

Functional Integrals and Statistical Physics*

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1. INTRODUCTION

THIS article discusses some work of the last few years on the "space-time" or "integral-over-all-paths" method in quantum mechanics, considering in particular its application to problems in statistical mechanics and its relation to the theory of Brownian motion. The method was first suggested by R. P. Feynman in his Princeton dissertation (see also Feynman 1948).¹

In its simplest form, the Feynman postulate is that the propagator or Green's function, $K(x't'; x''t'')$, for the wave function of a particle, defined by

$$\psi(x't') = \int K(x't'; x''t'') \psi(x''t'') dx'', \quad (1.1)$$

can be written as a certain integral over all paths $x(t)$ by which the particle can go from the point x'' at time t'' to the point x' at time t' :

$$K(x't'; x''t'') = A \int e^{(i/\hbar)S[x(t)]} d[x(t)], \quad (1.2)$$

where the action functional $S[x(t)]$ is defined as usual by

$$S[x(t)] = \int_{t''}^{t'} \mathcal{L} dt, \quad (1.3)$$

where \mathcal{L} is the Lagrangian.

The constant factor A is chosen to preserve the normalization of the wave function; its actual value depends on how the integral over paths is defined.

In principle, Feynman's postulate provides an alternative to the Schrödinger and Heisenberg methods for solving problems in ordinary quantum mechanics. Actually it is so difficult to calculate functional integrals that no one has succeeded in doing much more than simply verify that they lead to the same results as the Schrödinger equation in some particular cases. For a time there was considerable interest in functional integrals among field theorists. Although the method is not as useful for practical calculations as the perturbation theory using Feynman diagrams (Dyson 1949) in the cases where the latter method is applicable, it may turn out that for certain kinds of strong interactions

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¹References will be found in alphabetical order in the Bibliography at the end of the article.

the failure of perturbation theory will make it necessary to resort to numerical calculation of the appropriate functional integrals.

Recently the functional integral method has been applied to certain problems in statistical mechanics, such as superconductivity and the Bose-Einstein condensation. Its usefulness here stems from the fact that it permits one to consider various aspects of a problem separately; thus one can, for example, study the motions of individual particles in such a way that the motions of other particles, and their coupling through permutation statistics can be temporarily ignored; or, conversely, one can concentrate on the permutation statistics if that is believed to be more important.

In this review we do not attempt to cover Feynman's various papers on functional integrals, as these are easily accessible and provide the best introduction to the subject for physicists. Instead we discuss some of the more mathematical work, much of which is not otherwise available in English, but which will probably be useful to any one who wants to use the path-integral method.

2. FUNCTIONAL INTEGRALS IN THE THEORY OF BROWNIAN MOTION

Feynman's original discussion of his postulate made clear its physical interpretation, but did not make very precise the notion of an "integral over all paths." The type of integral which is used in Feynman's theory is one which was perhaps new in theoretical physics, but not in probability theory. In fact, the integral over trajectories introduced in (1.2) is almost the same as one used by Wiener (1923, 1924, 1930) in studying the trajectories which arise in Brownian motion. The relationship between Brownian motion and quantum theory has been discussed in several recent papers (Kac 1949; Montroll 1952; Gel'fand and Yaglom 1956; and Saito and Namiki 1956). This section is based on the paper by Gel'fand and Yaglom.

Consider a particle performing Brownian motion along the x axis under the action of random impulses (but not subject to any systematic force) starting at time $t=0$ at the origin of coordinates. On neglecting the inertia of the particle, the probability distribution for its position at time t satisfies the diffusion equation

$$\partial\psi/\partial t = D\partial^2\psi/\partial x^2; \quad (2.1)$$

if the motion is due to molecular bombardment, the constant can be related to the mass and size of the particle, and the temperature and viscosity of the

medium. Equation (2.1) has the solution

$$\psi(x,t) = (4\pi Dt)^{-\frac{1}{2}} \exp(-x^2/4Dt). \quad (2.2)$$

We choose units such that $D = \frac{1}{4}$. Then, for the probability that the value of the coordinate x_i of the particle at time t_1 will be in the interval $a_1 < x_1 < b_1$, at time t_2 in the interval $a_2 < x_2 < b_2$, etc., and at time t_n in the interval $a_n < x_n < b_n$, where $0 < t_1 < t_2 < \dots < t_n$, we have the formula

$$\begin{aligned} & [\pi^n t_1(t_2 - t_1) \dots (t_n - t_{n-1})]^{-\frac{1}{2}} \\ & \times \int_{a_1}^{b_1} \int_{a_2}^{b_2} \dots \int_{a_n}^{b_n} \exp \left\{ -\frac{x_1^2}{t_1} - \frac{(x_2 - x_1)^2}{t_2 - t_1} - \dots \right. \\ & \left. - \frac{(x_n - x_{n-1})^2}{t_n - t_{n-1}} \right\} dx_1 \dots dx_n. \quad (2.3) \end{aligned}$$

The expression (2.3) may be used to define a measure on the set of all functions $x(\tau)$ which satisfy the condition $x(0) = 0$ and we may take the limit as the time intervals go to zero. Wiener showed that this measure is completely concentrated on a set of continuous (but not differentiable) functions. The exponent in the expression (2.3) is just the kinetic energy integrated over the path, so that any class of trajectories which have infinite kinetic energy has zero measure; on the other hand, the instantaneous velocity may be infinite. This is because the important paths are those for which $(x_n - x_{n-1})/(t_n - t_{n-1})$ is of order $(t_n - t_{n-1})^{-\frac{1}{2}}$ which diverges in the limit when the time intervals go to zero.

We can use (2.3) to calculate the average value of any functional of the trajectories:

$$\begin{aligned} \int F\{x(\tau)\} d_w x & \equiv \frac{1}{N} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} F\{x(\tau)\} \\ & \times \exp \left\{ -\int_0^t \left[\frac{dx(\tau)}{d\tau} \right]^2 d\tau \right\} \prod_0^t dx(\tau), \quad (2.4) \end{aligned}$$

where N is a constant normalization factor determined by the condition $\int d_w x = 1$.

When $F\{x(\tau)\}$ depends only on the values of the function $x(\tau)$ at a finite number of points, the integral reduces to an ordinary integral over a finite number of dimensions. Thus, when F has the form

$$F\{x(\tau)\} = x(t_1)x(t_2) \dots x(t_k)$$

we obtain the standard formulas for the moments of a random process,

$$\int x(t) d_w x = 0,$$

and in general

$$\int x(t_1)x(t_2) \dots x(t_{2k+1}) d_w x = 0; \quad (2.5)$$

$$\int x(t_1)x(t_2) d_w x \equiv b(t_1, t_2) = \frac{1}{2} \min\{t_1, t_2\}$$

$$\begin{aligned} \int x(t_1)x(t_2) \dots x(t_{2k}) d_w x & \equiv b(t_1, t_2 \dots t_{2k}) \\ & = \sum b(t_{i_1}, t_{i_2}) b(t_{i_3}, t_{i_4}) \dots b(t_{i_{2k-1}}, t_{i_{2k}}), \quad (2.6) \end{aligned}$$

where the summation in the last formula extends over all possible partitions of the $2k$ indices $1, 2, \dots, 2k$ into k pairs:

$$(i_1, i_2), (i_3, i_4), \dots (i_{2k-1}, i_{2k}).$$

It is also possible to calculate Wiener integrals subject to the condition that both end points of the trajectories are fixed; we then have the so-called "conditional Wiener measure" on the space of continuous functions $x(\tau)$ which satisfy $x(0) = 0$ and $x(t) = X$. This measure can easily be generalized to include any other set of initial and final conditions. Denoting the normalized conditional measure by $d_{w(t,X)}x$, we have, instead of (2.5) and (2.6),

$$\int x(t_1) d_{w(t,X)}x = \frac{t_1}{t} X, \quad (2.7)$$

$$\begin{aligned} \int \left[x(t_1) - \frac{t_1}{t} X \right] \left[x(t_2) - \frac{t_2}{t} X \right] \dots \\ \times \left[x(t_{2k+1}) - \frac{t_{2k+1}}{t} X \right] d_{w(t,X)}x = 0, \quad (2.8) \end{aligned}$$

$$\begin{aligned} \int \left[x(t_1) - \frac{t_1}{t} X \right] \left[x(t_2) - \frac{t_2}{t} X \right] d_{w(t,X)}x & \equiv b_t(t_1, t_2) \\ & = t_1(t - t_2)/2t \quad (t_1 \leq t_2) \quad (2.9) \end{aligned}$$

$$\begin{aligned} \int \left[x(t_1) - \frac{t_1}{t} X \right] \left[x(t_2) - \frac{t_2}{t} X \right] \dots \\ \times \left[x(t_{2k}) - \frac{t_{2k}}{t} X \right] d_{w(t,X)}x & \equiv b_t(t_1, t_2 \dots t_{2k}) \\ & = \sum b_t(t_{i_1}, t_{i_2}) b_t(t_{i_3}, t_{i_4}) \dots b_t(t_{i_{2k-1}}, t_{i_{2k}}) \quad (2.10) \end{aligned}$$

(the summation in the last equation is the same as before).

