THE USE OF LAPLACE TRANSFORMS FOR EVALUATING THE PARTITION FUNCTION

A. A. ZAĬTSEV

Ivanovo Institute for Chemical Technology

Submitted to JETP editor March 21, 1960; resubmitted June 13, 1960

J. Exptl. Theoret. Phys. (U.S.S.R.) **39**, 1258-1262 (November, 1960)

The problem of the evaluation of the partition function can be reduced to the problem of finding the trace of the operator $(\hat{H} + p)^{-1}$ where $\hat{H}$ is the energy operator and p a complex parameter, if one uses Laplace transforms. One can use this fact to find the partition function for a fairly wide class of energy operators $\hat{H}$ in the form of a power series in 1/kT.

INTRODUCTION

If one wishes to evaluate the partition function

$$Q = \sum_n \exp(-E_n/kT)$$

of a physical system, there are some useful methods which enable one to evaluate Q without knowing the eigenvalues E_n of the energy operator $\hat{H}$ of that system; these are based upon the possibility to write the partition function as the trace of the operator $\exp(-\hat{H}/kT)$. We may mention here the method of expanding Q in a power series in $\hbar$ (see, for instance references 1 and 2) or in a power series in some other small parameter on which $\hat{H}$ may depend.

One is, however, not able to use such methods to expand Q in powers of T or 1/T, so as to be able to evaluate the thermodynamic functions in the corresponding temperature ranges. A formal expansion of Q in powers of 1/T by using the definition of the operator

$$\exp(-\hat{H}/kT) = 1 - \frac{1}{kT}\hat{H} + \frac{1}{(kT)^2}\frac{\hat{H}^2}{2!} - \frac{1}{(kT)^3}\frac{\hat{H}^3}{3!} + \cdots,$$

yields nothing, for although one can easily evaluate the matrix elements of the operator $\hat{H}^n/(kT)^n n!$ for not too large values of n in any suitable representation, the trace of such an operator turns out to diverge.

We shall give in the present paper a method for expanding the partition function in powers 1/kT, based upon the application of the Laplace transformation to the function Q(1/kT).

THE USE OF THE LAPLACE TRANSFORMATION FOR THE EVALUATION OF THE TRACE OF THE OPERATOR EXP $(-\tau\hat{H})$

When we use the Laplace transformation (see reference 3) we change from the function $Q(\tau)$, which is defined by the equation

$$Q(\tau) = \sum_n \exp(-\tau E_n)$$

(E_n are the eigenvalues of the Hamiltonian $\hat{H}$ of the system, and $\tau = 1/kT$) to its transform $\bar{Q}(p)$. One sees that the function $Q(\tau)$ satisfies all requirements necessary for it to have a Laplace transform.

The transform of the function $\exp(-\tau E_n)$ is the function $(E_n + p)^{-1}$,

$$\exp(-\tau E_n) \risingdotseq (E_n + p)^{-1}.$$

Using the fact that the Laplace transformation is a linear operator we find

$$\bar{Q}(p) = \sum_n \frac{1}{E_n + p} = \mathrm{Sp}\,\frac{1}{\hat{H} + p}. \tag{1}$$

When we have evaluated the trace of the operator $(\hat{H} + p)^{-1}$ we find the partition function by taking the inverse Laplace transform. The advantage of this method is that it is in most cases simpler to evaluate the trace of the operator $(\hat{H} + p)^{-1}$ than to evaluate the trace of the operator $\exp(-\tau\hat{H})$. This is connected, first, with the fact that one can use the Green function of the operator $\hat{H} + p$ to evaluate the trace of the operator $(\hat{H} + p)^{-1}$, and, second, with the possibility of using the results of a number of mathematical investigations which have been published recently. In these papers methods are developed for the evaluation of the trace of similar operators,[4,5] and we can use the results of these papers together with the method presented here to evaluate the partition function.*

If the Green function $G(\mathbf{r}, \mathbf{r}', p)$ of the operator $\hat{H} + p$ is known (see, for instance, reference 6) one can find $\bar{Q}(p)$ by means of the equation

*See references 7 and 8 for some applications of Eq. (1) in quantum statistics.

$$\overline{Q}(p)=\sum_n \frac{1}{E_n+p}=\int G(\mathbf{r},\mathbf{r},p)\,dv,$$

where dv is a volume element and where the integration is over the region where the operator $\hat{H}$ is defined.

