

Chapter 4

Quantum Statistics

Recall the (pure) states of a quantum system are described by vectors in Hilbert space, $|\phi\rangle$, and corresponding dual vectors, $\langle\phi|$. The inner product $\langle\phi|\psi\rangle$ satisfies

$$\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^*. \quad (4.1)$$

A state vector is a unit vector, a vector of unit norm,

$$\langle\phi|\phi\rangle = 1. \quad (4.2)$$

Physically, $\langle\phi|\psi\rangle$ represents a probability amplitude: That is, $|\langle\phi|\psi\rangle|^2$ is the probability of finding the system in the state $|\phi\rangle$ given that it was previously determined to be in (prepared in) the state $|\psi\rangle$. Suppose we introduce an orthonormal *basis* set $\{|j\rangle\}$:

$$\langle j|k\rangle = \delta_{jk}. \quad (4.3)$$

Such a set is *complete*. If $|\psi\rangle$ is any vector,

$$|\psi\rangle = \sum_j c_j |j\rangle, \quad c_j = \langle j|\psi\rangle. \quad (4.4)$$

That is,

$$|\psi\rangle = \sum_j |j\rangle \langle j|\psi\rangle, \quad (4.5)$$

or, since this is true for any state,

$$\sum_j |j\rangle \langle j| = 1. \quad (4.6)$$

The probability of finding the system in the state $|j\rangle$ is

$$P_j = |c_j|^2 = |\langle j|\psi\rangle|^2 = \langle j|\psi\rangle \langle\psi|j\rangle, \quad (4.7)$$

or if we define a “density operator” for the pure state $|\psi\rangle$ by

$$\rho = |\psi\rangle \langle\psi|, \quad (4.8)$$

the probability is

$$P_j = \langle j | \rho | j \rangle. \quad (4.9)$$

Note that ρ has the following properties:

$$\text{Tr } \rho = \langle | \rangle = 1, \quad (4.10)$$

$$\rho^2 = | \rangle \langle | \rangle \langle | \rangle = | \rangle \langle | \rangle = \rho. \quad (4.11)$$

Physical properties or “observables” are represented by linear operators, A , which carries a vector $|\phi\rangle$ to another vector $A|\phi\rangle$. The dual of this vector is $\langle\phi|A^\dagger$, where A^\dagger is the adjoint or Hermitian conjugate of A . A physical property is represented by a self-adjoint operator: $A = A^\dagger$. Eigenvectors of A represent states in which A assumes a definite value, its eigenvalue:

$$A|a'\rangle = a'|a'\rangle, \quad \langle a'|A = (a')^*\langle a'|, \quad (4.12)$$

where we’ve used the eigenvalue to label the vector. Note that for a self-adjoint operator

$$\langle a''|A|a'\rangle = a'\langle a''|a'\rangle = \langle a'|A|a''\rangle^* = (a'')^*\langle a''|a'\rangle, \quad (4.13)$$

from which conclude

1. If $a'' = a'$, $a' = (a')^*$, that is, the eigenvalues must all be real.
2. If $a' \neq a''$, $\langle a''|a'\rangle = 0$, which means that eigenvectors belonging to distinct eigenvalues are orthogonal.

The *expectation value* of A in a state $| \rangle$ is

$$\begin{aligned} \langle A \rangle &= \langle |A| \rangle = \sum_j \langle |j\rangle \langle j|A| \rangle \\ &= \sum_j \langle j|A| \rangle \langle |j\rangle = \sum_j \langle j|A\rho|j\rangle, \end{aligned} \quad (4.14)$$

or

$$\langle A \rangle = \text{Tr } A\rho = \text{Tr } \rho A. \quad (4.15)$$

Up to this point, we have been thinking of *pure states*. More generally, quantum systems will be found in *mixed states*. That is, we know only the probability p_n of finding the system in some pure state $|n\rangle$, described by the density operator

$$\rho = \sum_n |n\rangle p_n \langle n|, \quad (4.16)$$

where $\{|n\rangle\}$ is some complete set of states, and

$$\sum_n p_n = 1, \quad 1 \geq p_n \geq 0. \quad (4.17)$$

Now

$$\text{Tr } \rho = \sum_n \langle n|n\rangle p_n = 1, \quad (4.18)$$

as before, but now

$$\rho^2 = \sum_{n,n'} |n\rangle p_n \langle n|n'\rangle p_{n'} \langle n'| = \sum_n |n\rangle p_n^2 \langle n|, \quad (4.19)$$

so

$$\text{Tr } \rho^2 = \sum_n p_n^2 \leq 1, \quad (4.20)$$

where the trace of ρ^2 is one only if $p_n = 1$ for some n and zero otherwise. Thus,

$$\text{Tr } \rho^2 = 1 \quad (4.21)$$

characterizes a pure state.

