by \( 2\pi \), and \( I \) is the moment of inertia.

(2.) Each energy level is \((2\ell + 1)\) degenerate.

(3.) \( \phi_{\rho,\ell} = (2\ell + 1) \) for the identity element.
\[ \phi_{\rho,\ell} = -(2\ell + 1) \] for the \( C_2 \) element.

b. Spherical Tops

\[ E_\ell = \frac{\hbar^2}{2I} (\ell+1) \ell \quad \ell = 0,1,2,\ldots \]
\[ \beta E_\ell = \sigma (\ell+1) \ell \quad \sigma = \frac{\hbar^2}{2I} \kappa T \]

(2.) Each energy level is \((2\ell + 1)^2\) degenerate.

(3.) \( \phi_{\rho,\ell} = (2\ell + 1)^2 \) for the identity element.

\[ \phi_{\rho,\ell} = (2\ell + 1) \sum_{\kappa = -\ell}^{\ell} \cos \alpha_\rho \kappa \]
\[ = (2\ell + 1) \frac{\sin(2\ell + 1)\alpha_\rho \kappa}{\sin \frac{\alpha_\rho \kappa}{2}} \]

for classes involving a rotation by \( \alpha_\rho \) radians.
c. Symmetric Tops

(1.) \[ E_{\ell, \kappa} = \frac{\hbar^2}{2 I} (\ell + 1) \ell + \frac{\hbar^2}{2} \left( \frac{1}{I_c} - \frac{1}{I} \right) \kappa^2 \]

\[ \ell = 0, 1, 2, \ldots \quad \kappa = -\ell, - (\ell - 1), \ldots, \ell \]

\[ \beta E_{\ell, \kappa} = \sigma (\ell + 1) \ell + (\sigma_c - \sigma) \kappa^2 \]

I is one of the two equal moments of inertia, and \( I_c \) is the moment of inertia about the axis coincident with the principal symmetry axis.

\[ \sigma = \frac{\hbar^2}{2 I} \kappa T \]

\[ \sigma_c = \frac{\hbar^2}{2 I_c} \kappa T \]

(2.) The degeneracy is \( 2(2\ell + 1) \) when \( K \neq 0 \) and \( (2\ell + 1) \) when \( K = 0 \).

(3.) Classes designated by \( \rho \) involving rotations by the angle \( \alpha_\rho \) about the principal axis of symmetry have:

\[ \phi_{\rho, \ell, \kappa} = 2 (2\ell + 1) \cos(\alpha_\rho K) \text{ when } K \neq 0. \]

\[ = (2\ell + 1) \text{ when } K = 0. \]

On the other hand, those classes designated by the index \( \rho' \) involving \( C_2 \) rotations about an axis perpendicular to the principal axis of symmetry have:

\[ \phi_{\rho', \ell, \kappa} = 0 \text{ when } K \neq 0. \]

\[ = (-1)^\ell (2\ell + 1) \text{ when } K = 0. \]

C. The Other Eigenfunctions

Since the translational eigenfunction depends upon the center of mass coordinates, rotations of the molecule always leave it invariant.
This part of the wavefunction can therefore be ignored.

The electronic eigenfunctions must be in general determined experimentally. Since for most molecules, only the ground state is important in calculations at ordinary temperatures, we need only consider this state. The ground state of most molecules is totally symmetric.

The vibrational eigenfunction transformation properties for other than the ground and first excited states are complicated. In the ground state it is totally symmetric. The fundamentals are of the same symmetry as the normal coordinate of the excited mode. As with the electronic wavefunction, we will be primarily interested in the temperature range such that the molecule will be in its ground vibrational state.

Construction of the Spin Rotational Partition Functions.

Finally, we have enough information on hand to use equation (2.4).

We only consider molecules in their ground electronic-vibration state and therefore presuppose that:

$$\phi_{\rho, e} = 1, \quad \phi_{\rho, v} = 1$$

With this in mind, equation (2.4) can be written as:

\begin{equation}
\omega_{n}^{(3)} = \frac{1}{h} \sum_{\rho} h_{\rho} \chi_{\rho}^{(3)} \phi_{\rho, s} \phi_{\rho, n}
\end{equation}
Again, $\omega_n^{(\lambda)}$ is the number of independent linear combinations we can form of the proper symmetry for each energy, therefore, it is the weight or true degeneracy of the $n$th level.

The partition function becomes:

$$Z = \sum_n \omega_n^{(\lambda)} e^{-\beta E_n}$$  \hspace{1cm} (2.10)

Using (2.9) for $\omega_n^{(\lambda)}$ and interchanging the order of summation gives

$$Z = \frac{i}{\hbar} \sum_{\rho} h_\rho \chi_{\rho}^{(\lambda)} \phi_{\rho, s} \sum_n \phi_{\rho, n} e^{-\beta E_n}.$$  \hspace{1cm} (2.11)

The index $n$ runs over all energy levels.

The identity element is in a class by itself. For this class one gets:

$$\chi_I^{(\lambda)} = (-1)^{N_F - N_F} = +1$$

$$\phi_{i, s} = \prod_i (2S_i + 1)^{C(I, i)}$$

\(\phi_{i, n} = g_n\), the total number of rotational basis functions.

Segregation of the identity term in equation (2.11) gives

$$Z = \frac{i}{\hbar} \prod_i (2S_i + 1)^{C(I, i)} \sum_n g_n e^{-\beta E_n}$$

$$+ \frac{i}{\hbar} \sum_{\rho \neq I} h_\rho \chi_{\rho}^{(\lambda)} \phi_{\rho, s} \sum_n \phi_{\rho, n} e^{-\beta E_n}$$

$$= Z_d + Z_{ex}.$$
$Z_d$ can be said to have arisen from the ever present identity symmetry operation, and $Z_{ex}$ from the operations which actually interchange identical particles.

Using equation (2.11) along with the appropriate energy levels and traces, we are now able to construct the partition functions of the linear, spherical, and symmetric tops.

A. The Linear Molecule With a $C_2$ Element of Rotational Symmetry.

\[
Z = \frac{1}{2} \prod_i \left( 2S_i + 1 \right) C(I_i, i) \sum_{L=0}^{\infty} (2L+1) e^{-\sigma(L+1)L} \tag{2.13}
\]

\[
+ \frac{1}{2} \left( -1 \right)^{N_f} C(C_2, f) \prod_i \left( 2S_i + 1 \right) C(C_2, i) \sum_{L=0}^{\infty} (-1)^L (2L+1) e^{-\sigma(L+1)L}
\]

$N_f$ is the total number of Fermi nuclei. $C(C_2, i)$ is the rather clumsy notation for the number of cycles involving the type $i$ nuclei induced by the $C_2$ rotation. $C(C_2, f)$ is the analogous count of all cycles involving Fermi nuclei. $C(I, i)$ reduces to nothing more than the total number of nuclei of type $i$.

B. The Spherical Top.

\[
Z = \frac{1}{\hbar} \prod_i \left( 2S_i + 1 \right) C(I_i, i) \sum_{L=0}^{\infty} (2L+1)^2 e^{-\sigma(L+1)L} \tag{2.14}
\]

\[
+ \frac{1}{\hbar} \sum_{p \neq 1} \rho(-1)^{N_f} C(\rho, f) \prod_i \left( 2S_i + 1 \right) C(\rho, i) \sum_{L=0}^{\infty} (2L+1) \frac{\sin((2L+1)\alpha_p)}{\sin(\alpha_p/2)} e^{-\sigma(L+1)L}
\]
$\alpha_\rho$ is the angle of rotation of the $\rho$th class and $h_\rho$ is the number of elements in that class. Here we point out that it is not necessary to sum over the classes. We could have summed over all symmetry elements instead of over the classes.

**C. The General Symmetric Top**

\[
Z = \frac{i}{\hbar} \prod_i (2S_i + 1) C(i, i) \sum_{\ell = 0}^{\infty} (-1) \ell (\ell + 1) \sum_{\kappa = -\ell}^{\ell} e^{-\sigma(\ell+1)\ell} e^{-\lambda^2} \\
+ \frac{1}{\hbar} \sum_{\rho \neq \rho} (-1)^{N_\rho} C(\rho, \rho) \prod_i (2S_i + 1) C(i, i) \sum_{\ell = 0}^{\infty} (-1) \ell (\ell + 1) \sum_{\kappa = -\ell}^{\ell} \cos(\alpha_\rho \kappa) e^{-\lambda^2} \\
+ \frac{1}{\hbar} \sum_{\rho} (-1)^{N_\rho} C(\rho, \rho) \prod_i (2S_i + 1) C(i, i) \sum_{\ell = 0}^{\infty} (-1) \ell (\ell + 1) e^{-\sigma(\ell+1)\ell}
\]

As previously mentioned, $\sum_\rho$ denotes the sum over classes involving rotations about the principle axis and $\sum_\rho'$ denotes the sum over classes involving $C_2$ rotations perpendicular to the principle axis.

**Specific Examples**

A number of spin-rotational p.f. will now be constructed. We have seen that the p.f. can be written down from inspection of the cycle structure of the symmetry elements.
Example (1), CH$_4$, A Spherical Top.

The carbon nucleus is a boson and the hydrogen nucleus is a fermion.

$N_f$, the number of fermions, is four.

<table>
<thead>
<tr>
<th>T</th>
<th>I</th>
<th>4C$_3$</th>
<th>4C$_3^2$</th>
<th>3C$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle Structure</td>
<td>C$_1^1$H$_1^4$</td>
<td>C$_1^1$H$_1^1$H$_3^1$</td>
<td>C$_1^1$H$_1^1$H$_3^1$</td>
<td>C$_1^1$H$_2^2$</td>
</tr>
<tr>
<td>C($\rho$, H)</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>C($\rho$, C)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>C($\rho$, f)</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>(-1)$^4$C($\rho$, f)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Using equation (2.14) we get

\[
Z = \frac{1}{\text{Vol}} \left(2S_c + 1\right) \left(2S_h + 1\right)^4 \sum_{\ell=0}^{\infty} (2\ell+1)^2 \frac{1}{\ell+1} e^{-\sigma(\ell+1)\ell} \\
+ \frac{8}{\text{Vol}} \left(2S_c + 1\right) \left(2S_h + 1\right)^2 \sum_{\ell=0}^{\infty} (2\ell+1) \frac{\sin(2\ell+1)\pi/3}{\sin \pi/3} e^{-\sigma(\ell+1)\ell} \\
+ \frac{3}{\text{Vol}} \left(2S_c + 1\right) \left(2S_h + 1\right)^2 \sum_{\ell=0}^{\infty} (-1)^\ell (2\ell+1) e^{-\sigma(\ell+1)\ell}
\]

Because all of the permutations are even, we get the same result for CD$_4$. 
Example (2), $C_8H_8$, Cubane, a Spherical Top.

The number of fermions $(N_f)$ is 8.

