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The rotational partition function for linear molecules

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An important function in the statistical treatment of a gas of linear molecules is

$$S(\alpha) = \sum_{J=0}^{\infty}(2J+1)\,\mathrm{e}^{-\alpha J(J+1)}.$$

This sum is convenient to use mainly when α is large and alternate expressions, generally asymptotic expansions, are often used when α is small. In this paper, the sum is evaluated to yield a single expression that is valid for large and small values of α. The expression is composed of three terms, each of which involves the theta functions of Jacobi. One term is in the form of an integral, but is small relative to the other two and easily evaluated by numerical means. The expression is readily differentiated and can be used for the general evaluation of the rotational partition function for gases of linear molecules at all temperatures.

1. Introduction

The function defined by

$$S(\alpha) = \sum_{J=0}^{\infty}(2J+1)\,\mathrm{e}^{-\alpha J(J+1)} \tag{1}$$

is important in the statistical treatment of a gas of linear molecules. It is used to describe the contributions to the thermodynamic functions from the rotational motion of the individual molecules. The argument of this function represents the ratio $\alpha = \Theta_r/T$, Θ_r being a rotational temperature characteristic of the molecule and T being the temperature of the gas. The function $S(\alpha)$ constitutes the complete rotational contribution to the molecular partition function under the assumptions that the gas be ideal, that the rotation be described in terms of a rigid rotator uncoupled to any vibrational motions, that the molecules be nonsymmetric, and that they be in a $^1\Sigma$ electronic state. Although these assumptions are rather numerous and sometimes severe, the function $S(\alpha)$ still plays an important role when they are relaxed. It can be viewed as a zeroth order contribution to which corrections are applied. The derivatives of $S(\alpha)$ also play a role when the rigid rotator approximation is relaxed and coupling between the rotational and vibrational motions is introduced. The general statistical treatment of a gas of linear molecules involves the function $S(\alpha)$ and its derivatives.

From a purely computational viewpoint, $S(\alpha)$ and its derivatives can be calculated directly from equation (1). All the terms are positive, so that numerical errors due to cancellation of terms do not occur. Further, since α is always positive, the terms of the sum eventually become small enough to neglect. However, as α gets smaller, which corresponds to increasing the temperature of the gas, the number of terms needed to maintain a certain accuracy increases without bound. At some point, the evaluation of the sum becomes inconvenient.

At the other extreme, the Euler–MacLaurin sum formula [10] can be applied to obtain an asymptotic expansion for $S(\alpha)$ about $\alpha = 0$ (i.e., $T = \infty$). In addition to the direct application of the expansion formula [3], certain rearrangements have been proposed [7,8] which allow greater accuracy for moderate values of α. Since all such expansions are asymptotic, though, they necessarily diverge if either too many terms are included in the sum or the value of α gets too large.

The general procedure for evaluating $S(\alpha)$ is normally a combination of the two extremes. If α is smaller than some cutoff value (say, less than 0.7), one of the asymptotic expressions is used. If α is larger than the cutoff, the sum of equation (1) is used directly. Although such a procedure should be reliable for computational purposes, it is desirable to have a single expression that is convenient for all values of α. Such an expression is derived in this paper.

Because the sum in equation (1) is so similar to those that define the theta functions of Jacobi [10], it is natural to suggest that $S(\alpha)$ be expressed in terms of them [5,7]. Although it has generally been concluded that this cannot be done, the expression derived here is in terms of the theta functions.

The expression derived in this paper consists of three terms. Two terms, expressed in terms of well-known functions, contain the major contributions to the function, their sum yielding $S(\alpha)$ exactly in both the $\alpha \to 0$ and $\alpha \to \infty$ limits. The remainder is in the form of an integral. It never exceeds 0.175 and is generally less than this. The remainder has not been evaluated in closed form (except as an infinite sum, which is not generally useful), but it can be evaluated numerically to high accuracy with minor effort.

The rest of this paper is organized as follows. Section 2 presents the derivation of the expression for $S(\alpha)$. Section 3 discusses its properties and suggests some means for its evaluation. Section 4 presents the analogous expressions for the derivatives of $S(\alpha)$. Section 5 presents some conclusions.

2. Derivation of the expression

The form of the sum in equation (1) suggests that $S(\alpha)$ should be related to the first derivative of one of the theta functions. The closely related exchange rotational partition function [4], which differs from $S(\alpha)$ only by the additional factor of $(-)^J$ in the summand, can be expressed in just such a way. Attempts to find a direct relationship have not been successful, but the above reasoning suggests a slightly different approach. A new function can be defined that is similar to the theta functions but whose derivative is related to $S(\alpha)$. This function is found to obey a diffusion-type differential equation, the solution of which can be used to derive a closed-form expression for $S(\alpha)$.

