Abstract

In this continuation paper the theory is further extended to reveal the connection between its formal apparatus, dealing with microscopic quantities, and the formal apparatus of thermodynamics, related to macroscopic properties of large systems. We will also derive the Born-Sommerfeld quantization rules from the formalism of the infinitesimal Wigner-Moyal transformations and, as a consequence of this result, we will also make a connection between the later and the path integral approach of Feynman. Some insights of the relation between quantum mechanics and equilibrium states will be given as a natural development of the interpretation of the above results.

1 Introduction

We have already deserved much of our attention to the microscopic behavior of systems described by the Schrödinger equation, which we derived from Liouville’s equation together with the classical dynamical equations\[1\] -\[10\].

It remains now to try to establish the connection between this microscopic behavior and those macroscopic, which manifest themselves when the systems comprising the ensemble have a sufficiently large number of particles.

In the second and third sections of this paper we will make the connection between the microscopic quantities, derived from the quantum formalism, and the usual thermodynamics quantities (entropy, free energy, etc.) using the canonical ensemble model.

As everybody knows, in this approach we allow the systems (S) composing the ensemble to interact with a neighborhood (O), usually called the heat bath. In such cases, the interaction is still considered sufficiently feeble as to allow one to write a hamiltonian function \(H(q,p)\) for \(S\) not depending on the degrees
of freedom of $O$. The system $O$ is necessary only as a means of imposing its temperature $T$ upon system $S$.

## 2 Equilibrium and Quantum Formalism

According to Gibbs, in a state of equilibrium we shall have a canonical probability distribution defined as

$$F(q, p) = Ce^{-2\beta H(q, p)}, \quad (1)$$

where

$$2\beta = \frac{1}{K_B T}, \quad (2)$$

with $K_B$ being the Boltzmann constant, $T$ the absolute temperature and $C$ some normalization constant.

The Hamiltonian function may be written as

$$H(q, p) = \sum_{n=1}^{N} \frac{p_n^2}{2m_n} + V(q_1, \ldots, q_N), \quad (3)$$

where we are supposing systems $S$ with $N$ degrees of freedom with potential function not depending on velocities nor time.

Using the infinitesimal Wigner-Moyal transformation

$$\rho(q - \delta q/2, q + \delta q/2) = C \int F(q, p) e^{i \sum p_n \delta q_n / \hbar} dp, \quad (4)$$

the characteristic function becomes

$$\rho(q - \delta q/2, q + \delta q/2) = C \int e^{-2\beta \sum p_n^2 / 2m_n + V(q_1, \ldots, q_N)} \cdot e^{i \sum p_n \delta q_n / \hbar} dp_1 \ldots dp_n \quad (5)$$

which gives, performing the integral,

$$\rho(q - \delta q/2, q + \delta q/2) = C_1 e^{-2\beta V(q_1, \ldots, q_N)} e^{-\sum \frac{\hbar^2 (\delta q_n)^2}{2m_n}}. \quad (6)$$

Clearly, this characteristic function is a solution to the equation

$$- \sum_{n=1}^{N} \frac{\hbar^2}{m_n} \frac{\partial^2 \rho}{\partial q_n \partial (\delta q_n)} + \sum_{n=1}^{N} \frac{\partial \rho}{\partial q_n} (\delta q_n) \rho = 0, \quad (7)$$

obtained from the Liouville equation performing the infinitesimal transformation upon it.

As was already discussed, it may be possible to write the characteristic function in the format

$$\rho(q - \delta q/2, q + \delta q/2) = \psi^\dagger(q - \delta q/2; t) \psi(q + \delta q/2; t) \quad (8)$$
to be able to derive the Schrödinger equation related with the problem for the amplitudes. In this case, it is easy to see that the amplitudes \( \psi \) may be written as

\[
\psi(q; t) = \sqrt{C_3}e^{-\beta V(q_1, \ldots, q_N)}e^{-iEt},
\]

(9)
giving, for the characteristic function\[1\]

\[
\rho(q - \delta q/2, q + \delta q/2) = C_3e^{-2\beta \left[V(q_1, \ldots, q_N) + \frac{1}{8}\sum_n (\delta q_n)^2 \frac{\partial^2 V}{\partial q_n^2}\right]},
\]

(10)
Comparing the expression (10) with (6) we observe that it is necessary to have, around the point \( q = (q_1, \ldots, q_n) \) where the function is being evaluated

\[
\left. \frac{\partial^2 V}{\partial q_n^2} \right|_{\delta q_n=0} = \frac{m_n}{\beta^2 \hbar^2}, \tag{11}
\]

if we want to write the characteristic function as in (8) with the amplitudes given in (9).