<table>
<thead>
<tr>
<th>Cycle Structure</th>
<th>$C_1 H_1^8$</th>
<th>$C_3 H_1^2 H_3 H_1^2$</th>
<th>$C_2 H_2^4$</th>
<th>$C_4 H_4^2$</th>
<th>$C_2 H_2^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C(\rho, H)$</td>
<td>8</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>$C(\rho, C)$</td>
<td>8</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>$C(\rho, f)$</td>
<td>8</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>$(\rho - C(\rho, f))$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Equation (2.14) gives:

$$Z = \frac{1}{2^4} (2S_c + 1)^8 (2S_h + 1)^8 \sum_{l=0}^{\infty} (2l+1) e^{-\sigma(l+1)l}$$

$$+ \frac{8}{2^4} (2S_c + 1)^4 (2S_h + 1)^4 \sum_{l=0}^{\infty} (2l+1) \frac{\sin(2l+1) \pi/3}{\sin \pi/3} e^{-\sigma(l+1)l}$$

$$+ \frac{9}{2^4} (2S_c + 1)^4 (2S_h + 1)^4 \sum_{l=0}^{\infty} (-1)^l (2l+1) e^{-\sigma(l+1)l}$$

$$+ \frac{6}{2^4} (2S_c + 1)^2 (2S_h + 1)^2 \sum_{l=0}^{\infty} (2l+1) \frac{\sin(2l+1) \pi/4}{\sin \pi/4} e^{-\sigma(l+1)l}$$
Example (3) $B_{3}^6F_{6}^2$, A Symmetric Top.

This is a generalized cyclopropane-like system. We let

$B$ be a boson and $F$ a fermion. Also, we introduce the notation:

$$\sigma_{\kappa \ell} = \sigma(\ell+1) \ell + (\sigma_c - \sigma) K^z$$

<table>
<thead>
<tr>
<th>D$_3$</th>
<th>1</th>
<th>C$_3$</th>
<th>C$_3^2$</th>
<th>3C$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle Structure</td>
<td>$F_1^6B_1^3$</td>
<td>$F_3^2B_3^2$</td>
<td>$F_3^2B_3^1$</td>
<td>$F_2^3B_1^1B_2^1$</td>
</tr>
<tr>
<td>C$(\rho, F)$</td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>C$(\rho, B)$</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>C$(\rho, F)$</td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>$(-1)^{6-C(\rho, F)}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

From equation (2.15) we get:

$$Z = \frac{1}{6} \left(2S_F + 1\right)^6 \left(2S_B + 1\right)^3 \sum_{\ell=0}^{\infty} \sum_{\kappa = -\ell}^{\ell} (2\ell+1) e^{-\sigma_{\kappa \ell}}$$

$$+ \frac{2}{6} \left(2S_F + 1\right)^2 \left(2S_B + 1\right) \sum_{\ell=0}^{\infty} \sum_{\kappa = -\ell}^{\ell} (2\ell+1) \cos \frac{2\pi \kappa}{3} e^{-\sigma_{\kappa \ell}}$$

$$- \frac{3}{6} \left(2S_F + 1\right)^3 \left(2S_B + 1\right)^2 \sum_{\ell=0}^{\infty} (-1)^{\ell} (2\ell+1) e^{-\sigma(\ell+1)\ell}$$
Example (4) Benzene $C_6H_6$, A Symmetric Top.

Carbon nuclei have zero spin and are bosons. This allows us to ignore them. H can be a hydrogen nucleus or any fermion.

<table>
<thead>
<tr>
<th>$D_6$</th>
<th>I</th>
<th>2C$_6$</th>
<th>2C$_3$</th>
<th>C$_2$</th>
<th>3C$_2$</th>
<th>3C$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle Structure</td>
<td>H$_1^6$</td>
<td>H$_6^1$</td>
<td>H$_3^2$</td>
<td>H$_2^3$</td>
<td>H$_1^2$H$_2^2$</td>
<td>H$_2^3$</td>
</tr>
<tr>
<td>C($\rho$, H)</td>
<td>6</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>C($\rho$, f)</td>
<td>6</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>(-1)$^6$C($\rho$, f)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Using equation (2.15) and the notation introduced in the last example, we obtain:

$$Z = \frac{1}{i^2} (2S_H + 1)^6 \sum_{\ell=0}^{\infty} \sum_{\kappa=-\ell}^{\ell} (2\ell + 1) \Theta^{-(\ell+1)}$$

$$- \frac{3}{i^2} (2S_H + 1) \sum_{\ell=0}^{\infty} \sum_{\kappa=-\ell}^{\ell} (2\ell + 1) \cos \frac{\pi \kappa}{3} \Theta^{-(2\ell + 1)}$$

$$+ \frac{3}{i^2} (2S_H + 1)^2 \sum_{\ell=0}^{\infty} \sum_{\kappa=-\ell}^{\ell} (2\ell + 1) \cos \frac{2\pi \kappa}{3} \Theta^{-(2\ell + 1)}$$

$$- \frac{3}{i^2} (2S_H + 1)^3 \sum_{\ell=0}^{\infty} \sum_{\kappa=-\ell}^{\ell} (2\ell + 1) \Theta^{-(2\ell + 1)}$$

$$+ \frac{3}{i^2} (2S_H + 1)^4 \sum_{\ell=0}^{\infty} (-1)^\ell (2\ell + 1) \Theta^{-(3\ell + 1)}$$

$$- \frac{3}{i^2} (2S_H + 1)^3 \sum_{\ell=0}^{\infty} (-1)^\ell (2\ell + 1) \Theta^{-(4\ell + 1)}$$

.$$
If \( H \) were a boson, the only change is that all of the signs in front of the above six terms would be positive.

**Example (5) A Hypothetical Linear Molecule.**

\[
\text{C} \longrightarrow \text{B} \longrightarrow \text{A} \longrightarrow \text{B} \longrightarrow \text{C}
\]

We suppose that \( A \) and \( C \) are fermions and that \( B \) is a boson. We give this example only because it presents some generality.

<table>
<thead>
<tr>
<th>( C_2 )</th>
<th>I</th>
<th>( C_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle Structure</td>
<td>( A_1^1 B_1^1 C_1^2 )</td>
<td>( A_1^1 B_2^1 C_2^3 )</td>
</tr>
<tr>
<td>( C(\rho, A) )</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( C(\rho, B) )</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>( C(\rho, C) )</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>((-1)^3 C(\rho, f))</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

From equation (2.13) we get:

\[
\mathbb{Z} = \frac{1}{2} \left( 2S_A + 1 \right) \left( 2S_B + 1 \right) \left( 2S_C + 1 \right) \sum_{\ell = 0}^{\infty} \left( 2\ell + 1 \right) e^{-\sigma(\ell + 1)\ell}
\]

\[
-\frac{1}{2} \left( 2S_A + 1 \right)' \left( 2S_B + 1 \right)' \left( 2S_C + 1 \right)' \sum_{\ell = 0}^{\infty} (-1)\ell (2\ell + 1) e^{-\sigma(\ell + 1)\ell}
\]
III. A CLOSER LOOK AT THE PARTITION FUNCTION

The Partition Function as a Weighted Sum Over "Symmetry Functions." The p.f. of the general symmetric top (see equation (2.15)) can be written as follows:

\[ Z = \frac{1}{h} \sum_{\alpha} A_{\alpha} S(\alpha, t) + \frac{1}{h} \sum_{\alpha'} A_{\alpha'} S(\pi, 0) \]  

(3.1)

The sum over \( \alpha \) is over all symmetry elements about the principle axis of symmetry, and the sum over \( \alpha' \) is over those \( C_2 \) rotations about an axis perpendicular to this axis. The coefficient \( A_{\alpha} \) is given by:

\[ A_{\alpha} = (-i)^{N_f} C(\alpha, f) \prod_i (\epsilon s_i + \frac{1}{i}) C(\alpha, i) \]  

(3.2)

We remind ourselves of the notation. \( N_f - C(\alpha, f) \) is the number of Fermi nuclei in the molecule less the total number of cycles consisting of Fermi nuclei induced by the rotation of \( \alpha \) radians. Also, \( C(\alpha, i) \) is the number of cycles involving the \( i \)-th type of nucleus of spin \( s_i \). Next, we have set:

\[ S(\alpha, t) = \sum_{l=0}^{\infty} (2l+1) \epsilon^{-\sigma(l+1)} \sum_{k=-l}^{l} \epsilon^{-t \sigma} \cos(\alpha k), \]  

(3.3)
with
\[ t = \frac{\sigma_c}{\sigma} - 1 \]

or
\[ t = \frac{I}{I_c} - 1 \]

In the special case of the spherical top, \( Z \) becomes

\[ Z = \frac{1}{\hbar} \sum_{\alpha} A_{\alpha} S(\alpha, \sigma) \tag{3.4} \]

the sum now being over all symmetry elements. Specifically, we have

\[ S(\alpha, \sigma) = \sum_{\ell=0}^{\infty} (2\ell+1) \frac{\sin(2\ell+1) \frac{\alpha}{2}}{\sin \frac{\alpha}{2}} e^{-\sigma(\ell+1)\ell} \]

We note that for actual computations, we need only concern ourselves with the function \( S(\alpha, t) \). This function will be of such major importance in the ensuing pages that we give it the name "symmetry function." It is a function associated with each symmetry element of the molecule. Implicit in \( S(\alpha, t) \) are the independent parameters \( T \), the temperature, and \( I \), one of the two equal moments of inertia. However, it will be convenient to regard them as constants. To vary \( t \) then, we vary \( I_c \), the parallel moment of inertia.
If the usual high temperature approximation of setting the whole partition function equal to $Z_d$ is to be correct, the $S(\alpha, t)$ for $\alpha \neq 0$ must be small. Some of the interesting properties of the symmetry functions which lead to this and other results will now be discussed.

**Properties of the Symmetry Function.** $S(\alpha, t)$ in the low temperature form ($\sigma$’s $\gtrsim$ about 1), is

$$S(\alpha, t) = \sum_{l=0}^{\infty} (2l+1) e^{-\sigma(l+1)l} \sum_{k=-l}^{l} e^{-t \sigma k^2} \cos(\alpha k). \tag{3.5}$$

$S(\alpha, t)$, as one can readily verify, satisfies the heat equation.

$$\frac{\partial^2 S}{\partial \alpha^2} = \frac{1}{\sigma} \frac{\partial S}{\partial t} \tag{3.6}$$

S plays the role of temperature, $\alpha$ a coordinate, and $t$ the time. $S(\alpha, t)$ is a periodic and even function of $\alpha$, that is:

$$S(\alpha \pm \pi n, t) = S(\alpha, t)$$

$$S(-\alpha, t) = S(\alpha, t)$$

The above properties qualify the following interpretation of $S(\alpha, t)$. Given some initial temperature distribution about a ring;
the distribution's dependence on time and position is given by $S(\alpha, t)$, the symmetry function. The time variable is

$$\frac{I}{I_c} - 1.$$

Time being equal to zero corresponds to a spherical top ($I = I_c$). Time being negative corresponds to an oblate top ($I < I_c$). Time being positive corresponds to a prolate top ($I > I_c$). Then, the entire progression of the symmetry function in going from an extreme oblate top ($t = -\frac{1}{2}$), passing through the spherical top ($t = 0$), and going all the way to the linear molecule ($t = \infty$) is in complete analogy with the redistribution of heat about a ring from an initial temperature distribution of $S(\alpha, -\frac{1}{2})$ (see fig. 1 and fig. 2). $S(\alpha, -\frac{1}{2})$ is the symmetry function of a flat molecule. Times less than $-\frac{1}{2}$ are unphysical since $I_c$ can never be greater than twice $I$. The analogy with the heat flow problem gives us an intuitive feel for the symmetry functions. Having information about $S(\alpha, t)$ for some particular $t$, we can envision its form at another $t$ by referring to the familiar way heat redistributes itself.

**Consequences of the Heat Analogy.** $S(\alpha, t)$, as a consequence of satisfying the heat equation, has a number of interesting properties.

