Asymptotic expansion of the partition function for a rigid asymmetric top

M. I. Kaplan

All-union Scientific Research Institute for Petrochemical Processes
(Submitted July 27, 1973)
Zh. Eksp. Teor. Fiz. 65, 2522–2526 (December 1973)

A method for obtaining the asymptotic expansion in powers of $\hbar^2$ of the partition function corresponding to a rigid top of arbitrary symmetry is presented. Explicit expressions for the first three terms of this expansion are obtained. When two moments of inertia are equal the results reduce to the known formulas for the symmetric top.

In nonempirical calculations of thermodynamic functions of substances at the present time, one starts, in the majority of cases, from the classical integral for the partition function. Only in those rare situations in which explicit expressions for the energy levels are known is it possible to perform an exact summation over the states. However, e.g., for the case of a rigid asymmetric top, when there is no analytic dependence of the levels on an index, the difference between the exact rotational partition function and the classical partition function can approach 10% for light molecules. In this paper, quantum corrections to the classical partition function of a rigid top are calculated without explicit summation over the energy levels.

The Hamiltonian operator corresponding to free rotation of a solid about its center of inertia is

$$\hat{H}_0={}^1/_2(a\hat{L}_1^2+b\hat{L}_2^2+c\hat{L}_3^2), \qquad (1)$$

where $\hat{L}_i$ are the angular-momentum components along the internal coordinate axes, and $a>b>c$ are the inverse moments of inertia. Introducing the elliptical coordinates ρ_1 and ρ_2 on a unit sphere:

$$\xi^2=\frac{(a-\rho_1)(a-\rho_2)}{(a-b)(a-c)},\quad \eta^2=\frac{(b-\rho_1)(b-\rho_2)}{(b-a)(b-c)},\quad \zeta^2=\frac{(c-\rho_1)(c-\rho_2)}{(c-a)(c-b)},$$

we can write the operator H_0 in the form[1]

$$\hat{H}_0=-\frac{2\hbar^2}{\rho_1-\rho_2}\Big[\rho_2\sqrt{-P(\rho_1)}\frac{\partial}{\partial\rho_1}\Big(\sqrt{-P(\rho_1)}\frac{\partial}{\partial\rho_1}\Big)+\rho_1\sqrt{P(\rho_2)}\frac{\partial}{\partial\rho_2}\Big(\sqrt{P(\rho_2)}\frac{\partial}{\partial\rho_2}\Big)\Big]. \qquad (2)$$

Here $P(\rho)=(\rho-a)(\rho-b)(\rho-c)$.

With the condition that the square of the total angular momentum has the value $l(l+1)$, the equation for the eigenfunctions of the operator (2) admits a solution in the form of a product of two functions, of the variables ρ_1 and ρ_2 respectively, each of which is an eigenfunction of the operator

$$\hat{H}=\frac{\hbar^2}{2}\Big\{-4\sqrt{P(\rho)}\frac{\partial}{\partial\rho}\sqrt{P(\rho)}\frac{\partial}{\partial\rho}+l(l+1)\rho\Big\}. \qquad (3)$$

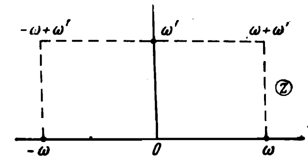
Introducing the new variable z by the formula $dz=d\rho/2\sqrt{P}$, we can write (3) in the following form:

$$\hat{H}={}^1/_2\hbar^2[\hat{p}^2+l(l+1)\rho(z)];\quad \hat{p}=-i\partial/\partial z. \qquad (4)$$

The equation for the eigenfunctions of the operator (4) is the Lamê equation in the Weierstrass form, and the function $\rho(z)$ coincides, to within a constant term, with the Weierstrass elliptic function. The half-periods of $\rho(z)$ are equal to

$$\omega=\frac{1}{2}\int_c^b\frac{d\rho}{\sqrt{P}}=\frac{1}{2}\int_a^\infty\frac{d\rho}{\sqrt{P}},$$

$$\omega'=\frac{1}{2}\int_b^a\frac{d\rho}{\sqrt{P}}=\frac{1}{2}\int_c^{-\infty}\frac{d\rho}{\sqrt{P}}.$$



The real axis in the ρ plane corresponds, in the z plane, to the boundary of a rectangle with vertices 0, ω, $\omega+\omega'$, ω' (see the figure), with $\rho(\omega)=a$, $\rho(\omega+\omega')=b$ and $\rho(\omega')=c$.

