

Lawrence Berkeley National Laboratory

Recent Work

Title

CLASSICAL-LIMIT QUANTIZATION OF NON-SEPARABLE SYSTEMS: PHASE SPACE DEEIVATION AM) ITS EQUIVALENCE TO THE DYNAMICAL QUANTUM CONDITION

Permalink

<https://escholarship.org/uc/item/20q6f6jp>

Author

Miller, William H.

Publication Date

1971-08-01

Submitted to Journal of
Chemical Physics

LBL-162
Preprint

c. 1

RECEIVED
LAWRENCE
RADIATION LABORATORY

OCT 22 1971

LIBRARY AND
DOCUMENTS SECTION

CLASSICAL-LIMIT QUANTIZATION OF NON-SEPARABLE SYSTEMS:
PHASE SPACE DERIVATION AND ITS EQUIVALENCE
TO THE DYNAMICAL QUANTUM CONDITION

William H. Miller

August 24, 1971

AEC Contract No. W-7405-eng-48

For Reference

Not to be taken from this room

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

LBL-162

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Classical-Limit Quantization of Non-Separable Systems: Phase Space
Derivation and Its Equivalence to the Dynamical Quantum Condition*

William H. Miller[‡]

Inorganic Materials Research Division, Lawrence Berkeley Laboratory
and Department of Chemistry; University of California,
Berkeley, California 94720

ABSTRACT

On the basis of simple phase space arguments a classical-limit quantization rule is derived for general non-separable systems. Although quite different in appearance, it is shown that this statistical quantum condition is actually equivalent to a dynamical quantum condition obtained previously. This equivalence is seen to imply a direct relation between the action integral $\oint dq \cdot p$ along the periodic trajectory whose energy is E and the volume of phase space with energy less than or equal to E .

I. INTRODUCTION

In a previous study of classical-limit eigenvalues for non-separable systems the classical quantization condition was derived and applied to several simple systems.¹ The derivation followed the approach of Gutzwiller², and classical quantization was seen to be intimately related to the periodic trajectories of the multi-dimensional system. The Bohr-Sommerfeld quantum condition for one-dimensional systems

$$(n + \frac{1}{2})\pi = \int dx \left\{ 2m [E - V(x)] / \hbar^2 \right\}^{\frac{1}{2}} \quad (1)$$

is the one-dimensional case of the general result¹.

In this paper we derive a classical-limit quantum condition for general non-separable systems from a completely different point of view, one based on classical phase space arguments. It is shown, however, that this statistical quantum condition is completely equivalent to the dynamical quantum condition obtained before¹. This equivalence is quite a remarkable feature when one realizes that the dynamical quantum condition¹ involves action integrals (i.e., line integrals along classical trajectories) evaluated along certain specific classical trajectories (the periodic trajectories of the system), whereas the statistical quantum condition to be developed below involves only phase space integrals. From a practical point of view the equivalence of the two approaches is important since one expects the statistical form of the quantum condition to be much simpler to apply to complicated systems.

Section II derives the statistical form of the quantum condition, shows its canonical invariance, and carries out the momentum part of the phase space integration. Section III discusses the connection with the

dynamical form of the quantum condition; this is based on a classical-limit approximation which is derived for the microcanonical density matrix. Section IV shows how constants of the motion other than the energy (e.g., total angular momentum and one of its components) can be accounted for in a unified manner.

II. STATISTICAL QUANTIZATION

Consider a general non-separable system with N degrees of freedom. If $\underline{q} \equiv (q_1, q_2, \dots, q_N)$ and $\underline{p} \equiv (p_1, p_2, \dots, p_N)$ are a set of canonical variables (i.e., coordinates and momenta) for the system, then the density of quantum states at any point $(\underline{q}, \underline{p})$ in phase space is the constant value h^{-N} , where $h \equiv 2\pi \hbar$ is Planck's constant; this is standard classical statistical mechanics.³ The total number n of quantum states with an energy less than or equal to E is therefore

$$n(E) = h^{-N} \int_{\underline{q}} dq \int_{\underline{p}} dp \theta \left[E - H(\underline{q}, \underline{p}) \right], \quad (2)$$

where $H(\underline{q}, \underline{p})$ is the classical Hamiltonian for the system, $\theta(x)$ is the unit step-function

$$\theta(x) = 1, \text{ if } x > 0 \\ 0, \text{ if } x < 0,$$

$$d\underline{q} \equiv dq_1 dq_2 \dots dq_N \\ d\underline{p} \equiv dp_1 dp_2 \dots dp_N,$$

and the integration is over all phase space. For the present we assume that there are no integral constants of the motion for the system other

than the energy itself; Section IV shows the simple modification that is required to remove this restriction.