As an example of the calculation of average values of functionals which depend on the entire trajectory, Gel'fand and Yaglom consider the functional

$$\exp \left\{ \lambda \int_0^t p(\tau) x^2(\tau) d\tau \right\},$$

where λ is a real number and $p(\tau) \geq 0$. The derivation may be found in Montroll's paper (Montroll 1952), so we simply give the results for the case $p(\tau) = 1$ which corresponds, in the quantum-mechanical case, to the simple harmonic oscillator:

$$\int \exp \left\{ \lambda \int_0^t x^2(\tau) d\tau \right\} d_w x = \left\{ \sec[t(\lambda^{\frac{1}{2}})] \right\}^{\frac{1}{2}} \quad (\lambda < \pi/2t) \quad (2.11)$$

$$\int \exp \left\{ \lambda \int_0^t x^2(\tau) d\tau \right\} d_{w(t,x)} x \\ = \{ (\lambda^{\frac{1}{2}}/\pi) \} \text{csc} [t(\lambda^{\frac{1}{2}})]^{\frac{1}{2}} \exp - \{ \lambda^{\frac{1}{2}} X^2 \cot(t\lambda^{\frac{1}{2}}) \}. \quad (2.12)$$

In general we are interested in finding the Wiener integral of functionals of the form

$$\exp \left\{ - \int_0^t V\{x(\tau)\} d\tau \right\},$$

and it is usually impossible to do this by the direct method of finding an explicit formula for the finite-dimensional integral and then passing to the limit of a continuous integral. We discuss some other methods in the next section.

Kac (1949) showed that the function

$$K(X,t) = \int \exp \left\{ - \int_0^t V\{x(\tau)\} d\tau \right\} d_{w(t,x)} x$$

is the solution which tends to zero as x goes to $\pm \infty$ of the differential equation

$$\partial K(X,t)/\partial t = \frac{1}{2} [\partial^2 K(X,t)/\partial X^2] - V(X)K(X,t) \quad (2.13)$$

and satisfies the condition $K(X,0) = \delta(X)$, where $\delta(X)$ is Dirac's delta function. More generally, the fundamental solution $K(X,t; X_0, t_0)$ of Eq. (2.13), which satisfies the condition $K(X, t_0; X_0, t_0) = \delta(x - x_0)$ when $t = t_0$, is

$$K(X,t; X_0, t_0) = \int \exp \left\{ - \int_{t_0}^t V\{x(\tau)\} d\tau \right\} d_{w(t_0 X; t, X)} x$$

Knowing the fundamental solution (or Green's function) for Eq. (2.13), we can construct the general solution for any arbitrary initial conditions $\psi(X, t_0) \equiv \psi_0(X)$:

$$\psi(X,t) = \int_{-\infty}^{\infty} K(X,t; X_0, t_0) \psi_0(X_0) dX_0.$$

The rigorous justification for the foregoing procedure has been given by Blanc-Lapierre and Fortet (1953) and Dinkin (1954, 1955), and provides a somewhat more sophisticated proof of the equivalence of the Feynman postulate and the Schrödinger equation. It can also be shown that for $t_0 < t_1 < t$

$$K(X,t; X_0, t_0) \\ = \int_{-\infty}^{\infty} K(X_1, t_1; X_0, t_0) K(X,t; X_1, t_1) dX_1 \quad (2.14)$$

which is formally the same as the Smoluchowski-Kolmogorov relation for the transition probabilities of a Markovian random process.

The only difference between the Wiener and Feynman integrals is the presence of the imaginary unit in the exponential. Although one can still carry out the same type of calculation, two consequences of this difference should be noted. In the first place, the measure functions which we usually use are real, nonnegative, and additive, and we can thus say that the measure of a set of paths is the probability that the path of the particle belongs to the set. But if the measure function is complex, this interpretation no longer makes sense, and in fact the correspondence between quantum mechanics and classical mechanics arises precisely from the fact that if \hbar is very small neighboring paths cancel out (because of the rapidly oscillating complex exponential) unless the action integral is stationary in that particular region of function space. Since the classical path is defined by the condition that the action integral is stationary, the quantum-mechanical theory must reduce to the classical one as \hbar goes to zero. (On the other hand, in the application to quantum statistics the imaginary unit disappears and one has again a simple Wiener integral.)

The second difference is that these rapidly oscillating integrals are not convergent, though they may easily be given a definite meaning by adding a small imaginary part to \hbar or to the mass, and then putting the imaginary part equal to zero after doing the calculation. With this prescription for evaluating the integrals (and with the proper definition of the normalization factor) Feynman's postulate gives the solution of the Schrödinger equation.

3. METHODS FOR CALCULATING FUNCTIONAL INTEGRALS

The rigorous methods used by Gel'fand and Yaglom to evaluate the functional integral for the harmonic oscillator seem to be too difficult to apply to other kinds of potential functions. We therefore consider some other methods which may be of use. Davison (1954), Burton and de Borde (1955), and Davies (1957) carried out the calculation of these integrals by representing the set of all possible paths going from x_0 to x in time t in terms of a complete set of orthogonal functions; by varying the coefficients of the functions in the expansion one runs through all the paths. Thus, they calculated the action integral for the infinite series, and then integrated over the coefficients of the functions. We first consider the method of Davison and of Burton and de Borde: we write the velocity as

$$\dot{x}(\tau) = (2\pi\hbar/mt) \sum_{n=0}^{\infty} a_n \phi_n(\tau/t), \quad (3.1)$$

where

$$\phi_n(Z) = \sqrt{2} \cos n\pi Z; \quad \phi_0(Z) = 1.$$

(τ is a "dummy" time variable running from 0 to t as the particle goes along the path.) The expansion for $x(\tau)$ is then obtained by integrating Eq. (3.1), subject to the initial condition $x_0 = x(0)$. (This condition fixes a_0 and leaves the other a_n arbitrary.) The Lagrangian

for the free particle is $mx^2/2$, so we have

$$\begin{aligned} \frac{i}{\hbar} \int_0^t L dt &= i\pi \sum_0^\infty a_n^2 = i\pi a_0^2 + i\pi \sum_1^\infty a_n^2; \\ a_0^2 &= (m/2\pi\hbar t)(x-x_0)^2 \\ K(x,t; x_0,0) &= \left(\frac{m}{2\pi i\hbar t}\right)^{\frac{1}{2}} \int_{-\infty}^\infty \frac{da_1}{i^{\frac{1}{2}}} \int_{-\infty}^\infty \frac{da_2}{i^{\frac{1}{2}}} \cdots \\ &\quad \times \int_{-\infty}^\infty \frac{da_n}{i^{\frac{1}{2}}} \cdots \exp\left(\frac{i}{\hbar} \int_0^t L dt\right) \\ &= \left(\frac{m}{2\pi i\hbar t}\right)^{\frac{1}{2}} \exp\left\{\frac{im}{2\hbar t}(x-x_0)^2\right\}. \end{aligned} \quad (3.2)$$

$$\begin{aligned} K(x,t; x_0,0) &= \left(\frac{m}{2\pi i\hbar t}\right)^{\frac{1}{2}} \left\{ \prod_{n=1}^\infty \left(1 - \frac{\omega^2 t^2}{n^2 \pi^2}\right)^{-\frac{1}{2}} \right\} \cdot \exp\left\{\frac{im t}{2\hbar} \left[\frac{(x-x_0)^2}{t^2} - \frac{1}{3}\omega^2(x^2 + xx_0 + x_0^2)\right]\right\} \\ &\quad \times \exp\left\{-\frac{im\omega^4 t^3}{\hbar\pi^4} \sum_1^\infty \frac{x^2 + x_0^2 - 2xx_0(-1)^n}{n^2(n^2 - (\omega t/\pi)^2)}\right\} \\ &= \left(\frac{m\omega}{2\pi i\hbar \sin\omega t}\right)^{\frac{1}{2}} \exp\left\{\frac{im\omega}{2\hbar} [(x^2 + x_0^2) \cot(\omega t) - 2xx_0 \csc(\omega t)]\right\}. \end{aligned} \quad (3.3)$$

In deriving Eq. (3.3) we have used the formulas

$$\begin{aligned} \int_{-\infty}^\infty \exp[i(\alpha x^2 + kx)] dx &= (i\pi/\alpha)^{\frac{1}{2}} \exp(-ik^2/4\alpha), \\ \prod_{n=1}^\infty \left(1 - \frac{z^2}{n^2}\right) &= \frac{\sin\pi z}{\pi z}, \\ \sum_{n=1}^\infty \frac{1}{n^2(n^2 - z^2)} &= \frac{1}{z^2} \left\{ \frac{1}{2z^2} - \frac{\pi}{2z} \cot(\pi z) - \frac{\pi^2}{6} \right\}, \\ \sum_{n=1}^\infty \frac{(-1)^n}{n^2(n^2 - z^2)} &= \frac{1}{z^2} \left\{ \frac{1}{2z^2} - \frac{\pi}{2z} \csc(\pi z) + \frac{\pi^2}{12} \right\}. \end{aligned}$$

Equation (3.3) is essentially the same as (2.12).