For the partition function Q corresponding to the operator (1), we can write the following expression:

$$Q=\frac{2}{\omega}\sum_{\substack{l=0\\k=-\infty}}^{\infty}(2l+1)\oint_C\exp\Big(-i\frac{2\pi kz}{\omega}\Big)\exp(-\beta\hat{H})\exp\Big(i\frac{2\pi kz}{\omega}\Big)dz, \qquad (5)$$

where $\beta=1/kT$, $\hat{H}$ is taken from (4), the factor $2l+1$ in the sum is a consequence of the degeneracy of the energy with respect to the value of the angular-momentum component along an external axis, and the integration contour C is the boundary of the rectangle with vertices ω, $\omega+\omega'$, $-\omega+\omega'$, $-\omega'$. Since the equality

$$\hat{p}^2\exp\Big(\frac{i2\pi kz}{\omega}\Big)=\exp\Big(\frac{i2\pi kz}{\omega}\Big)\Big(-\frac{2\pi k}{\omega}+\hat{p}\Big)^2$$

is valid, the expression (5) for Q can be transformed as follows:

$$Q=\frac{2}{\omega}\sum_{l,k}(2l+1)\oint_C\exp\Big\{-\varepsilon\Big[\Big(\hat{p}-\frac{2\pi k}{\omega}\Big)^2+l(l+1)\rho\Big]\Big\}dz, \qquad (6)$$

where $\epsilon=\beta\hbar^2/2$. To perform the summation over k, we can make use of a method analogous to that applied in the papers[2,3]. The basic idea of this method is as follows.

It is well known that if two operators $\hat{A}$ and $\hat{B}$ do not commute, then

$$\mathrm{Sp}\,[\exp(\hat{A}+\hat{B})]\neq\mathrm{Sp}\,[\exp(\hat{A})\cdot\exp(\hat{B})].$$

However, artificially introducing a dependence on a parameter, $A\equiv A(t_1)$ and $B\equiv B(t_2)$, we can write

$$\exp(\hat{A}+\hat{B})=\exp\Big(\int_0^1\hat{A}(t_1)dt_1\Big)\exp\Big(\int_0^1\hat{B}(t_2)dt_2\Big),$$

with the condition that

$$\hat{A}(t_1)\hat{B}(t_2)=\begin{cases}\hat{A}\hat{B} & \text{for } t_1\le t_2\\ \hat{B}\hat{A} & \text{for } t_1>t_2\end{cases} \qquad (7)$$

The expression (6) can now be written as follows:

$$Q=\frac{2}{\omega}\sum_{l,k}(2l+1)\oint_C\exp\Big\{-\varepsilon\Big[\int\hat{p}^2dt_1-\Big(\int\hat{p}\,dt_1\Big)^2+\frac{4\pi^2}{\omega^2}\Big(k-\frac{\omega}{2\pi}\int\hat{p}\,dt_1\Big)^2+l(l+1)\int\rho\,dt_2\Big]\Big\}dz. \qquad (8)$$

It should be noted that

$$\sum_k \exp\left[-\frac{4\pi^2}{\omega^2}\varepsilon\left(k-\frac{\omega}{2\pi}\int\hat{p}\,dt_1\right)^2\right]=\theta_3(q,x)e^{-qx^2}, \tag{9}$$

Since, for small q, the expansion

$$x=\frac{\omega}{2\pi}\int\hat{p}\,dt,\quad q=\frac{4\pi^2}{\omega^2}\varepsilon.$$

is valid (cf., e.g., [4]), in the following we can use the expression $\sqrt{\pi/q}=\omega/\hbar\sqrt{2\pi\beta}$ for the sum over k in (9).

