The Quantum Canonical Ensemble

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The phase space $\Gamma$ of quantum mechanics can be viewed as the complex projective space $\mathbb{CP}^n$ endowed with a Kählerian structure given by the Fubini-Study metric and an associated symplectic form. We can then interpret the Schrödinger equation as generating a Hamiltonian dynamics on $\Gamma$. Based upon the geometric structure of the quantum phase space we introduce the corresponding natural microcanonical and canonical ensembles. The resulting density matrix for the canonical $\Gamma$-ensemble differs from density matrix of the conventional approach. As an illustration, the results are applied to the case of a spin one-half particle in a heat bath with an applied magnetic field.

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I. QUANTUM PHASE SPACE

With a view to certain geometrical generalisations we reformulate the conventional quantum theory in the following manner. Consider a finite dimensional complex Hilbert space $\mathcal{H}_C^{n+1}$ with complex elements $Z^\alpha$. We identify the state vector $Z^\alpha$ with its multiples $\lambda Z^\alpha$ ($\lambda \in \mathbb{C} - \{0\}$) to obtain the complex projective space $\mathbb{CP}^n$. Here we use Greek indices ($\alpha = 0, 1, \cdots, n$) for vectors in $\mathcal{H}_C^{n+1}$, and regard $\mathbb{CP}^n$ as the true ‘state space’ of quantum mechanics. The complex conjugate of $Z^\alpha$ is written $\bar{Z}^\alpha$, with the Hermitian inner product $Z^\alpha \bar{Z}^\alpha$. We let the state vector $Z^\alpha$ represent homogeneous coordinates for $\mathbb{CP}^n$. Then, the complex conjugate of a point $P^\alpha$ in $\mathbb{CP}^n$ corresponds to the hyperplane $\bar{Z}^\alpha Z^\alpha = 0$. The points on this plane are the states orthogonal to the original state $P^\alpha$. Thus, $\mathbb{CP}^n$ is equipped with a complex conjugation operation that maps points to hyperplanes of codimension one, and vice-versa.

Distinct points $X^\alpha$ and $Y^\alpha$ are joined by a complex projective line $L^{\alpha\beta} = X^{[\alpha} Y^{\beta]}$, representing complex superpositions of the original two states. The quantum mechanical transition probability between two states $X^\alpha$ and $Y^\alpha$ is the cross ratio $\kappa = X^\alpha \bar{Y}_\alpha Y^\beta \bar{X}_\beta / X^\gamma \bar{X}_\gamma Y^\delta \bar{Y}_\delta$. If the system is in the state $Y^\alpha$ and a measurement is made with the projection operator $X^\alpha \bar{X}_\beta / X^\gamma \bar{X}_\gamma$, then $\kappa$ is the probability that the result is the eigenvalue unity. The angle $\theta$ defined by $\kappa = \cos^2(\theta/2)$ can be interpreted as the distance between the states $X^\alpha$ and $Y^\alpha$. Then if we set $\theta = ds$, $X^\alpha = Z^\alpha$, and $Y^\alpha = Z^\alpha + dZ^\alpha$, retaining terms to second order, we obtain the unitarily invariant Fubini-Study metric on the state space, given by

$$ds^2 = 8(Z^\alpha \bar{Z}_\alpha)^{-2} Z^{[\alpha} dZ^{\beta]} Z_{[\alpha} dZ_{\beta]} \quad .$$  \hfill (1)
Now suppose we write $H_\alpha^\beta$ for the Hamiltonian operator, assumed Hermitian. Then, if we set $\hbar = 1$, the Schrödinger equation reads $dZ^\alpha = iH_\alpha^\beta Z^\beta dt$. However, the projective Schrödinger equation

\[ Z^{[\alpha} dZ^{\beta]} = iZ^{[\alpha} H_\gamma^{\beta]} Z^\gamma dt , \]  

(2)

which eliminates the superfluous freedom associated with the scale of $Z^\alpha$, is defined directly on the state space.