Define the function

$$F(q,a) = \sum_{n=0}^{\infty} q^{(n+a)^2}. \tag{2}$$

The sum on the right hand side converges for all q such that $|q| < 1$ and for all complex a. The function $F(q,a)$ can be shown to be an entire function in a and, in general, a multiple-valued function in q with a branch point at $q = 0$. Introducing this function, equation (1) can be reexpressed as

$$S(\alpha) = -\frac{\mathrm{e}^{\alpha/4}}{\alpha} \frac{\partial}{\partial a} F(\mathrm{e}^{-\alpha}, a) \,|_{a=1/2} \,. \tag{3}$$

The theta functions can all be expressed in terms of $F(q,a)$. Specifically,[1]

$$\vartheta_4(z,q) = -1 + \mathrm{e}^{(2z+\pi)^2/4\ln^2 q} \left\{ F\left(q, \frac{\mathrm{i}(2z+\pi)}{2\ln q}\right) + F\left(q, -\frac{\mathrm{i}(2z+\pi)}{2\ln q}\right) \right\}. \tag{4}$$

The other three theta functions can be constructed directly from this one [10]. Inversion of this equation to give an expression for $F(q,a)$ in terms of the theta functions is not possible. All the theta functions contain a sum of the form $(F(q,a) + F(q,-a))$, so that, for arbitrary values of a, it is impossible to extract $F(q,a)$ with just one sign of a. For certain values of a, however, $F(q,a)$ can be related to the theta functions of zero argument (that is, $z = 0$). Of particular interest here are the two relations

$$\begin{aligned} F(q,0) &= \frac{1}{2}\big(\vartheta_3(0,q) + 1\big), \\ F(q,1/2) &= \frac{1}{2}\vartheta_2(0,q). \end{aligned} \tag{5}$$

By taking derivatives of equation (2) and comparing terms, it is readily worked out that $F(q,a)$ must satisfy the differential equation

$$\frac{\partial^2}{\partial a^2} F = \left[2\ln q + 4q(\ln q)^2 \frac{\partial}{\partial q} \right] F. \tag{6}$$

[1] In this and all other formulas, the notation of Whittaker and Watson [10] is used for the theta functions. Specifically,

$$\vartheta_4(z,q) = \sum_{n=-\infty}^{\infty} (-)^n q^{n^2} \mathrm{e}^{2n\mathrm{i}z}.$$

With the wide variety of notations in use, it is important that this be understood to avoid confusion with other work.

This can be converted to the more familiar diffusion-type equation by first letting $q = \mathrm{e}^{-1/4x}$ and introducing the new function

$$G(x,a) = \frac{1}{2x^{1/2}} F\bigl(\mathrm{e}^{-1/4x}, a\bigr). \tag{7}$$

Equation (6) now becomes

$$\frac{\partial^2 G}{\partial a^2} = \frac{\partial G}{\partial x}. \tag{8}$$

This differential equation is to be solved over the domain of real, non-negative values of x and a. At the boundaries, the function is found to have the required values

$$G(x,0) = \frac{1}{4x^{1/2}} \bigl(\vartheta_3(0, \mathrm{e}^{-1/4x}) + 1\bigr), \tag{9}$$

$$G(0,a) = 0. \tag{10}$$

As $a \to \infty$, we arrive at a third boundary condition,

$$\lim_{\alpha \to \infty} G(x,a) = 0. \tag{11}$$

It may be noted that the point, $x = a = 0$, is problematical, since the limits of the two equations (9) and (10) do not agree with each other. This is handled by removing an infinitesimal region about this point from the domain.

The differential equation (8) is most easily solved by performing a Laplace transform in x. Denote the transformed coordinate by s and the transformed function by $\widehat{G}(s,a)$. Using the boundary condition at $x = 0$, equation (8) is transformed to

$$\frac{\partial^2 \widehat{G}}{\partial a^2} = s\widehat{G}. \tag{12}$$

Using the boundary conditions in a, this equation is easily solved to give

$$\widehat{G}(s,a) = \widehat{G}(s,0)\, \mathrm{e}^{-\sqrt{s}a}, \tag{13}$$

where $\widehat{G}(s,0)$ refers to the Laplace transform of $G(x,0)$. The inverse Laplace transform is worked out as a convolution

$$G(x,a) = \int_0^x G(x-t,0) \frac{a}{2\sqrt{\pi t^3}}\, \mathrm{e}^{-a^2/4t}\, \mathrm{d}t. \tag{14}$$

The corresponding expression for $F(q,a)$ can be obtained with equation (7). For subsequent analysis, it is convenient to modify this by letting $q = \mathrm{e}^{-\alpha}$ and transforming the integration coordinate to $v = a^2(1/4t - \alpha)$. This leads to

$$F(\mathrm{e}^{-\alpha}, a) = \frac{\mathrm{e}^{-\alpha a^2}}{2\sqrt{\pi}} \left\{ \int_0^\infty \frac{\mathrm{e}^{-v}}{\sqrt{v}} \vartheta_3\bigl(0, \mathrm{e}^{-\alpha(1+\alpha a^2/v)}\bigr)\, \mathrm{d}v + \sqrt{\pi} \right\}. \tag{15}$$

Using this in equation (3) yields

$$S(\alpha) = \frac{1}{2}\,\mathrm{e}^{\alpha/4}\vartheta_2(0, \mathrm{e}^{-\alpha}) + \frac{\alpha \mathrm{e}^{-\alpha}}{2\sqrt{\pi}} \int_0^\infty \frac{\mathrm{e}^{-v}\mathrm{e}^{-\alpha^2/4v}}{v^{3/2}} \vartheta_3'\big(0, \mathrm{e}^{-\alpha(1+\alpha/4v)}\big)\,\mathrm{d}v, \tag{16}$$

where $\vartheta_3'(0, q)$ is the first derivative of $\vartheta_3(0, q)$ with respect to q.