First, by expanding it in a Taylor series about some time $t$ and using:
FIG. 1 An illustration of the time progression analogy.
\[
\frac{\partial^n S(\alpha, t)}{\partial t^n} \bigg|_{t=t_o} = \sigma^n \frac{\partial^{2n} S(\alpha, t_o)}{\partial \alpha^{2n}}
\]

gives

\[
S(\alpha, t-t_o) = \sum_{n=0}^{\infty} \frac{(t-t_o)^n}{n!} \sigma^n \frac{\partial^{2n} S(\alpha, t_o)}{\partial \alpha^{2n}}
\]

or

\[
S(\alpha, t-t_o) = e^{(t-t_o) \sigma D^2} S(\alpha, t_o),
\]

where

\[
D = \frac{\partial}{\partial \alpha}
\]

Also, it can be shown that when \( t \) is greater than \( t_o \), the above operation can be expressed as the integral: (See appendix 1)

\[
S(\alpha, t-t_o) = \left[4\pi \sigma (t-t_o) \right]^{-\frac{1}{2}} \int_{-\infty}^{\infty} S(\alpha + \xi, t_o) e^{-\frac{\xi^2}{4 \sigma (t-t_o)}} d\xi.
\]
When \( t \) is less than \( t_o \), it is given by

\[
S(\alpha, -|t-t_o|) = \left[ 4\pi \sigma |t-t_o| \right]^{-\frac{1}{2}} \int_{-\infty}^{\infty} S(\alpha + i\xi, t_o) e^{-\frac{\xi^2}{4\sigma(t-t_o)}} d\xi.
\]

(3.9)

Given a distribution at the time \( t_o \), we can find its distribution at any other time by the above relations. These time progression or regression relations are readily verified by using the low temperature form of \( S(\alpha, t) \) given by equation (3.3).

Using the heat flow analogy, we visualize that as \( t \) tends toward infinity, the heat should flow out evenly and the distribution will become linear. That is, \( S(\alpha, \infty) \) is independent of \( \alpha \). In regard to our molecule, we are then dealing with a linear molecule whose only rotational symmetry element about the principle axis is the identity. So, we use \( S(\alpha, \infty) \) as \( S(0, \infty) \). Now, referring back to the heat flow problem, we know that heat is conserved throughout the heat flow process. This implies that at any time \( t \),

\[
\int_{-\pi}^{+\pi} S(\alpha, t) d\alpha = \text{(constant)} \cdot \text{(total heat)},
\]

or using the fact that \( S(\alpha, \infty) \) is linear,

\[
\int_{-\pi}^{+\pi} S(\alpha, t) d\alpha = 2\pi S(0, \infty).
\]

(3.10)
This implies that the area under a plot of $S(\alpha, t)$ versus $\alpha$ is a constant for all $t$'s. (see fig. 2).
FIG. 2  A plot of $S(\alpha, t)$ at various times for $\sigma = 0.7$. 
IV. **HIGH TEMPERATURE EXPANSIONS.**

At temperatures high enough to produce moderately low values for the parameters \( \sigma \) and \( \sigma_c \) (0.1 and downward), the low temperature form of \( S(\alpha, t) \) is virtually useless for computation. One quickly finds \( S(\alpha, t) \), when \( \alpha \neq 0 \), to be a small number; however, it is difficult to tell how small without considerable labor. Also, its functional dependence upon the parameters involved is completely buried.

**The Approach Taken.** Our approach to obtaining the high temperature expansion of \( S(\alpha, t) \) is basically this. Relations (3.7), (3.8), and (3.9), give \( S(\alpha, t) \) in terms of \( S(\alpha, 0) \), the spherical top symmetry function. \( S(\alpha, 0) \) is closely related to one of the theta functions. The theta functions have two forms. One of these turns out to be a nice expansion of the spherical top symmetry function at high temperatures. Having on hand this one high temperature expression, we get the others by our time progression and regression relationships.

**Summary of the High Temperature Results.** Since the mathematics becomes rather involved in the following pages, we give the first term of the high temperature expansion of \( S(\alpha, t) \) now. To show its explicit dependence upon the variables \( \sigma \) and \( \sigma_c \), we write:

\[
S(\alpha, t) = S(\alpha, \sigma; \sigma_c).
\]
\[ S(\alpha, \sigma; \sigma_c) \sim \]

\[ e^{\frac{\alpha}{\sigma_c} \left( \frac{\alpha}{\sigma} \right)^2 \left( \frac{\sigma}{\sigma_c} \right) \left( \frac{\sigma_c}{\sigma} \right) \left( \frac{\sigma}{\sigma_c} \right)^2 e^{-\frac{\alpha^2}{4\sigma_c^2}}} \left[ 1 + \delta_{\alpha, \sigma} \right] \]

\[ \delta_{\alpha, \sigma} = 1 \text{ if } \alpha = \sigma \text{ and } \delta_{\alpha, \sigma} = 0 \text{ if } \alpha \neq \sigma. \] However, in the immediate neighborhood of \( \alpha = \sigma \) and \( \sigma = 2 \sigma_c \) (as would be the case for a flat molecule with a \( C_2 \) element of symmetry about the principle axis), we get:

\[ S(\sigma, \sigma = 2 \sigma_c) \sim \left( \frac{e^{\frac{\alpha}{\sigma_c} \left( \frac{\alpha}{\sigma} \right)^2 \left( \frac{\sigma}{\sigma_c} \right) \left( \frac{\sigma_c}{\sigma} \right) \left( \frac{\sigma}{\sigma_c} \right)^2 e^{-\frac{\alpha^2}{4\sigma_c^2}}} \right) \]

The exchange effects then vanish like \( T^\mu e^{-\lambda T} \) with increase in temperature. The exponential term easily dominates the qualitative behavior. In all instances we can interpret the combined \( \alpha \) and moment of inertia effects to mean that the smaller the distance we must move the nuclei to interchange identical particles, the greater will be the contribution of this symmetry function to the over-all partition function. This is epitomized by the domination of the contribution from the identity element.

Fig. 3 shows how a symmetry function varies with \( \alpha \) at a moderately high temperature. As the temperature gets higher, we
FIG. 3 A plot of $S(\alpha, -\frac{1}{2})$ for $\sigma = 0.1$. 
get something similar to a Dirac delta function centered at $\alpha$ equal to zero.

**The Spherical Top.** Since $S(\alpha, 0)$ plays such an important role in determining the high temperature behavior of $S(\alpha, t)$, we give it special attention. As we saw previously, the spherical top function is:

$$S(\alpha, 0) = \sum_{\ell=0}^{\infty} (2\ell+1) \frac{\sin(2\ell+1)\alpha}{\sin \frac{\alpha}{2}} e^{-\sigma(\ell+1)\ell} \quad (4.1)$$

It happens that $\vartheta_{2\ell}$, a theta function, is closely related to $S(\alpha, 0)$. 6

$$\vartheta_{2\ell}(\frac{\alpha}{2}, e^{-\sigma}) = 2 \sum_{\ell=0}^{\infty} \cos(2\ell+1)\alpha \frac{\alpha}{2} e^{-\sigma(\ell+\frac{1}{2})^2} \quad (4.2)$$

Comparison of (4.2) with (4.1) gives

$$S(\alpha, 0) = -\frac{i}{\alpha} \frac{\vartheta_{4\ell}}{\sin \frac{\alpha}{2}} \frac{1}{\vartheta_{2\ell}} \frac{\partial}{\partial \frac{\alpha}{2}} \vartheta_{2\ell}(\frac{\alpha}{2}, e^{-\sigma}).$$

Fortunately, Jacobi's transformation of theta functions gives us an alternate form for $\vartheta_{2\ell}$. 6

$$\vartheta_{2\ell}(\frac{\alpha}{2}, e^{-\sigma}) = (\frac{\pi}{\sigma})^{\frac{1}{2}} e^{\frac{-\alpha^2}{4\sigma}} \sum_{\eta=-\infty}^{\infty} (-1)^{\eta} e^{\frac{-\eta^2\pi^2}{\sigma}} \cosh \eta \frac{n\alpha}{\sigma} \quad (4.3)$$
Upon regrouping of terms, the above can be shown to be equivalent to

\[ \mathcal{Q}_2 \left( \frac{\alpha}{2}, e^{-\sigma} \right) = (\frac{\pi}{\sigma})^{\frac{1}{2}} \sum_{n=\pm \infty}^{\infty} (-1)^n e^{-(\alpha + 2n\pi)^2 / 4\sigma}. \]  \hspace{1cm} (4.4)

\( S(\alpha, 0) \) is then given by

\[ S(\alpha, 0) = \]  \hspace{1cm} (4.5)

\[ e^{\sigma_4 \left( \frac{\pi}{\sigma} \right)^2 \frac{1}{\sigma}} \sum_{n=\pm \infty}^{\infty} (-1)^n \left[ \frac{\sinh n\pi \alpha / \sigma}{\sin \alpha / 2} \right] e^{-\frac{n^2 \pi^2}{\sigma}}. \]

or using equation (4.4), we have

\[ S(\alpha, 0) = \]  \hspace{1cm} (4.6)

\[ e^{\sigma_4 \left( \frac{\pi}{\sigma} \right)^2 \frac{1}{\sigma}} \sum_{n=\pm \infty}^{\infty} (-1)^n \frac{\alpha + 2n\pi}{\sin \alpha / 2} e^{-\frac{(\alpha + 2n\pi)^2}{4\sigma}}. \]

Taking the limit of (4.5) or (4.6) as \( \alpha \) goes to zero, we obtain

\[ S(0, 0) = e^{\sigma_4 \left( \frac{\pi}{\sigma} \right)^2 \frac{1}{\sigma}} \sum_{n=\pm \infty}^{\infty} (-1)^n e^{-\frac{n^2 \pi^2}{\sigma}} \left[ 1 - \frac{2n^2 \pi^2}{\sigma} \right] \]  \hspace{1cm} (4.7)
We now have extremely good converging series for all terms which go into the spherical top spin-rotational p.f. At moderately low $\sigma$'s, only the first terms need be kept. (It should be mentioned here that the alternate forms for $S(0, 0)$ and $S(\pi, 0)$ have been used by others.\(^7\), \(^8\))

$Z_{d}$ is the portion of the whole partition function involving the identity element.

$$Z_{d} = \frac{1}{\hbar} \ S(0, 0) \ \frac{C(I, i)}{\prod (2s_{l} + 1)}$$

We have

$$Z_{d} = \frac{1}{\hbar} \ \frac{C(I, i)}{\prod (2s_{l} + 1)} \ \epsilon^{\sigma/4 \left( \frac{\pi}{\sigma} \right)^{1/2} \frac{1}{\sigma}} \left[ 1 + O(\sigma^{-1} \epsilon^{-(2\pi)^2}) \right] \quad (4.8)$$

However, if $\alpha \neq 0$, we get

$$S(\alpha, 0) \ \overset{\sigma \to 0}{\sim} \ \epsilon^{\sigma/4 \left( \frac{\pi}{\sigma} \right)^{1/2} \frac{1}{\sigma}} \frac{\alpha}{\sigma} \frac{\alpha/2}{\sin \alpha/2} \left( 1 + \delta_{\alpha, \pi} \right) \quad (4.9)$$

As explained previously, $\delta_{\alpha, \pi}$ is a kronecker delta between $\alpha$ and $\pi$. $S(\alpha, 0)$, for $\alpha \neq 0$, is the symmetry function associated with $Z_{ex}$. Therefore, $Z_{ex}$ vanishes powerfully with increase in temperature (decrease in $\sigma$) while $Z_{d}$ increases. $Z_{d}$ is a good approximation to
the entire p.f. at all, but extremely low temperatures. The smaller the interchange angle, the larger the contribution of the corresponding $S(\alpha, 0)$ to the total p.f. Table 1 gives the numerical value of $S(\alpha, 0)$ at various values of $\alpha$ with $\sigma$ equal to 0.1. It indicates the rapidity with which the exchange effects fall off. The temperature at which $\sigma$ equals 0.1 for methane corresponds to the modest temperature of only about 77° Kelvin.