An explicit expression for the Green function is known only for some simple operators, for instance for the operator $d^2/dx^2 + p$ and its determination is connected with appreciable difficulties. It is therefore natural to use other methods which are based upon an application of Eq. (1) to evaluate $\overline{Q}(p)$.

EXPRESSIONS FOR $Q(\tau)$ FOR DIFFERENT CASES

The final result of a calculation of the partition function is independent of the set of basis functions in which the trace of the operator $(\hat{H}+p)^{-1}$ is evaluated. For some particular cases one can use directly the results of a paper by Dikiĭ[4] to evaluate the trace of the operator $(H+p)^{-1}$; in that paper he found an expression for the trace of the operator $[-d^2/dx^2 + V(x) + p]^{-1}$.

In Dikiĭ's paper the operator $\hat{H}$ had to satisfy the condition that all odd derivatives of the potential energy $V(x)$ vanish at the end points of the interval $0-\pi$, and the eigenfunctions ψ_n of this operator had to satisfy the boundary conditions $\psi(0)=\psi(\pi)=0$. The trace was evaluated in the basis of the functions $\sqrt{2/\pi}\sin nx$.

Let our energy operator be of the form

$$\hat{H}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)$$

and let it satisfy all conditions mentioned a moment ago. We find then from theorem (5.1) of Dikiĭ's paper[4]

$$\mathrm{Sp}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)+p\right)^{-1}$$

$$=\frac{m}{\hbar^2}\sum_{k=0}^{\infty}\frac{(-1)^k}{p^{k+1/2}}\left(\frac{\hbar^2}{2m}\right)^{k+1/2}\int_0^{\pi}A_{2k}\left(k-\frac{1}{2},x\right)dx$$

$$+\sum_{k=0}^{\infty}\frac{(-1)^k}{p^{k+1}}\left(\frac{\hbar^2}{2m}\right)^k\sum_{l=0}^{2k}(2i)^{l-2k-2}[A_l^{(2k-l)}(k,0)$$

$$+A_l^{(2k-l)}(k,\pi)].$$

Here k, l, m, and s are integers;

$$A_l(s,x)=\sum_{m=0}^{l}C^s_{(l+m)/2}B_{l,m}(x),$$

where $C^s_{(l+m)/2}$ is a binomial coefficient, and the functions $B_{1,m}$ are determined by the recurrence relations: $B_{0,0}(x)=1$, and $B_{1,m}(x)=0$ if either l or $m<0$,

$$B_{l,m}(x)=-B''_{l-2,m}(x)+V(x)\,2m\hbar^{-2}B_{l-2,m}(x)$$
$$+2iB'_{l-1,m-1}(x).$$

Using operational techniques to change over from $\overline{Q}(p)$ to its inverse Laplace transform we find, according to what we said earlier, the initial expression for the partition function $Q(\tau)$

$$Q(\tau)=\frac{1}{2}\sum_{k=0}^{\infty}(-1)^k\frac{\tau^{k-1/2}}{\Gamma(k+1/2)}\left(\frac{\hbar^2}{2m}\right)^{k-1/2}\int_0^{\pi}A_{2k}(k-1/2,x)\,dx$$

$$+\sum_{k=0}^{\infty}\frac{\tau^k}{k!}\left(-\frac{\hbar^2}{2m}\right)^k\sum_{l=0}^{2k}(2i)^{l-2k-2}[A_l^{(2k-l)}(k,0)$$

$$+A_l^{(2k-l)}(k,\pi)], \tag{2}$$

where Γ is the gamma function.

If the form of the operator $\hat{H}$, the region in which it is defined, or the boundary conditions imposed on its eigenfunctions are different, the equation for $Q(\tau)$ will have a different form.