An alternative way of viewing this structure is to regard $CP^n$ as a real manifold $\Gamma$ of dimension $2n$, equipped with a Riemannian metric $g_{ab}$ and a compatible symplectic structure $\Omega_{ab}$, satisfying $g^{ab} \Omega_{ac} \Omega_{bd} = g_{cd}$ and $\nabla_a \Omega_{bc} = 0$. We use Roman indices ($a = 1, 2, \ldots, 2n$) for tensorial operations in the tangent space of $\Gamma$. The Schrödinger equation then takes the form of a Hamiltonian flow $\xi^a = 2\Omega^{ab} \nabla_b H$ on $\Gamma$. Here the generating function $H(x)$ is given at each point $x$ in $\Gamma$ by the expectation $H_\beta^\alpha \Pi_\alpha^\beta(x)$ of the Hamiltonian operator, where $\Pi_\alpha^\beta(x) = Z^\beta \Pi_\alpha^\beta / Z^\gamma \Pi_\gamma^\beta$ is the projection operator for the point $x \in \Gamma$ represented by the state vector $Z^\alpha(x)$. Thus, in quantum mechanics the dynamical trajectories are given by a symplectic flow on the quantum phase space $\Gamma$, generated by the Hamiltonian function $H(x)$. The flow is necessarily a Killing field, satisfying

\[ \nabla_{(a} \xi_{b)} = 0 , \]  

(3)

where $\xi_a = g_{ab} \xi^b$. In other words, the isometries of the Fubini-Study metric on $\Gamma$ can be lifted to $H_{2n+1}^\mathbb{C}$ to yield unitary transformations. Conversely, given the Killing field we recover the observable function $H(x)$ on $\Gamma$, up to an additive constant, by use of the relation

\[ \Omega^{ab} \nabla_a \xi_b = 2(n+1)(H - \bar{H}) , \]  

(4)

where $\bar{H} = H_\alpha^\alpha / (n+1)$ is the average of the eigenvalues of $H_\alpha^\beta$.

**II. QUANTUM MICROCANONICAL POSTULATES**

In this paper we use the metrical symplectic geometry of the quantum phase space as the basis for a reexamination of the traditional hypotheses of quantum statistical mechanics. To this end, we observe that the quantum phase space $\Gamma$ admits a natural foliation by the $(2n-1)$-dimensional hypersurfaces $\mathcal{E}_E$ determined by level values $H(x) = E$ of the Hamiltonian function. The number of quantum mechanical microscopic configurations (pure states) with expected energy in the small range $E$ to $E + \Delta E$ is then given by $\Omega(E)\Delta E$, where the state density $\Omega(E)$ for energy $E$ is

\[ \Omega(E) = \int_{\mathcal{E}_E} \frac{\nabla_a H \sigma^a}{(\nabla_b H \nabla^b H)} . \]  

(5)

Here $d\sigma^a = g^{ab} \epsilon_{bc} \cdots d\sigma^d$ is the natural vector-valued $(2n-1)$-form on $\Gamma$. In the case of an isolated quantum mechanical system with energy in the given small range, we can adopt the notion of the microcanonical ensemble, and identify the entropy by use of the Boltzmann relation $S(E) = \ln(\Omega(E)\Delta E)$. Here, we implicitly assume what might be called the *quantum microcanonical postulate*, which asserts that for an isolated system in equilibrium all states on
a given energy surface in the quantum phase space are equally probable. As a consequence, the temperature of such a system is given by \( \beta = dS(E)/dE \), where \( \beta = 1/kT \). Thus for an isolated quantum system with expected energy \( E \) the equilibrium configuration is given by a uniform distribution on the energy surface \( \mathcal{E}_E \), with entropy \( S(E) \) and temperature \( T(E) \) as given above. The corresponding probability density function on \( \Gamma \), which we call the microcanonical \( \Gamma \)-distribution, is

\[
\mu_E(x) = \delta(H(x) - E)/\Omega(E) .
\]  

(6)

It is a straightforward exercise to verify that the state density \( \Omega(E) = \int_\Gamma \delta(H(x) - E)dV \), which appears here as a normalisation factor, is consistent with expression (5).

