2 Density matrix

2.1 Statistical ensembles

In most real situations, even in most experiments, the microscopic state of physical system cannot be fully defined in all aspects, rather a limited set of macroscopic quantities (such as the temperature) is controlled. Macroscopic characterizations are consistent with many microstates and it is the topic of statistical physics to build up their connection. The statistical description of physical system means to switch from uniquely determined (micro)states of mechanical system to ensemble (set) of states, of which each member ε is assigned probability weight $w_\varepsilon \geq 0$ (obeying $\sum_\varepsilon w_\varepsilon = 1$). Experimental results are then postulated to be related to the average (mean) value $\langle\rangle$ of the observable f in statistical ensemble defined as[5]

$$\langle f \rangle \equiv \sum_\varepsilon w_\varepsilon f_\varepsilon. \tag{17}$$

The reader should be reminded that several important ensembles have been specified in the elementary course of classical statistical physics. In equilibrium the weights w_ε are derived from the energy ϵ_ε of the member ε. The *microcanonical ensemble* is defined by the uniform distribution

$$w_\varepsilon \propto \delta(E - \epsilon_\varepsilon) \tag{18}$$

over the equally-sized cells ε of phase space on the energy shell E and serves as a model for isolated systems. Similarly, the thermostatted systems (at temperature T) are represented by Boltzmann weights

$$w_\varepsilon \propto e^{-\beta\epsilon_\varepsilon}, \qquad \beta \equiv 1/(k_B T) \tag{19}$$

of the *canonical ensemble*. Finally, open systems exchanging particles with a reservoir correspond to the *grand canonical ensemble* and the weights

$$w_\varepsilon \propto e^{\beta\bar{\mu}N_\varepsilon - \beta\epsilon_\varepsilon} \tag{20}$$

represent the modulation of the variable number of particles N_ε in microstate ε by the chemical potential $\bar{\mu}$. A subtle analysis of the Gibbs

[5]The use of $\sum$ symbol in Eq. (17) silently assumes that the set $\{\varepsilon\}$ can be indexed by integers, i.e. it is countable. This convenient assumption can be relaxed for more general mathematical structures delimited by axiomatization worked out in Appendix. A great result of the next section 2.2 leaves such extensions insignificant as countable quantum ensembles with equivalent experimental expectations can always be constructed along Eq. (28), see discussion below Eq. (25) and footnote 61 in Appendix.

paradox suggests correction factor $1/N_\varepsilon!$ to Eq. (20) when the classical particles are declared indistinguishable. This discussion will be postponed to Eq. (94) where the Gibbs paradox is resolved in an elegant way within the quantum framework of many-particle states.

2.2 Statistical operator

In quantum mechanics the microscopic states are represented by wave functions. The quantum statistical ensemble is thus a set of wave functions $|\psi_\varepsilon\rangle$ (normalized $\langle\psi_\varepsilon|\psi_\varepsilon\rangle = 1$) with probability weights w_ε. System of wave functions $\{\varepsilon\}$ can be very large, but it is effectively simplified when the two layers of probability (the classical weights w and the rules for quantum meaurement) are combined into an object directly related to probabilities of (usually smaller system of) measurement outcomes.

The probability of finding certain discrete outcome a of the quantity $\hat{A}$ in quantum measurement is proportional to the square of the wave function projection $P(a) \equiv |\langle\psi_\varepsilon|\phi_a\rangle|^2$ (on the normalized function $|\phi_a\rangle$ representing the result a). In the statistical ensemble we have

$$\langle P(a)\rangle = \sum_\varepsilon w_\varepsilon |\langle\psi_\varepsilon|\phi_a\rangle|^2 = \sum_\varepsilon w_\varepsilon \langle\psi_\varepsilon|\phi_a\rangle\langle\phi_a|\psi_\varepsilon\rangle = \sum_\varepsilon w_\varepsilon \langle\psi_\varepsilon|\hat{D}_a|\psi_\varepsilon\rangle$$

where the projector $\hat{D}_a \equiv |\phi_a\rangle\langle\phi_a|$ is introduced to represent the outcome a. Similarly, for the mean expectation value of general observable A we have

$$\langle A\rangle = \sum_a a\langle P(a)\rangle = \sum_{a,\varepsilon} a w_\varepsilon \langle\psi_\varepsilon|\hat{D}_a|\psi_\varepsilon\rangle = \sum_\varepsilon w_\varepsilon \langle\psi_\varepsilon|\hat{A}|\psi_\varepsilon\rangle,$$