$$\theta_3(q,x)=\sqrt{\frac{\pi}{q}}\exp(qx^2)\,[1+O(e^{-\pi^2/q^2})],$$

The partition function takes the following form:

$$Q=\frac{2}{\hbar\sqrt{2\pi\beta}}\oint_c dz\exp\left\{-\varepsilon\left[\int\hat{p}^2\,dt_1-\left(\int\hat{p}\,dt_1\right)^2\right]\right\}$$
$$\times\sum_l(2l+1)\exp\left[-\varepsilon l(l+1)\int\rho\,dt_2\right] \tag{10}$$

or

$$Q=\frac{2}{\hbar\sqrt{2\pi\beta}}\oint_c dz\exp\left\{-\varepsilon\left[\int\hat{p}^2\,dt_1-\left(\int\hat{p}\,dt_1\right)^2\right]\right\}I\left(\varepsilon\int\rho\,dt_2\right)$$

where

$$I(s)=\sum_{l=0}^{\infty}(2l+1)\exp[-sl(l+1)].$$

In the neighborhood of $s=0$, the expansion

$$I(s)=\frac{1}{s}-\frac{2}{3}+\frac{1}{15}s-\dots. \tag{11}$$

is valid for I(s)[5,6]. It is clear that only the first term in (11) will give a non-zero contribution to the partition function. The subsequent terms vanish after the integration, since they have only one singular point—a pole at $z=0$—inside the contour C.

Expanding the first exponential in the integrand in (10) in a series, we obtain an asymptotic expansion of Q in powers of ħ. The first term of this expansion will be

$$Q=\frac{2}{\hbar\sqrt{2\pi\beta}}\oint_c\frac{dz}{\varepsilon\rho(z)}. \tag{12}$$

Two simple zeros of the function ρ are positioned on the imaginary axis, symmetrically about the point $z=\omega'$. One of these is positioned inside the integration contour. Therefore,

$$Q_0=\frac{2}{\hbar\sqrt{2\pi\beta}}\frac{2\pi i}{i\varepsilon\cdot2\sqrt{abc}}=\sqrt{\frac{\pi}{\tau_a\tau_b\tau_c}},\quad \tau_i=\beta\hbar^2/2I_i. \tag{13}$$

This result coincides with the expression obtained from classical mechanics for the partition function of an asymmetric top.

The next term in the expansion (10) will be

$$Q_1=\frac{2}{\hbar\sqrt{2\pi\beta}}\oint_c dz\left\{-\varepsilon\left[\int_0^1\hat{p}^2\,dt_1-\left(\int_0^1\hat{p}\,dt_1\right)^2\right]\right\}I\left(\varepsilon\int_0^1\rho\,dt_2\right). \tag{14}$$

We transform the first integral in the square brackets in accordance with the rule (7):

$$\int_0^1\hat{p}^2\,dt_1\,I\left(\varepsilon\int_0^1\rho\cdot dt_2\right)=\sum_{l=0}^{\infty}(2l+1)\int_0^1 e^{-\varepsilon\rho t l(l+1)}\hat{p}^2e^{-\varepsilon\rho(1-t)l(l+1)}\,dt$$
$$=-\frac{1}{6}\sum_l(2l+1)l(l+1)\varepsilon\frac{\partial^2\rho}{\partial z^2}e^{-\varepsilon\rho l(l+1)}=-\frac{\varepsilon}{6}\frac{\partial^2\rho}{\partial z^2}\frac{\partial I(\varepsilon\rho)}{\partial(\varepsilon\rho)}.$$

Analogously, for the second integral in (14) we can obtain

$$\left(\int_0^1\hat{p}\,dt_1\right)^2 I\left(\varepsilon\int_0^1\rho\,dt_2\right)=\frac{\varepsilon}{12}\frac{\partial^2\rho}{\partial z^2}\frac{\partial I(\varepsilon\rho)}{\partial(\varepsilon\rho)}.$$

Taking into account that

$$\frac{\partial^2\rho}{\partial z^2}=\frac{1}{\sqrt{P}}\frac{\partial P}{\partial\rho}\frac{\partial\rho}{\partial z}=2\frac{\partial P}{\partial\rho},$$

and using (11), for Q_1 we can write

$$Q_1=\frac{2}{\hbar\sqrt{2\pi\beta}}\oint_c dz\,\varepsilon\frac{\varepsilon}{12}\frac{1}{\rho^2\varepsilon^2}\frac{\partial^2\rho}{\partial z^2}=\frac{1}{3\hbar\sqrt{2\pi\beta}}\oint_c dz\frac{\partial P}{\partial\rho}\frac{1}{\rho^2}.$$