A general measurable function \( F(x) \) on \( \Gamma \) represents a nonlinear observable in the sense of [1,5]. We interpret \( F(x) \) as the conditional expectation \( \langle F \rangle_x \) of the observable \( F \) in the pure state \( x \). The unconditional expectation of \( F \) in the microcanonical \( \Gamma \)-ensemble is then given by

\[
\langle F \rangle_E = \int_\Gamma F(x)\mu_E(x)dV .
\]  

(7)

Providing we only consider linear observables, the state is fully characterised by \( \mu_\beta^\alpha(E) \). Now suppose \( W(E) \) denotes the total phase space volume for states such that \( H(x) \leq E \). Then the density matrix \( \mu_\beta^\alpha(E) \) can be calculated explicitly by use of the formula

\[
\mu_\beta^\alpha(E) = \left( \frac{\partial W(E)}{\partial H} \right)^{-1} \frac{\partial W(E)}{\partial H^\beta} .
\]  

(8)

III. CANONICAL \( \Gamma \)-ENSEMBLE

Next, we motivate a construction for the corresponding canonical ensemble, representing the situation where a quantum mechanical system is in contact with a heat bath at a fixed temperature. The results we obtain are related to those that follow from the conventional density matrix for the canonical state, though differ in certain essential respects. First we note that the projection operator \( \Pi_\alpha^\beta(y) \), for a given state \( y \), can itself be thought of as the density matrix corresponding to a mass distribution \( \delta_y(x) \) on \( \Gamma \), concentrated at the point \( y \). Therefore, we can write \( \Pi_\alpha^\beta(y) = \int_\Gamma \Pi_\beta^\alpha(x)\delta_y(x)dV \). Then the conventional density matrix of quantum statistical mechanics, which we denote \( r_\alpha^\beta \), is determined by a point mass distribution with density

\[
r(x) = Z(\beta)^{-1} \sum_k e^{-\beta E_k}\delta_{y_k}(x)
\]  

(9)

on \( \Gamma \), concentrated at the energy eigenstates \( y_k \), with \( E_k \) being the corresponding eigenvalues and \( Z(\beta) = \sum_k e^{-\beta E_k} \) the associated partition function. Hence, for the conventional density matrix we have
\[ r_\beta^\alpha = Z(\beta)^{-1} \sum_k e^{-\beta E_k} \Pi_\beta^\alpha(y_k) . \] (10)

It should be evident that, despite its general usefulness and wide acceptance as a fundamental basis for quantum statistical mechanics, the conventional density matrix \( r_\beta^\alpha \) is in some respects unnatural in the absence of some mechanism forcing the system to energy eigenstates, since its phase space distribution is characterised by \( \delta_{y_k}(x) \). Thus we are led to consider an alternative expression, suggested by the geometry of \( \Gamma \), in which we do not assume a concentration on eigenstates.

Consider two systems I and II and let them make contact to form a combined system I+II. We suppose that the systems only interact weakly, so the support of the resulting state on the quantum phase space \( \Gamma_{1+2} \) of the combined system is concentrated on the product \( \Gamma_{1,2} \subset \Gamma_{1+2} \) of the phase spaces \( \Gamma_1 \) and \( \Gamma_2 \) for the systems I and II. We have in mind the situation where system I represents a heat bath with a given inverse temperature \( \beta \), while II represents a small system immersed in the bath. We wish to calculate the probability density \( p(E_2) \) that system II lies on the energy surface \( \mathcal{E}_{E_2} \) in \( \Gamma_2 \), conditional on the total energy of the combined system I+II lying in the small range \( E \) to \( E + \Delta E \). Now, according to the quantum microcanonical hypothesis, the equilibrium distribution over the energy surface \( \mathcal{E}_E \) in \( \Gamma_{1,2} \) is uniform. Therefore, conditional on a given value \( E \) for the combined system I+II, the joint probability density function \( p_E(E_1, E_2) \) for system I to lie on \( \mathcal{E}_{E_1} \) in \( \Gamma_1 \) and for system II to lie on \( \mathcal{E}_{E_2} \) in \( \Gamma_2 \) is

\[
p_E(E_1, E_2) = \frac{\delta(E - E_1 - E_2)\Omega_1(E_1)\Omega_2(E_2)}{\Omega_{1,2}(E)} . \] (11)