Some further progress is possible with the integral. Since it vanishes exponentially for large α, it is reasonable to focus on the case where α is small. As α decreases, the integrand becomes dominated by the theta function. For a given value of v (assumed to be non-zero), the integrand behaves as

$$\frac{\mathrm{e}^{-v}\mathrm{e}^{-\alpha^2/4v}}{v^{3/2}} \vartheta_3'\big(0, \mathrm{e}^{-\alpha(1+\alpha/4v)}\big) \underset{\alpha\to 0}{\sim} \vartheta_3'(0, \mathrm{e}^{-\alpha}) \frac{\mathrm{e}^{-v}}{(v+\alpha/4)^{3/2}}. \tag{17}$$

To extract the small α behavior, then, this term is subtracted and added to the integrand, the added part being integrated in closed form. The result is

$$S(\alpha) = \frac{1}{2}\,\mathrm{e}^{\alpha/4}\vartheta_2(0, \mathrm{e}^{-\alpha}) + 2\sqrt{\frac{\alpha}{\pi}}\,\mathrm{e}^{-\alpha}\vartheta_3'(0, \mathrm{e}^{-\alpha})\left(1 - \frac{1}{2}\sqrt{\pi\alpha}\,\mathrm{e}^{\alpha/4}\mathrm{erfc}\big(\sqrt{\alpha}/2\big)\right) + \mathrm{e}^{-\alpha}R(\alpha), \tag{18}$$

where

$$R(\alpha) = \frac{\alpha}{2\sqrt{\pi}} \int_0^\infty \mathrm{e}^{-v}\left(\frac{\mathrm{e}^{-\alpha^2/4v}}{v^{3/2}}\vartheta_3'\big(0, \mathrm{e}^{-\alpha(1+\alpha/4v)}\big) - \frac{1}{(v+\alpha/4)^{3/2}}\vartheta_3'(0, \mathrm{e}^{-\alpha})\right)\mathrm{d}v. \tag{19}$$

3. Some properties of the functions

The derived expression for $S(\alpha)$ is given as a sum of three terms. The first two are closed-form expressions of well-known functions and the final term contains a remaining integral. Although it is not obvious, these three terms are easily evaluated for all values of α. The behavior of these three terms will be analyzed in this section and a general procedure for their evaluation outlined.

Consider just the first two terms of equation (18) for now. These closed-form expressions contain elementary functions whose computation is a straightforward matter. The exponential function and even the complementary error function can be found in many computers' math libraries. The theta functions are not so common and are worth a few comments here.

There are four different theta functions, only three of which are needed for an evaluation of $S(\alpha)$. Further, although the theta functions are generally defined as having two arguments, only one is non-zero in the expressions derived here. Formulas for the functions needed here are

$$\begin{aligned}
\vartheta_2(0,q) &= 2\sum_{n=0}^{\infty} q^{(n+1/2)^2},\\
\vartheta_3(0,q) &= 1+2\sum_{n=1}^{\infty} q^{n^2},\\
\vartheta_4(0,q) &= 1+2\sum_{n=1}^{\infty} (-)^n q^{n^2},\\
\vartheta_3'(0,q) &= 2\sum_{n=1}^{\infty} n^2 q^{n^2-1}.
\end{aligned} \tag{20}$$

Whenever $q < 0.05$, all these sums achieve sixteen-digit accuracy within four terms. For $q > 0.05$, the functions can be transformed, using what is known as Jacobi's imaginary transformation [10], to a form that converges just as rapidly. The formulas of importance here are:

$$\begin{aligned}
\vartheta_2(0,\mathrm{e}^{-\alpha}) &= \left(\frac{\pi}{\alpha}\right)^{1/2} \vartheta_4\bigl(0,\mathrm{e}^{-\pi^2/\alpha}\bigr),\\
\vartheta_3'(0,\mathrm{e}^{-\alpha}) &= \frac{\pi^{1/2}}{\mathrm{e}^{-\alpha}\alpha^{5/2}}\left\{\frac{\alpha}{2}\vartheta_3\bigl(0,\mathrm{e}^{-\pi^2/\alpha}\bigr) - \pi^2\mathrm{e}^{-\pi^2/\alpha}\vartheta_3'\bigl(0,\mathrm{e}^{-\pi^2/\alpha}\bigr)\right\}.
\end{aligned} \tag{21}$$

If $\mathrm{e}^{-\alpha} > 0.05$, then $\mathrm{e}^{-\pi^2/\alpha} < 0.05$, and the sums defining the functions on the right-hand sides converge rapidly – within four terms for sixteen-digit accuracy. The evaluation of the theta functions is therefore rapid regardless of the value of α.

Consider the first term of equation (18) more closely. For reference purposes, denote it by

$$T_1 = \frac{1}{2}\,\mathrm{e}^{\alpha/4}\vartheta_2(0,\mathrm{e}^{-\alpha}). \tag{22}$$

This term is important mainly for large values of α. It can be obtained from a direct analysis of the sum in equation (1). After breaking up the factor of $(2J+1)$ in the summand and separating the expression into two sums, there results

$$S(\alpha) = 2\sum_{J=0}^{\infty} J\,\mathrm{e}^{-\alpha J(J+1)} + T_1. \tag{23}$$

The importance of T_1 for large values of α is a consequence of the fact that the first term of the sum in equation (1) (i.e., the $J = 0$ term) becomes the most important in this regime. This first term is contained entirely in T_1. For large values of α, T_1 approaches unity. As α gets smaller, on the other hand, T_1 grows as $\alpha^{-1/2}$. However, the function $S(\alpha)$ grows as α^{-1} for small α, so that the important contribution in this regime is due to the remaining sum in equation (23).