If there are $n(E)$ quantum states below E , however, then $n(E)$ must be the quantum number for the eigenvalue whose energy is E ; i.e., the function $n(E)$ defined in Equation (2) is the inverse function of the classical-limit eigenvalue function $E(n)$. When one allows n to take on only integer values, therefore, Equation (2) is the desired classical quantum condition.

It is quite simple to show that the form of Equation (2) is invariant to a canonical transformation. If $\tilde{Q} \equiv (Q_1, Q_2, \dots, Q_N)$ and $\tilde{P} \equiv (P_1, P_2, \dots, P_N)$ are any other set of canonical variables, then one knows that

$$d\tilde{q} d\tilde{p} = d\tilde{Q} d\tilde{P}$$

$$H(\tilde{q}, \tilde{p}) = H(\tilde{Q}, \tilde{P}) \quad ,$$

so that Equation (2) has the same form regardless of the particular set of canonical variables one chooses in order to carry out the calculation.

One may without restriction, therefore, take the variables to be the Cartesian coordinates and momenta of the system, so that the Hamiltonian is of the form

$$H(\tilde{q}, \tilde{p}) = \sum_{i=1}^N p_i^2 / 2m_i + V(\tilde{q}) \quad . \quad (3)$$

Because of the relatively simple way the momenta enter in the Hamiltonian in Equation (3), the integral over them in Equation (2) can be performed.

The momentum integral

$$\int_{\tilde{p}} dp \equiv \int dp_1 \int dp_2 \cdots \int dp_N$$

with the ranges of integration restricted to account for the step-function integrand,

$$\sum_{i=1}^N p_i^2 / 2m_i \leq E - V(\tilde{q}) \quad ,$$

is the form of a Dirichlet integral, and using standard integral formulas⁴ one obtains

$$\int_{\tilde{p}} dp \theta [E - H(\tilde{q}, \tilde{p})] = \left[(2m_1)(2m_2) \cdots (2m_N) \right]^{\frac{1}{2}} \times \Gamma(\frac{1}{2})^N \Gamma(1 + \frac{N}{2})^{-1} [E - V(\tilde{q})]^{N/2} \quad . \quad (4)$$

With Equation (4), therefore, the classical quantum condition in Equation (2) becomes

$$n(E) = \left(\frac{2m}{4\pi\hbar^2} \right)^{N/2} \Gamma(1 + \frac{N}{2})^{-1} \int_{\tilde{q}} dq [E - V(\tilde{q})]^{N/2} \quad , \quad (5)$$

where

$$m \equiv (m_1 m_2 \cdots m_N)^{1/N} \quad .$$

One can quite readily verify that Equation (5) reduces to the Bohr-Sommerfeld condition [Equation (1)] for the case of one degree of freedom ($N = 1$).

The quantum number function $n(E)$ of Equations (2) and (5) is the microcanonical (fixed energy) version of the partition function $Q(T)$ for canonical (fixed temperature) systems. The relation between the two is:

$$Q(T) = \int_0^{\infty} dn \exp \left[-E(n)/kT \right] = \int_0^{\infty} dE n'(E) \exp \left[-E/kT \right] ;$$

$Q(T)$ is also given by Equation (2) with the replacement

$$\theta[E - H(\underline{q}, \underline{p})] \rightarrow \exp[-H(\underline{q}, \underline{p})/kT] .$$

and by Equation (5) with the replacement

$$\Gamma(1 + \frac{N}{2})^{-1} [E - V(\underline{q})]^{N/2} \rightarrow (kT)^{N/2} \exp[-V(\underline{q})/kT] .$$

III. DYNAMICAL QUANTIZATION AND ITS EQUIVALENCE TO STATISTICAL QUANTIZATION

First we re-derive, in a somewhat different manner, the classical quantization condition obtained previously;¹ not only is the derivation below simpler and more physically transparent, but it also clears up the inconsistencies in some of Gutzwiller's results.^{2c}