Here, \( \Omega_1(E_1) \) and \( \Omega_2(E_2) \) are the state densities for the energy surfaces \( \mathcal{E}_{E_1} \) in \( \Gamma_1 \) and \( \mathcal{E}_{E_2} \) in \( \Gamma_2 \), and the state density \( \Omega_{1,2}(E) \) for the energy surface \( \mathcal{E}_E \) in \( \Gamma_{1,2} \) is

\[
\Omega_{1,2}(E) = \int_{-\infty}^{\infty} \Omega_1(E - \epsilon)\Omega_2(\epsilon)d\epsilon . \] (12)

Our goal is to calculate the conditional probability density for system II to have energy \( E_2 \). This is given by \( p(E_2) = \int_{-\infty}^{\infty} p_E(E_1, E_2)dE_1 \), which implies

\[
p(E_2) = \frac{\Omega_1(E - E_2)\Omega_2(E_2)}{\Omega_{1,2}(E)} . \] (13)

Since system I, the heat bath, is in equilibrium, by the microcanonical hypothesis it has entropy \( S_1(E_1) = \ln(\Omega_1(E_1)\Delta E) \), and hence temperature \( \beta(E_1) = \partial S_1/\partial E_1 \). If \( E_2 \ll E \), then to first order in \( E_2 \) we have \( \Omega_1(E - E_2) = \Omega_1(E)e^{-\beta E_2} \), where \( \beta(E_1) \) is the inverse temperature of the heat bath. As a consequence we deduce that the probability density \( p(E_2) \) for system II to lie on the energy surface \( \mathcal{E}_{E_2} \) in \( \Gamma_2 \) is given by \( p(E_2) = \Omega_2(E_2)e^{\beta E_2}/\int_{-\infty}^{\infty} \Omega_2(\epsilon)e^{\beta \epsilon}d\epsilon \). More succinctly, now we drop the subscript 2, and regard the conditioning as implicit in the specification of the parameter \( \beta \). Then for the probability density of the energy distribution on \( \Gamma \) we have

\[
p(\epsilon) = \frac{\Omega(\epsilon)\exp(-\beta \epsilon)}{Z(\beta)} , \] (14)
where $\Omega(\epsilon)$ is the state density on $\Gamma$ per unit of energy and $Z(\beta) = \int_{-\infty}^{\infty} \Omega(\epsilon) \exp(-\beta \epsilon) d\epsilon$ is the partition function. By the quantum canonical postulate we mean the assumption that a small quantum system in equilibrium with a heat bath will be in a state characterised by a distribution over the energy surfaces of $\Gamma$ with density (14), having a uniform distribution on each such surface. The corresponding probability density function $\rho_\beta(x)$ on $\Gamma$ is

$$\rho_\beta(x) = \frac{\exp(-\beta H(x))}{Z(\beta)}, \quad (15)$$

which we call the canonical $\Gamma$-distribution. Alternatively, we can write $\rho_\beta(x) = \int p(\epsilon)\mu_\epsilon(x) d\epsilon$, expressing $\rho_\beta(x)$ as a weighted average of microcanonical ensembles, where $p(\epsilon)$ is given as in (14). The associated density matrix for the canonical $\Gamma$-distribution is therefore

$$\rho_{\alpha\beta}(T) = \int_\Gamma \Pi_{\alpha\beta}^\alpha(x)\rho_\beta(x)dV. \quad (16)$$