The second term in equation (18) will be denoted by

$$T_2 = 2\sqrt{\frac{\alpha}{\pi}}\,\mathrm{e}^{-\alpha}\vartheta_3'(0,\mathrm{e}^{-\alpha})\left(1 - \frac{1}{2}\sqrt{\pi\alpha}\,\mathrm{e}^{\alpha/4}\mathrm{erfc}(\sqrt{\alpha}/2)\right). \tag{24}$$

Clearly, it is an approximation to the remaining sum in equation (23). For large values of α, T_2 decays exponentially, while for small values of α, it grows as α^{-1}. This term describes the small α behavior of $S(\alpha)$ while T_1 describes the large α behavior.

We can view the sum of the two terms, $T_1 + T_2$, as a first approximation for the function, $S(\alpha)$; denote it by $S_0(\alpha)$. This approximation is found to be fairly good. In fact, in the two limits $\alpha \to 0$ and $\alpha \to \infty$, it is readily shown that the correct limiting values are obtained:

$$S_0(\alpha) \underset{\alpha\to 0}{\sim} \frac{1}{\alpha}, \qquad S_0(\alpha) \underset{\alpha\to\infty}{\sim} 1. \tag{25}$$

For intermediate values of α, the approximation deviates from the exact result, but the deviation is relatively small. The approximate and exact functions are compared in figure 1. From the fairly good agreement, it is clear that only a modest approximation for $R(\alpha)$ should provide a very good approximation for $S(\alpha)$.

Now, consider the third term of equation (18),

$$T_3 = \mathrm{e}^{-\alpha}R(\alpha), \tag{26}$$

where $R(\alpha)$ is given by equation (19). Because $R(\alpha)$ is expressed as an integral, this term is not as easily evaluated as the other two. However, it does have some desirable properties that allow some accurate approximations.

The integrand used to define $R(\alpha)$ is given by

$$I(v) = \mathrm{e}^{-v}\left(\frac{\mathrm{e}^{-\alpha^2/4v}}{v^{3/2}}\vartheta_3'\big(0,\mathrm{e}^{-\alpha(1+\alpha/4v)}\big) - \frac{1}{(v+\alpha/4)^{3/2}}\vartheta_3'(0,\mathrm{e}^{-\alpha})\right). \tag{27}$$

It is the difference of two terms, the first term being encountered in the original expression for $S(\alpha)$ (see equation (16)) and the second term being the small α limit of the first. $I(v)$ is negative for all values of v so that T_3 is negative for all α. For a given non-zero value of v, $I(v)$ vanishes in the limit $\alpha \to 0$.

To evaluate $R(\alpha)$ reliably, it is important to understand the v-dependence of the integrand. The v-dependence changes with α, but overall, the integrand is localized to the small v region. As v gets large, both terms in $I(v)$ approach the same limit. The difference therefore goes to zero faster than either term alone. The infinite-ranged integral can then be replaced by a finite-ranged one to a good approximation. The cut-off to use in generating the finite-ranged integral varies with α, so it is useful to investigate this.

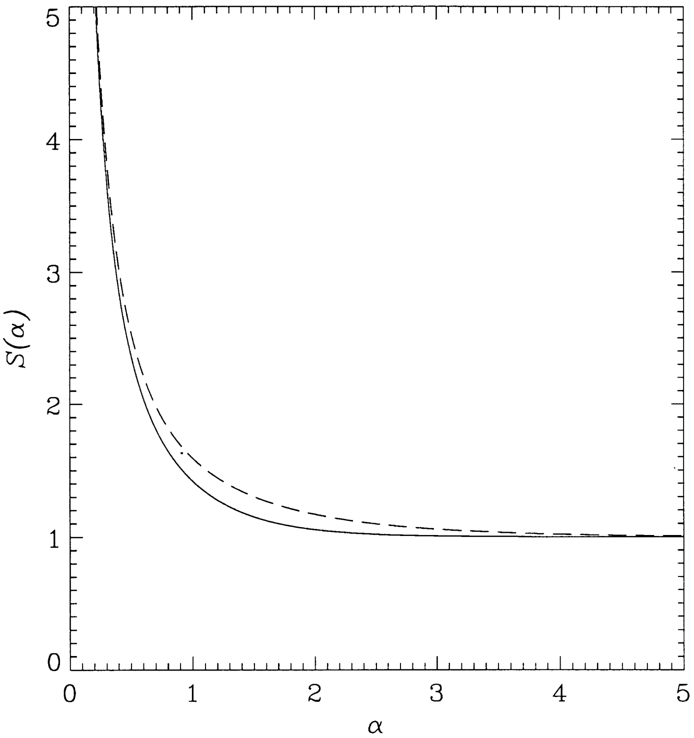

Figure 1. Comparison of $S_0(\alpha)$ (dashed line) and $S(\alpha)$ (solid line).