Burton and de Borde point out that one can derive the energy levels from (3.3) by using the well-known formula for the Green's function in terms of the wave functions,

$$K(x,t; x_0,0) = \sum_n \psi_n(x) \psi_n^*(x_0) e^{-iE_n t/\hbar}. \quad (3.4)$$

Thus we have

$$\begin{aligned} \int dx K(x,t; x_0,0) &= \sum_{n=0}^\infty e^{-iE_n t/\hbar} \\ &= \left(\frac{m\omega}{2\pi i\hbar \sin\omega t}\right)^{\frac{1}{2}} \int dx \exp\left\{\frac{im\omega x^2}{\hbar} (\cot\omega t - \csc\omega t)\right\} \\ &= \sum_{n=0}^\infty e^{-(n+\frac{1}{2})i\omega t}, \end{aligned} \quad (3.5)$$

so that the energy levels are $E_n = (n + \frac{1}{2})\hbar\omega$.

The propagator goes to $\delta(x-x_0)$ as $t \rightarrow 0$, as required by Eq. (1.1).

For the harmonic oscillator we have $L = (m/2) \times (\dot{x}^2 - \omega^2 x^2)$. On using the same expansion as before, we have

$$\begin{aligned} \frac{i}{\hbar} \int_0^t L dt &= \frac{im t}{2\hbar} \left\{ \frac{(x-x_0)^2}{t^2} - \frac{\omega^2}{3}(x^2 + xx_0 + x_0^2) \right. \\ &\quad \left. + i \sum_{n=1}^\infty \left\{ \pi \left(1 - \frac{\omega^2 t^2}{n^2 \pi^2}\right) a_n^2 \right. \right. \\ &\quad \left. \left. - \left(\frac{\omega t}{n\pi}\right)^2 \left(\frac{4\pi m}{\hbar t}\right)^{\frac{1}{2}} [x_0 - (-1)^n x] a_n \right\} \right\}, \end{aligned}$$

Burton and de Borde used a similar method for finding the Green's function for a two-dimensional rigid rotator.

Davies used a slightly different method, expanding the coordinate $x(t)$ instead of its derivative in a Fourier series. Thus Davies includes discontinuous paths, whereas Davison's method includes paths which are continuous but may have discontinuous derivatives. The two methods give the same result for the cases where they have been applied. Davies used a cosine series, so that the condition on the end points of the path resulted in a condition on the sum of coefficients, which was handled by inserting a delta function in the integral. We simplify the calculation by using instead the expansion

$$x(\tau) = \frac{\tau\Delta}{t} + \sum_1^\infty a_n \sin\left(\frac{n\pi\tau}{t}\right),$$

where Δ is the difference between the final and initial values of x . We specialize to the case where the Lagrangian is $L = \frac{1}{2}m\dot{x}^2 - \frac{1}{2}k(x^2 - \frac{1}{2}\Delta)^2$.

On carrying out the integration, we have

$$\begin{aligned} \int L d\tau &= \Delta^2 \left(\frac{m}{2t} - \frac{k t}{24}\right) + \frac{k t \Delta}{\pi} \sum_{n=2,4,\dots} \frac{a_n}{n} \\ &\quad + \frac{1}{4} \sum_{a_n^2} [(\pi^2 m n^2 / t) - k t]. \end{aligned}$$

The integration over the a_n gives the normalization factor (which can be shown to be the same as before)

and we have

$$\begin{aligned}
 K(\Delta, t; 0, 0) &\sim \exp \left\{ \frac{i}{\hbar} \left[\Delta^2 \left(\frac{m}{2t} - \frac{kt}{24} \right) - \sum_n \frac{k^2 \Delta^2 t^2}{n^2 \pi^2} \frac{1}{(\pi^2 m n^2 / t) - kt} \right] \right\} \\
 &= \exp \left\{ \frac{i \Delta^2 (km)^{\frac{1}{2}}}{\hbar} \left[\frac{1}{\theta} - \frac{\theta}{3} - \frac{2\theta}{\pi^2} \sum_{j=1}^{\infty} \left(\frac{\theta}{\pi} \right)^2 \zeta(2j+2) \right] \right\} \\
 &= \exp \left\{ \frac{i \Delta^2 (km)^{\frac{1}{2}}}{\hbar} \cot \theta \right\}, \tag{3.6}
 \end{aligned}$$

where $\theta = (t/2)(k/m)^{\frac{1}{2}}$ and $\zeta(x)$ is the Riemann zeta function. Equation (3.6) is equivalent to (2.12) and (3.3).

These elaborate calculations tend to obscure the fact (originally noted by Feynman) that the only contribution to the exponential part of the transformation function comes from the classical path, for the harmonic oscillator; the integration over the other paths just determines the normalization factor, which is already fixed by the condition (2.14). This can be seen by taking

$$x(\tau) = \Delta \sin \tau (k/m)^{\frac{1}{2}} / \sin t (k/m)^{\frac{1}{2}} \tag{3.7}$$

which is the classical path for the Lagrangian

$$L = \frac{1}{2} m \dot{x}^2 - \frac{1}{2} k (x - \frac{1}{2} \Delta)^2,$$

and carrying out the calculation as before.

This fact can be proved more generally as follows (Morette 1951; Kilmister 1957): changing to new variables $\tau^* = \tau/t$ and $x = x^*t$ (which leaves the action integral the same), we may write a typical path as

$$x^*(\tau^*) = x_c(\tau^*) + f(\tau^*),$$

where $x_c(\tau^*)$ is the classical path and $f(\tau^*)$, is any function which satisfies $f(0) = f(1) = 0$. The Lagrangian function may be written

$$L = \frac{1}{2} m (\dot{x}_c + \dot{f})^2 - V(x_c + f).$$

Assuming that V can be expanded in a Taylor series about the path $x^* = x_c$ for all values of τ^* considered, we have

$$\begin{aligned}
 L = L_c + (m \dot{x}_c \dot{f} - V_c' f) + \frac{1}{2} (m \dot{f}^2 - V_c'' f^2) \\
 - \frac{1}{6} V_c''' f^3 + \dots, \tag{3.8}
 \end{aligned}$$

where L_c is the Lagrangian calculated as a function of τ for the classical path, and dashes denote differentiation with respect to x . Hence

$$S = S_0 + \frac{1}{2} S_2 + \frac{1}{6} S_3 + \dots,$$

where

$$S_0 = \int_0^1 L_c dt, \quad S_2 = \int_0^1 (m \dot{f}^2 - V_c'' f^2) dt,$$

$$\begin{aligned}
 S_1 = \int_0^1 (m \dot{x}_c \dot{f} - V_c' f) dt = \int_0^1 m (\dot{x}_c f + x_c \dot{f}) dt \\
 = [m \dot{x}_c f]_0^1 = 0.
 \end{aligned}$$

We see that S_0 depends only on x_c ; if V_c'' is constant,

then S_2 depends only on f , while S_3, S_4 , etc., are all zero. In this case $\exp\{iS/\hbar\}$ splits into a product of two factors, of which one depends only on the classical path, and the other only on f . We can now sum over any set of functions f_1, f_2, \dots , etc., and obtain the result

$$K[x^*(1), 1; x^*(0), 0] = A \exp\{iS_0/\hbar\}, \tag{3.9}$$

where the constant is $\sum_t \exp[iS_2\{f\}/\hbar]$ and does not depend on the end points.

The statement that V'' is constant implies that

$$V = a + bx + \frac{1}{2} cx^2$$

which is just the potential of a harmonic oscillator with arbitrary center of force.

In problems involving other potentials, we might expect to get a fairly good approximation by using the classical path to calculate the Green's function; however, in most problems of interest in quantum mechanics the classical path itself is a very complicated function when written in the form $x(\tau)$, even for the Kepler problem [though it appears to be simple when written $r(\theta)$]. The technique of expanding around the classical path is discussed in more detail in Sec. 8.