IV. TWO-STATE SYSTEM

To illustrate how the consequences of the canonical $\Gamma$-distribution (15) differ from those of the conventional treatment in terms of the density matrix $r_{\alpha\beta}$, we study the example of a spin one-half particle in a heat bath. First we review briefly the geometry of the Schrödinger dynamics for a spin one-half particle. The quantum phase space in this case is $\mathbb{C}P^1$, which can be viewed as a sphere $S^2$. The poles of the sphere correspond to the energy eigenstates, with eigenvalues $E_0 = -\hbar$ and $E_1 = \hbar$, and the Schrödinger trajectories are generated by a rigid rotation of the sphere about the axis through the poles, the two stationary points. This rotation gives rise to a Killing field on the sphere, where the angular velocity is $2\hbar$, the energy difference between the poles. Thus the Schrödinger evolution generates a latitudinal circle. Now we introduce a complex Hilbert space with coordinates $Z^\alpha (\alpha = 0, 1)$ which we regard as homogeneous coordinates for $\mathbb{C}P^1$. The complex conjugate of $Z^\alpha$ is the ‘plane’ $\bar{Z}^\alpha$ in $\mathbb{C}P^1$, which in this dimension is a point. The point corresponding to $\bar{Z}^\alpha$ is $\bar{Z}^\alpha = \epsilon^{\alpha\beta} Z_\beta$, where $\epsilon^{\alpha\beta}$ is the natural symplectic form on the two-dimensional Hilbert space. The formalism in this case is equivalent to the algebra of two-component spinors. By use of the spinor identity $2X^{[\alpha} Y^{\beta]} = \epsilon^{\alpha\beta} X^\gamma Y^\gamma$, where $X^\alpha \epsilon_{\alpha\beta} = X_\beta$, we obtain $ds^2 = 4Z_\alpha dZ^\alpha \bar{Z}_\beta d\bar{Z}^\beta/\bar{(\bar{Z}_\gamma Z^\gamma)}^2$ for the Fubini-Study metric, and $Z_\gamma dZ^\gamma = iH_{\alpha\beta} Z^\alpha Z^\beta dt$ for the projective Schrödinger equation. The Hamiltonian has the representation

$$H_{\alpha\beta} = 2\hbar \frac{P_{(\alpha} \bar{P}_{\beta)}}{P^\gamma P^\gamma}, \quad (17)$$

where $P^\alpha$ and $\bar{P}^\alpha$ are the stationary points, satisfying $H_{\beta\alpha} P^\beta = \hbar P^\alpha$ and $H_{\beta\alpha} \bar{P}^\beta = -\hbar \bar{P}^\alpha$. It follows that the velocity of the trajectory through $\Gamma$ is

$$\frac{ds}{dt} = 2\hbar \sin \theta, \quad (18)$$

a special case of the Anandan-Aharonov relation [4]. Here, $\theta$ is the distance from $Z^\alpha$ to $P^\alpha$, given by the angular coordinate measured down from the north pole. The transition
probability from $Z^\alpha$ to the north pole $P^\alpha$ is $(1 + \cos \theta)/2$, and for the evolutionary trajectory we obtain

\[ Z^\alpha = \cos(\theta/2)e^{i(ht+\phi)}P^\alpha + \sin(\theta/2)e^{-i(ht+\phi)}\bar{P}^\alpha, \tag{19} \]

where $\theta$ and $\phi$ are the initial coordinates on the sphere for the state at $t = 0$. The vector $Z^\alpha$ is normalised by setting $P^\alpha \bar{P}_\alpha = -\bar{P}_\alpha P^\alpha = 1$. The expectation $E$ of the energy for this state is $E = \hbar \cos \theta$, and its variance is $\hbar^2 \sin^2 \theta$.

With this in mind we now examine the situation where the spin one-half particle is immersed in a heat bath. The conventional density matrix $r^\alpha_\beta(T)$ for the system in this case can be expressed as a superposition of projection operators onto energy eigenstates, with Boltzmann weights:

\[ r^\alpha_\beta = \frac{-e^{-\beta E_0}\bar{P}^\alpha P_\beta + e^{-\beta E_1}P^\alpha \bar{P}_\beta}{e^{-\beta E_0} + e^{-\beta E_1}}. \tag{20} \]

This can also be written $r^\alpha_\beta = Z^{-1}\exp(-\beta H^\alpha_\beta)$. The fact that $r^\alpha_\beta$ has trace unity follows from the normalisation condition. For the expected energy $H^\alpha_\beta r^\beta_\alpha$ we then obtain $E = -\hbar \tanh(\beta \hbar)$.