Consider matrix elements of the fixed-energy projection operator

$$P(\underline{q}_2, \underline{q}_1; E) \equiv \langle \underline{q}_2 | \delta(E-H) | \underline{q}_1 \rangle ; \quad (6)$$

this is the microcanonical density matrix. The delta function operator is conveniently expressed as the Fourier transform of the propagator (time evolution operator)

$$\delta(E - H) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dt \exp(iEt/\hbar) \exp(-iHt/\hbar), \quad (7)$$

so that Equation (6) becomes

$$P(\underline{q}_2, \underline{q}_1; E) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dt \exp(iEt/\hbar) \langle \underline{q}_2 | \exp(-iHt/\hbar) | \underline{q}_1 \rangle . \quad (8)$$

We seek the classical-limit approximation for the diagonal elements of this density matrix, i.e., the classical-limit approximation for the particle density at fixed energy E. This is accomplished by using Equation (8) with the classical-limit approximation for the propagator,^{5,2a}

$$\langle \underline{q}_2 | \exp(-iHt/\hbar) | \underline{q}_1 \rangle = \sum \left[(2\pi i \hbar)^N \det \left(\frac{\partial \underline{q}_2}{\partial \underline{p}_1} \right)_{\underline{q}_1} \right]^{\frac{1}{2}} \times \exp \left[i\phi(\underline{q}_2, \underline{q}_1; t) / \hbar \right] , \quad (9)$$

where the phase function ϕ is the classical action computed along the classical trajectory that goes from \underline{q}_1 to \underline{q}_2 in time t,

$$\phi(\underline{q}_2, \underline{q}_1; t) = \int_0^t dt' \underline{p} \cdot \dot{\underline{q}} - H(\underline{q}, \underline{p}) ,$$

and the summation in Equation (9) indicates a sum over all such trajectories that go from \underline{q}_1 to \underline{q}_2 in time t.

Proceeding as in references 1 and 2d, one evaluates the time integral in Equation (8) by stationary phase. For the diagonal elements ($\underline{q}_1 = \underline{q}_2 \equiv \underline{q}$) one argues as before^{1,2d} that only periodic trajectories can contribute, so that stationary phase evaluation of the integral in Equation (8) gives

$$P(\underline{q}, E) \equiv P(\underline{q}_2, \underline{q}_1; E)_{\underline{q}_2 = \underline{q}_1 \equiv \underline{q}} = \sum_{k=-\infty}^{\infty} f(\underline{q}) \exp \left[ik(\Phi(E)/\hbar - \pi l/2) \right] . \quad (10)$$

The phase $\Phi(E)$ in Equation (10) is the action integral

$$\Phi(E) = \int_0^{\tau} dt \underline{p} \cdot \dot{\underline{q}} \equiv \oint \underline{dq} \cdot \underline{p} , \quad (11)$$

where $[\underline{q}(t), \underline{p}(t)]$ is the⁶ periodic trajectory with energy E, and τ is

its period. The sum in Equation (10) is a sum over all times $t = k\tau$, $k = 0, \pm 1, \pm 2, \dots$ which are the points of stationary phase in the integral over t in Equation (8); physically this corresponds to the fact that there are classical trajectories that go from \underline{q} back to \underline{q} in time $t = 0, \pm\tau, \pm 2\tau, \dots$. All the dependence on \underline{q} in Equation (10) is contained in the function $f(\underline{q})$ which will be discussed in detail below. [In reference 1 it appears implicitly that the function $f(\underline{q})$ may be different for different terms in the sum in Equation (10); this is not the case. Since reference 1 made no use of the coordinate dependence, this had no effect on the conclusions therein.] The integer l in Equation (10) is a constant which is defined and discussed in reference 1.