Expression (10) is equivalent to take

\[
\rho_{eq}(q) = e^{-2\beta V(q_1, \ldots, q_N)}
\]

(12)
as the probability density function for the thermodynamic equilibrium, defined upon configuration space, and express the characteristic function as

\[
\rho(q - \delta q/2, q + \delta q/2) = \rho_{eq}(q + \delta q/2) = \rho_{eq}(q - \delta q/2)
\]

(13)
if we have

\[
\left. \frac{\partial V}{\partial q_n} \right|_{\delta q_n=0} = 0 \tag{14}
\]
at the considered point. The point to which we have both (11) and (14) satisfied defines, as known, a mechanical equilibrium point for the considered physical system.

This means that the characteristic function, for this specific problem where we consider an ensemble of systems \( S \) in thermal equilibrium with a reservoir \( O \), can be considered as the probability density function when evaluated at points infinitesimally distant from the systems’ mechanical equilibrium situations.

Obviously, the density \( \rho_{eq}(q) \) is the function obtained from the characteristic function (3) taking the limit \( \delta q_n, n = 1, \ldots, N \) or, what is equivalent, performing

1As is expected, the terms having order greater than or equal to 3 in \( \delta q \) shall not be considered since this variable is considered infinitesimal. Its second power shall be maintained because of the derivative \( \partial/\partial(\delta q) \) we have in equation (2) above for the characteristic function.

2Indeed, it will be also correct to use this property to get the functional description of the probability amplitudes, as given by equation (4), this, of course, neglecting the phase factor that remains ambiguous.
the integration of the probability density function defined on phase-space \( \rho_{eq}(q) \) with respect to the variables \( p_n, n = 1, \ldots, N \). This is also consistent with the expression

\[
\rho_{eq}(q) = \psi^\dagger(q; t)\psi(q; t),
\]

as expected.

The development above furnishes a very well-defined physical interpretation for the characteristic function:

*The characteristic function is obtained from the probability density, the later being taken at infinitesimally distant points from the mechanical equilibrium situation of the system.*

This connection between the separation \( \rho_{eq}(q) \) of the characteristic function—that allows the very derivation of the Schrödinger equation—and the fact that we are dealing with systems infinitesimally near the mechanical equilibrium points, make one recall the physicists first intuitions at the beginning of this century. The above conclusions, although derived for a particular problem, gives us a first insight on the validity of the Bohr postulates as they were first formulated in the early days of quantum formalism.

We may go further and ask which Schrödinger equation is related with the amplitude \( \psi \). In this case, substituting this amplitude into the Schrödinger equation

\[
-\sum_{n=1}^{N} \frac{\hbar^2}{2m_n} \frac{\partial^2}{\partial q_n^2} + V(q_1, \ldots, q_N)\psi = E\psi,
\]

we get

\[
\sum_{n=1}^{N} \frac{\beta\hbar^2}{2m_n} \frac{\partial^2 V}{\partial q_n^2} + V(q_1, \ldots, q_N) - \sum_{n=1}^{N} \frac{\beta^2\hbar^2}{2m_n} \left( \frac{\partial V}{\partial q_n} \right)^2 = E
\]

from which we may write, using equations (11) and (14)

\[
E = V(q_1^0, \ldots, q_N^0) + N K_B T ,
\]

where \( q_n^0 \) represents the mechanical equilibrium point related with this degree of freedom. The second term on the right-hand side of equation (18) represents the energy related with the reservoir \( O \); in such case this reservoir may be interpreted as consisting of \( N \) independent harmonic oscillators, each one contributing, as prescribed by the equipartition theorem with the energy \( K_B T \).

It is interesting to note, from expression (4) for the characteristic function, seen as obtained from the density \( \rho_{eq}(q) \) that, for the cases where the absolute temperature tends to zero, any departure \( \delta q \) from zero, whatever small, gives origin to an extremely small density of states, or, as implied, it is extremely

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3See last note.

4In the next section this connection will be made clear.

5Note that we are using the Boltzmann \( \rho_{eq}(q) \) ‘classical’ distribution function, for which this result applies.
unprobable to find the systems out of this mechanical equilibrium point, for this temperature. Because of equation (18) we have

\[ E = V(q_1^0, ..., q_N^0), \]

and it is as if the reservoir does not exist.

3 Connection with Thermodynamics

As a consequence of the approach of the last section, it is possible to establish a connection between the microscopic entities of the quantum formalism and the macroscopic description given by thermodynamics.