Next we apply the canonical $\Gamma$-distribution to this problem. For this ensemble the probability distribution of the energy in the spin one-half case is

\[ p(E)dE = -2\pi Z(\beta)^{-1} \sin \theta \exp(-\beta h \cos \theta)d\theta, \tag{21} \]

where $E = \hbar \cos \theta$. The normalisation condition on the density function $p(E)$ implies $Z(\beta) = 4\pi(\beta \hbar)^{-1}\sinh(\beta \hbar)$, from which the expected energy $E = -\partial \ln Z/\partial \beta$ can be deduced. The result is $E = kT - \mu B \coth(\mu B/kT)$. Here we have reinstated Boltzmann’s constant $k$, the particle’s magnetic moment $\mu$, and the external magnetic field strength $B$, with $\hbar = \mu B$. The behaviour of the energy for the cases considered above is sketched in Fig. 1. It is clear that the increase in magnetisation, when the temperature decreases, is slower in the canonical $\Gamma$-distribution than for the conventional ensemble. This is because the latitudinal circles closer to the equator have larger weights than those closer to the poles. In Fig. 2 we plot the relationship between the specific heat and the temperature.

We note that in the case of the canonical $\Gamma$-ensemble the heat capacity for this system is nonvanishing at zero temperature. For many bulk substances, on the other hand, the heat capacity vanishes as zero temperature is approached. Therefore, it would be interesting to enquire if a single electron has a different behaviour. To that end, we note that in the case of a general two state system, with energy eigenvalues $E_0$ and $E_1$, the density matrix of the canonical $\Gamma$-distribution, in the basis of energy eigenstates, is

\[ \rho^\alpha_\beta = -\left[ \frac{1}{\beta(E_0 - E_1)} + \frac{1}{1 - e^{-\beta(E_1 - E_0)}} \right] \bar{P}^\alpha P_\beta + \left[ \frac{1}{\beta(E_1 - E_0)} + \frac{1}{1 - e^{-\beta(E_0 - E_1)}} \right] P^\alpha \bar{P}_\beta. \tag{22} \]

This expression can be contrasted with the conventional result for such a system, given in formula (20). In fact it is not difficult to obtain analogous expressions in higher dimensions, some of which may characterise other systems that can be implemented in experiments to determine whether the $\Gamma$-distribution introduced here provides a better account of phenomena in certain situations.
V. DISCUSSION

The foregoing constructions are based on the quantum microcanonical postulate, which for an isolated system in equilibrium implies a uniform distribution over any energy surface of the quantum phase space. We therefore enquire whether this postulate can be derived from the basic principles of quantum mechanics. This would follow, e.g., if quantum dynamics were ergodic on the energy surfaces $\mathcal{E}_E$. In the example of the spin one-half particle, ergodicity is indeed guaranteed by the periodicity of the Schrödinger evolution and the dimensionality of the energy surface.

In higher dimensions, the generic energy surface $\mathcal{E}_E$ is parameterised by $(n-1)$ angular parameters and $n$ phase variables. For each fixed set of angular variables we obtain an $n$-torus $T^n$ in $\mathcal{E}_E$, and by varying the angular parameters the energy surface is foliated by an $(n-1)$-dimensional family of such tori. If we assume that the Hamiltonian is nondegenerate, and that the ratios $E_i/E_j$ ($i \neq j$) of the energy eigenvalues are irrational, then the Schrödinger evolution is nonperiodic on each $T^n$. As a result, ergodicity is guaranteed on the toroidal energy subsurfaces. On the other hand, unitary evolution does not change the angular parameters on $\mathcal{E}_E$. It follows that the energy surfaces are not fully ergodic with respect to the Schrödinger equation, and that we cannot deduce the microcanonical postulate directly from the principles of quantum mechanics. It would be interesting to see if this postulate could be derived as a consequence of a suitable generalisation of ordinary quantum mechanics, e.g., nonlinear or stochastic quantum dynamics.

To summarise, we have formulated quantum mechanical analogues of the microcanonical and canonical ensembles by consideration of the geometry of the quantum phase space. In particular, a key distinction in our proposal is that phase space weightings are fully taken into account in the construction of equilibrium ensembles, whereas in the conventional approach such weights arise only in the event of energy eigenvalue degeneracies. We are thus able to give a coherent meaning to the quantum microcanonical ensemble, and derive an expression for the corresponding density matrix, a construction that is missing in the conventional theory. It may be that for bulk substances there is a further component to the dynamics, perhaps due to internal interactions at low temperature, that forces the quantum phase space to contract down to the lattice of energy eigenstates, with appropriate multiplicities. In that case we recover the conventional theory. It would be interesting to determine, by suitable measurements on quantum mechanical systems, whether the ensembles introduced here are indeed appropriate.

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