If α is large, the first term in the integrand becomes small for all values of v, and at some point becomes negligible. For large enough α,

$$I(v) \underset{\alpha\to\infty}{\sim} -\vartheta_3'(0, \mathrm{e}^{-\alpha}) \frac{\mathrm{e}^{-v}}{(v+\alpha/4)^{3/2}}. \tag{28}$$

In this regime, the integrand decays exponentially with v and the integral can be effectively cut off when the exponential function is small relative to unity.

For smaller values of α, the first term in equation (27) becomes more important and begins to cancel the second before the exponential factor cuts off the integral. This cancellation occurs at steadily smaller values of v as α is decreased. How this cut-off varies with α can be deduced as follows. The small α behavior of the integrand is determined by the Jacobi imaginary transformation (see equation (21)). When α is less than some threshold, call it α_m, the transformation formula can be well approximated by

$$\vartheta_3'(0, \mathrm{e}^{-\alpha}) \approx \frac{\pi^{1/2}}{2\,\mathrm{e}^{-\alpha}\alpha^{3/2}}. \tag{29}$$

In this regime, both terms in the integrand yield the same approximate value (differing only by exponentially small terms), so that the integral is effectively cut off when $\alpha(1+\alpha/4v)$ is smaller than the threshold value, α_m. In terms of v, the integral is cut off when

$$v > \frac{\alpha^2}{4(\alpha_m - \alpha)}. \tag{30}$$

For small values of α, this cut-off decreases as α^2. This does not mean that the integral vanishes in the limit of small α. On the contrary, the integral approaches a non-zero limit. For $v = 0$, the first term of the integrand vanishes while the second increases in magnitude as $\alpha^{-3/2}$. Further, all of the derivatives of the first term are zero at $v = 0$, meaning that this term stays close to zero for a range of small values of v. Although the effective range of integration decreases with α, its evaluation remains important to the limit of $\alpha \to 0$.

The localized nature of the integrand suggests a simple numerical integration. A 129-point Romberg integration [9] was used over a finite range in v. The upper limit used for the integration was

$$v_{\max} = 10\left(-\frac{3}{4} + \left[(3/4)^2 + (\alpha/2)^2\right]^{1/2}\right). \tag{31}$$

With this procedure, T_3 was computed to within 0.0001 of the exact result for all values of α. This does require the evaluation of the integrand over 129 points and may be considered time consuming. However, it is not necessary to monitor the size of the terms, nor to consider whether the range of α is appropriate.

Although numerical integration is accurate, an analytic evaluation or even approximation for T_3 would be desirable. Before concluding this section, then, some of the analytic properties of $R(\alpha)$ will be discussed and an *ad hoc* approximation presented.

The integral can be evaluated by expanding the first theta function in equation (19), integrating term by term, and recombining at the end. The resulting expression is

$$\begin{aligned} R(\alpha) = {} & 2\sum_{n=1}^{\infty} n\, \mathrm{e}^{-\alpha(n^2+n-1)} - 2\left(\frac{\alpha}{\pi}\right)^{1/2} \vartheta_3'(0, \mathrm{e}^{-\alpha}) \\ & \times \left(1 - \frac{1}{2}\sqrt{\pi\alpha}\, \mathrm{e}^{\alpha/4} \mathrm{erfc}(\sqrt{\alpha}/2)\right). \end{aligned} \tag{32}$$

Clearly, this expression is not of any use for computational work; one might as well use the original definition of $S(\alpha)$. However, it does allow the determination of the correct behavior of this function in the $\alpha \to 0$ and $\alpha \to \infty$ limits.

For large α, equation (32) yields

$$\begin{aligned} R(\alpha) & \underset{\alpha\to\infty}{\sim} -4\left(\frac{\alpha}{\pi}\right)^{1/2}\left(1 - \frac{1}{2}\sqrt{\pi\alpha}\, \mathrm{e}^{\alpha/4}\mathrm{erfc}(\sqrt{\alpha}/2)\right) + (\text{exponential terms}) \\ & \underset{\alpha\to\infty}{\sim} -\frac{8}{\sqrt{\pi\alpha}} + \mathrm{O}\left(\alpha^{-3/2}\right). \end{aligned} \tag{33}$$

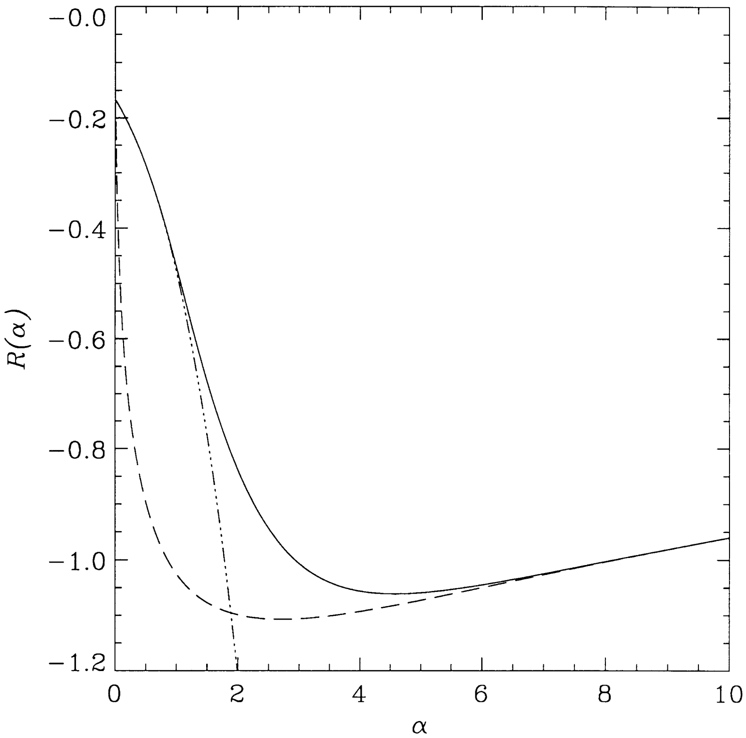

Figure 2. $R(\alpha)$ as a function of α (solid line). Also shown are the large (dashed) and small (dash-dotted) limiting forms of equations (33) and (34).