Let the operator $\hat{H}$ depend on three coordinates and let it be of the usual form of a single particle Hamiltonian

$$\hat{H}=-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r}).$$

Generalizing the results of Dikiĭ's paper[4] to the three-dimensional case we write the operator $(\hat{H}+p)^{-1}$ in the form

$$\frac{1}{\hat{H}+p}=\sum_{l=0}^{\infty}\sum_{m,k,j=0}^{l}B_{l,m,k,j}(\mathbf{r})\left(\frac{\partial}{\partial x}\right)^m\left(\frac{\partial}{\partial y}\right)^k\left(\frac{\partial}{\partial z}\right)^j$$

$$\times\left(-\frac{\hbar^2}{2m}\nabla^2+p\right)^{-1-(l+m+k+j)/2}. \tag{3}$$

Our problem is thus to determine the coefficients $B_{l,m,k,j}$ in such a way that the equation indeed holds, i.e., that if we multiply both sides of Eq. (3) by $\hat{H}+p$ they turn out to be equal. Let us multiply both sides of the equation from the left by $\hat{H}+p$ and let us interchange the positions of the ∇^2 and the operator multiplying the function $B_{l,m,k,j}$ by using the commutation relations

$$\nabla^2(B_{l,m,k,j}f)=(\nabla^2B_{l,m,k,j})f+B_{l,m,k,j}(\nabla^2 f)$$

$$+2\frac{\partial B_{l,m,k,j}}{\partial x}\frac{\partial f}{\partial x}+2\frac{\partial B_{l,m,k,j}}{\partial y}\frac{\partial f}{\partial y}+2\frac{\partial B_{l,m,k,j}}{\partial z}\frac{\partial f}{\partial z}.$$

Equating the coefficients of the same powers of

$$\left(\frac{\partial}{\partial x}\right)^m\left(\frac{\partial}{\partial y}\right)^k\left(\frac{\partial}{\partial y}\right)^j\left(-\frac{\hbar^2}{2m}\nabla^2+p\right)^n,$$

we find recurrence relations for the functions $B_{l,m,k,j}$: $B_{l,m,k,j}=0$, if either l, m, k, or j are less than zero; $B_{0,0,0,0}=1$

$$B_{l,m,k,j}=\frac{\hbar^2}{2m}\Big(\nabla^2B_{l-2,m,k,j}+\frac{2m}{\hbar^2}V(\mathbf{r})B_{l-2,m,k,j}$$

$$+2\frac{\partial B_{l-1,m-1,k,j}}{\partial x}+2\frac{\partial B_{l-1,m,k-1,j}}{\partial y}+2\frac{\partial B_{l-1,m,k,j-1}}{\partial z}\Big). \tag{4}$$

We note also that $B_{l,m,k,j} = 0$, if $m + k + j > 1$, or if $l + m + k + j$ is an odd number, as is proved at once by induction with respect to l.

Let our operator $\hat{H}$ be defined in a finite, but sufficiently large region of the volume b. We can then use Eq. (3) for the operator $\overline{Q}(p)$ and evaluate the trace in the base of the orthonormal functions $u = v^{-1/2} \exp[i(k_l x + k_m y + k_n z)]$ (replacing the summation over the possible values of **k** by an integration over $dk_1 dk_2 dk_3$) and so get the following expression for $\overline{Q}(p)$

$$\overline{Q}(p) = \frac{1}{(2\pi)^3} \int_v dv \int d\mathbf{k} \sum_{l=0}^{\infty} \sum_{m=0}^{l} \sum_{k=0}^{l-m} \sum_{j=0}^{l-m-k} B_{l,m,k,j} \times (ik_1)^m (ik_2)^k (ik_3)^j \left[\frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2) + p\right]^{-1-(l+m+k+j)/2} \quad (5)$$

(the limits of the summation are changed here in correspondence to the fact that $B_{l,m,k,j} = 0$, if $m + k + j > 1$).