4. APPROXIMATE METHODS²

In looking for an approximate method for evaluating functional integrals, it is natural to try replacing the infinite-dimensional integral by a finite-dimensional one. There are several different ways in which this could be done. Cameron (1951) has investigated two possible numerical integration rules, which are based on approximating the functional $F\{x(\tau)\}$ in Eq. (2.4) by a finite series of trigonometric functions.

Following Cameron, we define

$$\alpha_j(t) = 2^{\frac{1}{2}} \sin(j - \frac{1}{2})\pi t; \quad \beta_j(t) = 2^{\frac{1}{2}} \cos(j - \frac{1}{2})\pi t, \tag{4.1}$$

$$\phi(s, t) = \begin{cases} 2^{-\frac{1}{2}} \operatorname{sgn}(s) & (0 \leq |s| < t \leq 1) \\ 0 & (0 \leq t \leq |s| \leq 1) \end{cases} \tag{4.2}$$

$$\psi_n(\xi, t) = \psi_n(\xi_1, \dots, \xi_n, t) = \frac{2}{\pi} \sum_{j=1}^n \frac{\xi_j \alpha_j(t)}{2j-1}. \tag{4.3}$$

Let C be the space of continuous functions $x(t)$ on the interval $(0 \leq t \leq 1)$ which satisfy $x(0) = 0$, and let C'

² See also Sec. 8.

be the larger space of functions which are continuous except perhaps at one point where they must have a finite jump. The n th approximation to a function $x(t)$ in C' is

$$x^n(t) = \sum_{j=1}^n \alpha_j(t) \int_0^1 x(s) \alpha_j(s) ds \\ = - \sum_{j=1}^n \frac{\alpha_j(t)}{2j-1} \int_0^1 \beta_j(s) dx(s). \quad (4.4)$$

When $x(t)$ is the function $\phi(t)$ defined previously, we have

$$\phi^n(s,t) = \frac{2^{\frac{1}{2}}}{\pi} \sum_{j=1}^n \frac{\alpha_j(t) \beta_j(s) \operatorname{sgn}(s)}{2j-1}. \quad (4.5)$$

The "rectangle rule" for the evaluating functional integrals gives the expression

$$I_n = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e_n(\xi) F\{\psi_n(\xi,t)\} d\xi_1 \cdots d\xi_n, \quad (4.6)$$

where the measure function $e_n(\xi)$ is defined by [cf. Eq. (2.3)]

$$e_n(\xi) = \pi^{-n/2} \exp(-\xi_1^2 - \cdots - \xi_n^2). \quad (4.7)$$

It is plausible enough (and is proved rigorously by Cameron) that, provided $F\{x(t)\}$ is a reasonably well-behaved functional,

$$\lim_{n \rightarrow \infty} I_n = \int_0^T F\{x(t)\} d_w x, \quad (4.8)$$

where the right-hand side is the functional integral which we wish to calculate.

Unfortunately, the limit is not approached very rapidly; Cameron computed I_n for the case

$$F = \left[\int_0^1 [x(s)]^2 ds \right]^2 \quad (4.9)$$

and found that the error incurred by using the n -fold integral instead of its limit was $O(n^{-1})$, not even $o(n^{-1})$. [$a_n = O(n^{-1})$ means that a number n_0 exists such that $|na_n| < K$ whenever $n > n_0$, where K is independent of n ; $a_n = o(n^{-1})$ means that $\lim na_n = 0$ as $n \rightarrow \infty$.] Thus in order to increase the accuracy by one decimal place one would have to increase n by a factor of 10, which makes this approximation rather impractical.

Cameron discovered that by making a slight modification in the formula (4.6) it is possible to obtain much more rapid convergence. This modification involves adding one extra variable, using the functions ϕ^n defined previously; the new formula, which Cameron

called his "Simpson's rule" is

$$J_n = \frac{1}{2} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e_n(\xi) d\xi_1 \cdots d\xi_n \\ \times \int_{-1}^1 F\{\psi_n(\xi,t) + \phi(s,t) - \phi^n(s,t)\} ds. \quad (4.10)$$

This formula was designed so that the extra terms, after integration, would exactly cancel out the error due to using the finite series (4.3) instead of the infinite series, provided that F was a "third-degree polynomial functional" of the form

$$F\{x\} = K_0 + \sum_{\nu=1}^s \int_0^1 \cdots \int_0^1 x(s_1) \cdots \\ \times x(s_\nu) ds_1 \cdots ds_\nu K_\nu(s_1 \cdots s_\nu), \quad (4.11)$$

where $K_0 = F\{x_0\}$ and the coefficients K_ν are assumed to be of bounded variation in $s_1 \cdots s_\nu$ for every x_0 .

Cameron showed that, in general, the difference between J_n and $\lim J_n$ as $n \rightarrow \infty$ was $O(n^{-2})$; and in the special case (4.9) it was even more accurate than this, the error being $O(n^{-3})$ with a fairly small constant multiplying the n^{-3} .

It would appear that Cameron's "Simpson's rule" could be applied to the evaluation of Feynman integrals, making the appropriate modifications to take into account the fact that both ends of the path are fixed, but so far this does not seem to have been attempted.

The analogy with Brownian motion suggests that the Monte Carlo method might be used to evaluate functional integrals. This method has been used by Gel'fand and Chentsov (1956) to evaluate the following integral which arises in the theory of electrons in polar crystals (Feynman 1955):

$$K(T) = \int \exp \left\{ \frac{\alpha}{2\sqrt{2}} \int_0^T \int_0^T \frac{e^{-|t-s|}}{|x(t) - x(s)|} dt ds \right\} d_w x. \quad (4.12)$$

Gel'fand and Chentsov were mainly interested in finding the lowest eigenvalue, which is simply

$$E_0(\alpha) = - \lim_{T \rightarrow \infty} \frac{1}{T} \ln K(T), \quad (4.13)$$

and they did not give very many details of their method, although it appears to have given fairly good results (see also Gel'fand, Frolov, and Chentsov 1958). Similar methods have been suggested by Kac and Cohen (1952).

Finally we consider an even simpler method (Brush 1957a) which can be used to estimate functional integrals of more complicated functionals, although probably not with very great accuracy. It is based on integrating over a set of parabolic paths which satisfy the

given conditions. We illustrate the method for the harmonic oscillator problem, where

$$L = \frac{1}{2}mx^2 - \frac{1}{2}k(x - \frac{1}{2}\Delta)^2. \quad (4.14)$$

The particle is required to go from $x=0$ to $x=\Delta$ in time T . We write the path in the form

$$x(t) = \frac{\Delta t}{T} + \frac{\alpha t}{T} \left(1 - \frac{t}{T}\right) \quad (4.15)$$

and integrate over all values of α . The result is

$$K(\Delta, T; 0, 0) = (\text{const}) \exp \left\{ \frac{i\Delta^2(km)^{\frac{1}{2}}}{4\hbar^2} \left(\frac{1}{\theta} - \frac{\theta}{3} \right) \right\}, \quad (4.16)$$

where $\theta = (T/2)(k/m)^{\frac{1}{2}}$.

This result may be compared with the exact propagator [Eq. (3.6)]. Since $(1/\theta - \theta/3)$ is the beginning of the Taylor expansion of $\cot\theta$ for $\theta^2 < \pi^2$, it is a very good approximation to the correct result, e.g., for $\theta=1$, $(1/\theta - \theta/3) = 0.667$, while $\cot\theta = 0.642$. The result (4.16) is also obtained if we integrate over a set of paths of the form

$$x(t) = (\Delta t/T) + \alpha \sin(\pi t/T). \quad (4.17)$$

For more complicated potential functions we do not know how accurate the method is; at least it has the advantage that it can actually be carried out numerically for any given potential. This has been done for the case of two helium atoms interacting with a Lennard-Jones (6-12) potential (Brush 1957b, 1958).

5. QUANTUM-MECHANICAL PARTITION FUNCTION

We now derive an expression for the partition function in terms of functional integrals, and show that it can be written as a power series in \hbar , the zero-order term being the classical partition function. This expansion was first used by Wigner (1932) and Kirkwood (1933), who gave the first few terms of the series; alternative derivations have been given by Khalatnikov (1952) and by Goldberger and Adams (1952). We follow the method of Yaglom (1956).