This behavior is due solely to the second term of the integrand; the first term is exponentially small. For small α, the Euler–MacLaurin sum formula can be used to rearrange the first term of equation (32) to give

$$R(\alpha) \underset{\alpha\to 0}{\sim} -\frac{1}{6} - \frac{11}{60}\alpha - \frac{241}{2520}\alpha^2 - \frac{7}{240}\alpha^3 - \frac{1277}{332640}\alpha^4 - \cdots . \tag{34}$$

In this range, the second term of the integrand cancels out a major contribution from the first. The sum in equation (34) comes entirely from the remaining part of the first term. The small and large α limits are therefore due to the separate terms in the integrand. The behavior in these limits is markedly different as can be seen in figure 2 where $R(\alpha)$ is plotted along with the large and small α forms. Trying to find an approximation that models both regions correctly is a numerical challenge.

There are many ways to model this function, some more empirical than others. One approximation that is accurate to within 0.002 for all α is constructed as follows. It is first noted that $R(\alpha)$ is multiplied by $e^{-\alpha}$, so that more emphasis will be given to the small α behavior. When α is small, the integrand increases in magnitude near $v = 0$ and becomes more localized in this region. For larger α, the integrand behaves as an exponential. A function that has these features is

$$I_a(v) = A\,\mathrm{e}^{-av-bv^2}, \tag{35}$$

where A, a and b are functions of α designed to give the desired behavior. Using this integrand, the approximation

$$R_a(\alpha) = \frac{\alpha}{2\sqrt{\pi}} \int_0^\infty I_a(v)\,\mathrm{d}v \tag{36}$$

is proposed. The parameter A is designed to get the magnitude correctly near $v = 0$, a is expected to approach 1 as α increases, and b is expected to increase as α^{-4} as α decreases. The $v = 0$ limit of the integrand and its first derivative can be worked out in closed form, suggesting the values

$$A = -\frac{8}{\alpha^{3/2}}\vartheta_3'(0, \mathrm{e}^{-\alpha}), \qquad a = \frac{\alpha + 6}{\alpha}. \tag{37}$$

The other parameter will be rewritten as $b = \beta/\alpha^4$, and β will be chosen to give the correct small α limit for $R_a(\alpha)$.

The integral can be evaluated in closed form, leading to $\beta = 36\pi$ and

$$R_a(\alpha) = -\frac{\alpha^{3/2}\vartheta_3'(0, \mathrm{e}^{-\alpha})}{3\sqrt{\pi}}\,\mathrm{e}^{\alpha^2(\alpha+6)^2/144\pi}\mathrm{erfc}\left(\frac{\alpha(\alpha + 6)}{12\sqrt{\pi}}\right). \tag{38}$$

This approximation yields the correct $\alpha \to 0$ and $\alpha \to \infty$ limits. However, it does not model the function well inbetween. To improve the approximation, it is multiplied by a function of the form

$$P(\alpha) = 1 + \frac{\sum_{j=1}^{3} c_j \alpha^j}{1 + \gamma\alpha^3}. \tag{39}$$

The coefficients c_j are chosen to get the first few terms of the small α expansion (34) correctly. The denominator is introduced to damp out the function as α gets larger and γ is chosen empirically to get the best agreement inbetween. Direct calculation leads to

$$\begin{aligned} c_1 &= \frac{1}{10} + \frac{1}{\pi}, \quad c_2 = -\frac{11}{420} + \frac{1}{60\pi} + \frac{1}{\pi^2}, \\ c_3 &= -\frac{13}{840} - \frac{33}{280\pi} + \frac{1}{10\pi^2} + \frac{1}{\pi^3}. \end{aligned} \tag{40}$$

By trying several values of γ, optimum agreement with the exact result was obtained with a value of $\gamma = 0.12$. Comparison of $\mathrm{e}^{-\alpha}R_a(\alpha)P(\alpha)$ with T_3 showed a maximum deviation of 0.002.

4. Derivatives of $S(\alpha)$

Because $S(\alpha)$ is expressed in terms of analytic functions, its derivatives are readily evaluated from equation (18). Explicit formulas for the first two derivatives will be given here. Higher derivatives are obtained in the same way.

