

Appendix B. Review of the density matrix

B.1. The density matrix in the coordinate representation

If a system is completely isolated then we can, in principle, given the Hamiltonian, solve the Schroedinger equation to find the eigen functions and energy levels. This is the most complete description we can have in quantum mechanics.

However in many applications it is of interest to have a way to describe “subsystems”, which are part of (and coupled to) a larger system, or

alternatively involve a smaller set of coordinates. Our knowledge of the system is then less than that needed for a complete quantum mechanical description.

To discuss such problems we will start by assuming we have the wavefunction for the *entire* system, which we write as

$$\Psi = \Psi(x,y,t). \quad (\text{B.1})$$

Here x stands for the coordinates of the subsystem, $x_1, x_2 \dots$, and y has all the remaining coordinates, $y_1, y_2 \dots$, the combination x, y then describing the total system.

Suppose we have an operator \hat{f} which acts *only* on the coordinates of the subsystem,¹ x . We may then write its expectation value as

$$\bar{f}(t) = \int dx dy \Psi^*(x,y,t) \hat{f}(x) \Psi(x,y,t). \quad (\text{B.2})$$

Since we do not “need” the y dependence it is convenient to “integrate it out”. We do this by introducing a quantity

$$\rho(x, x', t) = \int dy \Psi(x, y, t) \Psi^*(x', y, t); \quad (\text{B.3})$$

this function is called the *density matrix*, and has units of a probability density in x space. Note that, unlike the usual probability density $\rho(x)$ in quantum mechanics, which depends only on the

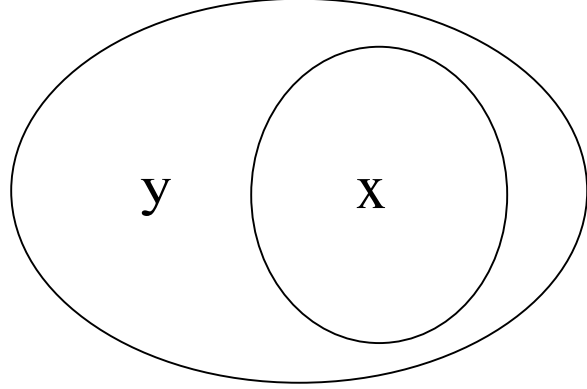


Figure B.1 A schematic representation of an entire system, described by the coordinates x and y , together with a sub system, involving only coordinates x .

¹ As an example, consider the energy operator; i.e., we might want to know the energy of our subsystem.

set of variables x , the density matrix depends on *two positions*, x and x' .² The expectation value of \hat{f} is then seen to be given by

$$\bar{f} = \int dx \left[\hat{f}(x) \rho(x, x', t) \right]_{x' \rightarrow x}. \quad (\text{B.4})$$

Eq. (B.4) is interpreted in the following way: we first operate on $\rho(x, x', t)$ with $\hat{f}(x)$, then take the limit $x' \rightarrow x$, and finally integrate over all x . Eq. (B.3) can be interpreted as a matrix in position space; the “continuous indices” are x and x' . From the definition we have

$$\rho(x, x', t) = \rho^*(x', x, t); \quad (\text{B.5})$$

i.e., ρ is Hermitian.

The representation of a system by a density matrix is the most general possible description of a quantum system. A special case is when $\rho(x, x', t) = \Psi(x, t) \Psi^*(x', t)$; this is referred to as *pure* system on which we will elaborate at greater length in section B.5. Here the $\Psi(x, t)$ can be associated with some operator (e.g. the Hamiltonian) the eigen functions of which yield a set of specific experimental outcomes. In the general case no such set exists.