The Euler-Maclaurin summation formula for $Z_d$ gives the first term of equation (4.9). One might venture to say that the Euler-Maclaurin expression picks up the contribution from rotations by 0-radians. Corrections to this come from rotations by full multiples of 2\pi radians. With this qualitative picture of the origin of the various terms, it is easy to see that $Z_{ex}$ which arises from rotations of \pi or less, will vanish less rapidly than the corrections to the Euler-Maclaurin approximation for $Z_d$.

**The Symmetric Top.** Letting $t_0$ equal zero in equation (3.7) yields:

$$S(\alpha, t) = e^{t\sigma \frac{\partial^2}{\partial \alpha^2}} S(\alpha, 0)$$

(4.10)

We now proceed to perform the indicated operation using $S(\alpha, 0)$ in its high temperature form in hopes of obtaining a high temperature
Table I.

$S(\alpha, 0)$ vs. $\alpha$ for $\sigma = 0.1$

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$S(\alpha, 0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>57.468 822 445</td>
</tr>
<tr>
<td>$\pi/4$</td>
<td>12.615 830 545</td>
</tr>
<tr>
<td>$2\pi/4$</td>
<td>00.133 687 398</td>
</tr>
<tr>
<td>$3\pi/4$</td>
<td>00.000 068 765</td>
</tr>
<tr>
<td>$\pi$</td>
<td>00.000 000 003</td>
</tr>
</tbody>
</table>
expansion of $S(\alpha, t)$.

In what follows we do many manipulations which we do not attempt to rigorously justify. However, since we have on hand the low temperature expansions to check our results, we feel partially justified in assuming that if the results agree, we have at least developed an asymptotic expansion of the symmetry functions.

Equation (4.6) for $S(\alpha, 0)$ and the above relation gives

$$S(\alpha, t) =$$

$$B \sum_{\kappa = -\infty}^{\infty} e^{t \sigma} \frac{\partial^2}{\partial (\alpha + 2\pi \kappa)^2} \left\{ \frac{(\alpha + 2\pi \kappa)/2}{\sin(\alpha + 2\pi \kappa)/2} e^{-\frac{(\alpha + 2\pi \kappa)^2}{4\sigma}} \right\}.$$  

We used

$$B = \epsilon^{\gamma_4 + \frac{\pi}{\sigma}} \frac{\epsilon^2}{\sigma}.$$ 

Let $\gamma_\kappa = (\alpha + 2\pi \kappa)$ and concentrate for the time being on one term of the above. Then, it is our task to evaluate an expression of the type:

$$T = \epsilon^{t \sigma} \frac{\partial^2}{\partial y^2} \left\{ \frac{y_2 \csc y_2}{y_2} e^{-\frac{y_2^2}{4\sigma}} \right\}.$$  

(4.12)
\[ T = \sum_{n=0}^{\infty} \frac{(t \sigma)^n}{n!} D^n \left\{ \frac{y_2}{2} \csc \frac{y_2}{2} \ e^{-\frac{y_2^2}{4 \sigma}} \right\} \]

(4.13)

\[ = \sum_{n=0}^{\infty} \frac{(t \sigma)^n}{n!} \sum_{j=0}^{2n} \binom{2n}{j} D^j \frac{y_2}{2} \csc \frac{y_2}{2} \ D^{2n-j} \ e^{-\frac{y_2^2}{4 \sigma}} \]

\[ D^n = \frac{\partial^n}{\partial y^n} \]

Using the definition of Hermite polynomials:

\[ H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2} \]

and the relation

\[ H_{2n-j}(\xi) = \frac{(2n-j)!}{(2n)!} 2^j \frac{d^j}{d\xi^j} H_{2n}(\xi) , \]

equation (4.13) is converted to

\[ T = e^{-\frac{y_2^2}{4 \sigma}} \sum_{j=0}^{\infty} \frac{(t \sigma)^j}{j!} \sum_{n=0}^{\infty} \binom{2n}{j} \frac{y_2}{2} \csc \frac{y_2}{2} \cdot \frac{d^j}{d\xi^j} \cdot \frac{\xi^n}{n!} H_{2n}(\frac{y_2}{2 \sqrt{\sigma}}). \]
The sum over $n$ can be carried out.\footnote{9}

$$
\sum_{n=0}^{\infty} \left( \frac{x}{y} \right)^n \frac{1}{n!} \frac{y}{2n} H_{2n} \left( \frac{y}{x \sqrt{\sigma}} \right) = \frac{1}{(1+t)^{\frac{1}{\sqrt{2}}} \sqrt{\sigma}} \int e^{\frac{y^2}{4\sigma}} \frac{t}{1+t} \ .
$$

Using this, we get

$$
T = (4.14)
$$

$$
(1+t)^{-\frac{1}{4}} \sqrt{\sigma} \int e^{\frac{y^2}{4\sigma}} \sum_{j=0}^{\infty} \frac{(-2\sigma)^j}{j!} \int \frac{y_j}{2} \csc \frac{y_j}{2} \int e^{\frac{y^2}{4\sigma}} \frac{t}{1+t} \ .
$$

Recognizing the connection of the last derivative of the above with Hermite polynomials and using their explicit form (along with the substitution $\delta = \frac{t}{1+t}$), we can establish

$$
D^j e^{\frac{\delta y^2}{4\sigma}} = \frac{j!}{\sigma^j} e^{\frac{\delta y^2}{4\sigma}} \sum_{n=0}^{\infty} \frac{1}{n!} \left( \frac{\delta \sigma}{4} \right)^n \frac{1}{(j-2n)!} \left( \frac{\delta y}{2} \right)^{j-2n}.
$$

Placing this in equation (4.14) gives

$$
T = (1-\delta)^{\frac{1}{2}} \sqrt{\sigma} e^{-\frac{y^2}{4\sigma}} (1-\delta) .
$$

$$
\cdot \sum_{n=0}^{\infty} \frac{1}{n!} \left( \frac{\delta \sigma}{4} \right)^n \sum_{j=2n}^{\infty} \frac{1}{(j-2n)!} \left( \frac{\delta y}{2} \right)^{j-2n} (-2)^j D^j \frac{y}{2} \csc \frac{y}{2} .
$$
Let us introduce a new index:

\[ m = j - 2n \]

Then, we get

\[ T = (1 - \sigma)^{\frac{j}{2}} e^{- \frac{y^2}{4\sigma} (1 - \sigma)} \cdot \sum_{n=0}^{\infty} \frac{(\delta \sigma)^n}{n!} \sum_{m=0}^{\infty} \frac{(-\delta y)^m}{m!} D^{m+2n} y^{\frac{1}{2}} csc y^{\frac{1}{2}}. \]

Noting that the sum over \( m \) is merely the Taylor series expansion of

\[ \frac{\partial^{2n}}{\partial (1 - \delta) y^{2n}} \left\{ \frac{y^{\frac{1}{2}} (1 - \delta) csc y^{\frac{1}{2}} (1 - \delta)}{y^{\frac{1}{2}} (1 - \delta) csc y^{\frac{1}{2}} (1 - \delta)} \right\}, \]

we finally obtain

\[ T = (1 - \sigma)^{\frac{j}{2}} e^{- \frac{y^2}{4\sigma} (1 - \sigma)}. \quad (4.15) \]

\[ \cdot \sum_{n=0}^{\infty} \frac{(\delta \sigma)^n}{n!} \frac{\partial^{2n}}{\partial y^{2n}} \left\{ \frac{y^{\frac{1}{2}} (1 - \delta) csc y^{\frac{1}{2}} (1 - \delta)}{y^{\frac{1}{2}} (1 - \delta) csc y^{\frac{1}{2}} (1 - \delta)} \right\}. \]

Using the above in the original expression (4.11), we get
\[ S(\alpha, \sigma; \sigma_c) = \]

\[ e^{\frac{\pi^2}{4} \left( \frac{\sigma}{\sigma_c} \right)^2} \frac{1}{\sigma} \sum_{n=0}^{\infty} \frac{(\delta \sigma)^n}{n!} \sum_{\kappa = -\infty}^{\infty} e^{-\frac{(\alpha + 2\pi \kappa)^2}{4\sigma_c}} \frac{\partial^{2n}}{\partial \xi_{2\kappa}^{2n}} \frac{\sigma_c}{\kappa \csc \xi_{2\kappa}} \]

We used:

\[ S(\alpha, \sigma; \sigma_c) = S(\alpha, t) \]

\[ \xi_{2\kappa} = (\alpha + 2\pi \kappa) \left( 1 - S \right) / 2 \]

The parameter \( S \) appears to be a natural quantity for the problem.

\[ \delta = \frac{t}{1 + t} = -\frac{\sigma}{\sigma_c} + 1 = 1 - \frac{I_c}{I} \]

It ranges in value from -1 to +1. Its value is -1 for the flat molecule, 0 for the spherical top, and +1 for the linear molecule.

Writing the result in the form:

\[ S(\alpha, \sigma; \sigma_c) = e^{\frac{\pi^2}{4} \left( \frac{\sigma}{\sigma_c} \right)^2} \frac{1}{\sigma} \sum_{\kappa = -\infty}^{\infty} e^{-\frac{(\alpha + 2\pi \kappa)^2}{4\sigma_c}} \sum_{n=0}^{\infty} a_{\kappa} \left( \frac{\delta \sigma}{4} \right)^n \frac{1}{n!} \]
We have for the first few $a_{n,k}$'s:

$$a_{n,k} = \frac{\partial^{2n}}{\partial x_k^{2n}} \frac{x_k}{\csc x_k}$$

$$a_{0,k} = \frac{x_k}{\csc x_k}$$

$$a_{1,k} = \frac{x_k}{\csc x_k} \csc x_k \csc x_k \cot x_k - 2 \cot x_k \csc x_k$$

$$a_{2,k} = \cot x_k \csc x_k + 18 \frac{x_k}{\csc x_k} \csc x_k \csc x_k \cot x_k + \frac{x_k}{\csc x_k} \csc x_k \cot x_k$$

$$- 20 \cot x_k \csc x_k \cot x_k - 4 \csc x_k \cot x_k \csc x_k$$

$$a_{3,k} = 61 \frac{x_k}{\csc x_k} \csc x_k \csc x_k + 39 \frac{x_k}{\csc x_k} \csc x_k \csc x_k \cot x_k + 179 \frac{x_k}{\csc x_k} \csc x_k \cot x_k$$

$$+ \frac{x_k}{\csc x_k} \cot x_k \csc x_k \cot x_k - 36 \csc x_k \cot x_k \csc x_k \cot x_k - 6 \cot x_k \csc x_k \cot x_k$$

At high enough temperatures such that $\sigma$ and $\sigma_c$ are small, it suffices to keep only the first term. Reverting back to our original notation, we get

\begin{equation}
S(\alpha,t) \sim \frac{\sigma}{\alpha} \left[ \frac{\pi}{(1+t)\sigma} \right]^{1/2} \frac{\alpha}{2(1+t)} \csc x \frac{\alpha}{2(1+t)} e^{-\frac{\alpha^2}{4\sigma(1+t)}} (1 + \delta_{\alpha,\pi})
\end{equation}
This accounts for the peaked structure of the curves in figures 2 and 3.

Note that for the spherical top, $\zeta$ equals zero. Only the $Q_{\sigma, \kappa}$ terms contribute. This results in a much faster converging high temperature expansion for the spherical top.

