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Evaluation of the Density Matrix for an Ensemble of Anharmonic Oscillators by a Path Integral Approach

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Abstract

Considering the Feynman path integral representation for the configuration-space density matrix for an ensemble of anharmonic oscillators, we determine the 'stationary paths' near which the integrand remains stationary. By taking the path integral to be saturated by contributions from the neighborhood of the path which maximizes the integrand we evaluate the density matrix explicitly in analytic form. This seems to be the first such evaluation of a path integral for a system not describable by a quadratic Hamiltonian. We also comment briefly on the question of analyticity with respect to the perturbation parameter.

1. *Introduction*

Recent investigations using a variety of approaches have led to a number of results, exact as well as approximate, relating to the dependence of the energy eigenvalues E_n of an anharmonic oscillator on the parameter λ representing the strength of the anharmonic (quartic) part of the potential. In particular, it has been proved by a rigorous analysis (Simon, 1970) that the eigenvalue E_n (for any fixed n), considered as a function of λ, has a singularity at the origin of the complex λ plane. The nature of the singularity itself, which is quite complicated, has been unraveled (Simon, 1970; Bender and Wu, 1968; 1969).

On the other hand, it has been shown (Löffel *et al.*, 1969; Graffi *et al.*, 1970) that the formal expression for E_n as a (divergent) power series in λ, which results from the Rayleigh-Schroedinger perturbation theory on treating the anharmonic term as a perturbation, can be approximated by a sequence of Padé approximants whose values converge to the correct eigenvalues of H. The success of the Padé approximants is in contrast to the experience with renormalized perturbation theory, which has been shown to be incapable of yielding a convergent series in terms of the renormalized parameters (Jaffe, 1965). Approximate formula in closed form for the energy levels have also been obtained recently from a semiclassical approach (Mathews and Eswaran, 1972).

While the analyticity properties of, and the processes of approximation to, the energy eigenvalues have thus been rather well explored, the same cannot be said of other quantities of interest like the propagator $\langle x_2 t_2 | x_1 t_1 \rangle$. The perturbation expansion is believed to diverge in this case, too, but no rigorous results seem to be known. An interesting procedure for obtaining an approximate expression for the propagator was outlined some years ago by Lam (1967). It is based on the Feynman path integral representation (Feynman, 1948; Feynman and Hibbs, 1965)

$$\langle x_2 t_2 | x_1 t_1 \rangle = \int \mathscr{D}x \cdot \exp\left[i \int L(x(t), \dot{x}(t))\, dt \right] \tag{1.1}$$

where Dx denotes integration over all paths going from x_1 at t_1 to x_2 at t_2. The explicit evaluation of path integrals is notoriously difficult, and the cases of the free particle and the harmonic oscillator seem to be the only ones for which a complete evaluation of (1.1) has been possible so far. However in the case of the anharmonic oscillator, with

$$V(x) = \tfrac{1}{2}\mu w^2 x^2 + \tfrac{1}{4}\mu\lambda w^2 x^4 \tag{1.2}$$

(μ = mass of the oscillator), Lam (1967) evaluated (1.1) using the stationary phase approximation (see footnote 1). The resulting expression turned out to be nonanalytic in λ at $\lambda = 0$. The nonanalyticity was found to be related to the existence of a multiplicity of possible *classical* trajectories obeying the specific boundary conditions.

Our aim in this paper is to evaluate explicitly another quantity having a path integral representation, namely the (unnormalized) configuration space density matrix ρ for a canonical ensemble, defined by

$$\rho(x_2, x_1; \tau) = \langle x_2 | e^{-\tau H/\hbar} | x_1 \rangle \tag{1.3}$$

Here H is the Hamiltonian, and

$$\tau = \beta\hbar = \hbar/kT \tag{1.3a}$$

[1] The stationary phase method has been applied recently to a system characterized by a nonpolynomial Lagrangian (Sarkar, 1973).