Since it is a geometric series, one can readily show that

$$\sum_{k=-\infty}^{\infty} \exp(ikA) = 0$$

provided

$$A \neq 2\pi \times (\text{integer}) ;$$

if $A = 2\pi \times (\text{integer})$, however, the sum is ∞ . More generally, one has that

$$\sum_{k=-\infty}^{\infty} \exp(ikA) = \sum_{n=-\infty}^{\infty} \delta(A/2\pi - n) , \quad (12)$$

so that Equation (10) becomes

$$P(\underline{q}, E) = f(\underline{q}) \sum_{n=0}^{\infty} \delta[\Phi(E)/h - l/4 - n], \quad (13)$$

where the sum is started at 0 since $\Phi(E)/h - \ell/4 > -1$. Each term in Equation (10) thus contributes equally to the particle density, and all the multiple passes over the periodic trajectory enter simply to give the delta function factor in Equation (13).

The formal quantum mechanical expression for the particle density is

$$P(\tilde{q}, E) = \sum_{n=0}^{\infty} |\psi_n(\tilde{q})|^2 \delta(E - E_n) , \quad (14)$$

where E_n are the eigenvalues and $\psi_n(\tilde{q})$ the corresponding normalized eigenfunctions for the system; i.e., the density for energy E has a delta function singularity when E is equal to an eigenvalue E_n and is zero otherwise. It is seen that the classical-limit approximation in Equation (13) also has this property⁷, and that the classical-limit eigenvalue relation is (as obtained previously¹)

$$\Phi(E) = h (n + \ell/4) , \quad (15)$$

$n = 0, 1, \dots$: i.e., the quantum number function $n(E)$, the inverse function of which the classical eigenvalue function $E(n)$, is

$$n_d(E) \equiv h^{-1} \Phi(E) , \quad (16)$$

where the subscript "d" signifies that this is the quantum number function obtained by this dynamical derivation. In Equation (16) we have discarded the fraction $\ell/4$ and will not bother with it in further discussion.

With the definition in Equation (16), the classical-limit approximation for the particle density [Equation (13)] may be written

$$P(\underline{q}, E) = f(\underline{q}) \sum_{n=0}^{\infty} \delta[n_d(E) - n] , \quad (17)$$

or since

$$\delta[n_d(E) - n] = \delta(E - E_n)/n_d'(E) ,$$

this becomes

$$P(\underline{q}, E) = \sum_{n=0}^{\infty} \left[f(\underline{q})/n_d'(E) \right] \delta(E - E_n) . \quad (18)$$

Comparing this classical-limit approximation in Equation (18) with the formal quantum mechanical expression in Equation (14), one identifies the classical-limit approximation for the square of the wavefunction for eigenstate n ,

$$|\psi_n(\underline{q})|^2 = f(\underline{q})/n_d'(E) . \quad (19)$$

It is of considerable interest, therefore, to determine more precisely the function $f(\underline{q})$ appearing above, not only for its interpretation in terms of the wavefunction [Equation (19)], but also because it is essential in making the connection between the dynamical quantum condition derived in this section and the statistical quantum condition derived in the previous section.

Since $f(\underline{q})$ is the same for all terms in Equation (10), we may determine it by considering any single term. In particular, we choose to evaluate it for the term $k = 0$; this term is the contribution to the particle density from the "trajectory" that goes from q back to q in zero time. To determine its contribution to the integral over t in

Equation (8), it is easiest to return to Equation (8) itself; for in the limit $\underline{q}_2 \rightarrow \underline{q}_1$, and small t , the classical-limit propagator in Equation (9) can be constructed explicitly. Thus in this limit

$$\underline{q}_2 \approx \underline{q}_1 + \underline{p}_1 t/m ,$$

so that

$$\det \begin{pmatrix} \underline{q}_2 \\ \underline{p}_1 \end{pmatrix}_{\underline{q}_1} = (t/m)^N ,$$

and also

$$\phi(\underline{q}_2, \underline{q}_1; t) \approx m |\underline{q}_2 - \underline{q}_1|^2 / 2t - V(\underline{q})t ;$$

the diagonal elements of the propagator in the limit of small t are thus given by

$$\langle \underline{q} | \exp(-iHt/\hbar) | \underline{q} \rangle = (2\pi i \hbar t/m)^{-\frac{N}{2}} \exp[-iV(\underline{q})t/\hbar] . \quad (20)$$

The contribution to the diagonal elements of the density matrix from this $t = 0$ trajectory, denoted by $P_0(\underline{q}, E)$, is therefore

$$P_0(\underline{q}, E) = (2\pi \hbar)^{-1} \int_{-\infty}^{\infty} dt (2\pi i \hbar t/m)^{-\frac{N}{2}} \exp \left\{ i \left[E - V(\underline{q}) \right] t / \hbar \right\} \quad (21)$$

If the path of the t -integral is distorted infinitesimally below the real axis at $t = 0$, then one can evaluate the following integral

$$\int_{-\infty}^{\infty} dt t^{-N/2} e^{iAt} = 2\pi i (iA)^{\frac{N}{2} - 1} \Gamma\left(\frac{N}{2}\right)^{-1} \quad (22)$$

by closing the path of integration in the upper half complex t -plane.