Table 2 gives comparisons of $S(\alpha, t)$ calculated from the above form and from the low temperature expansion (equation (3.5)). These and other similar calculations give us confidence in equation (4.17). Table 3 gives numerical values for $S(\alpha, t)$ calculated from equation (4.17). The temperature selected is high enough such that the low temperature form is practically impossible to sum directly.

We note, however, that in the neighborhood of $\frac{\alpha}{2(t + \tau)}$ being equal to $\pi$, equation (4.17) gives something indefinite. This means that it is not useful for calculating the high temperature limiting form of the symmetry function of a flat molecule involving a $C_2$ rotation about the principle axis. This probably suggests a different $\sigma$ dependence for this particular function. $S(\pi, -\frac{1}{2})$, the function under question, will be handled by the integral technique in the next section.
Table 2. Comparisons of approximations to $S(\alpha, t)$ using the high temperature form given by equation (4.16) to the values predicted by the low temperature expansion given by equation (3.5).
Table 3. $S(\alpha, t)$ for $\sigma = 0.0257$. This corresponds to $T = 298^\circ C$ for methane.

<table>
<thead>
<tr>
<th></th>
<th>$S(\alpha, 0)$</th>
<th>$S(\alpha, 2)$</th>
<th>$S(\alpha, \infty)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>432</td>
<td>250</td>
<td>39.2</td>
</tr>
<tr>
<td>$\pi/3$</td>
<td>$1.06 \times 10^{-2}$</td>
<td>7.18</td>
<td>39.2</td>
</tr>
<tr>
<td>$2\pi/3$</td>
<td>$1.54 \times 10^{-16}$</td>
<td>$1.70 \times 10^{-4}$</td>
<td>39.2</td>
</tr>
<tr>
<td>$\pi$</td>
<td>$2.74 \times 10^{-39}$</td>
<td>$6.62 \times 10^{-12}$</td>
<td>39.2</td>
</tr>
</tbody>
</table>
The Special Case of $S(\pi, -\frac{1}{2})$. Let us now concentrate our attention on the flat molecule symmetry function involving a $C_2$ symmetry operation about the principal symmetry axis. As was mentioned, this seems to possess a high temperature form which differs from that of the other symmetry functions.

Resorting to the solution of the heat equation for previous times (equations (3.9) and (4.5) with $t_0 = 0$), and performing a few elementary manipulations, we get:

$$S(\pi, -\frac{1}{2}) = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\sigma(\ell+1)^2} \sum_{n=-\infty}^{\infty} (-1)^n \frac{\xi}{\sigma^2} e^{\frac{\xi^2}{4\sigma}} \tag{4.19}$$

$$= \frac{\sqrt{2}}{\sqrt{\pi}} \frac{\xi_0}{\sigma^2} \sum_{n=-\infty}^{+\infty} (-1)^n \frac{\xi}{4\sigma} e^{-(2n+1)^2 \frac{\xi^2}{4\sigma}}.$$

$$\int_{-\infty}^{+\infty} \left[ \frac{(2n+1)\xi}{\sigma} \cos(2\pi n t) + \frac{\xi}{\sigma} \sin(2\pi n t) \right] e^{-\frac{\xi^2}{4\sigma}} d\xi.$$  

We keep the $n$ equal zero and $n$ equal minus one terms only. This will certainly be a valid approximation when $\sigma$ is small because of the exponential factor following the summation sign.
\[ S(\pi - \frac{1}{2}) = \]

\[
\sqrt{\pi} \frac{\sigma^{\sigma/2}}{\sigma^{\sigma/2}} \exp \left( -\frac{\pi^2}{2\sigma} \right) \int_{-\infty}^{\infty} \left[ \frac{\pi^2}{2\sigma} \cos \frac{\pi \xi}{2\sigma} + \frac{i\pi}{\sigma} \sin \frac{\pi \xi}{2\sigma} \right] \frac{\exp^{\xi^2/4\sigma}}{\cosh \xi/2} d\xi
\]

We now set about the task of getting an estimate of the above rather formidable integral.

We denote the first term of the integral by \( I \).

\[
I = \int_{-\infty}^{\infty} \frac{\exp^{\xi^2/4\sigma}}{\cosh \xi/2} \cos \frac{\pi \xi}{2\sigma} d\xi
\]

\[
= \int_{-\infty}^{\infty} \frac{\exp^{\xi^2/4\sigma} - \frac{i\pi}{\sigma} \xi}{\cosh \xi/2} d\xi
\]

This integral defied all of the more obvious attempts to estimate it. However, Mordell in 1920, provided us with a very elegant result which transforms the integral into another one with much more pleasant properties.\(^{10}\) In complete analogy with the theta function transformation of equation (4.3), Mordell established the remarkable result:
\[
\int_{-\infty}^{\infty} e^{\frac{\pi i \omega t^2 - 2 \pi t x}{\cosh \pi t}} \, dt = \frac{1}{\sqrt{(i\omega)}} \int_{-\infty}^{\infty} e^{-\frac{\pi i \chi}{\omega} (t-i\chi)^2} \, dt,
\] (4.21)

where the imaginary part of \( \omega \) must be positive. We can cast \( I \) into this form by making the substitution: \( \xi = 2\pi t \).

\[
I = 2\pi \int_{-\infty}^{\infty} \frac{e^{-\frac{\pi^2 t^2}{\sigma^2} - \frac{i \pi t}{\sigma}}}{\cosh \pi t} \, dt
\]

Comparison with the left hand side of equation (4.21) shows:

\[
\omega = \frac{i \pi}{\sigma}
\]

\[
\chi = \frac{i \pi}{2\sigma}
\]

Making these substitutions in the right hand side, one establishes that

\[
I = 2 \sqrt{\pi \sigma} \, e^{-\frac{\pi^2}{4\sigma}} \int_{-\infty}^{\infty} \frac{e^{-\sigma t^2 - \pi t}}{\cosh \pi t} \, dt
\]

We note the pleasant fact that this form of \( I \) shows no oscillation of the integrand and is thus more amenable to approximate treatments.
The derivative of Mordell's relation with respect to $x$ gives us the analogous transformation for the second part of the integral of equation (4.20) which we call $I'$:

$$I' = \int_{-\infty}^{\infty} \xi e^{-\xi^2/4\sigma} \frac{\sin \pi \xi}{\cosh \pi \xi/2} \, d\xi$$

$$= 4\sigma \sqrt{\pi \sigma} \int_{-\infty}^{\infty} \left( t + \frac{\pi}{2\sigma} \right) e^{-\sigma \left( t + \frac{\pi}{2\sigma} \right)^2} \cos \pi t \, dt$$

Integrating by parts, this goes to

$$I' = -2\pi \sqrt{\pi \sigma} e^{-\frac{\pi^2}{4\sigma}} \int_{-\infty}^{\infty} \sinh \pi t \left( e^{-\sigma \left( t + \frac{\pi}{2\sigma} \right)^2} \int_{-\infty}^{\infty} \frac{e^{-\sigma t^2 - \pi t}}{\cosh^2 \pi t} \, dt \right) \, dt$$

Using $I$ and $I'$ in equation (4.20) for $S(\pi, -\frac{1}{2})$ gives

$$S(\pi, -\frac{1}{2}) = 4\sqrt{\pi} e^{-\frac{\pi^2}{4\sigma}} \int_{-\infty}^{\infty} \frac{e^{-\sigma t^2 - \pi t}}{1 + e^{\frac{2\pi t}{\sigma}}} \, dt \quad (4.22)$$

The integral we now have to contend with is well behaved and can easily be evaluated numerically. We shall content ourselves with its evaluation in the limit of $\sigma$ going to zero.
Making an obvious change in variable, we get:

\[
\int_{-\infty}^{\infty} \frac{e^{-\sigma t^2}}{(1 + e^{\frac{2\pi}{\sigma} t})^2} \, dt = \frac{1}{\sqrt{\sigma}} \int_{-\infty}^{\infty} \frac{e^{-\frac{\alpha^2}{\sigma} x}}{(1 + e^{\frac{2\pi}{\sigma} x})^2} \, dx
\]

We note the numerator of the integrand is a gaussian and the other factor

\[
\frac{1}{(1 + e^{\frac{2\pi}{\sigma} x})^2}
\]

behaves like a step function as \( \sigma \) diminishes (See fig. 4). Therefore as \( \sigma \) decreases, the value of the integral approaches that of

\[
\frac{1}{2} \sqrt{\frac{\pi}{\sigma}} \int_{-\infty}^{\infty} e^{-x^2} \, dx = \frac{1}{2} \sqrt{\frac{\pi}{\sigma}}
\]

Therefore in the limit of \( \sigma \) going to zero, \( S(\pi, -\frac{1}{2}) \) assumes the following form:

\[
S\left(\pi, -\frac{1}{2}\right) \xrightarrow[\sigma \to 0]{\sigma} 2\sqrt{\alpha} \ e^{\sigma^2/4} \left(\frac{\pi}{\sigma}\right)^{\frac{3}{2}} e^{-\frac{\alpha^2}{4\sigma c}} \tag{4.23}
\]

Indeed, this symmetry function does show a slightly different \( \sigma \) dependence. Its exponentially decreasing nature remains the same.
FIG. 4 A is a plot of $(1 + e^{3\pi t})^{-2}$ against $t$. B is a plot of $e^{-\sigma t}$ against $t$. C is the area which represents the integral over the product of these two functions for $\sigma = 0.1$. 
For \( \frac{\alpha}{2(1+z)} \) not equal to \( \pi \) we got

\[
S(\alpha, t) \sim T^{\frac{3\alpha}{2}} e^{-\lambda T},
\]

while for \( \frac{\alpha}{2(1+z)} \) equal to \( \pi \), we have

\[
S(\pi, -\frac{1}{2}) \sim T^{\frac{\mu}{2}} e^{-\lambda T}.
\]

The above result for the high temperature forms of \( S(\pi, -\frac{1}{2}) \) agrees with the extrapolated values of \( S(\pi, -\frac{1}{2}) \) calculated at various \( \sigma \)'s using the low temperature expansion.

The **Linear Molecule as a Limiting Case of a Symmetric Top**.

We now consider \( \sigma_c \) tending toward infinity as is the case for the linear molecule. The high temperature equations developed thus far are good only when \( \sigma_c \) is small. We shall find that physically this is not an important restriction.

The quantity \( \sigma_c \) becoming large \( (l_c \to 0) \) implies that \( t \) gets large also.

\[
t = \frac{\sigma_c}{l} - 1
\]
It is convenient here to examine \( S(\alpha, t) \) in the limit of \( t \) going to infinity in a different form than that of equation (3.8). We use the equivalent solution of the heat equation for positive times as is discussed in appendix 1.

We get

\[
S(\alpha, t) = \frac{1}{2\pi} \int_{-\pi}^{+\pi} S(\xi, 0) \left[ \sum_{n=\infty}^{+\infty} \cos n(\alpha - \xi) e^{-n^2\sigma t} \right] d\xi
\]

Now, in the limit of \( t \) tending toward infinity, only the \( n \) equal to zero term contributes.

\[
S(\alpha, \infty) = \frac{1}{2\pi} \int_{-\pi}^{+\pi} S(\xi, 0) d\xi
\]

This is merely a restatement that "heat" is conserved. In intermediate instances (such that \( t \) is not identically infinite) one must use more terms involving \( \sigma \). Therefore, we would expect a different \( \sigma \) dependence as indeed is the case. The fact that in actual physical situations, \( t \) is either a relatively small quantity or identically infinite accounts for the rather discontinuous transition of the symmetry functions in going to the linear molecule. That is, physically, we
can find symmetric tops corresponding to times up from \(-\frac{1}{2}\) to let us say about 20. However, we must wait until \(t\) equals \(\infty\) to realize another physical example (the linear molecule).