(k = Boltzmann's constant, T = absolute temperature). The partition function Z of the ensemble is of course expressible in terms of ρ

$$Z(\tau) \equiv \operatorname{tr} e^{-\tau H/\hbar} = \int_{-\infty}^{\infty} \rho(x, x; \tau)\, dx \tag{1.4}$$

The path integral expression for ρ is

$$\rho(x_2, x_1; \tau) = \int \mathscr{D}x \exp\left[-\frac{1}{\hbar}\int_0^\tau E(u)\, du\right] \tag{1.5}$$

wherein $\mathscr{D}x$ stands for integration over all paths $x(u)$, $0 \leqslant u \leqslant \tau$, subject to

$$x(0) = x_1, \qquad x(\tau) = x_2 \tag{1.6}$$

(The variable u, like τ, has the dimensions of time). E is a function of $x(u)$ and $\dot{x}(u) \equiv dx(u)/du$, and has a form identical to the classical expression for the energy: $E = \frac{1}{2}\mu\dot{x}^2 + V(x)$.

The integrand of the functional integral (1.5) is a maximum for a path $x_m(u)$ which minimizes the quantity $\int E du$. Since $\int E du$ is stationary with respect to variations about such a path, the "minimum path" $x_m(u)$ is a stationary path and is therefore determined by the Euler-Lagrange equation

$$\mu\ddot{x} - V'(x) = 0 \tag{1.7}$$

corresponding to the variational principle $\delta \int E du = 0$, together with the boundary conditions (1.6). It is known (Brush, 1961) that on approximating (1.5) by the contribution to it from paths in the neighborhood of $x_m(u)$, one gets (see footnote 2)

$$\rho \sim \left[\frac{\mu}{2\pi\hbar^2 D(x_2, x_1; \tau)}\right]^{1/2} \exp\left[-\frac{1}{\hbar}\int_0^\tau E_m\, du\right] \tag{1.8}$$

where $E_m(u) = E(x_m(u), \dot{x}_m(u))$, and $D(x_2, x_1; \tau)$—to be abbreviated hereafter as $D(\tau)$—is to be obtained by solving the following equation:

$$\mu \frac{d^2 D(u)}{du^2} = [V''(x)]_{x=x_m} D(u) \tag{1.9a}$$

$$D(0) = 0, \dot{D}(0) = \hbar^{-1} \tag{1.9b}$$

The dependence of $D(u)$ on x_1, x_2 enters through the minimum path x_m which is involved in (1.9a).

We shall carry through the complete evaluation of ρ, analytically, in the above approximation (which is the counterpart of the saddle point approximation often used in the evaluation of ordinary integrals). As far as we know, this is the first time that such an explicit evaluation of a path integral has been

[2] Equation (1.8) is the first term in an expansion analogous to the asymptotic series obtained on evaluating an ordinary integral by the method of steepest descents. A systematic method for generating further terms in the expansion will be reported separately.

presented for any system not describable by a quadratic Hamiltonian. It is also of interest that unlike other approximation schemes considered in the recent literature (Siegel and Burke, 1972) the approximation (1.8) which we have employed is not perturbative in the potential or any part of it.

2. *Minimum Trajectories for the Anharmonic Oscillator*

In the following we refer to a trajectory $x_m(u)$ which minimises $\int E du$ as a minimum trajectory. For an anharmonic oscillator characterized by (1.2), the equation (1.7) for $x_m(u)$ reduces to

$$\ddot{x}_m - w^2 x_m - \lambda w^2 x_m{}^3 = 0 \tag{2.1}$$

By a single quadrature one finds that the Lagrange function

$$L \equiv \tfrac{1}{2}\mu\dot{x}^2 - \tfrac{1}{2}\mu w^2 x^2 - \tfrac{1}{4}\mu\lambda w^2 x^4 \tag{2.2}$$

is a constant on the path $x(u) = x_m(u)$. Integration of this equation leads to explicit expressions for $x_m(u)$ in terms of Jacobian elliptic functions. It turns out that there are three different forms applicable in different ranges of values of L.