To reach this goal we may define the free energy

\[ F_G(q_1, ..., q_N) = V(q_1, ..., q_N), \]

such that

\[ F_G = -K_B T \ln(\psi^\dagger(q)\psi(q)). \]

Expressing the entropy function as

\[ S = K_B \ln(\psi^\dagger(q)\psi(q)), \]

we find

\[ F_G = -TS. \]

Equation (22) represents the desired connection between microscopic properties, described by the probability amplitudes satisfying a Schrödinger equation, and the macroscopic behavior of the system, described by the entropy and its related functions.

4 The Bohr-Sommerfeld Rules

It seems curious, at first sight, that in equation (13) the characteristic function may be interpreted, at least in this particular case, as the probability density in configuration space taken at a point \( \delta q/2 \) apart from the equilibrium situation—and not \( \delta q \) as one might think.

Indeed, if we write

\[ \rho(q - \delta q/2, q + \delta q/2; t) = \int e^{i\frac{\hbar}{\delta q} F(q, p; t)} dp \]

and interpret \( p = -i\hbar \partial / \partial q \), then we end with the formal identification

\[ \rho(q + \delta q; t) = \int e^{\delta q \frac{\partial}{\partial q} F(q, p; t)} dp. \]
Such an approach would be, however, misleading. As was already shown \[1\]-\[10\], the function \( p \) is taken into the above cited operator only when it is acting upon the probability amplitudes and not when it is acting upon the density function, as in equation (24).

We may go to a representation of \( F(q, p; t) \), based on phase space probability amplitudes, imposing that we may write it from a function

\[
f(q, p; p'; t) = \phi^\dagger(q, 2p - p'; t)\phi(q, p'; t),
\]

such that

\[
F(q, p; t) = \int_{-\infty}^{+\infty} f(q, p; p'; t) dp' = \int_{-\infty}^{+\infty} \phi^\dagger(q, 2p - p'; t)\phi(q, p'; t) dp'.
\]

(27)

In this case, the integration in (24) becomes, using the convolution theorem, given by

\[
\rho(q - \delta q/2, q + \delta q/2; t) = T_F\{\phi^\dagger(q, p; t)\}T_F\{\phi(q, p'; t)\},
\]

(28)

where \( T_F\{\phi\} \) represents the Fourier transform of the function \( \phi \).

Now, writing

\[
\psi(q + \delta q/2; t) = T_F\{\phi(q, p; t)\} = \int e^{i\frac{\pi}{\hbar}p\delta q} \phi(q, p; t) dp,
\]

(29)

such that

\[
\psi^\dagger(q - \delta q/2; t) = T_F\{\phi(q, p; t)\} = \int e^{i\frac{\pi}{\hbar}p\delta q} \phi^\dagger(q, p; t) dp,
\]

(30)

we reach\[6\], in expression (28),

\[
\rho(q - \delta q/2, q + \delta q/2; t) = \psi^\dagger(q - \delta q/2; t)\psi(q + \delta q/2; t),
\]

(31)

as was previously \[\text{imposed}\].

The expressions (29) and (30) may be used to make the bridge between this formalism and the one proposed by Bohr and latter deepened by Sommerfeld, known as the ‘old quantum theory’.

\[6\]Note that the equations (29) and (30) are compatible with the formal identification \( p = -i\hbar\partial/\partial q \), since

\[
\psi(q + \delta q/2; t) = \int e^{i\frac{\pi}{\hbar}p\delta q} \phi(q, p; t) dp = \int \phi(q + \delta q/2, p; t) dp,
\]

giving the correct displacement we found for the density function.

\[7\]The constraint given by equations (26) and (27) is similar, therefore, to the imposition that we have done directly upon the characteristic function \[31\] in other papers.
In this case, considering expression (29), for example, we may note that it consists in an integral transformation with a nucleus given by

\[ K_{p(q)}(q + \delta q, q) = e^{i \bar{h} p(q) \delta q}. \]  

(32)

If the system is periodic—indeed independently of being a libration or a rotation [11]—then we may perform a succession of transformations taking

\[ \psi(q + Q; t) = \pm \psi(q; t), \]  

(33)

where \( Q \) is the period (in q-space) of the movement and the signal \( \pm \) takes into account the fact that we are dealing with amplitudes and not with densities, leaving the choice of the signs undefined.