We also note that the above relation says that

\[
\lim_{t \to \infty} S(\alpha, t)
\]

is independent of \(\alpha\) and therefore equal to \(S(0, \infty)\). We interpret this in the following manner. Since \(t\) goes to \(\infty\) as a result of \(I_c\) vanishing, the nuclei have to pack close around the principle symmetry axis. The interchange distances become very small and all symmetry elements begin to contribute to the partition function equally. However, as we noted, no such molecules exist in nature.

The Direct Partition Functions. The direct partition functions deserve some special attention. The asymptotic Euler-Maclaurin development of the linear molecule direct partition function is straightforward and well known. A tedious double application of the Euler-Maclaurin sum formula has been done by Miss Viney. She gets several terms of the symmetric top direct partition function. Kassel conjectured the general answer from his work involving a numerical technique of determining the coefficients of Miss Viney's expansion. We extract the same result from the high temperature
expansion of $S(\alpha, 0)$, the spherical top symmetry function, by employing the solutions of the heat equation for future and past times. The similarities between the linear and symmetric top high temperature direct partition functions are shown.

We begin our discussion by starting with equation (4.16) evaluated at \( \alpha \) equal to zero; this being an expression for \( Z_d \) without the spin factor.

\[
S(\alpha, \sigma; \sigma_c) =
\]

\[
e^{-\mu \left( \frac{\alpha \pi}{\sigma} \right)^2} \frac{1}{\sigma} \sum_{\kappa=0}^{\infty} \left( 2^{\kappa} \kappa \right)^{n/2} \sum_{n=-\infty}^{\infty} e^{-\frac{(2\pi \kappa)^2}{4 \sigma_c^2}} \left\{ \frac{\partial^{2n}}{\partial \xi^{2n}} \xi \frac{\partial^{2n}}{\partial \xi \xi} c \csc \xi \right\} 2\pi \kappa (\kappa - \delta)/2
\]

If \( \sigma_c \) is small, the \( k \) equal zero term will certainly predominate (We note, however, that \( \sigma_c \) is infinite for the linear molecule). This amounts to throwing away terms on the order of

\[
-\mu \sigma_c^{-\mu} e^{-\frac{(2\pi \kappa)^2}{4 \sigma_c^2}}
\]

where \( \mu \) is a small constant. We might interpret this as throwing away all contributions from interchanges involving rotations of \( 2\pi \), \( 2 \cdot 2 \pi \), \( 3 \cdot 2 \pi \), etc. and keeping the contribution from a rotation of 0-radians.
\[ S(0, \sigma; \sigma_c) = \]

\[ \Theta^{\sigma/4} \left( \frac{\pi}{\sigma_c} \right)^{1/2} \frac{1}{\sigma} \sum_{n=0}^{\infty} \left( \frac{8\sigma}{4} \right)^n \frac{1}{n!} \left\{ \frac{\partial^{2n}}{\partial \xi^{2n}} \xi \csc \xi \right\}_{\xi=0} \]

\[ \frac{\partial^{2n}}{\partial \xi^{2n}} \xi \csc \xi \bigg|_{\xi=0} = (4^{n-1} 2) B_n \]

The \( B_n \) are Bernoulli numbers.

\[ B_0 = -\frac{1}{2}, \quad B_1 = \frac{1}{6}, \quad B_2 = \frac{1}{2}, \quad B_3 = \frac{1}{2}, \quad B_4 = \frac{1}{30}, \ldots \]

So, we get

\[ S(0, \sigma; \sigma_c) = \]

\[ \Theta^{\sigma/4} \left( \frac{\pi}{\sigma_c} \right)^{1/2} \frac{1}{\sigma} \sum_{n=0}^{\infty} \left( \frac{8\sigma}{4} \right)^n \frac{4^{n-2}}{4^n} B_n \left\{ 1 + \Theta(\sigma^{-\mu} e^{-\pi^2/\sigma_c}) \right\}. \]

We get for \( Z_d \),

\[ (4.27) \]

\[ Z_d = S(0, \sigma; \sigma_c) \frac{1}{\pi} \prod_i (2s_i + 1) \]
The product goes over all nuclei.

\[ S(0, \sigma; \sigma_c) \sim \]

\[ \exp \left( \frac{\pi}{\sigma_c} \right) \frac{1}{\sigma} \left[ 1 + \frac{1}{2} \delta \sigma + \frac{7}{480} \left( \delta \sigma \right)^2 + \frac{31}{8064} \left( \delta \sigma \right)^3 + \frac{127}{92160} \left( \delta \sigma \right)^4 \ldots \right] \]

Next, we use the integral approach to arrive at the above result. Equation (3.9) gives \( S(0, t) \) for times previous to \( t_0 = 0 \) (oblate tops).

\[ S(0, -|t|) = \sqrt{4\pi\sigma^{-1}t} \int_{-\infty}^{+\infty} S(i\xi, 0) e^{-\frac{\xi^2}{4\sigma^{-1}t}} d\xi \]

Putting in expression (4.5) for \( S(i\xi, 0) \), we get

\[ S(0, -|t|) = C \sum_{n = -\infty}^{+\infty} (-1)^n e^{-\frac{n^2 \pi^2}{\sigma}} \cdot \int_{-\infty}^{+\infty} \left[ \frac{\xi}{2} \cos \frac{n \pi \xi}{\sigma} - n \pi \sin \frac{n \pi \xi}{\sigma} \right] \frac{e^{-\frac{\xi^2}{4\sigma^{-1}t} \left( \frac{t}{1} - 1 \right)}}{\sinh \frac{\xi}{2}} d\xi \]

where

\[ C = \exp \left( \frac{\pi}{\sigma} \right) \frac{1}{\sqrt{4\pi\sigma^{-1}t}} \cdot \frac{1}{\sqrt{4\pi\sigma^{-1}t}} \]
Similarly, for future times (prolate tops), we have

\[ S(0, t) = C \sum_{n=-\infty}^{+\infty} (-1)^n e^{-\frac{n^2 \pi^2}{\sigma^2}} \cdot \left( \int_{-\infty}^{+\infty} \left[ \frac{\xi/2}{\cosh n \pi \xi/\sigma} - n \pi \sinh n \pi \xi/\sigma \right] \frac{e^{-\xi^2/(4\sigma)}(1/2t+1)}{\sin \xi/2} d\xi \right) \]  

where, as is discussed in appendix I, the principal value of the integral is to be taken.

Keeping only the \( n \) equal zero terms, we have

\[ S(0, t) = C \int_{-\infty}^{+\infty} \frac{\xi/2}{\sinh \xi/2} \frac{e^{-\xi^2/(4\sigma)}(1/2t-1)}{d\xi} \] (oblate) \hspace{1cm} (4.32)

\[ S(0, t) = C \int_{-\infty}^{+\infty} \frac{\xi/2}{\sin \xi/2} \frac{e^{-\xi^2/(4\sigma)}(1/2t+1)}{d\xi} \] (prolate) \hspace{1cm} (4.32)

Both are to be multiplied by the factor

\[ \left[ 1 + O \left( e^{-\pi^2/\sigma \xi} \right) \right] . \]
The extreme prolate top; the linear molecule, as we have seen, takes the special form:

\[ S(\phi, \infty) = \frac{1}{2\pi} \int_{-\pi}^{+\pi} S(\xi, \phi) \, d\xi \]  

(4.34)

Employing the high temperature \( S(\xi, 0) \) in the form of equation (4.6), we get

\[ S(\phi, \infty) = \frac{1}{2\pi} \, e^{\sigma/4} \left( \frac{\pi}{\sigma} \right)^{1/4} \, \frac{1}{\sigma} \sum_{n=-\infty}^{+\infty} \int_{-\pi}^{+\pi} \frac{\xi + 2n\pi}{\sin(\xi + 2n\pi)/2} \, e^{-\frac{(\xi + 2n\pi)^2}{4\sigma}} \, d\xi. \]

This is the same as

\[ S(\phi, \infty) = \frac{1}{2\pi} \, e^{\sigma/4} \left( \frac{\pi}{\sigma} \right)^{1/4} \, \frac{1}{\sigma} \int_{-\infty}^{+\infty} \frac{\xi/2}{\sin(\xi/2)} \, e^{-\frac{\xi^2}{4\sigma}} \, d\xi. \]  

(4.36)

Let us rewrite (4.32) and (4.33) and make the substitution

\[ \delta = \frac{t}{1+t} \quad \text{or} \quad t = \frac{\delta}{1-\delta}. \]
\[ S(\text{oblate}) \approx (4 \pi \sigma \varepsilon_{181})^{-\frac{1}{2}} e^{\sigma/4} \left(\frac{\pi}{\sigma}\right)^{\frac{1}{2}} \frac{i}{\sigma} \int_{-\infty}^{+\infty} \frac{\xi/2 e^{-\xi^2/4 \sigma}}{\sinh \xi/2} \, d\xi \]  
(4.37)

\[ S(\text{prolate}) \approx (4 \pi \sigma \varepsilon_{4 \sigma})^{-\frac{1}{2}} e^{\sigma/4} \left(\frac{\pi}{\sigma}\right)^{\frac{1}{2}} \frac{i}{\sigma} \int_{-\infty}^{+\infty} \frac{\xi/2 e^{-\xi^2/4 3 \sigma}}{\sin \xi/2} \, d\xi \]  
(4.38)

\[ S(\text{linear}) = \frac{1}{2\pi} e^{\sigma/4} \left(\frac{\pi}{\sigma}\right)^{\frac{1}{2}} \frac{i}{\sigma} \int_{-\infty}^{+\infty} \frac{\xi/2 e^{-\xi^2/4 \sigma}}{\sin \xi/2} \, d\xi \]  
(4.39)

The three very similar integrals above may be evaluated asymptotically in the following manner. Since when \( \sigma \) is small, most of the contribution to the integral is around \( \xi \) equal to zero, we reason that the first few terms of the expansion of

\[ \frac{\xi/2}{\sinh \xi/2} \quad \text{or} \quad \frac{\xi/2}{\sin \xi/2} \]

should give an accurate picture of its affect on the integral, at least for small \( \sigma \). We then integrate term by term. Calling

\[ I(x) = (4 \pi x)^{-\frac{1}{2}} \int_{-\infty}^{+\infty} \frac{\xi/2 e^{-\xi^2/4 x}}{\sin \xi/2} \, d\xi \]
We get
\[ I(x) \xrightarrow{x \to a} \sum_{n=0}^{\infty} \frac{x^n}{n!} \frac{4^{n-2}}{4^n} B_n. \tag{4.40} \]

The integral in equation (4.37) is merely \( I(-x) \). Therefore we see that,
\[ S(\sigma; \delta) \approx e^{\sigma/4} \left( \frac{\pi}{\sigma_c} \right)^{1/2} \frac{1}{\sigma} I(\sigma \delta), \tag{4.41} \]
an expression which applies to both the prolate and oblate tops.