(a) For negative L one has

$$x_m(u) = A\ nc(\nu u + \gamma; k) \tag{2.3}$$

where the modulus k, amplitude A and the parameter ν (proportional to the frequency) of the elliptic function nc (reciprocal of cn) are related by

$$A^2 = \frac{1}{\lambda}\left(\frac{\nu^2}{w^2} - 1\right), \qquad k^2 = \frac{1}{2}\left(1 + \frac{w^2}{\nu^2}\right) \tag{2.4}$$

and γ is a phase constant. These may in turn be expressed in terms of L which determines the value of ν

$$\left(\frac{\nu^2}{w^2}\right)^2 - 1 = \frac{4|L|\lambda}{\mu w^2} \tag{2.5}$$

Note that in this regime, $\nu > w$.

(b) If $0 < (4L\lambda/\mu w^2) < 1$, the solution takes the form

$$x_m(u) = A\ sc(\nu u + \gamma) \tag{2.6}$$

with

$$A^2 = \frac{2}{\lambda}\left(1 - \frac{\nu^2}{w^2}\right), \qquad k^2 = \left(2 - \frac{w^2}{\nu^2}\right) \tag{2.7}$$

$$\frac{2\nu^2}{w^2} - 1 = \left(1 - \frac{4L\lambda}{\mu w^2}\right)^{1/2} \tag{2.8}$$

(c) When $(4L\lambda/\mu w^2) > 1$, the solution is somewhat more complicated

$$x_m(u) = \left(\frac{Q}{\lambda^2}\right)^{1/4} \frac{1 + \rho sc(\nu t + \gamma)}{1 - \rho sc(\nu t + \gamma)} \tag{2.9}$$

where

$$Q = 4L\lambda/\mu w^2 \tag{2.10}$$

$$\rho = (Q^{1/2} + 1)^{-1/2} [(4Q)^{1/4} - (Q^{1/2} - 1)^{1/2}] \tag{2.11}$$

$$\nu = (w/2\rho)(Q^{1/2} + 1)^{1/2}, \qquad k^2 = 1 - \rho^4 \tag{2.12}$$

One can show that for a given initial value x_1 of $x(u)$ at $u = 0$, a solution of the first type (2.3) exists only if the value prescribed for x_2 is between the two roots of the equation

$$x_1^2 + x_2^2 - 2x_1x_2 \cosh w\tau = \tfrac{1}{2}\lambda x_1^2 x_2^2 \tag{2.13}$$

The value $x_2 = x_1$ lies within this range. For x_2 lying outside this range, the minimum paths are of the type (b) or (c) depending on the actual value of x_2.

In the evaluation of (1.8) in the following, we shall assume that x_1, x_2 are such as to lead to minimum paths of the type (2.3). The boundary conditions (1.6) then become

$$x_1 = A\, nc(\gamma, k), \qquad x_2 = A\, nc(\nu\tau + \gamma, k) \tag{2.14}$$

Now, the *nc* function of modulus k has a real period $4K(k)$—where K is the complete elliptic integral of the first kind—and its behaviour is somewhat like that of the secant function: it is an even function and it has an infinite discontinuity whenever the value of the argument passes through an odd multiple of K. Such discontinuties are not admissible in any path which is to minimize $\int E\, du$. So the parameters of the *nc* function in the present case must be such that

$$-K(k) < \gamma < \nu\tau + \gamma < K(k) \tag{2.15}$$

The two equations (2.14) are to be solved for ν and γ (remembering that A and k are also functions of ν). It can be verified that there exists one solution which satisfies the constraint (2.15) also. It will be understood in the following that the parameters ν, γ appearing in the equation (2.7) for the minimum path are given by this solution.

3. *Evaluation of* ρ

The quantities $\int E_m(u)\, du$ and D occurring in (1.8) will now be evaluated explicitly. The former can be written, after an integration by parts and use of equation (1.7), as

$$\int_0^\tau E_m(u)\,du = \tfrac{1}{2}\mu(x_m\dot{x}_m)\Big|_0^\tau + \int_0^\tau (V - \tfrac{1}{2}xV')\Big|_{x=x_m} du \tag{3 1}$$

With V and x_m given by (1.2) and (2.3) this becomes (see footnote 3)

$$\int_0^\tau E_m(u)\,du = \tfrac{1}{2}\mu x_m\dot{x}_m\Big|_0^\tau - \tfrac{1}{4}\mu\lambda w^2 \int_0^\tau x_m{}^4\,du$$

$$= \Big(\tfrac{1}{2}\mu A^2 \nu\, nc^3 v\ snv\ dnv - \frac{\mu\lambda w^2 A^4}{12k'^4\nu}\,[k'^2 nc^3 v\ snv\ dnv$$

$$- 2(2k^2 - 1)\{ncv\ snv\ dnv - E(amv, k) + k'^2 v\}$$

$$+ k^2k'^2 v]\Big)\Big|_{u=0}^{u=\tau} \tag{3.2}$$

where $v = \nu u + \gamma$.