We consider the partition function for a particle of mass m moving in three-dimensional space in a potential field $V(\mathbf{x}) = V(x_1 x_2 x_3)$. It is assumed that $V \rightarrow \infty$ as $x_1^2 + x_2^2 + x_3^2 \rightarrow \infty$, but is nonsingular everywhere else. We wish to evaluate

$$Q = \sum_n e^{-\beta E_n}, \quad (5.1)$$

where the E_n are the eigenvalues of the operator

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^3 \frac{\partial^2}{\partial x_i^2} + V(\mathbf{x}). \quad (5.2)$$

We use the fact that the Green's function for the differential equation

$$\frac{\partial \varphi(\mathbf{x}, t)}{\partial t} = \frac{1}{4} \sum_{i=1}^3 \frac{\partial^2 \varphi(\mathbf{x}, t)}{\partial x_i^2} - V(\mathbf{x}) \varphi(\mathbf{x}, t) \quad (5.3)$$

can be written as an integral in function space

$$K(\mathbf{x}, t; \mathbf{x}_0) = \int_{C_t; \mathbf{x} - \mathbf{x}_0} \exp \left\{ - \int_0^t V[\mathbf{x}_0 + \mathbf{x}(\tau)] \right\} \times d_{w(t; \mathbf{x} - \mathbf{x}_0)} \mathbf{x}(\tau) \quad (5.4)$$

where the integration is over all continuous vector functions $\mathbf{x}(\tau)$ on the interval $(0, t)$ satisfying the conditions $\mathbf{x}(0) = 0$, $\mathbf{x}(t) = \mathbf{x} - \mathbf{x}_0$. To apply Eq. (5.4), we note that the Green's function $K(\mathbf{x}, t; \mathbf{x}_0)$ may be expanded in a double Fourier series of normalized eigenfunctions of the corresponding elliptic differential operator

$$L = -\frac{1}{4} \sum_{i=1}^3 \frac{\partial^2}{\partial x_i^2} + V(\mathbf{x}),$$

giving the well-known expression

$$K(\mathbf{x}, t; \mathbf{x}_0) = \sum_n e^{-\lambda_n t} \varphi_n(\mathbf{x}) \varphi_n(\mathbf{x}_0). \quad (5.5)$$

We now put $\mathbf{x} = \mathbf{x}_0$ and integrate over \mathbf{x} , so that we obtain

$$\begin{aligned} \sum_n e^{-\lambda_n t} &= \int \int \int_{-\infty}^{\infty} K(\mathbf{x}, t; \mathbf{x}) dx_1 dx_2 dx_3 \\ &= \int \int \int_{-\infty}^{\infty} \left(\int_{C_t; 0} \exp \left\{ - \int_0^t V[\mathbf{x} + \mathbf{x}(\tau)] d\tau \right\} \right. \\ &\quad \left. \times d_{w(t, 0)} \mathbf{x}(\tau) \right) dx_1 dx_2 dx_3. \end{aligned} \quad (5.6)$$

The eigenvalues of the operator (5.2) are clearly the same as those of the operator

$$L_1 = -\frac{1}{4} \sum_{i=1}^3 \frac{\partial^2}{\partial x_i^2} + V \left[\frac{\sqrt{2}\hbar}{m^{\frac{1}{2}}} \mathbf{x} \right], \quad (5.7)$$

since this operator is obtained from H by a change of scale factor in the x_i . Therefore we have

$$\begin{aligned} Q &= \int \int \int_{-\infty}^{\infty} \left(\int_{C_{\beta; 0}} \exp \left\{ - \int_0^{\beta} V \left[\frac{\sqrt{2}\hbar}{m^{\frac{1}{2}}} (\mathbf{x} + \mathbf{x}(\tau)) \right] d\tau \right\} \right. \\ &\quad \left. \times d_{w(\beta, 0)} \mathbf{x}'(\tau) \right) dx_1 dx_2 dx_3. \end{aligned} \quad (5.8)$$

Thus the quantum-mechanical partition function can be written as an integral over certain imaginary "motions" of the particle; it may perform conditional Brownian motion, returning to its starting point after a "time" $\beta = 1/kT$.

We now make the substitution

$$X_i = \frac{\sqrt{2}}{m^{\frac{1}{2}}} \hbar x_i \quad (5.9)$$

and then expand the function

$$\exp\left\{-\int_0^\beta V\left[\mathbf{X}+\left(\frac{\sqrt{2}}{m^{\frac{1}{2}}}\right)\hbar\mathbf{x}(\tau)\right]d\tau\right\}$$

in a power series in the parameter \hbar ; this gives the required expansion of Q . We use the formulas

$$\int_{C_{t,X}} d_{w(t,X)}\mathbf{x}(\tau)=\frac{\exp(-X^2/t)}{(\pi t)^{\frac{3}{2}}};$$

$$\int_{C_{t,0}} d_{w(t,0)}\mathbf{x}(\tau)=\frac{1}{(\pi t)^{\frac{3}{2}}}. \quad (5.10)$$

The zero-order term in the expansion of (5.8) is then

$$\left(\frac{m}{2\pi\beta\hbar^2}\right)^{\frac{3}{2}}\int\int\int\exp[-\beta V(\mathbf{X})]dX_1dX_2dX_3. \quad (5.11)$$

This is the same (apart from a constant factor) as the classical phase integral.

To obtain the higher-order terms, one simply writes out the Taylor expansion of the exponential function and applies the formulas (2.7)–(2.10) for the moments of a conditional random process. Since the potential is non-singular, all the odd terms vanish (cf. DeWitt 1960), so we can write

$$Q=\left(\frac{m}{2\pi\beta\hbar^2}\right)^{\frac{3}{2}}[Q_0+\hbar^2Q_2+\hbar^4Q_4+\dots], \quad (5.12)$$

where

$$Q_0=\int\int\int\exp[-\beta V(\mathbf{X})]dX_1dX_2dX_3.$$

The second term is

$$Q_2=\frac{1}{m}\left\{\int\int\int\int V_i(\mathbf{X})V_j(\mathbf{X})\exp[-\beta V(\mathbf{X})]dX_1dX_2dX_3\right.$$

$$\cdot\delta_{ij}\int_0^\beta\int_0^\beta b(\tau_1,\tau_2)d\tau_1d\tau_2-\int\int\int\int V_{ij}(\mathbf{X})$$

$$\times\exp[-\beta V(\mathbf{X})]dX_1dX_2dX_3\cdot\delta_{ij}\int_0^\beta b(\tau,\tau)d\tau\left\}$$

$$=\frac{\beta^3}{24m}\left\{\int\int\int\int\left[(\text{grad}V)^2-\frac{2}{\beta}\Delta V\right]e^{-\beta V}dX_1dX_2dX_3\right\}$$

$$=-\frac{\beta^3}{24m}\int\int\int\int[\text{grad}V(\mathbf{X})]^2$$

$$\times\exp[-\beta V(\mathbf{X})]dX_1dX_2dX_3, \quad (5.13)$$

where $V_i=\partial V/\partial X_i$ and $V_{ij}=\partial^2 V/\partial X_i\partial X_j$; we have integrated by parts, using the assumption that the potential is unbounded at infinity, to obtain the final expression.

The evaluation of the next term yields the result (see Yaglom 1956 for details)

$$Q_4=\frac{\beta^2}{8m^2}\int\int\int\int\frac{1}{720}\{[(\beta\text{grad}V)^2]$$

$$+12(\beta\Delta V)^2-8(\beta\text{grad}V)^2(\beta\Delta V)\}$$

$$\times e^{-\beta V}dX_1dX_2dX_3. \quad (5.14)$$

6. IDEAL BOSE-EINSTEIN AND FERMI-DIRAC GASES

We now show how one may use the free-particle propagator [see, e.g., Eq. (3.2)] to derive the partition function for the ideal Bose-Einstein and Fermi-Dirac gases. This development is independent of the functional-integral formalism, inasmuch as the free-particle propagator can be derived by other methods (ter Haar 1954, p. 185; Montroll and Ward 1958).