Similarly for the linear molecule, we have
\[ S(\sigma, \infty) \approx e^{\sigma/4} \frac{1}{\sigma} I(\sigma). \tag{4.42} \]

Equation (4.41) is only a verification of our previous result. However, in this form, we now see a similarity between the symmetric top \( Z_d \) and that of the extreme linear molecule.

\[ Z_d(\text{symmetric top}) = \frac{1}{\hbar} \sqrt{\ell(2s_{\ell} + 1)} \left( \frac{\pi}{\sigma_c} \right)^{1/4} \frac{1}{\sigma} e^{\sigma/4} I(\sigma \delta) \tag{4.43} \]

\[ Z_d(\text{linear}) \approx \frac{1}{\hbar} \sqrt{\ell(2s_{\ell} + 1)} e^{\sigma/4} \frac{1}{\sigma} I(\sigma). \tag{4.44} \]
V. A NOTE ON THE ASYMMETRIC TOP.

As we mentioned at the start, the asymmetric rotor p.f. is difficult to examine because of the complicated pattern of its energy levels. However, we can use the density matrix formalism to write down the spin-rotational p.f. in a form comparable to that given for the symmetric top. The symmetric top functions are used as basis functions.

The result appears to have little quantitative value, but it does show some similarity with the formalism given for the symmetric top:

1. There are contributions to the p.f. from each element of rotational symmetry.

2. The contributions from the symmetry elements other than the identity involves sums which alternate in sign.

Being qualitatively the same as the description of the symmetric top p.f., this is reasonable justification for keeping only the contribution from the identity element at all but extremely low temperatures. That is, the terms associated with the non-identity elements of symmetry tend to cancel themselves.

Because we can do very little with the result, we omit the details and merely give the spin-rotational p.f. Appendix 2 gives some of the details. Asymmetric tops can have one $C_2$ element of
rotational symmetry (the $C_2$ group) or three mutually perpendicular $C_2$ elements (the $D_2$ group). Examples are water with $C_2$ symmetry and ethylene with $D_2$ symmetry.

**Asymmetric Top With $D_2$ Symmetry.**

$$G(\xi) = (-1)^N f - C(C_\xi, f) \prod_i (2s_i + 1) C(C_\xi, i).$$

$C_a, C_b, C_c$ are rotations of $\pi\tau$ about a, b, and c principle axis.

$$Z = \frac{i}{4} \prod_i (2s_i + 1) C(I, i) \sum_{l=0}^\infty \sum_{\kappa=-l}^l (2l+1) \langle l, \kappa | e^{-\beta H} | l, \kappa \rangle$$

$$+ \frac{i}{4} G(a) \sum_{l=0}^\infty \sum_{\kappa=-l}^l (2l+1) (-1)^l \langle l, -\kappa | e^{-\beta H} | l, \kappa \rangle$$

$$+ \frac{i}{4} G(b) \sum_{l=0}^\infty \sum_{\kappa=-l}^l (2l+1) (-1)^{l+\kappa} \langle l, -\kappa | e^{-\beta H} | l, \kappa \rangle$$

$$+ \frac{i}{4} G(c) \sum_{l=0}^\infty \sum_{\kappa=-l}^l (2l+1) (-1)^\kappa \langle l, \kappa | e^{-\beta H} | l, \kappa \rangle$$

(5.1)
Asymmetric Top With \( C_2 \) Symmetry.

\[ Z = \frac{1}{2} \sum \frac{\pi_i}{\xi_i} \sum_{\ell=0}^{\infty} (2\ell+1) \langle \ell, \kappa | e^{-\beta H} | \ell, \kappa \rangle \]

\[ + \frac{1}{2} G(\alpha) \sum_{\ell=0}^{\infty} \sum_{\kappa=-\ell}^{\ell} (2\ell+1) (-1)^\ell \langle \ell, -\kappa | e^{-\beta H} | \ell, \kappa \rangle \]

Let:

\[ A = \frac{\hbar^2}{2 I_\alpha} \]

\[ B = \frac{\hbar^2}{2 I_\beta} \]

\[ C = \frac{\hbar^2}{2 I_\gamma} \]

The matrix elements of the above can in principle be determined from the relation:

\[ H | \ell, \kappa \rangle = \left[ \frac{A+B}{2} \ell(\ell+1) + (C - \frac{A+B}{2}) \kappa^2 \right] | \ell, \kappa \rangle \]

\[ + \left( \frac{A-B}{2} \right) \left[ \frac{1}{2} C_\kappa C_{\kappa+1} | \ell, \kappa+2 \rangle + \frac{1}{2} C_\kappa C_{\kappa-1} | \ell, \kappa-2 \rangle \right]. \]
\[ C_K = \sqrt{\ell(\ell+1) - \kappa(1+\ell)} \]
\[ C_K' = \sqrt{\ell(\ell+1) - \kappa(\kappa-1)} \]

From analogy with the symmetric top, we conjecture that the exchange effects vanish exponentially with increase in temperature. At moderately high temperatures, each non-identity term of the p.f. is likely to be proportional to

\[ T^\mu e^{-\lambda T} \]

The parameter \( \mu \) is probably 3/2 except for certain special ratios of the three moments of inertia. The quantity \( \lambda T \) will almost certainly be \( \frac{\pi^2}{4 \sigma_{\xi}^2} \) where \( \sigma_{\xi} \) involves the moment of inertia about the actual axis of interchange.

\[ \sigma_{\xi} = \frac{I^2}{2 I_{\xi} k T} \]
VI. NON-COMBINING SPECIES.

Up to now, we have tacitly assumed that equilibrium exists between all spin-rotational states. However, in the absence of a catalyst, this is found not to be the case. Due to the lack of the proper types of perturbation, equilibrium between the various nuclear spin states is slow. Thermodynamically, we must consider the system of molecules to be a mixture of several non-interconverting components. The thermodynamics of mixtures applies.

Those molecules with nuclear spin states which form a basis for the same irreducible representation will, in accordance with the exclusion principle, have the same set of allowed rotational levels. Having identical partition functions, their fractional amounts will be the same at all temperatures, even at true equilibrium. It is therefore convenient to group those spin species of the same symmetry together. An extensive property $P$, is therefore given by

$$P = \sum_{\lambda} X_{\lambda} P_{\lambda}.$$  

$X_{\lambda}$ is the fraction of molecules with spin functions of symmetry $\lambda$. $P_{\lambda}$ is the associated thermodynamic property of that component.

The number of times an irreducible representation $\lambda$ occurs in a reducible representation is given by equation (2.3). We
denote this number by \( \mathcal{V}_S^{(\lambda)} \) and consider the reducible representation furnished by all the nuclear spin functions.

\[
\mathcal{V}_S^{(\lambda)} = \frac{1}{\hbar} \sum_{\rho} h_{\rho} \chi_{\rho}^{(\lambda)} \phi_{\rho,S}
\]

(6.1)

\( \chi_{\rho}^{(\lambda)} \) is taken from the character table. \( \phi_{\rho,S} \), as we discussed previously, is \( \prod_{i} (2S_i + 1)^{C(\rho_i)} \). This determines \( \mathcal{V}_S^{(\lambda)} \); the number of sets of spin functions having the same symmetry properties as is specified by the irreducible representation \( \lambda \).

In close analogy with the true equilibrium p.f., we now construct the p.f. of the \( \lambda \) nuclear spin species of the spherical top.

\[
Z_{\lambda} = \mathcal{V}_S^{(\lambda)} \sum_{\alpha} (-i)^{N_f - C(\alpha, \tau)} \chi_{\alpha}^{(\lambda)} S(\alpha, 0)
\]

(6.2)

The sum is over all rotation symmetry elements. \( \chi_{\alpha}^{(\lambda)} \) is obtained from the character table of the group involved. \( S(\alpha, 0) \) is the much discussed spherical top symmetry function.

Likewise for the \( \lambda \) component of a collection of symmetric tops, we get

\[
Z_{\lambda} = \mathcal{V}_S^{(\lambda)} \frac{1}{\hbar} \sum_{\alpha} (-i)^{N_f - C(\alpha, \tau)} \chi_{\alpha}^{(\lambda)} S(\alpha, \tau)
\]

(6.3)

\[
+ \mathcal{V}_S^{(\lambda)} \frac{1}{\hbar} \sum_{\alpha'} (-i)^{N_f - C(\alpha', \tau')} \chi_{\alpha'}^{(\lambda)} S(\pi, 0)
\]
For our purposes, the important point to note is that the partition function of each spin species can still be regarded as a sum over symmetry functions. Therefore, even if equilibrium is not achieved between the various spin species, all of our previous discussion still applies to the separate components.

As an example a system of non-combining species, we select methane. We give the p.f. for the various components of methane. The rotational group associated with methane is T. It has the following character table.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>4C₃</th>
<th>4C₃²</th>
<th>3C₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ε</td>
<td>1</td>
<td>e^{2πi/3}</td>
<td>e^{-2πi/3}</td>
<td>1</td>
</tr>
<tr>
<td>ε*</td>
<td>1</td>
<td>e^{-2πi/3}</td>
<td>e^{2πi/3}</td>
<td>1</td>
</tr>
<tr>
<td>T</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cycle Structure</th>
<th>H₁⁴</th>
<th>H₁¹H₃¹</th>
<th>H₁¹H₃¹</th>
<th>H₂²</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(μ, H)</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>(-l)Nₓ C(μ, f)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
First we determine the p.f. of the species associated with the A irreducible representation. From equation (6.1), we get

\[ Z_S^A = \frac{1}{12} \left( 2^4 + 8 \cdot 2^2 + 3 \cdot 2^2 \right) = 5 \]

Using equation (6.2) gives

\[ Z_A = \frac{5}{12} S(0,0) + \frac{5 \cdot 8}{12} S\left(\frac{2\pi}{3},0\right) + \frac{5 \cdot 3}{12} S(\pi,0). \]  

(6.4)

Likewise for the other components we get:

\[ Z_S^e = Z_S^{e^*} = \frac{1}{12} \left[ 2^4 + (e^{2\pi i/3} + e^{-2\pi i/3}) 4 \cdot 2^2 + 3 \cdot 2^2 \right] = 1 \]

\[ Z_e = \frac{1}{12} S(0,0) - \frac{4}{12} S\left(\frac{2\pi}{3},0\right) + \frac{3}{12} S(\pi,0) \]

\[ Z_{e^*} = \frac{1}{12} S(0,0) - \frac{4}{12} S\left(\frac{2\pi}{3},0\right) + \frac{3}{12} S(\pi,0) \]

Since \( e \) and \( e^* \) have identical partition functions we group them together under the notation \( E \):

\[ Z_E = \frac{2}{12} S(0,0) - \frac{8}{12} S\left(\frac{2\pi}{3},0\right) + \frac{6}{12} S(\pi,0). \]  

(6.5)
\[ V_s T = \frac{1}{12} (3 \cdot 2^4 - 3 \cdot 2^2) = 3 \]

\[ Z_T = \frac{9}{12} S(0,0) - \frac{9}{12} S(\pi,0) \quad (6.6) \]

At high temperatures only the \( S(0,0) \) fail to vanish. We get:

\[ Z_A \xrightarrow{T \to \infty} \frac{5}{12} S(0,0) \]

\[ Z_E \xrightarrow{T \to \infty} \frac{2}{12} S(0,0) \]

\[ Z_T \xrightarrow{T \to \infty} \frac{9}{12} S(0,0) \]

The equilibrium high temperature limiting ratios of the various components is therefore:

5 : 2 : 9
VII. A NUMERICAL EXAMPLE

We now give a sample calculation of the thermodynamic quantities $E$, the internal energy and $C$, the rotational heat capacity. We select methane at equilibrium and at a temperature of 77° Kelvin ($\sigma = 0.1$).