Next, to determine D, we have to solve equation (1.9a) which becomes, in the present case

$$\frac{d^2D}{du^2} = w^2\,[1 + 3\lambda A^2 nc^2(\nu u + \gamma; k)]D$$

$$= \nu^2\,[(k^2 - k'^2) + 6k'^2 nc^2(\nu u + \gamma; k)]D \tag{3.3}$$

The last form is obtained from equations (2.4). In the harmonic oscillator limit ($\lambda \to 0$, $k' \to 0$, $\nu \to w$ and $nc \to \cosh$) the solution of the above equation which satisfies the initial conditions (1.9b) is readily seen to be $(\hbar w)^{-1}\sinh wu$. The solution we seek for $\lambda \neq 0$ has to be such as to tend to this function when the limit $\lambda \to 0$ is taken. Examination of simple combinations of elliptic functions which tend to a sinh function in this limit leads one to the combination

$$D_1 = \frac{sn(\nu u + \gamma)\,dn(\nu u + \gamma)}{cn^2(\nu u + \gamma)} \tag{3.4}$$

which satisfies equation (1.9a). Though it does not satisfy the initial conditions (1.9b) it can be used to generate the solution which does. In fact, by writing

[3] Integrals of elliptic functions and their combinations may be found from the Tables in Gradshteyn and Ryzhik (1965). A concise presentation of the main properties of elliptic functions may be found in Bowman (1953).

the general solution as

$$D = gD_1$$

where g is to be determined by substitution in (1.9a), one gets (on using the fact that D_1 already satisfies that equation)

$$D_1 \frac{d^2 g}{du^2} + 2 \frac{dD_1}{du}\frac{dg}{du} = 0 \tag{3.5}$$

and hence

$$g = c_1 + \int \frac{c_2}{{D_1}^2}\, du \tag{3.6}$$

Particulars of evaluation of this integral and imposition of the boundary conditions on $D(u)$ are given in the Appendix. The final result is

$$D(\tau) = -(snv\ dnv\ cn^2 v)_{u=0} \cdot (snv\ dnv\ nc^2 v)_{u=\tau} \times \frac{\left[\dfrac{k^2 cnv}{snv\ dnv} + (k^2 - k'^2)E(am(v+K), k) + k'^2(v+K)\right]\Bigg|_{u=0}^{u=\tau}}{\hbar\nu[k^2 cn^4 v + 2k'^2(k^2 - k'^2)\, sn^2 v]_{u=0}} \tag{3.7}$$

where once again $v = \nu u + \gamma$. The expression for the matrix element $\rho(x_2, x_1; \tau)$ is obtained on substituting (3.2) and (3.7) in (1.8). Some simplification is possible for the diagonal matrix element ($x_1 = x_2 = x$). In this case one has $\gamma = -\frac{1}{2}\nu\tau$ and hence

$$\begin{aligned}\rho(x_1 x; \tau) = {} & \left[\frac{\mu\nu}{2\pi\hbar} \cdot \frac{k^2 cn^4 \tfrac{1}{2}\nu\tau + 2k'^2(k^2 - k'^2) sn^2 \tfrac{1}{2}\nu\tau}{sn\tfrac{1}{2}\nu\tau \cdot dn\tfrac{1}{2}\nu\tau(2k^2 cn\tfrac{1}{2}\nu\tau + k'^2 \nu\tau\, sn\tfrac{1}{2}\nu\tau\, dn\tfrac{1}{2}\nu\tau)}\right]^{1/2} \\ & \times \exp\left\{-\frac{\mu A^2 \nu}{\hbar}\, sn\tfrac{1}{2}\nu\tau\ nc^3\tfrac{1}{2}\nu\tau\, dn\tfrac{1}{2}\nu\tau \right. \\ & \cdot \left[1 - \frac{\lambda w^2 A^2}{6k'^4 \nu^2}(k'^2 - 2(k^2 - k'^2) cn^2 \tfrac{1}{2}\nu\tau)\right] \\ & \left. + \frac{(2 - 3k^2)\mu\lambda w^2 A^4 \tau}{12 k'^2 \hbar}\right\}\end{aligned} \tag{3.8}$$