On replacing i/\hbar by $\beta=1/kT$, the "thermal propagator" which takes N particles from a point \mathbf{r} at time β may be written

$$K^{(N)}(\mathbf{r}'\beta';\mathbf{r}\beta)$$

$$=K_0^{(N)}(\mathbf{r}_1'\dots\mathbf{r}_N'\beta';\mathbf{r}_1\dots\mathbf{r}_N\beta)$$

$$=\prod_{j=1}^N\frac{\exp\{-\frac{1}{2}m(\mathbf{r}_j'-\mathbf{r}_j)^2/\hbar^2(\beta'-\beta)\}}{[(2\hbar^2\pi/m)(\beta'-\beta)]^{\frac{3}{2}}}$$

$$=\prod_{j=1}^N K_0(\mathbf{r}_j'\beta_j';\mathbf{r}_j\beta). \quad (6.1)$$

According to Eq. (5.8) the partition function, ignoring statistics, is just

$$Q=\int K^{(N)}(\mathbf{r}\beta;\mathbf{r}0)d\mathbf{r}$$

$$=\int\dots\int K_0^{(N)}(\mathbf{r}_1\dots\mathbf{r}_N\beta;\mathbf{r}_1\dots\mathbf{r}_N0)d^3\mathbf{r}_1\dots d^3\mathbf{r}_N$$

$$=V^N[2\hbar^2\pi\beta/m]^{3N/2}. \quad (6.2)$$

For particles obeying Bose-Einstein (Fermi-Dirac) statistics, the wave function of the system, and hence also the propagator, must be symmetrical (antisymmetrical) with respect to permutations of the particles. In terms of the Brownian motion analogy, we may say that the N particles start out at time 0 (corresponding to infinite temperature) at a specified set of positions $(\mathbf{r}_1\dots\mathbf{r}_N)$ and perform Brownian motion until a time β has elapsed. One then discards all the N -particle trajectories thus generated except those which leave the

N particles at the original set of positions. Since the particles are indistinguishable, one must include trajectories for which the final configuration is some permutation of the original one. One is thus led to the propagator (Montroll and Ward 1958)

$$\begin{aligned} K^{(N)}(\mathbf{r}_1' \cdots \mathbf{r}_N', \beta'; \mathbf{r}_1 \cdots \mathbf{r}_N, \beta) \\ = \frac{1}{N!} \left| \begin{array}{ccc} K_0(\mathbf{r}_1' \beta'; \mathbf{r}_1 \beta) & \cdots & K_0(\mathbf{r}_1' \beta'; \mathbf{r}_N \beta) \\ \vdots & & \vdots \\ K_0(\mathbf{r}_N' \beta'; \mathbf{r}_1 \beta) & \cdots & K_0(\mathbf{r}_N' \beta'; \mathbf{r}_N \beta) \end{array} \right| \\ = (1/N!) \det_N(\mathbf{r}' \beta'; \mathbf{r} \beta), \end{aligned} \quad (6.3)$$

which is correct for Fermi-Dirac statistics; for Bose-Einstein statistics the determinant is to be replaced by the permanent.

It is convenient to introduce the grand partition function, which is in this case

$$\Omega = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int \cdots \int \det_N(\mathbf{r}, \beta; \mathbf{r}0) d^3 \mathbf{r}_1 \cdots d^3 \mathbf{r}_N. \quad (6.4)$$

On expanding the determinant (permanent) one obtains

$$\begin{aligned} \Omega = \sum_{N=0}^{\infty} z^N \sum_{\substack{\mathbf{r}_t \\ (\sum_t t = N)}} \prod_{t=1}^{\infty} \frac{(\pm 1)^{(t+1)r_t} (A_t/t)^{r_t}}{(r_t)!} \\ = \exp \left\{ \sum_{t=1}^{\infty} (\pm z)^{t+1} (A_t/t) \right\}, \end{aligned} \quad (6.5)$$

where

$$\begin{aligned} A_t = \int \cdots \int_r K_0(\mathbf{r}_1 \beta; \mathbf{r}_1 0) K_0(\mathbf{r}_t \beta; \mathbf{r}_{t-1} 0) \cdots \\ \times K_0(\mathbf{r}_3 \beta; \mathbf{r}_2 0) \cdot K_0(\mathbf{r}_2 \beta; \mathbf{r}_1 0) d^3 \mathbf{r}_1 \cdots d^3 \mathbf{r}_t. \end{aligned} \quad (6.6)$$

Each A_t can now be represented as a graph on a torus of tubal circumference β ; these graphs were called "torons" by Montroll and Ward. A permutation cycle of k particles may be represented by a graph in which a single "particle" goes around the torus k times.

Evaluation of (6.6) yields the result (Montroll and Ward 1958)

$$A_t = \frac{V}{(2\pi\hbar)^3} \int_0^{\infty} 4\pi p^2 \exp(-t\beta p^2/2m) dp, \quad (6.7)$$

and hence

$$\log \Omega = \mp \frac{4\pi V}{(2\pi\hbar)^3} \int_0^{\infty} p^2 \log \{ 1 \mp z \exp(-\beta p^2/2m) \} dp, \quad (6.8)$$

where the upper sign holds for Bose-Einstein statistics and the lower for Fermi-Dirac statistics. [One abstains from the final integration in (6.7) in order to obtain (6.8) in closed form.]

7. LIQUID HELIUM

In order to investigate the λ transition of liquid helium, Feynman (1953) tried to use a partition function

similar to (6.4), representing the effect of interatomic forces by an "effective mass" instead of a potential function. The problem is thus reduced to adding up contributions from various permutations of the atoms. Kikuchi (1954) simplified this model still further by considering a lattice system: all the atoms are required to be situated on a regular lattice at time 0, and must return to this configuration or some permutation thereof at time β . In Kikuchi's original model, only those permutations were allowed which could be made up of superpositions of cycles in which each atom moved at most one lattice spacing. The approximate partition function for this model was

$$Q \sim \sum g(L) e^{-ATL}, \quad (7.1)$$

where $A = m'd^2k/2\hbar^2$, d = lattice spacing, m' = effective mass, and e^{-AT} is the propagator for one atom to move a distance d in time β . Each permutation in the sum consists of cycles, or "polygons," and L atoms take part in the permutation. $g(L)$ is a combinatorial factor specifying the number of ways that polygons can be drawn, by connecting nearest-neighbor points of the lattice, so that the total number of "sides" (total length of all polygons) is L .

It should be noted that (7.1) omits most of the physical properties of helium, such as phonon and roton excitations, which are described by other theories; the assumption is that one can factor out the permutation part of the partition function and thus pick out the part which gives the discontinuity in the specific heat.

Kikuchi used an approximate method to evaluate $g(L)$ and obtained a second-order transition (discontinuous specific heat) at a temperature $T = 2.9$ (m/m') $^\circ\text{K}$, so that one gets the observed transition temperature by choosing the ratio m'/m (effective mass over real mass) equal to 1.3. The shape of the specific heat curves is fairly good near the lambda point, but at lower temperatures (7.1) predicts a negative specific heat.

In recent work, Kikuchi and his co-workers found a way to remove the restriction to nearest-neighbor permutations, and thus succeeded in eliminating the negative specific heat (see Kikuchi *et al.* 1960).

In writing (7.1) it is assumed that the propagator for all permutations is the same. This assumption seems most in error for the "two-sided polygons," in which two atoms simply change places, since here they must "go around" each other, whereas in larger cycles the atoms can move directly from one lattice point to the next. Consequently, an attempt was made to eliminate this propagator using the approximate method described at the end of Sec. 4. If one treats two-sided polygons separately, the partition function may be written (Brush 1957b)

$$Q \sim \sum g_R(L) e^{-ATL\xi R/2}, \quad (7.2)$$

where ξ is the propagator for two-sided polygons, $R/2$ is the number of two-sided polygons included in a permutation, and $g_R(L)$ is the total number of ways that

polygons can be drawn by connecting nearest-neighbor points of the lattice so that the total number of sides is L and the total number of these sides contributed by two-sided polygons is R (Brush 1958). The partition function (7.2) can also be generalized to describe systems with mixtures of isotopes, or to include the possibility of vacant lattice sites (Brush 1958; Hecht 1958).

8. ELECTRON-PHONON SYSTEM*

The most extensive application of the technique of functional integration has been made by Abé (1954). Abé first derived a path-integral formula for the density matrix and applied it to the harmonic oscillator; although this development overlaps some of the material which we have already presented, it is useful in understanding the more technical calculation for the electron-phonon system.