With the integral formula of Equation (22), Equation (21) becomes

$$P_0(\underline{q}, E) = \left(\frac{2m}{4\pi\hbar^2} \right)^{N/2} \Gamma\left(\frac{N}{2}\right)^{-1} \left[E - V(\underline{q}) \right]^{N/2 - 1} \quad (23)$$

Equation (23) is the contribution to the integral over t in Equation (8) which is associated with the "zero-time trajectory"; since this contribution is identified with the $k = 0$ term in Equation (10), one sees that the sought-after function $f(\underline{q})$ which appears in Equations (10), (13), (17), (18), and (19) is precisely the function P_0 of Equation (23):

$$f(\underline{q}) = P_0(\underline{q}, E) \quad (24)$$

This is a most important relation. Another important property of the function P_0 is

$$n_s'(E) = \int d\underline{q} P_0(\underline{q}, E) \quad (25)$$

where $n_s(E)$ is the statistical quantum number function of Equation (5) of the previous section; Equation (25) is easily obtained by differentiating Equation (5) with respect to E and noting Equation (23).

With $f(\underline{q})$ now determined to be $P_0(\underline{q}, E)$ of Equation (23), one may integrate Equation (19) over coordinate space. Since the wavefunctions are normalized and in light of Equation (25), one obtains

$$1 = n_s'(E)/n_d'(E) \quad ,$$

or

$$n_s(E) = n_d(E) \quad (26)$$

to within a possible constant. This equality of the statistical and dynamical quantum number functions is the desired connection; i.e., the

two quantization conditions are identical.

In terms of the function $P_0(q, E)$ of Equation (23), the square of the wavefunction for state n is

$$|\psi_n(q)|^2 = P_0(q, E) / \int dq P_0(q, E) \quad , \quad (27)$$

with $E = E_n$. For the one-dimensional case ($N = 1$) one can readily verify that Equation (27) gives the usual classical result.

In concluding this section we again note the quite dissimilar origins of the two quantum number functions $n_s(E)$ and $n_d(E)$. Equation (2) defines $n_s(E)$ as a rather straight-forward phase space integral, which can be reduced to the configuration integral in Equation (5). Equation (16), on the other hand, defines $n_d(E)$ in terms of the action integral of Equation (11); this action integral is evaluated along one specific trajectory, namely the periodic trajectory with energy E . As has been shown, however, these two prescriptions give the same result. Equation (26) , implying the following relation between the action integral over the periodic trajectory with energy E and the volume of phase space with energy less than or equal to E :

$$h^{-1} \oint_C dq \cdot p = h^{-N} \int dq \int dp \theta[E - H(q, p)] \quad , \quad (28)$$

the closed curve C over which the line integral is taken being the periodic trajectory with energy E .

IV. CONSTANTS OF THE MOTION OTHER THAN THE ENERGY

All of the discussion so far has assumed that there were no constants of the motion other than the energy itself; in this case n is the only quantum number of the system, it being simply the "counting quantum number" that orders the states in a sequence with increasing energy. If other constants of the motion exist (e.g., total angular momentum and one of its components), the function $n(E)$ is still the total number of states less than or equal to E - but this is not the most useful quantity in this case.

Consider, for example, the system which is one particle in three dimensions in a spherically symmetric potential well, so that ℓ and m are conserved quantities. Then the function $n(E)$ is

$$n(E) = \sum_{\ell, m} n_{\ell}(E) = \sum_{\ell=0} (2\ell + 1) n_{\ell}(E) ,$$

where $n_{\ell}(E)$ is the radial quantum number; i.e., $n_{\ell}(E)$ is the number of states, all of whose angular momentum is ℓ , that lie below the value E . In situations where such conserved quantities exist, one wishes to take account of them and construct the "counting quantum number" for each subspace separately [such as $n_{\ell}(E)$], rather than the gross "counting quantum number" $n(E)$ which orders all eigenvalues irrespective of their classification according to the other "good quantum numbers".