The elliptic functions appearing here may expressed in terms of x

$$cn\tfrac{1}{2}\nu\tau = (A/x),\ sn\tfrac{1}{2}\nu\tau = \left(1 - \frac{A^2}{x^2}\right)^{1/2},\ dn\tfrac{1}{2}\nu\tau = \left(k'^2 + \frac{k^2 A^2}{x^2}\right)^{1/2} \tag{3.9}$$

The τ– dependence will then enter only through the value of k which is determined implicitly by the first of equations (3.9). The integral of the expression (3.8) over x finally gives the partition function Z.

4. *Discussion*

We have remarked earlier that the approximation (1.8) to the functional integral (1.5) is analogous to the saddle point approximation in ordinary integration. The validity of the saddle point approximation is known to depend on the existence of a large parameter which ensures very fast decrease of the integrand as one moves away from the saddle point. In the present case one would look for such a parameter in the argument of the exponential function in (1.5): By defining the nondimensional variables

$$y = \lambda^{1/2} x \quad \text{and} \quad u' = (u/\tau) \tag{4.1}$$

one can write the exponent as

$$-\frac{1}{\hbar}\int_0^\tau E(u)\,du = -\frac{\mu w^2 \tau}{2\lambda\hbar}\int_0^1 \left[\frac{1}{w^2\tau^2}\left(\frac{dy}{du'}\right)^2 + y^2 + y^4\right] du' \tag{4.2}$$

The nondimensional parameter $(\mu w^2 \tau/2\lambda\hbar) \equiv (\mu w^2/2\lambda kT)$ determines how fast the exponent in (1.5) changes when $y(u')$ is varied from the minimum path. Our approximation may be considered good when this parameter is large. This is the case, in particular, when the anharmonicity (characterised by λ) is small. It may be verified in fact that in the limit $\lambda \to 0$, the approximation (1.8) together with (3.1), (3.2) and (3.7) tends to the exact result $\rho^{(0)}$ of the harmonic oscillator case, namely

$$\rho^{(0)}(x_1, x_2; \tau) = \left(\frac{\mu w}{2\pi\hbar \sinh w\tau}\right)^{1/2} \exp\left\{-\frac{\mu w}{2\hbar \sinh w\tau} \cdot [(x_1^2 + x_2^2)\cosh w\tau - 2x_1x_2]\right\} \tag{4.3}$$

Another point of interest concerns the correspondence between ρ and the propagator G. One can obtain G from ρ by formal replacement of τ by it, and the representation (1.5) is consistent with this fact. Lam (1967) has observed that in the stationary phase approximation to the path integral representation for G, there exists an infinite number of stationary-phase paths which contribute to G, and that the contributions from all but one of these have a manifestly nonanalytic λ-dependence (involving the exponential of λ^{-1}). The contribution from the exceptional path alone is the counterpart of our approximation to ρ, and is obtainable from the latter by the replacement $\tau \to it$. This is because there is only a single 'minimum path' which is relevant in the case of ρ—all other paths which satisfy (2.1) and (1.6) have infinite discontinuities. Thus the analyticity with respect to λ does not appear in quite the same light in the *approximate* expressions for G and ρ.