With the use of the identity

$$e^{-\beta H} = \lim_{\epsilon \rightarrow 0} (1 - \epsilon H)^{\beta/\epsilon}, \quad (8.1)$$

the density matrix may be defined as

$$\begin{aligned} \rho(q', q_0; \beta) &= \langle q' | e^{-\beta H} | q_0 \rangle \\ &= \lim_{\epsilon \rightarrow 0} \left\langle q' \left| \frac{(1 - \epsilon H)(1 - \epsilon H) \cdots (1 - \epsilon H)}{J = \beta/\epsilon \text{ factors}} \right| q_0 \right\rangle. \end{aligned} \quad (8.2)$$

(For convenience we treat J as an integer.) According to the usual rules of quantum mechanics we may insert a complete set of states, $\sum | \rangle \langle |$ between each pair of factors in (8.2):

$$\begin{aligned} \rho(q', q_0; \beta) &= \lim_{\epsilon \rightarrow 0} \int \langle q' | 1 - \epsilon H | q_{J-1} \rangle dq_{J-1} \\ &\quad \times \langle q_{J-1} | 1 - \epsilon H | q_{J-2} \rangle dq_{J-2} \cdots dq_2 \\ &\quad \times \langle q_2 | 1 - \epsilon H | q_1 \rangle dq_1 \langle q_1 | 1 - \epsilon H | q_0 \rangle. \end{aligned} \quad (8.3)$$

Now suppose the Hamiltonian has the form

$$H \equiv (1/2m) \hat{p}_{\text{op}}^2 + V(q), \quad (8.4)$$

where \hat{p}_{op} is the usual momentum operator. Then

$$\begin{aligned} \langle q' | 1 - \epsilon H | q \rangle &= \int \langle q' | \hat{p}' \rangle d\hat{p}' \\ &\quad \langle \hat{p}' | 1 - \epsilon [(\hat{p}_{\text{op}}^2/2m) + V(q)] | q \rangle \\ &= \int \langle q' | \hat{p}' \rangle d\hat{p}' \langle \hat{p}' | q \rangle \\ &\quad \times \{ 1 - \epsilon [(\hat{p}'^2/2m) + V(q)] \}, \end{aligned} \quad (8.5)$$

* This section is based on a translation-summary of Abé's work which was kindly sent to me by Dr. R. Kikuchi.

where $\langle q' | \hat{p}' \rangle$ has been inserted so that the operator H can be treated as a c number. $\langle q' | \hat{p}' \rangle$ is an eigenfunction of the momentum operator and is defined as

$$\langle q' | \hat{p}' \rangle = h^{-1/2} e^{ip'q'/\hbar}. \quad (8.6)$$

We now replace $1 - \epsilon [(\hat{p}'^2/2m) + V(q)]$ by the corresponding exponential; the error incurred here is $O(\epsilon^2)$, so that the total error from all the β/ϵ factors is still only $O(\epsilon\beta)$. We then do the momentum integral and obtain

$$\begin{aligned} \langle q' | 1 - \epsilon H | q \rangle &= \frac{1}{h} \int \exp[i(q' - q)\hat{p}'/\hbar] \\ &\quad \times \exp\{-[\hat{p}'^2/2m + V(q)]\} d\hat{p}' + O(\epsilon^2) \\ &= \frac{1}{h} \left(\frac{2\pi m}{\epsilon} \right)^{1/2} \exp[-(m/2\epsilon\hbar^2)(q' - q)^2 \\ &\quad - \epsilon V(q)] + O(\epsilon^2). \end{aligned} \quad (8.7)$$

On substituting (8.7) into (8.3), we find

$$\begin{aligned} \rho(q', q_0; \beta) &= \lim_{\epsilon \rightarrow 0} \int \exp\left\{ - \left[\frac{m}{2\epsilon\hbar^2} \sum_{i=0}^{J-1} (q_{i+1} - q_i)^2 \right. \right. \\ &\quad \left. \left. + \sum_{i=0}^{J-1} \epsilon V(q_i) \right] \right\} \times \frac{dq_1}{A} \frac{dq_2}{A} \cdots \frac{dq_{J-1}}{A} \frac{1}{A}, \end{aligned} \quad (8.8)$$

where $1/A \equiv (1/h)(2\pi m/\epsilon)^{1/2}$, and $q_J \equiv q'$. This expression is a functional integral of the type discussed in Sec. 2 [see (2.3)], and thus in the limit we can write it as

$$\begin{aligned} \rho(q', q_0; \beta) &= K(q', q_0; \beta) \\ &= \int \exp\left\{ - \int_0^\beta V(q(\tau)) d\tau \right\} d_{w(0, q_0; \beta, q')} q(\tau). \end{aligned} \quad (8.9)$$

Abé then gave a systematic method for approximating the path integral, which is equivalent to an explicit evaluation of Eq. (3.9). Consider the integral

$$I \equiv \int \exp\{-f(q_0 \cdots q_J)\} \frac{1}{A} \prod_{i=1}^{J-1} dq_i/A, \quad (8.10)$$

where

$$f(q_0 \cdots q_J) \equiv \sum_{i=0}^{J-1} \left[\frac{m}{2\hbar^2} \epsilon \left(\frac{q_{i+1} - q_i}{\epsilon} \right)^2 + \epsilon V(q_i) \right]$$

and $1/A = (1/h)(2\pi m/\epsilon)^{1/2}$. The values of f near its minimum give the largest contribution to (8.10), so we expand f with respect to the q_i and retain up to second-order terms. On denoting by q_i^* the value of q_i which makes f a minimum, we write

$$\begin{aligned} f(q_0, \cdots, q_J) &= f(q_0, q_1^*, \cdots, q_{J-1}^*, q_J) \\ &\quad + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 f}{\partial q_i \partial q_j} \right)^* \xi_i \xi_j, \end{aligned} \quad (8.11)$$

where $\xi_i \equiv q_i - q_j^*$. On substituting (8.11) into (8.10), we have

$$I = e^{-f^*} \int_{-\infty}^{\infty} \exp \left[-\frac{1}{2} \sum_{i,i} \left(\frac{\partial^2 f}{\partial q_i \partial q_j} \right)^* \xi_i \xi_j \right] \frac{1}{A} \prod_{i=1}^J \frac{d\xi_i}{A}. \quad (8.12)$$

In order to calculate f^* , Abé takes the minimum condition,

$$\left(\frac{\partial f}{\partial q_i} \right)^* = \frac{m q_i^* - q_{j-1}^*}{\hbar^2 \epsilon} - \frac{m q_{i+1}^* - q_i^*}{\hbar^2 \epsilon} + \epsilon \left(\frac{\partial V}{\partial q_i} \right)^* = 0 \quad (8.13)$$

and lets $\epsilon \rightarrow 0$, so that it becomes

$$(m/\hbar^2)(d^2q/dt^2) = \hbar^2(dV/dq); \quad q(0) = q_0, \quad q(\beta) = q'. \quad (8.14)$$

To evaluate the remaining integral in (8.12), one must reduce the quadratic form in the exponent to a sum of squares. This can be done by standard methods, and the result is

$$I = \frac{e^{-f^*}}{h} \left(\frac{2\pi m}{\epsilon} \right)^{\frac{1}{2}} \frac{1}{\pi^{(J-1)/2}} \int \exp \left(-\sum_{i=1}^{J-1} \lambda_i \eta_i^2 \right) \times \prod_{i=1}^{J-1} d\eta_i = e^{-f^*} \frac{(2\pi m)^{\frac{1}{2}}}{h} \frac{1}{(D_{J-1})^{\frac{1}{2}}}, \quad (8.15)$$

where

$$D_{J-1} \equiv \prod_{i=1}^{J-1} \lambda_i \quad (8.16)$$

and the λ_i are determined by the equations

$$\lambda_1 = S_1, \quad \lambda_i + (1/\lambda_{i-1}) = S_i; \quad i = 2, 3, \dots, J-1 \quad (8.17)$$

$$S_i \equiv 2 + (\epsilon^2 \hbar^2 / m) (\partial^2 V / \partial q_i^2). \quad (8.18)$$

In order to determine D_{J-1} , it is convenient to introduce also

$$D_i = \epsilon \prod_{j=1}^i \lambda_j. \quad (8.19)$$

On combining (8.19) with (8.17), one obtains a difference equation for D_i :

$$D_i S_{i+1} = \epsilon \left(\prod_{j=1}^i \lambda_j \right) \left(\lambda_{i+1} + \frac{1}{\lambda_i} \right) = D_{i-1} + D_{i+1}. \quad (8.20)$$

On substituting (8.18) for S_i and letting $\epsilon \rightarrow 0$, we obtain finally

$$m(d^2D/dt^2) = \hbar^2(\partial^2V/\partial q^2)_{q=q(t)}D, \quad (8.21)$$

where $q(t)$ is determined by (8.14). The initial conditions for $D(t)$ are found by looking at $D_1 = \epsilon S_1$ and $D_2 = \epsilon(S_1 S_2 - 1)$ in the limit $\epsilon \rightarrow 0$, and it is easily shown that $D(0) = 0$ and $D'(0) = 1$.