Consider each term separately. The first term and its first two derivatives are given by

$$\begin{aligned} T_1 &= \frac{1}{2}\,\mathrm{e}^{\alpha/4}\vartheta_2(0,\mathrm{e}^{-\alpha}), \\ T_1' &= \frac{1}{4}T_1 - \frac{1}{2}\,\mathrm{e}^{-3\alpha/4}\vartheta_2'(0,\mathrm{e}^{-\alpha}), \\ T_1'' &= \frac{1}{16}T_1 + \frac{1}{4}\,\mathrm{e}^{-3\alpha/4}\vartheta_2'(0,\mathrm{e}^{-\alpha}) + \frac{1}{2}\,\mathrm{e}^{-7\alpha/4}\vartheta_2''(0,\mathrm{e}^{-\alpha}), \end{aligned} \tag{41}$$

where the primes on the theta functions denote differentiation with respect to q while those on T_1 denote differentiation with respect to α. For reference purposes,

$$\begin{aligned} \vartheta_2'(0,q) &= 2\sum_{n=0}^{\infty}(n+1/2)^2 q^{n^2+n-3/4}, \\ \vartheta_2''(0,q) &= 2\sum_{n=0}^{\infty}(n+1/2)^2(n^2+n-3/4)q^{n^2+n-7/4}. \end{aligned} \tag{42}$$

As with the other theta functions, Jacobi's imaginary transformation can be applied to these functions to ensure rapid convergence for all values of q.

For the second term,

$$\begin{aligned} T_2 &= 2\sqrt{\frac{\alpha}{\pi}}\,\mathrm{e}^{-\alpha}\vartheta_3'(0,\mathrm{e}^{-\alpha})\left(1-\frac{1}{2}\sqrt{\pi\alpha}\,\mathrm{e}^{\alpha/4}\mathrm{erfc}(\sqrt{\alpha}/2)\right), \\ T_2' &= 2\sqrt{\frac{\alpha}{\pi}}\,\mathrm{e}^{-\alpha}\Bigg\{\vartheta_3'(0,\mathrm{e}^{-\alpha})\left[\frac{2-3\alpha}{4\alpha}+\frac{3\alpha-4}{8\alpha}\sqrt{\pi\alpha}\,\mathrm{e}^{\alpha/4}\mathrm{erfc}(\sqrt{\alpha}/2)\right] \\ &\quad - \mathrm{e}^{-\alpha}\vartheta_3''(0,\mathrm{e}^{-\alpha})\left[1-\frac{1}{2}\sqrt{\pi\alpha}\,\mathrm{e}^{\alpha/4}\mathrm{erfc}(\sqrt{\alpha}/2)\right]\Bigg\}, \\ T_2'' &= 2\sqrt{\frac{\alpha}{\pi}}\,\mathrm{e}^{-\alpha}\Bigg\{\vartheta_3'(0,\mathrm{e}^{-\alpha})\left[\frac{9\alpha^2-10\alpha-4}{16\alpha^2}+\frac{24-9\alpha}{32\alpha}\sqrt{\pi\alpha}\,\mathrm{e}^{\alpha/4}\mathrm{erfc}(\sqrt{\alpha}/2)\right] \\ &\quad + \mathrm{e}^{-\alpha}\vartheta_3''(0,\mathrm{e}^{-\alpha})\left[\frac{5\alpha-2}{2\alpha}+\frac{4-5\alpha}{4\alpha}\sqrt{\pi\alpha}\,\mathrm{e}^{\alpha/4}\mathrm{erfc}(\sqrt{\alpha}/2)\right] \\ &\quad + \mathrm{e}^{-2\alpha}\vartheta_3'''(0,\mathrm{e}^{-\alpha})\left[1-\frac{1}{2}\sqrt{\pi\alpha}\,\mathrm{e}^{\alpha/4}\mathrm{erfc}(\sqrt{\alpha}/2)\right]\Bigg\}. \end{aligned} \tag{43}$$

The theta function derivatives are

$$\begin{aligned}\vartheta_3''(0,q) &= 2\sum_{n=1}^{\infty} n^2(n^2-1)q^{n^2-2},\\ \vartheta_3'''(0,q) &= 2\sum_{n=1}^{\infty} n^2(n^2-1)(n^2-2)q^{n^2-3}.\end{aligned} \tag{44}$$

The derivatives of the third term are best evaluated over several levels. Thus,

$$\begin{aligned}T_3 &= \mathrm{e}^{-\alpha}R(\alpha),\\ T_3' &= \mathrm{e}^{-\alpha}\{-R(\alpha)+R'(\alpha)\},\\ T_3'' &= \mathrm{e}^{-\alpha}\{R(\alpha)-2R'(\alpha)+R''\},\end{aligned} \tag{45}$$

where

$$\begin{aligned}R(\alpha) &= \frac{\alpha}{2\sqrt{\pi}}\int_0^{\infty} H(\alpha,v)\,\mathrm{d}v,\\ R'(\alpha) &= \frac{1}{\alpha}R(\alpha)+\frac{\alpha}{2\sqrt{\pi}}\int_0^{\infty} H'(\alpha,v)\,\mathrm{d}v,\\ R''(\alpha) &= \frac{1}{\sqrt{\pi}}\int_0^{\infty} H'(\alpha,v)\,\mathrm{d}v+\frac{\alpha}{2\sqrt{\pi}}\int_0^{\infty} H''(\alpha,v)\,\mathrm{d}v.\end{aligned} \tag{46}$$