Proceeding more generally, suppose there are L conserved quantities P_1, P_2, \dots, P_L ; the quantities P_i are functions of the coordinates and momenta $(\underline{q}, \underline{p})$ and will typically be some kind of angular momentum. One first carries out a canonical transformation to a new set of canonical

variables \tilde{Q} and \tilde{P} such that the first L of the new momenta are the conserved quantities P_i themselves. If $P_i = \hbar k_i$, $i = 1, \dots, L$ are the fixed values of the conserved quantities, then the number of states less than or equal to E with these fixed values of the conserved quantities is

$$n(E, k_1, k_2, \dots, k_L) = h^{-(N-L)} \int dQ_{L+1} \dots dQ_N \times \int dP_{L+1} \dots \int dP_N \theta [E - H(\tilde{Q}, \tilde{P})] \quad (29)$$

The coordinates Q_i , $i = 1, \dots, L$ conjugate to the conserved momenta P_i do not appear in the Hamiltonian, and the fixed values of P_i appear only as parameters in the Hamiltonian; i.e., Equation (29) is simply an example of the general Equation (2) for the reduced system of $(N-L)$ degrees of freedom.

Noting, however, that⁸

$$\int dQ_i \int dP_i \delta [P_i/\hbar - k_i] = 2\pi\hbar = h \quad ,$$

for $i = 1, \dots, L$, one may equivalently write Equation (29) as

$$n(E, k_1, \dots, k_L) = h^{-N} \int d\tilde{Q} \int d\tilde{P} \delta(P_1/\hbar - k_1) \times \dots \delta(P_L/\hbar - k_L) \theta [E - H(\tilde{Q}, \tilde{P})] \quad ,$$

and if variables of integration are changed back to the original set of canonical variables (\tilde{q}, \tilde{p}) , one obtains the final result

$$n(E, k_1, \dots, k_L) = h^{-N} \int d\tilde{q} \int d\tilde{p} \delta [P_1(\tilde{q}, \tilde{p})/\hbar - k_1] \times \dots \delta [P_L(\tilde{q}, \tilde{p})/\hbar - k_L] \theta [E - H(\tilde{q}, \tilde{p})] \quad (30)$$

The only modification of Equation (2), therefore, is that one inserts

delta functions in the integrand of the phase space integral to insure that only that region of phase space contributes for which the conserved quantities have their specified values. The inverse function of $n(E, k_1, \dots, k_L)$ gives $E_n(k_1, \dots, k_L)$, the eigenvalues of the system as a function of the quantum numbers k_i for the conserved momenta and the "counting quantum number" n which orders the eigenvalues of each subspace.

REFERENCES

- * Acknowledgement is made to the donors to the Petroleum Research Fund, administered by the American Chemical Society, and to the U.S. Atomic Energy Commission for support of this research.
- † Alfred P. Sloan Fellow.
1. W. H. Miller, J. Chem. Phys., to be published.
 2. M. G. Gutzwiller, (a) J. Math. Phys., 8, 1979 (1967); (b) *ibid.*, 10, 1004 (1969); (c) *ibid.*, 11, 1791 (1970); (d) *ibid.*, 12, 343 (1971).
 3. See, for example, K. Huang, Statistical Mechanics, Wiley, N. Y., 1963, pp. 139 et seq.
 4. See, for example, K. Denbigh, The Principles of Chemical Equilibrium, Cambridge U. P., Cambridge, 1963, pp. 385-386.
 5. R. P. Feynman and A. R. Hibbs, Quantum Mechanics and Path Integrals, McGraw-Hill, N. Y., 1965, p. 29.
 6. The fact that the periodic trajectory is uniquely determined by the energy (if there are no other constants of the motion) is discussed in reference 1.
 7. The diagonal elements of the density matrix obtained in reference 2c do not vanish for $E \neq E_n$.
 8. The variables (Q_i, P_i) , $i = 1, \dots, L$ are actually angle-action variables, so that the limits of the Q_i integral are 0 and 2π .

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720