The nucleus of this transformation is given by

\[ \psi(q + Q; t) = \int K_{p(q)}(q + Q, q) \phi(q, p; t) dp, \]  

(34)

such that

\[ K_{p(q)}(q + Q, q) = \lim_{N \to \infty} \prod_{n=1}^{N} K_{p(q+(n-1)\delta q)}(q + n\delta q, q + (n-1)\delta q), \]  

(35)

where we made

\[ N\delta q = Q, \]  

(36)

being necessary to take the limit \( N \to \infty \) since \( \delta q \) is infinitesimal.

Using the expression (32) for the nucleus, we may write equation (35) as

\[ \lim_{N \to \infty} K_{p(q)}(q + Q, q) = e^{i \bar{h} \sum_{n=0}^{N} p(q + n\delta q) \delta q}. \]  

(37)

The sum in the exponent above is clearly an integral taken along one period \( Q \) of the system displacement on phase-space or, mathematically,

\[ K_{p(q)}(q + Q, q) = e^{i \bar{h} \int p(q) dq}. \]  

(38)

Due to the periodicity condition (33) we shall have

\[ K_{p(q)}(q + Q, q) = \pm 1, \]  

(39)

such that

\[ \int p(q) dq = \begin{cases} 2n\pi \bar{h} = nh & \text{if } K_{p(q)}(q + Q, q) = +1 \\ 2n\pi \bar{h} + \pi \bar{h} = (n + 1/2)\hbar & \text{if } K_{p(q)}(q + Q, q) = -1 \end{cases}, \]  

(40)

\footnote{We wrote \( p(q) \) to make it clear that, in the phase space, the system follows a trajectory such that this functional identification is always possible. Indeed, considering a conservative system, we may write the hamiltonian as \( H(q,p) = \alpha \), where \( \alpha \) is a constant, and obtain \( p \) as a function of \( q \).}
implying that the choice between the quantum number \( n \) or \( n + 1/2 \) is related with the transformation properties of the amplitude with respect to a translation by its period on configuration space.

This result shows that the appearance of half-integral quantum numbers is expected even within the ‘old’ quantum theory, something that could not be predicted using the historical development of this theory.

Therefore, it explains why some systems will be described by half-integral quantum numbers associated with them (as the harmonic oscillator) and others will not (as the hydrogen atom).

The conditions (36) are precisely those of Bohr-Sommerfeld for the stability of periodic systems, as we wished to derive.

In this sense, the present section reveals the intimate connection, for periodic systems, between the ‘old’ quantum theory and that one considered ‘contemporary’, represented by the Schrödinger equation. Such a connections was indeed expected if one does not intend to consider the very similar results obtained by both theories (e.g. for the energy spectrum of the hydrogen atom) as being ‘accidental’.

The important difference between both approaches is that, while the one based on the Schrödinger equation refers to ensembles, that one based on the Bohr-Sommerfeld rules applies to each periodic system composing this ensemble and is capable of explaining these systems stability, as individual constituents of the ensemble considered.

5 Path Integrals

The approach of the last section may be slightly modified to allow us to find the relation existing between the Schrödinger formal apparatus and the one related with Feynman’s path integrals.

To attain this goal, we shall use in (29)

\[
\frac{p\delta q}{\delta t} = \frac{\delta q}{\delta t} \Delta t,
\]

where we take formally

\[
\frac{\delta q}{\delta t} = \dot{q},
\]

meaning that \( \delta q \) is being taken along a specific trajectory of the system.

\[\text{It is, indeed, related with the type of periodicity we are dealing with. If the movement is a libration it will have turning points which will introduce the extra phase } \pi/2 \text{ responsible for the } 1/2 \text{ above. If this movement is a rotation it will not have these turning points associated with it and the } 1/2 \text{ factor will be absent. In fact, if the domain of the coordinate is finite we expect the } 1/2 \text{ factor to appear while if the domain of validity of } q \text{ is infinite, this factor will not be present.}\]

\[\text{We may take the variation of a trajectory in a more general way using the expression}\]

\[
\Delta q = \delta q + \dot{q} \Delta t.
\]
We may now use
\[ \dot{q} = L(q, \dot{q}; t) - E, \]  
where \( L \) is the classical lagrangean function and \( E \) is the energy (here supposed constant) of the system considered. In this case, expression (29) becomes
\[ \psi(q(t + \delta t/2)) = \int e^{\frac{i}{\hbar}[L(q, \dot{q}; t) - E]\delta t} \phi(q, \dot{q}; t) J\left(\frac{p}{\dot{q}}\right) d(\dot{q}), \]  
where
\[ J\left(\frac{p}{\dot{q}}\right) = \frac{dp}{d\dot{q}} \]  
is the jacobian of the transformation \((q, p) \rightarrow (q, \dot{q})\).