since $\hat{A} = \sum_a a\hat{D}_a$. The way to an efficient representation of a quantum statistical ensemble becomes obvious after we use the properties of tracing

$$\begin{aligned}\langle P(a)\rangle = \sum_\varepsilon w_\varepsilon \langle\psi_\varepsilon|\hat{D}_a|\psi_\varepsilon\rangle &= \sum_\varepsilon w_\varepsilon \mathrm{Tr}|\psi_\varepsilon\rangle\langle\psi_\varepsilon|\hat{D}_a \\ &= \mathrm{Tr}\{\hat{D}_a \sum_\varepsilon w_\varepsilon |\psi_\varepsilon\rangle\langle\psi_\varepsilon|\} \qquad (21)\end{aligned}$$

or, in complete analogy

$$\langle A\rangle = \sum_\varepsilon w_\varepsilon \langle\psi_\varepsilon|\hat{A}|\psi_\varepsilon\rangle = \sum_\varepsilon w_\varepsilon \mathrm{Tr}|\psi_\varepsilon\rangle\langle\psi_\varepsilon|\hat{A} = \mathrm{Tr}\{\hat{A}\sum_\varepsilon w_\varepsilon|\psi_\varepsilon\rangle\langle\psi_\varepsilon|\}.$$

The outcomes of measurement on a quantum statistical ensemble are thus well-represented by an object

$$\hat{\rho} \equiv \sum_{\varepsilon} w_\varepsilon |\psi_\varepsilon\rangle\langle\psi_\varepsilon| \tag{22}$$

quadratic in wave functions $|\psi_\varepsilon\rangle$, which is called a *statistical operator*, or somewhat colloquially when in operator notation, but quite commonly a *density matrix*.

The postulates of quantum theory thus prescribe the probability

$$\langle P(a)\rangle = \mathrm{Tr}\ \hat{D}_a\hat{\rho} \tag{23}$$

for measuring the value a in a quantum statistical ensemble. Similarly, the observable A has mean value

$$\langle A\rangle = \mathrm{Tr}\ \hat{A}\hat{\rho}.$$

Example: In the standard σ_z representation of spin, let the z-spin polarizations $|\uparrow\rangle = (1,0)^T$ and $|\downarrow\rangle = (0,1)^T$ occur with probabilities $w_\uparrow$ and $w_\downarrow$, respectively. The density matrix is

$$\hat{\rho} = \begin{pmatrix} w_\uparrow & 0 \\ 0 & w_\downarrow \end{pmatrix}. \tag{24}$$

Similarly, if the ensemble is composed from x-polarized states $|\uparrow_x\rangle = (1,1)^T/\sqrt{2}$ and $|\downarrow_x\rangle = (-1,1)^T/\sqrt{2}$ with probabilities $w_{\uparrow_x}, w_{\downarrow_x}$ the density matrix reads

$$\hat{\rho} = \frac{w_{\uparrow_x}}{2}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} + \frac{w_{\downarrow_x}}{2}\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & w_{\uparrow_x} - w_{\downarrow_x} \\ w_{\uparrow_x} - w_{\downarrow_x} & 1 \end{pmatrix}. \tag{25}$$

In the previous example, setting $w_\uparrow = w_\downarrow = 1/2$ (in Eq. (24)) and similarly $w_{\uparrow_x} = w_{\downarrow_x} = 1/2$ in Eq. (25) yields the same (unit) density matrix $\hat{\rho} = \hat{1}/2$ representing the nonpolarized spin statistics. Obviously, the quantum statistical ensemble (i.e. the values w, and the states $|\psi\rangle$) cannot be unambiguously reconstructed from the density matrix. Still, all statistical ensembles sharing the same density matrix have also the same expectations for any future measurement; in this (observatory) sense the density matrix represents unambiguously the predictions of future measurements within our understanding of quantum mechanics.

The central tenet of the density matrix concept is that we work in the same probabilistic way with uncertainties basing the statistical ensemble and with the inherent unpredictability of quantum measurements. This way the costly construction of probabilistic measure[6] (261) over the

[6] Stochastic process (see Appendix) is an adequate framework for unabridged definition of quantum ensemble.