As was shown in example (1), the spin-rotational partition function is

$$Z = \frac{4}{3} S(0,0) + \frac{8}{3} S(\frac{2}{3} \pi, 0) + S(\pi, 0)$$

$$Z_d = \frac{4}{3} S(0,0)$$

$$Z_{ex} = \frac{8}{3} S(\frac{2}{3} \pi, 0) + S(\pi, 0)$$

Equation (4.17) gives,

$$Z_d = \frac{4}{3} e^{\frac{\sigma}{2} \mu (\pi)^{\frac{1}{2}} \frac{1}{\sigma}}$$

$$= \frac{4}{3} e^{\frac{\sigma}{2} \mu (\pi)^{\frac{1}{2}} \frac{1}{\sigma}} (e^{\frac{\sigma}{2} \mu^2 - 2}) e^{-\frac{\pi^2}{\sigma}}$$

$$= 76.63 + 4.1 \times 10^{-39}$$
The first term is given by the Euler-Maclaurin sum formula. The second term is a trivial nonanalytic correction to this formula.

From equation (4.16) we get,

\[
Z_{ex} \approx \frac{16}{9} \frac{\pi}{\lambda^3} \epsilon^\sigma \left( \frac{\pi}{\sigma} \right)^{2/3} \frac{1}{\lambda} \epsilon^{-\frac{\pi^2}{2\sigma}} + \epsilon^{\sigma/4} \left( \frac{\pi}{\sigma} \right)^{3/2} \epsilon^{-\frac{\pi^2}{4\sigma}}
\]

\[
= 3.203 \times 10^{-3} + 3.47 \times 10^{-9}
\]

\[
= 3.203 \times 10^{-3}
\]

The contribution from the larger angle may be ignored (the last term of the above).

We now proceed to calculate \( E \) and \( C \). The authors of reference 8 show that if a partition function is broken into two parts such as,

\[
Z = Z_d + Z_{ex},
\]

then the internal energy may be expressed as

\[
\frac{E}{RT} = \frac{E_d}{RT} + \frac{Z_{ex}}{Z_{ex} + Z_d} \left[ \frac{E_{ex}}{RT} - \frac{E_d}{RT} \right].
\]
We used:
\[
\frac{E_d}{RT} = -\beta \frac{d}{d\beta} \ln Z_d
\]
\[
\frac{E_{ex}}{RT} = -\beta \frac{d}{d\beta} \ln Z_{ex}
\]

Likewise, they get for the heat capacity,
\[
\frac{C}{R} = \frac{C_d}{R} + \frac{Z_{ex}}{Z_{ex} + Z_d} \left[ \frac{C_{ex}}{R} - \frac{C_d}{R} \right]
\]
\[
+ \frac{Z_{ex} Z_d}{(Z_{ex} + Z_d)^2} \left[ \frac{E_{ex}}{RT} - \frac{E_d}{RT} \right]^2
\]

where
\[
\frac{C_d}{R} = \beta^2 \frac{d^2}{d\beta^2} \ln Z_d
\]
\[
\frac{C_{ex}}{R} = \beta^2 \frac{d^2}{d\beta^2} \ln Z_{ex}
\]

The so defined exchange thermodynamic functions have no real physical meaning. The first term on the right of these equations is the thermodynamic function we would calculate if we were to use the direct partition function only. The other terms are corrections to this approximation.

If we express all of our rotational partition functions in terms of \( \sigma \) and \( t \) (not \( \sigma \) and \( \sigma_c \)) we may change \( \beta \) to \( \sigma \) in the above formulas.
Using the preceding expressions, we readily obtain the following (methane, \( \sigma = 0.1 \)).

\[
\frac{Z_{ex}}{Z_{ex} + Z_d} = 4.18 \times 10^{-5}
\]

\[
E_d/RT = \frac{3}{2} - \sigma/4
\]

\[= 1.475\]

\[
E_{ex}/RT = \frac{3}{2} - \sigma/4 - \frac{\pi^2}{9} \sigma
\]

\[= -9.491\]

\[
E/RT = 1.475 - 4.6 \times 10^{-4}
\]

\[
E_{ex}/R - E_d/RT = -4.6 \times 10^{-4}
\]

\[
C_d/R = \frac{3}{2}
\]

\[
C_{ex}/R = \frac{3}{2} - \frac{2\pi^2}{9} \sigma
\]

\[= -20.43\]

\[
C/R = 1.500 + 4.1 \times 10^{-3}
\]

\[
C/R - C_d/R = 4.1 \times 10^{-3}
\]
VIII. CONCLUDING REMARKS

We have tried to present here a rather exhaustive analysis of exchange effects in the rotating symmetric top. From an experimental point of view, these effects are of little importance. The spin-rotational statistical effects influence the thermodynamic properties only at low temperatures (except, of course, for the already well characterized light diatomics). At these temperatures, hardly any of the gas phase remains. It is hoped, however, that the familiarity of exchange effects gained from a theoretical study of this model provides some intuitive guide to understanding the exchange effects in other systems.
APPENDIX 1

Fourier's Ring Problem. In the problem of the flow of heat about a ring, the solution to the heat equation must be periodic. This suggest an expansion of the solution in a Fourier series with the addition of an $e^{-nt}$ factor such that it satisfies the heat equation.

\[
\frac{\partial^2 T}{\partial \alpha^2} = \frac{1}{\sigma} \frac{\partial T}{\partial t}
\]

$T$ is the temperature and $\sigma$ is the coefficient of thermal conductivity.

\[
T(\alpha, t) = \sum_{n=\infty}^{\infty} \left( a_n \cos n\alpha + b_n \sin n\alpha \right) e^{-n^2\sigma t} \tag{1}
\]

We consider only the even distributions about the ring. $T(\alpha, t)$ is then an even function of $\alpha$ and can be expressed as a Fourier cosine series.

\[
T(\alpha, t) = \sum_{n=-\infty}^{\infty} a_n \cos n\alpha e^{-n^2\sigma t} \tag{2}
\]

\[
T(\alpha, 0) = \sum_{n=-\infty}^{\infty} a_n \cos n\alpha \tag{3}
\]

\[
a_n = \frac{1}{2\pi} \int_{-\pi}^{\pi} T(\alpha, 0) \cos n\alpha \, d\alpha
\]
Placing this in equation (2), we get

\[ T(\alpha, t) = \frac{1}{2\pi} \sum_{n = -\infty}^{\infty} \int_{-\pi}^{\pi} T(\alpha', 0) \cos n\alpha \cos n\alpha' \, d\alpha' \, e^{-n^2 \sigma t}. \tag{4} \]

Using the trigonometric identity

\[ \cos n\alpha \cos n\alpha' = \cos(n(\alpha - \alpha')) - \sin n\alpha \sin n\alpha', \]

and the fact that the integral over the sine portion vanishes, we get

\[ T(\alpha, t) = \frac{1}{2\pi} \int_{-\pi}^{\pi} T(\alpha', 0) \left[ \sum_{n = -\infty}^{\infty} \cos(n(\alpha - \alpha')) e^{-n^2 \sigma t} \right] d\alpha'. \tag{5} \]

Recognizing the portion in brackets to be a theta function and using its alternate form gives:

\[ T(\alpha, t) = \frac{1}{\sqrt{4\pi \sigma t}} \sum_{n = -\infty}^{\infty} \int_{-\pi}^{\pi} T(\varepsilon', 0) e^{-\frac{(\alpha - \varepsilon' + 2n\pi)^2}{4\sigma^2 t}} \, d\varepsilon'. \tag{6} \]

The above can be written in several alternate forms. Making the change in variable \( y = \varepsilon - 2n\pi \) and noting that

\[ T(y + 2n\pi, 0) = T(y, 0), \]
we obtain
\begin{equation}
T(\alpha, t) = \frac{1}{\sqrt{4\pi \sigma t}} \sum_{\eta = -\infty}^{+\infty} \int_{(2\eta+1)i\pi}^{(2\eta+1)i\pi} T(y, 0) e^{-\frac{(\alpha - y)^2}{4\sigma t}} \, dy.
\end{equation}

Finally, letting \( y = \xi + \alpha \), we get the result
\begin{equation}
T(\alpha, t) = \frac{1}{\sqrt{4\pi \sigma t}} \int_{-\infty}^{+\infty} T(\alpha + \xi, 0) e^{-\frac{\xi^2}{4\sigma t}} \, d\xi.
\end{equation}

It is of some importance to note that the above expression is equivalent to equation (6) which involves integration over \( T(\xi, 0) \) only in the range \(-\pi\) to \(+\pi\). Therefore, as long as the initial distribution is well behaved in this region, any apparent trouble arising from the use of (8) with its infinite limits can be removed by working backwards to equation (6). This is equivalent to taking the principle value interpretation of the infinite integral.
APPENDIX 2

The Asymmetric Top. We approach the asymmetric top p.f. using the formalism of the density matrix in the coordinate representation. Z, the canonical p.f., is given by

\[ Z = \int \rho(\tau) \, d\tau. \]

The integration is over all spatial coordinates and \( \rho(\tau) \), the density function, is given by:

\[ \rho(\tau) = \sum_i \left[ \phi_i^*(\tau) \right] e^{-\beta H} \left[ \phi_i(\tau) \right] \]

H is the asymmetric top Hamiltonian and \( \beta = \frac{1}{\pi T} \). The \( \phi_i(\tau) \) are any complete set of functions with which we can expand the true eigenfunctions of our system. We choose these to be the spin-rotational eigenfunctions of the symmetric top. The notation \( [\phi_i(\tau)] \) means that the functions have been properly symmetrized and normalized. Using the projection operators of group theory, we have\(^{13}\)

\[ \left[ \phi_i(\tau) \right] = \frac{1}{h} \sum_{\mathcal{G}} \chi^{(\lambda)}(\mathcal{G}) \hat{G} \phi_i(\tau). \]
\( \lambda \) is the one dimensional irreducible representation specified by the exclusion principle. \( \hat{G} \) is a symmetry operation which now operates on the eigenfunctions.

\( Z \) is now given by:

\[
Z = \sum_{i} \int \left[ \frac{i}{\hbar} \sum_{G} \chi_{(G)}^{(a)} \hat{G} \phi_{i}(\tau) \right] e^{-\beta \hat{H}} \left[ \frac{i}{\hbar} \sum_{G'} \chi_{(G') \hat{G}'} \phi_{i}(\tau) \right] d\tau
\]

Following Hill's arguments, we eliminate one of the sums such that

\[
\sum_{G} \sum_{G'} \rightarrow h \sum_{G}
\]

\[
Z = \sum_{i} \int \frac{i}{\hbar} \sum_{G} \chi_{(G)}^{(a)} \left[ \hat{G} \phi_{i}(\tau) \right] e^{-\beta \hat{H}} \phi_{i}(\tau) d\tau
\]

Recognizing that the only spin functions which survive the integration over the spin coordinates (because of orthogonality) are the ones which the operator \( \hat{G} \) doesn't change, we get after integration over the spin coordinates:

\[
Z = \frac{i}{\hbar} \sum_{G} \chi_{(G)}^{(a)} \chi_{s,G} \sum_{i} \langle \hat{G} \phi_{i}^{\ast}(\tau) | e^{-\beta \hat{H}} | \phi_{i}(\tau) \rangle
\]
where, as was derived in the text,

\[ \chi^{(a)}(\mathcal{G}) = (-1)^{N_f} \mathcal{C}(\mathcal{G}, \mathcal{f}) \]

\[ \chi_{s_i \mathcal{G}} = \prod_{i} (2s_i + 1) \mathcal{C}(s_i, i) \]

Davydov gives the transformation properties of the \( \phi_i(\tau) \) for the symmetric top. Using these, we can arrive at expressions (5.1) and (5.2) presented in the text.
References