The final expression for the density matrix is thus

$$\rho(q', q; \beta) = \frac{(2\pi m)^{\frac{1}{2}}}{\hbar [D(\beta, q_0, q')]^{\frac{1}{2}}} \times \exp \left(-\int_0^\beta \left\{ \frac{m}{2\hbar^2} \left(\frac{dq}{dt} \right)^2 + V[q(t)] \right\} dt \right), \quad (8.22)$$

where q is determined by

$$\frac{m}{\hbar^2} \frac{d^2q}{dt^2} = \frac{\partial V}{\partial q}; \quad q(0) = q_0 \quad \text{and} \quad q(\beta) = q' \quad (8.14a)$$

and D is determined by

$$\frac{m}{\hbar^2} \frac{d^2D}{dt^2} = D \left(\frac{\partial^2 V}{\partial q^2} \right)_{q=q(t)}; \quad D(0) = 0, \quad (dD/dt)_{t=0} = 1. \quad (8.23)$$

For the case of a simple harmonic oscillator,

$$V(q) + \frac{1}{2} m \omega^2 q^2, \quad (8.24)$$

Eqs. (8.14) and (8.23) can be solved exactly, and we obtain

$$q(t) = \frac{1}{\sinh(\hbar\omega\beta)} [q_0 \sinh(\hbar\omega(\beta-t)) + q' \sinh(\hbar\omega t)];$$

$$D(t) = (1/\hbar\omega) \sinh(\hbar\omega t),$$

$$\rho(q', q_0; \beta) = \left[\frac{m\omega}{2\pi\hbar \sinh(\hbar\omega\beta)} \right]^{\frac{1}{2}} \times \exp \left[-\frac{m\omega}{4\hbar} \left\{ (q' - q_0)^2 \coth \frac{\hbar\omega\beta}{2} + (q' + q_0)^2 \tanh \frac{\hbar\omega\beta}{2} \right\} \right]. \quad (8.25)$$

As expected from the proof at the end of Sec. 3, this approximation gives the exact result for the harmonic oscillator; (8.25) is equivalent to (2.12), (3.3), and (3.6).

So far we have simply rederived the well-known propagator for the harmonic oscillator; however, Abé's method can deal with the more difficult problem of the electron-phonon system. He assumes the Hamiltonian has the form

$$H = \left[\sum_i \frac{p_i^2}{2m} + V(x) \right] + \sum_k \left[M \omega_k \alpha_k(x) q_k + \gamma_k(x) p_k \right] + \sum_k \left(\frac{M \omega_k^2}{2} q_k^2 + \frac{p_k^2}{2m} \right), \quad (8.26)$$

where x represents the electron coordinates, and the index k numbers the phonon modes. $V(x)$, $\alpha_k(x)$, and $\gamma_k(x)$ are some functions of the electron coordinates which we do not need to specify, since we solve only the

phonon part of the problem. Since (8.26) does not have any cross terms between different modes of phonons, we may discuss the path integral for only one mode at a time and drop the subscript k .

The relevant part of the Hamiltonian is then

$$H(p, q) = \frac{p^2}{2M} + \gamma p + V(q); \quad V(q) = \frac{M\omega^2 q^2}{2} + M\omega\alpha q. \quad (8.27)$$

Because of the term linear in p , we do not use (8.8); instead, we go back to (8.7) and write

$$\begin{aligned} \langle q' | 1 - \epsilon H | q \rangle &= \frac{1}{h} \int \exp \left\{ i(q' - q)p/\hbar - \epsilon \frac{p^2}{2M} - \epsilon \gamma p - \epsilon V(q) \right\} \\ &= \left(\frac{2\pi M}{\epsilon \hbar^2} \right)^{\frac{1}{2}} \exp \left\{ -\frac{\epsilon M}{2\hbar^2} \left(\frac{q' - q}{\epsilon} + i\hbar\gamma \right)^2 - \epsilon V(q) \right\}. \end{aligned} \quad (8.28)$$

The exponent in (8.10) is therefore

$$f(q_0 \cdots q_J) = \sum_{i=0}^{J-1} \left[\frac{M\epsilon}{2\hbar^2} \left(\frac{q_{i+1} - q_i}{\epsilon} + i\hbar\gamma_i \right)^2 + \epsilon V(q_i) \right],$$

and the path is now determined by

$$(d^2q/dt^2) - \hbar^2\omega^2 q = \hbar^2\omega\alpha + (\hbar/i)d\gamma/dt \quad (8.29)$$

instead of (8.14). The solution of (8.29) is

$$\begin{aligned} q(t) &= \frac{q_0 \sinh[\hbar\omega(\beta - t) + q] \sinh(\hbar\omega t)}{\sinh(\hbar\omega\beta)} - B \frac{\sinh(\hbar\omega t)}{\sinh(\hbar\omega\beta)} \\ &\quad + \hbar \int_0^\beta \{ \alpha(S) \sinh[\hbar\omega(t - S)] \\ &\quad - i\gamma(S) \cosh[\hbar\omega(t - S)] \} dS, \end{aligned} \quad (8.30)$$

where

$$B \equiv h \int_0^\beta \{ \alpha(S) \sinh[\hbar\omega(\beta - S)] - i\gamma(S) \cosh[\hbar\omega(\beta - S)] \}.$$

The "classical" path therefore gives a contribution

$$\begin{aligned} P(q', q_0) &\equiv \lim_{\epsilon \rightarrow 0} f^* = \int_1^\beta \left\{ \frac{M}{2\hbar^2} \left(\frac{dq}{dt} + i\hbar\gamma \right)^2 + V[q(t)] \right\} dt \\ &= \frac{M\omega}{2\hbar \sinh(\hbar\omega\beta)} \left[(q_0^2 + q'^2) \cosh(\hbar\omega\beta) \right. \\ &\quad \left. - 2q_0q' + 2Aq' + 2Bq_0 + 2C \right], \end{aligned} \quad (8.31)$$

where

$$\begin{aligned} A &\equiv \hbar \int_0^\beta [\alpha(t) \sinh(\hbar\omega t) + i\gamma(t) \cosh(\hbar\omega t)] dt \\ C &\equiv -\hbar^2 \int_0^\beta dt \int_0^t dS \{ \alpha(t) \sinh[\hbar\omega(\beta - t)] \\ &\quad - i\gamma(t) \cosh[\hbar\omega(\beta - t)] \} \\ &\quad \times [\alpha(S) \sinh(\hbar\omega S) + i\gamma(S) \cosh(\hbar\omega S)]. \end{aligned}$$

The equation for D (8.23) is unaffected by the presence of the additional term $i\hbar\gamma$, so D is still given by

$$D = \sinh(\hbar\omega\beta)/\hbar\omega$$

and therefore the density matrix is

$$\rho(q', q_0; \beta) = \left[\frac{M\omega}{2\pi\hbar \sinh(\hbar\omega\beta)} \right]^{\frac{1}{2}} e^{-\nu(q' - q_0)}. \quad (8.32)$$

Further discussion of this problem may be found in Abé's original paper.

9. CONCLUDING REMARKS

We have not discussed any of the applications of functional integrals in quantum field theory, since these applications involve a new mathematical problem, that of noncommuting operators in the exponent; this subject was considered outside the scope of the present study. A partial list of references to papers on field theory is given in the second part of the Bibliography, as well as some other papers not specifically mentioned in the text. For a brief survey Chap. VII in the textbook by Bogolyubov and Shirkov (1957) is suggested.

It must be admitted that so far no important results seem to have been obtained by the use of functional integrals which could not have been obtained by other methods, and that a considerable amount of work will have to be done if practical computation techniques are to be developed comparable to those available in ordinary quantum mechanics. On the other hand, the space-time viewpoint restores to the physicist some of the conceptual advantages of classical mechanics, in which one could imagine atoms following definite trajectories even if one could not actually see them. Quantum mechanics replaced this pictorial representation by an abstract mathematical formalism, which produced correct results for observable quantities but failed to give an intuitive understanding of events on the microscopic level.

Feynman's postulate does not imply that the particle "really" executes the motions over which one integrates; it simply means that the particle *behaves as though it did*, and therefore it is legitimate to use physical intuition in looking for valid approximation methods. It is hoped that some of the methods of evaluating functional integrals discussed here may prove useful to those who are interested in developing such approximations.

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Theory of Thermal Conductivity of Solids at Low Temperatures

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INTRODUCTION

THIS review provides an introduction to the present theoretical understanding of certain aspects of the lattice thermal conductivity of solids at low temperatures. An attempt is made to collect the various methods used in the analysis of experiments. The adequacy and range of validity of these methods are evaluated, and suggestions are made concerning possible theoretical and experimental investigations which seem desirable.

A few selected topics are discussed thoroughly, instead of attempting a complete survey. This restriction forces the omission of a detailed discussion of some interesting topics, such as the interactions of lattice vibrations with spin waves, excitons, and electrons, but the author feels that in order to understand these latter phenomena it is first necessary to be able to evaluate with confidence the effect of certain defects that are nearly always present in a crystal. (Detailed comparison with experiment is not made here.)

Therefore most of this paper is devoted to a discussion of strain-field scattering, mass-difference scattering, and boundary effects. In order to understand the influence of these scattering mechanisms on the thermal conductivity of a perfect crystal, it is necessary to give a discussion of the three-phonon processes which arise from the anharmonic forces. Much of the discussion is

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