B.2. Time evolution of the density matrix

Let us develop an equation of motion for the density matrix. Following Landau and Lifshitz, rather than treating the general case we will limit our discussion to the pure case where $\rho(x, x', t) = \Psi(x, t) \Psi^*(x', t)$ since this form must also satisfy the general equation. We then have

$$\begin{aligned} \dot{\rho}(x, x', t) &= \frac{\partial}{\partial t} \Psi(x, t) \Psi^*(x', t) \\ &= \left[\dot{\Psi}(x, t) \Psi^*(x', t) + \Psi(x, t) \dot{\Psi}^*(x', t) \right]. \end{aligned}$$

We now insert the Schrodinger equation for both $\dot{\Psi}(x, t)$ and $\dot{\Psi}^*(x, t)$ obtaining

$$\dot{\rho}(x, x', t) = \frac{1}{i\hbar} \left[\left(\hat{H} \Psi(x, t) \right) \Psi^*(x', t) - \Psi(x, t) \left(\hat{H}'^* \Psi^*(x', t) \right) \right]$$

where in the general case (where we integrate over the y coordinates) \hat{H} is that part of the Hamiltonian that acts only on the coordinates x of $\Psi(x, y, t)$ while \hat{H}'^* acts only on the coordinates x' of $\Psi^*(x', y, t)$. The subsequent time evolution will then be governed by

² In the language of function space $\rho(x)$ is a vector and $\rho(x, x')$ is a matrix.

$$i\hbar\dot{\rho}(x,x',t) = (\hat{H} - \hat{H}'^*)\rho(x,x',t). \quad (\text{B.6})$$

B.3. The density matrix in terms of a basis set

Rather than expressing the density matrix as a continuous function of the set of variables x, x' , we can use any complete set of states $\Psi_n(x,t)$ (spanning the space of x) to express it as a matrix whose indices number the states in our set. Such an expansion will have the form

$$\rho(x,x',t) = \sum_{m,n} \rho_{mn} \Psi_n^*(x',t) \Psi_m(x,t). \quad (\text{B.7})$$

We now assume the basis chosen involves the set of eigenfunctions of \hat{H} acting in x space. Note that instead of a single set of coefficients a_n involving an index n , which are used to expand an arbitrary wave function, $\sum_n a_n \psi_n(x) e^{-(i/\hbar)E_n t}$, we must consider a more general expansion

where the coefficients have *two* indices, n, m . We rewrite (B.7) as

$$\rho(x,x',t) = \sum_{m,n} \rho_{mn} \Psi_n^*(x') \Psi_m(x) e^{\frac{i}{\hbar}(E_n - E_m)t}. \quad (\text{B.8})$$

Using (B.5) we have

$$\rho_{nm} = \rho_{mn}^*; \quad (\text{B.9})$$

i.e., the matrix ρ_{nm} is also Hermitian; ρ_{nm} is also called the density matrix, or, more precisely, the density matrix represented in an energy basis where n and m number the energy eigenvalues.

The mean value of an operator \hat{f} *that operates only in the space of x* is clearly

$$\begin{aligned} \int dx \hat{f} \rho(x,x',t) |_{x=x'} &= \sum_{m,n} \rho_{mn} \int dx \Psi_n^*(x) \hat{f} \Psi_m(x) e^{i\omega_{nm}t} \\ &= \sum_{m,n} \rho_{mn} f_{nm} e^{i\omega_{nm}t}. \end{aligned}$$

We can write this as

$$\int dx [\hat{f} \rho(x,x',t)]_{x=x'} = \sum_{m,n} \rho_{mn}(t) f_{nm}, \quad (\text{B.10})$$

where we wrote $\rho_{mn}(t) = \rho_{mn} e^{i\omega_{nm}t}$.

