

# The density matrix

A review of the quantum theory starts with the definition of the term “state”. Generally, the term “state” refers to a thermodynamic state, i. e. macroscopic variables such as pressure, temperature, density etc needed to specify a system, are given. In mechanics, of course, state variables are microscopic, and a state is specified by giving the positions and velocities of all particles as a function of time. Obviously, this does not generalize to the quantum theory very easily, thus in our work we will try to adhere as closely as possible to the first meaning, but it needs to be understood in a particular way to employ such an interpretation for quantum systems. This lecture follows the review article by U. Fano [Rev. Mod. Phys. **29**, 74 (1957)] on the subject.

The basic building blocks in the quantum theory are energy eigenstates  $|\psi_i\rangle$ ;

$$H|\psi_i\rangle = E_i|\psi_i\rangle \quad (1)$$

where  $|\psi_i\rangle$  is a eigenstate vector, sometimes written  $|i\rangle$ . A general state vector could be a superposition of eigenstates

$$|\psi^{(\nu)}\rangle = \sum_i a_i^{(\nu)} |\psi_i\rangle \quad (2)$$

where the superscript  $\nu$  is just an index to indicate that many different state vectors can be formed via superposition of energy eigenstates. The coefficient  $a_i^{(\nu)}$  is also called an amplitude. In general, it may be a function of time, for example  $a_i^{(\nu)}(t) = a_i^{(\nu)}(0)e^{-iE_it/\hbar}$ . The time variable will usually not be written explicitly, just  $a_i^{(\nu)}$ .

Now if  $Q$  is some operator that could refer to a physical quantity, i. e. angular momentum, then the matrix element of  $Q$  with the state vector  $|\psi^{(\nu)}\rangle$  is,

$$\langle \psi^{(\nu)} | Q | \psi^{(\nu)} \rangle = \sum_{ii'} a_i^{(\nu)} a_{i'}^{(\nu)*} \langle \psi_{i'} | Q | \psi_i \rangle. \quad (3)$$

A physical system could be composed of different microscopic components, namely, atoms or molecules, with different state vectors  $|\psi^{(\nu)}\rangle$  with weights  $w(\nu)$ . In that case the *expectation value* of  $Q$ , denoted by  $\langle Q \rangle$ , is

$$\langle Q \rangle = \sum_{\nu, ii'} w(\nu) a_i^{(\nu)} a_{i'}^{(\nu)*} \langle \psi_{i'} | Q | \psi_i \rangle = \sum_{ii'} \rho_{ii'} Q_{i'i} = Tr[\rho Q] \quad (4)$$

where the density matrix element  $\rho_{ii'}$  is defined as

$$\rho_{ii'} = \sum_{\nu} w(\nu) a_i^{(\nu)} a_{i'}^{(\nu)*} \quad (5)$$

and  $Q_{i'i} = \langle \psi_{i'} | Q | \psi_i \rangle$  is the matrix element of  $Q$  in a basis of energy eigenstates. The operator  $\rho$  is defined as

$$\rho = \sum |\psi_i \rangle \rho_{ii'} \langle \psi_{i'}| \quad (6)$$

Quite generally, in the quantum theory we consider that the state of a system with  $n$  eigenstates is defined by all of its  $n \times n$  density matrix elements. If the *eigenvalues* of the density matrix are all equal 0 except one (which equals  $\sum_i |a_i|^2$ ) then the system is said to be in a *pure state*. Otherwise it is in a *mixed state*. Usually the density matrix is normalized so that  $\sum_i \rho_{ii} = \text{Tr}[\rho] = 1$ . In this case, the expectation value of  $Q$  is also called the mean value.

Only if the system is in a pure state it can it be described by a state vector

$$|\psi \rangle = \sum_i a_i |\psi_i \rangle \quad (7)$$

in which case  $\rho = |\psi \rangle \langle \psi|$  if the state vector is normalized to unity.

In summary, by the term “state of a system” we will understand as a state of a micro *or* macroscopic system defined by its complete density matrix. With that understanding, not all states are characterized by a state vector. Only pure states for which  $\rho = |\psi \rangle \langle \psi|$  are defined by a state vector. Energy eigenstates are a special type of state vector. Clearly the density matrix describes states that are similar to those familiar from classical mechanics.

To make closer contact with the thermodynamic state consider that one could obtain the expectation value of a set of  $n^2$  operators  $Q^{(s)}$  by a series of measurements. These expectation values give a set on  $n^2$  linear equations relating  $\langle Q^{(s)} \rangle$  to the  $n^2$  parameters  $\rho_{ii'}$ . If the linear relations are independent, then the equations can be inverted to obtain  $\rho$ , therefore one can also say that the state of a system is defined by the expectation values of  $n^2$  measurable quantities. From the mean values one can determine that the system is in a state with  $\rho = \exp[-H/kT]/\text{Tr}[\exp(-H/kT)]$ , for example. See the paper by Fano for further discussion. For our purposes it is sufficient to understand that we use either the density matrix or a set of expectation values to define the state of a system.

Terminology introduced that you should know:

1. Energy eigenstate.
2. Pure state and state vector.
3. Mixed state and density matrix.

In actual calculations one usually computes a state function or eigenfunction. These are defined in terms of state vectors as

$$\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle \quad (8)$$

$$\psi_i(\mathbf{r}) = \langle \mathbf{r} | \psi_i \rangle \quad (9)$$

where  $|\mathbf{r}\rangle$  is an eigenstate of the position operator  $\mathbf{r}$ .

Another concept that we shall use frequently is “energy level” or simply “level”. As you know, states of atoms or molecules in the gas phase almost always have degenerate magnetic substates as required by rotational invariance. The group of all such states of the same energy is called an energy level. Thus we say that an excited hydrogen atom (nonrelativistic) is in the  $n$ 'th energy level if we only know the excitation energy and do not know more details about the state.

**States in photo-transitions** Initial states. How do you know what the initial state is in any process? How do you know classically? (You might measure temperature, pressure, volume, etc). Let us consider a simple example, namely, the fluorescent light bulb. Initially, mercury atoms get excited, but the excitation process does not single out a direction in space. We say the initial state is isotropic. This could mean (1) the initial state has  $J=0$ , or (2) the initial state has  $J \neq 0$  and all magnetic substates are equally occupied, that is  $\rho_{M_i, M'_i} = \delta_{M_i, M'_i} / (2J_i + 1)$ .