The integrands are given by

$$\begin{aligned}H(\alpha,v) &= \mathrm{e}^{-v}\left\{\frac{\mathrm{e}^{-\alpha^2/4v}}{v^{3/2}}\vartheta_3'\big(0,\mathrm{e}^{-\alpha(1+\alpha/4v)}\big)-\frac{1}{(v+\alpha/4)^{3/2}}\vartheta_3'(0,\mathrm{e}^{-\alpha})\right\},\\ H'(\alpha,v) &= \mathrm{e}^{-v}\left\{-\frac{\alpha\mathrm{e}^{-\alpha^2/4v}}{2v^{5/2}}\vartheta_3'\big(0,\mathrm{e}^{-\alpha(1+\alpha/4v)}\big)\right.\\ &\quad -\frac{2v+\alpha}{2v^{5/2}}\,\mathrm{e}^{-\alpha}\mathrm{e}^{-\alpha^2/2v}\vartheta_3''\big(0,\mathrm{e}^{-\alpha(1+\alpha/4v)}\big)\\ &\quad \left.+\frac{3}{8(v+\alpha/4)^{5/2}}\vartheta_3'(0,\mathrm{e}^{-\alpha})+\frac{\mathrm{e}^{-\alpha}}{(v+\alpha/4)^{3/2}}\vartheta_3''(0,\mathrm{e}^{-\alpha})\right\},\\ H''(\alpha,v) &= \mathrm{e}^{-v}\left\{\frac{\alpha^2-2v}{4v^{7/2}}\,\mathrm{e}^{-\alpha^2/4v}\vartheta_3'\big(0,\mathrm{e}^{-\alpha(1+\alpha/4v)}\big)\right.\\ &\quad +\frac{4v^2-2v+8v\alpha+3\alpha^2}{4v^{7/2}}\,\mathrm{e}^{-\alpha}\mathrm{e}^{-\alpha^2/2v}\vartheta_3''\big(0,\mathrm{e}^{-\alpha(1+\alpha/4v)}\big)\\ &\quad +\frac{(2v+\alpha)^2}{4v^{7/2}}\,\mathrm{e}^{-2\alpha}\mathrm{e}^{-3\alpha^2/4v}\vartheta_3'''\big(0,\mathrm{e}^{-\alpha(1+\alpha/4v)}\big)\\ &\quad -\frac{15}{64(v+\alpha/4)^{7/2}}\vartheta_3'(0,\mathrm{e}^{-\alpha})-\frac{3+4v+\alpha}{4(v+\alpha/4)^{5/2}}\,\mathrm{e}^{-\alpha}\vartheta_3''(0,\mathrm{e}^{-\alpha})\\ &\quad \left.-\frac{\mathrm{e}^{-2\alpha}}{(v+\alpha/4)^{3/2}}\vartheta_3'''(0,\mathrm{e}^{-\alpha})\right\}.\end{aligned} \tag{47}$$

Clearly, these expressions become increasingly unwieldy. Nevertheless, they are exact and readily evaluated on a computer. Further, the integrals involved in the derivatives of T_3 contain integrands that are localized and can be accurately evaluated numerically.

5. Conclusions

The infinite sum of equation (1) has been evaluated in closed form as a sum of three terms. The significance of this result can be seen on two levels. The most obvious is on a formal level. In the first place, Statistical Mechanics textbooks commonly state that the sum cannot be evaluated (three examples are [1,2,6]). The expression derived here contradicts this statement. Second, functional analysis of $S(\alpha)$ is more easily achieved with the closed-form expression than it is with the infinite sum. Finally, the derivatives of $S(\alpha)$ are more easily evaluated with the functional expression and their properties more easily analyzed than with the infinite sum.

The more practical significance of this result is that there is a single expression for the rotational partition function that is accurate and equally convenient at all temperatures. Direct summation is also accurate at all temperatures, but it becomes increasingly awkward at higher temperatures due to the slower convergence. Several asymptotic expansions have been derived that are more efficient for higher temperatures, but they are inaccurate at lower temperatures. Use of McDowell's expression [7], for example, becomes inaccurate for HCl below 10 K, while it becomes inaccurate for H_2 below 60 K. The expression derived here is accurate at all temperatures and is as easily evaluated at high as at low temperatures.

Derivatives of $S(\alpha)$ are also of interest, and the expression derived here has certain advantages over both the infinite sum and the asymptotic expansions. Term by term differentiation of the infinite sum can be performed and numerically evaluated, but the slow convergence at higher temperatures is worse for these expressions than for the original sum. On the other hand, differentiation of the asymptotic expansion is not necessarily reliable.[2] Exact expressions for the derivatives can be evaluated from the expression derived here and evaluated accordingly. They are accurate and easily evaluated at all temperatures.

The weakest part of the expression is the function $R(\alpha)$, expressed here as an integral. A simple approximation is to ignore this term, leading to what has been referred to as $S_0(\alpha)$. This seems to work fairly well but comparisons of the rotational partition functions with the exact results for several molecules show noticeable differences; in particular, there is an inherent error of $1/6$ for higher temperatures. The approximation suggested in equations (38) and (39) requires about 10 percent more computational effort than ignoring the function and is quite accurate. For higher accuracy, the integral can be evaluated numerically; 129-point Romberg integration ensures

[2] According to Whittaker and Watson [10, p. 153], "it is not in general permissible to differentiate an asymptotic expansion."

evaluation to within 0.0001. Even so, an analytic evaluation of this remaining term would be desirable. It is still possible that a solution could be found.

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