Now let's consider the expectation value of some physical observable A in a mixed state:

$$\langle A \rangle = \sum_n p_n \langle n|A|n \rangle = \text{Tr} \sum_n |n\rangle p_n \langle n|A = \text{Tr } \rho A. \quad (4.22)$$

The trace is independent of basis. Indeed, such a new basis is related to the old by a unitary transformation,

$$|j\rangle = U|j\rangle, \quad \langle j| = \langle j|U^\dagger, \quad (4.23)$$

where $U^\dagger = U^{-1}$. Therefore, in the new basis,

$$\begin{aligned} \langle A \rangle &= \sum_j \langle j|\rho A|j\rangle = \sum_j \langle j|U^{-1}\rho AU|j\rangle \\ &= \text{Tr}(U^{-1}\rho AU) = \text{Tr}\rho AUU^{-1} \\ &= \text{Tr}\rho A = \langle A \rangle. \end{aligned} \quad (4.24)$$

Recall, classically, we had Liouville's theorem for the phase-space distribution:

$$\frac{d\rho}{dt} = 0 = \frac{\partial \rho}{\partial t} + \{\rho, H\}, \quad (4.25)$$

in terms of the Poisson bracket. What happens for the quantum density operator? Recall, in the Schrödinger picture, the time evolution of states is given by the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t}|t\rangle = H|t\rangle. \quad (4.26)$$

The density operator

$$\rho(t) = \sum_n p_n |n, t\rangle \langle n, t| \quad (4.27)$$

then satisfies

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \rho(t) &= \sum_n p_n H|n, t\rangle \langle n, t| - \sum_n p_n |n, t\rangle \langle n, t| H \\ &= [H, \rho], \end{aligned} \quad (4.28)$$

in terms of the commutator,

$$[A, B] \equiv AB - BA. \quad (4.29)$$

Therefore the quantum-mechanical Liouville equation is

$$\frac{\partial}{\partial t}\rho(t) + \frac{1}{i\hbar}[\rho, H] = 0. \quad (4.30)$$

Note that upon comparison with Eq. (4.25) we have the correspondence principle relation:

$$\frac{1}{i\hbar}[\ , \] \rightarrow \{ \ , \ }. \quad (4.31)$$

We will usually be interested in stationary distributions, for which

$$\frac{\partial}{\partial t}\rho(t) = 0 \Rightarrow [\rho, H] = 0. \quad (4.32)$$

Suppose the observable $A = A(q_i, p_i)$ is not *explicitly* time dependent. Then, for a stationary distribution

$$0 = \frac{d}{dt}\langle A \rangle = \text{Tr} \left(A \frac{\partial}{\partial t} \rho \right) = -\frac{1}{i\hbar} \text{Tr} ([\rho, H]A) \quad (4.33)$$

in the Schrödinger picture. This must be true for all A , in particular for $A = |j\rangle\langle k|$, so we conclude that $[\rho, H] = 0$.

This result will also be true in the Heisenberg picture, where states are time independent, but operators move. The two pictures are related by a unitary transformation,

$$A_H(t) = U^{-1}(t)A_S U(t), \quad | \rangle_H = U^{-1}(t)|t\rangle_S, \quad (4.34)$$

where the unitary time evolutionary operator satisfies

$$i\hbar \frac{d}{dt}U(t) = H_S U(t) = U(t)H_H. \quad (4.35)$$

The Heisenberg picture Hamiltonian is time independent,

$$i\hbar \frac{d}{dt}H_H = [H_H, H_H] = 0, \quad (4.36)$$

whereas the other observables satisfy

$$i\hbar \frac{d}{dt}A_H = [A_H, H_H]. \quad (4.37)$$

The density operator depends on time in the Schrödinger picture, so it satisfies in the Heisenberg picture

$$\begin{aligned} i\hbar \frac{d}{dt}\rho_H &= [\rho_H, H_H] + U^{-1} \left(i\hbar \frac{\partial}{\partial t} \rho_S \right) U \\ &= [\rho_H, H_H] - U^{-1}[\rho_S, H_S]U = [\rho_H, H_H] - [\rho_h, H_H] = 0, \end{aligned} \quad (4.38)$$

as must be.

In the Heisenberg picture

$$\begin{aligned} 0 &= \frac{d}{dt}\langle A \rangle = \text{Tr} \rho \frac{d}{dt} A \\ &= \frac{1}{i\hbar} \text{Tr} \rho [A, H] = \frac{1}{i\hbar} \text{Tr} [H, \rho] A, \end{aligned} \quad (4.39)$$

so again we conclude that

$$[\rho, H] = 0. \quad (4.40)$$

This says, once again, that ρ is a constant of the motion, and the only reasonable choice, if translational or rotational invariance is not present, is

$$\rho = \rho(H). \quad (4.41)$$

Thus in the basis in which the energy is diagonal,

$$\rho(H) = \sum_{l,k} p(E_l) |E_l, k\rangle \langle E_l, k|, \quad (4.42)$$

where $p(E_l) = \rho(E_l)$ and k labels quantum numbers other than the energy.