It may be pertinent to remark, in this context, on the conjecture that if the change of sign of the perturbation parameter λ results in a drastic change in the behavior of the system (as in the case of the anharmonic oscillator) then physical quantities pertaining to the system, considered as functions of λ, should be singular at $\lambda = 0$. While the behavior of the energy levels and of the propagator of the anharmonic oscillator conforms to this conjecture, it would be well to take note of an even simpler example where the conjecture is not borne out. The example has to do with the harmonic oscillator, considered as a perturbed free particle, the perturbation parameter being w^2. The energy levels, being proportional to w, have a branch point at $w^2 = 0$. But the density matrix (4.3)—or the propagator—is analytic (see footnote 4) at $w^2 = 0$. It appears that in aggregating the contributions from all the energy eigenstates to the propagator, the singularity (which is present in the individual energy eigenvalues) gets softened. It may be a safe conjecture that in general, the propagator has a smoother dependence than the energy levels have on any perturbation parameter.

Appendix

Evaluation of

$$\int \frac{cn^4(\nu u + \gamma)}{sn^2(\nu u + \gamma)\, dn^2(\nu u + \gamma)}\, du \tag{A.1}$$

is facilitated by reexpressing the integrand as

$$\frac{cn^4 v}{sn^2 v\, dn^2 v} = k'^2 \frac{sn^4(v + K)}{cn^2(v + K)} = k'^2 [nc^2(v + K) + cn^2(v + K) - 2] \tag{A.2}$$

using the properties of elliptic functions (see, for example section 8.15, Gradshteyn and Ryzhik, 1965). The recurrence formula (section 5.13, Gradshteyn and Ryzhik, 1965)

$$\begin{aligned}\int cn^m\alpha\, d\alpha = [(m-1)k^2]^{-1}\Big[(m-2)(2k^2-1)\int cn^{m-2}\alpha\, d\alpha \\ + (m-3)k'^2\int cn^{m-4}\alpha\, d\alpha + cn^{m-3}\alpha\; sn\alpha\, dn\alpha\Big]\end{aligned} \tag{A.3}$$

together with the result that

$$\int cn^2\alpha\, d\alpha = k^{-2}\, [E(am\alpha, k) - k'^2\alpha] \tag{A.4}$$

enables us to write (A.1) as

$$\begin{aligned}&(k'^2/\nu)\int (nc^2\alpha + cn^2\alpha - 2)\, d\alpha \\ &= \frac{1}{\nu k^2}\left[k^2 \frac{sn\alpha\, dn\alpha}{cn\alpha} + (k'^2 - k^2)E(am\alpha, k) - k'^2\alpha\right]\end{aligned} \tag{A.5}$$

[4] The material difference between this example and the case of the anharmonic oscillator, on which the question of analyticity seems to hinge, is the nonuniqueness, in the latter case, of the classical trajectories which connect specified initial and final configurations. While the harmonic oscillator has only one such trajectory, the anharmonic oscillator has an infinite number (Lam, 1967).

where $\alpha = \nu u + \gamma + K$. Substituting this for the integral in (3.6) and returning to the variable $v = \alpha - K$, we obtain

$$D = \frac{snv\,dnv}{cn^2 v}\left[c_1 - \frac{c_2}{\nu k^2}\left\{k^2 \frac{cnv}{snv\,dnv} + (k'^2 - k^2)E(am(v+K),k) - k'^2(v+K)\right\}\right] \tag{A.6}$$

The initial conditions (9b) on D require that at $u = 0$, the factor in square brackets in (A.6) should vanish and that its derivative multiplied by $(snv\,dnv/cn^2 v)$ should be equal to $(1/\hbar)$. The former condition gives c_1 in terms of c_2 and the latter reduces to

$$\frac{1}{\hbar} = \left(\frac{snv\,dnv}{cn^2 v}\right)_{u=0}\left(-\frac{c^2}{k^2}\right)\left[\frac{k^2(k^2 sn^2 v\,cn^2 v - dn^2 v)}{sn^2 v\,dn^2 v} + (k^2 - k'^2)(-k'^2/dn^2 v) + k'^2\right]_{u=0} \tag{A.7}$$

After a little manipulation one gets

$$c_2 = \left\{\frac{k^2\,snv\,dnv\,cn^2 v}{\hbar[k^2 cn^4 v + 2k'^2(k^2 - k'^2)sn^2 v]}\right\}_{u=0} \tag{A.8}$$

Introducing in (A.6) the values of c_2 and c_1 thus determined, we obtain the expression (3.7) for D.

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