B.4. Equation of motion in the energy representation

We now obtain the equation of motion for $\rho_{mn}(t)$ which is the counter part of that obtained for the coordinate representation. Inserting (B.8) into (B.6) gives

$$i\hbar \sum_{m',n'} \dot{\rho}_{m'n'}(t) \psi_n^*(x') \psi_{m'}(x) = (\hat{H} - \hat{H}'^*) \sum_{m',n'} \rho_{m'n'}(t) \psi_n^*(x') \psi_{m'}(x).$$

Multiplying both sides by $\psi_n(x') \psi_m^*(x)$, integrating over dx and dx' and making use of the orthonormality of our basis set we get

$$\begin{aligned} i\hbar \dot{\rho}_{mn}(t) &= \sum_{m',n'} \int dx dx' \psi_n(x') \psi_m^*(x) (\hat{H} - \hat{H}'^*) \rho_{m'n'}(t) \psi_n^*(x') \psi_{m'}(x) \\ &= \sum_{m'} \hat{H}_{mm'} \rho_{m'n}(t) - \sum_{n'} \hat{H}_{n'n} \rho_{mn'}(t) \\ &= \sum_l \left[\hat{H}_{ml} \rho_{ln}(t) - \rho_{ml}(t) \hat{H}_{ln} \right] \end{aligned} \quad (B.11a)$$

or equivalently

$$\dot{\hat{\rho}} = \frac{i}{\hbar} [\hat{\rho}, \hat{H}]; \quad (B.11b)$$

note this equation of motion for $\hat{\rho}$ has the *opposite sign* of that in the Heisenberg equation of motion.

B.5. Properties of the density matrix; pure and mixed states

Let us now establish some general properties of the density matrix. From Eq. (B.3) we see that $\rho(x,x,t)$ is the probability of finding the particle(s) at the space-time point(s) (x,t) . This *must be positive definite*. Now the quantities $\Psi_n^*(x,t)$ and $\Psi_m(x,t)$ in Eq. (B.8) oscillate in space and time. If we freeze space-time and regard these as arbitrary complex quantities ξ_n^* and ξ_m , then the condition $\rho(x,x) > 0$ is equivalent to

$$\sum_{m,n} \rho_{mn} \xi_n^* \xi_m > 0.$$

This places restrictions on the coefficients (familiar from the theory of quadratic forms) which are

$$\rho_{nn} \geq 0 \quad (B.12a)$$

and

$$\rho_{nn} \rho_{mm} - |\rho_{mn}|^2 > 0. \quad (B.12b)$$

In the “pure” case, where the coordinates x encompass *all* the degrees of freedom of the motion, we have from (B.3) and (B.8)

$$\rho(x, x', t) = \left(\sum_n a_n^* \Psi_n^*(x', t) \right) \left(\sum_m a_m \Psi_m(x, t) \right)$$

or

$$\rho_{mn} = a_m a_n^* . \quad (B.13)$$

(If m, n range from 1, N , then a Hermitian matrix, ρ_{mn} , has N^2 independent real entries³ while a matrix formed from $a_m a_n^*$ has N independent complex entries or $2N$ real ones. We can test if we have the pure case by examining the square of the density matrix, in which we would have

$$\begin{aligned} (\rho^2)_{mn} &= \sum_l \rho_{ml} \rho_{ln} = \sum_l a_m a_l^* a_l a_n^* = a_m a_n^* \sum_l |a_l|^2 \\ &= a_m a_n^* \end{aligned} \quad (B.14)$$

where we used the normalization of our wavefunction in the last step. Comparing Eq. (B.13) with Eq. (B.14) we see that the criteria for the pure case is

$$(\rho^2)_{mn} = (\rho)_{mn} ; \quad (B.15)$$

i.e., the density matrix is *equal to its square*. This property provides a simple test of whether a given density matrix describes a pure or a mixed state.

Additional Reading

For a discussion of the density matrix in statistical physics see section 5 of *Statistical Physics Part I*, L. D. Landau and E. M. Lifshitz, Pergamon Press, Oxford (1980).

³ For a Hermitian matrix the diagonal elements are real and there are a total of N ; the off diagonal elements occur as complex conjugate pairs and the number of independent complex elements is $N(N-1)/2$ corresponding to $N(N-1)$ real constants. The total number of real independent parameters is then $N(N-1) + N = N^2$.