Only terms proportional to ρ^{-1} and ρ^{-2} give a contribution to the integral:

$$Q_1=\frac{1}{3\hbar\sqrt{2\pi\beta}}\oint_c dz\left[-\frac{2(a+b+c)}{\rho}+\frac{ab+ac+bc}{\rho^2}\right]$$

After simple transformations, the first quantum correction to the classical expression (13) for the partition function acquires the form

$$Q_1=\left(\frac{\pi}{\tau_a\tau_b\tau_c}\right)^{1/2}\left[\frac{1}{6}(\tau_a+\tau_b+\tau_c)-\frac{1}{12}\left(\frac{\tau_a\tau_b}{\tau_c}+\frac{\tau_a\tau_c}{\tau_b}+\frac{\tau_b\tau_c}{\tau_a}\right)\right]. \tag{15}$$

The next term in the expansion of (10) will be

$$Q_2=\frac{1}{\hbar\sqrt{2\pi\beta}}\oint_c dz\left\{-\varepsilon\left[\int_0^1\hat{p}^2\,dt_1-\left(\int_0^1\hat{p}\,dt_1\right)^2\right]\right\}I\left(\varepsilon\int_0^1\rho\,dt_2\right). \tag{16}$$

Here, in the same way as before, by performing transformations in accordance with the rule (7) we can bring the expression (16) to the following form:

$$Q_2=\frac{\hbar}{288}\sqrt{\frac{\beta}{2\pi}}\oint dz\left[\frac{14}{5}\left(\frac{\partial^2\rho}{\partial z^2}\right)^2\frac{1}{\rho^3}-\frac{\partial^4\rho}{\partial z^4}\frac{1}{\rho^2}\right]. \tag{17}$$

The function under the integral sign, as already noted earlier, has a singularity at the point corresponding to $\rho=0$. Performing calculations analogous to those given above, we can bring (17) to the form

$$Q_2=\frac{1}{12}\sqrt{\frac{\pi}{N}}\left\{\frac{RS^2}{N}-\frac{4}{5}S-\frac{6}{5}R^2-\frac{7}{40}\frac{S^4}{N^2}\right\}, \tag{18}$$

where

$$N=\tau_a\tau_b\tau_c,\quad R=\sum\tau_i,\quad S=\frac{1}{2}\sum_{i\neq k}\tau_i\tau_k\quad(i,k=a,b,c).$$

Thus, the first three terms in the expansion of the partition function in powers of ħ will be

$$Q=\sqrt{\frac{\pi}{N}}\left\{1+\frac{1}{3}\left(R-\frac{1}{4}\frac{S^2}{N}\right)+\frac{1}{12}\left(\frac{RS^2}{N}-\frac{4}{5}S-\frac{6}{5}R^2-\frac{7}{40}\frac{S^4}{N^2}\right)\right\}. \tag{19}$$

The terms enclosed in the first round brackets are proportional to $\hbar^2$, those in the second to $\hbar^4$, and so on. For $a=b\neq c$, formula (19) becomes

$$Q=\sqrt{\frac{\pi}{\tau_0^2\tau_1}}\left[1+\frac{1}{12}\left(4\tau_0-\frac{\tau_0^2}{\tau_1}\right)+\frac{1}{480}\left(32\tau_0^2-24\frac{\tau_0^3}{\tau_1}+7\frac{\tau_0^4}{\tau_1^2}\right)+\dots\right], \tag{20}$$

which coincides with the results obtained in[6] for the symmetric top.

[1]I. Lukach and Ya. A. Smorodinskiĭ, Zh. Eksp. Teor. Fiz. **57**, 1342 (1969) [Sov. Phys.—JETP **30**, 728 (1970)].
[2]R. P. Feynman, Phys. Rev. **84**, 108 (1951).
[3]I. M. Khalatnikov, Dokl. Akad. Nauk SSSR **87**, 539 (1952).
[4]E. T. Whittaker and G. N. Watson, A Course of Modern Analysis, Cambridge University Press, 1927 (Russ. transl. Fizmatgiz, M., 1963 (vol. 2)).
[5]L. S. Kassel, J. Chem. Phys. **4**, 276 (1936).
[6]I. E. Viney, Proc. Camb. Phil. Soc. **29**, 407 (1933).

Translated by P. J. Shepherd
263