The nucleus of the, infinitesimal in time, transformation (44) is given by
\[ K_{\dot{q}(t)}(t + \delta t, t) = \left[ \lim_{N \rightarrow \infty} \prod_{n=1}^{N} J\left(\frac{p(t_n)}{\dot{q}(t_n)}\right) e^{\frac{i}{\hbar}[L(q(t_n), \dot{q}(t_n); t) - E]\delta t} \right], \]  
such that the transformation between two times \( t_a = 0 \) and \( t_b = t \) may be written
\[ K_{\dot{q}(t)}(t_b, t_a) = \lim_{N \rightarrow \infty} \prod_{n=1}^{N} K_{\dot{q}(t+n(\delta t), t+n(\delta t))}(t + n(1)\delta t, t + (n-1)\delta t), \]  
where
\[ N\delta t = t_b - t_a, \]  
making it necessary to take the limit \( N \rightarrow \infty \), since \( \delta t \) is infinitesimal.

Regrouping the terms in (47) we may find the expression
\[ K_{\dot{q}(t)}(t_b, t_a) = \left[ \lim_{N \rightarrow \infty} \prod_{n=1}^{N} J\left(\frac{p(t_n)}{\dot{q}(t_n)}\right) \right] e^{\frac{i}{\hbar} \lim_{N \rightarrow \infty} \sum_{n=1}^{N} [L(q(t_n), \dot{q}(t_n); t) - E]\delta t}, \]  
where we put
\[ t_n = t + (n-1)\delta t, \]  
where, here, \( \delta q \) means that we take this variation between distinct trajectories. As we wish to vary the time along one trajectory, we shall make \( \delta q = 0 \) and use the expression (29)—with the necessary notational alterations. It is important to stress here that the interpretation of this more general variation is the one in which we are representing the same real trajectory on the configuration space, varying only the velocity with which the point \( q(t) \) moves along it. Using this variation, it is possible to show that
\[ \Delta \int_{t_1}^{t_2} p\dot{q} dt = \Delta \int_{q(t_1)}^{q(t_2)} p dq = 0, \]  
and is such that if the system is periodic in time and we take the integral above for only one period, we recover the results of the previous section. The last expression is known as the Least Action Principle.
and supposed that each limit exists. In the appropriate limit, we get

\[ K_{\dot{q}(t)}(t_b, t_a) = Ae^{\int L(q, \dot{q}; t) dt} e^{-\frac{\hbar}{2} E(t_b - t_a)}, \quad (51) \]

if we put

\[ A = \lim_{N \to \infty} \prod_{n=1}^{N} J \left( \frac{p(t_n)}{\dot{q}(t_n)} \right). \quad (52) \]

Now, writing

\[ S_{cl}[t_b, t_a] = \int_{t_a}^{t_b} L(q, \dot{q}; t) dt, \quad (53) \]

we finally get the desired result

\[ K_{\dot{q}(t)}(t_b, t_a) = Ae^{\frac{\hbar}{2} S_{cl}[t_b, t_a]} e^{-\frac{\hbar}{2} E(t_b - t_a)}. \quad (54) \]

This last expression or its infinitesimal equivalent \[ (56) \], is exactly the one we obtain in the path integral approach of the quantum formalism \[ [14] \]. The derivation method above has also the advantage of giving the mathematical expression of the constant \( A \), as in \[ (52) \].

This finally establishes the connection between the various methods of quantization we have studied in this paper.

6 Conclusions

In this paper we have derived many important relations of the formal apparatus of quantum mechanics. We will use this last section to make a resumé of these relations, trying to fix the relevance of each one of them within the theoretical approach proposed by ourselves since the first paper of this series.

We may begin stressing the relevance of determining the physical interpretation of the characteristic function (even for a specific example) by fixing its relation with the probability density in configuration space.

Following the derived result, and making its generalization, we can consider the quantum mechanical formalism as representing a statistical mechanics in configuration space in which one studies the dynamic behavior of physical systems which were infinitesimally dislocated from their mechanical equilibrium situation. This establishes the relation between quantum mechanics and historical equilibrium considerations, which are in the origin of the formalism. Besides, it was possible to establish the connection between the quantum formalism and thermodynamics, by means of the entropy function.

Another important achievement was the derivation of the formal connection of the quantization formalisms: one based on Schrödinger equation and the other based on the quantization rules of Bohr-Sommerfeld; with the important distinction made that the former refers to ensembles while the latter to individual systems.
Finally, it was possible to link the Schrödinger formalism with the Feynman path integral approach, fixing the interpretation of the infinitesimal parameter once more.

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