To change over from $\overline{Q}(p)$ to $Q(\tau)$ we must find the inverse transform corresponding to the transform

$$\left[\frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2) + p\right]^{-1-(l+m+k+j)/2}$$

We use the following property of the transforms: $\bar{f}^{(n)}(p) \doteqdot (-1)^n \tau^n f(\tau)$. We have therefore

$$\left[\frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2) + p\right]^{-1-(l+m+k+j)/2} = (-1)^{(l+m+k+j)/2}\left[\left(\frac{l+m+k+j}{2}\right)!\right]^{-1} \frac{\partial^{(l+m+k+j)/2}}{\partial p^{(l+m+k+j)/2}}\left[\frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2) + p\right]^{-1} \doteqdot \tau^{(l+m+k+j)/2}\left[\left(\frac{l+m+k+j}{2}\right)!\right]^{-1} \times \exp\left\{-\tau\frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2)\right\}.$$

Substituting this expression into (5) we get

$$Q(\tau) = \frac{1}{(2\pi)^3}\int dk \int_v dv \sum_{l=0}^{\infty}\sum_{m=0}^{l}\sum_{k=0}^{l-m}\sum_{j=0}^{l-m-k} \tau^{(l+m+k+j)/2} \times \left[\left(\frac{l+m+k+j}{2}\right)!\right]^{-1} B_{l,m,k,j}(ik_1)^m (ik_2)^k (ik_3) \times \exp\left\{-\tau\frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2)\right\}. \quad (6)$$

We integrate now over k_1, k_2, and k_3. It is clear that if m, k, or j is odd, the integral

$$I = \int d\mathbf{k}\,(ik_1)^m (ik_2)^k (ik_3)^j \exp\left\{-\tau\frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2)\right\}$$

vanishes, while for even m, k, and j it is equal to

$$I = (-1)^{(m+k+j)/2}\frac{m!\,k!\,j!}{2^{m+k+j}}\left[\left(\frac{m}{2}\right)!\left(\frac{k}{2}\right)!\left(\frac{j}{2}\right)!\right]^{-1} \times \pi^{3/2}\left(\frac{\hbar^2}{2m}\tau\right)^{-[(m+k+j)/2]-3/2}$$

Substituting this expression into (6) we find the final expression for $Q(\tau)$

$$Q(\tau) = \frac{1}{8}\left(\pi\frac{\hbar^2}{2m}\tau\right)^{-3/2}\sum_{l=0}^{\infty}\sum_{m=0}^{l}\sum_{k=0}^{l-m}\sum_{j=0}^{l-m-k}\left(-\frac{\hbar^2}{2m}\right)^{-(m+k+j)/2}\tau^{l/2} \times \frac{m!\,k!\,j!}{2^{m+k+j}}\left[\left(\frac{m}{2}\right)!\left(\frac{k}{2}\right)!\left(\frac{j}{2}\right)! \times \left(\frac{l+m+k+j}{2}\right)!\right]^{-1}\int_v B_{l,m,k,j}\,dv. \quad (7)$$

The summation is over even values of l, m, k, and j.

One can use this expression to evaluate the partition function for an arbitrary form of the potential energy $V(\mathbf{r}) = V(x, y, z)$, and the functions $B_{l,m,k,j}$ are determined from $V(\mathbf{r})$ using the recurrence relations (4). The method could immediately be generalized to the case where the energy operator depends on a larger number of coordinates.

I express my gratitude to Professor I. N. Godnev for a useful discussion of the problems considered here.

[1] L. D. Landau and E. M. Lifshitz, Статистическая физика (Statistical Physics), Gostekhizdat, 1951 [Pergamon, 1958].

[2] I. M. Khalatnikov, Doklady Akad. Nauk SSSR **87**, 539 (1952).

[3] M. A. Lavrent'ev and B. V. Shabat, Методы теории функций комплексного переменного (Methods of the theory of functions of a complex variable), Gostekhizdat, 1951.

[4] L. A. Dikiĭ, Usp. Mat. Nauk **13**, 111 (1958).

[5] I. M. Gel'fand, Usp. Mat. Nauk **2**, 191 (1956).

[6] R. Courant and D. Hilbert, Methoden der mathematischen Physik, Vol. 1, Springer, 1931.

[7] J. E. Kimball, J. Chem. Phys. **18**, 626 (1950).

[8] K. M. Watson, Phys. Rev. **103**, 489 (1956).

Translated by D. ter Haar
236