10.2: The Density Matrix and Density Operator

In general, the many-body wave function $\Psi(q_1, \ldots, q_{3N}, t)$ is far too large to calculate for a macroscopic system. If we wish to represent it on a grid with just 10 points along each coordinate direction, then for $N = 10^{23}$, we would need $10^{10^{23}}$ total points, which is clearly enormous.

We wish, therefore, to use the concept of ensembles in order to express expectation values of observables $\langle A \rangle$ without requiring direct computation of the wavefunction. Let us, therefore, introduce an ensemble of systems, with a total of Z members, and each having a state vector $|\Psi^{(\alpha)}\rangle$, $\alpha = 1, \cdots, Z$. Furthermore, introduce an orthonormal set of vectors $\langle \phi_k | \phi_j \rangle = \delta_{ij}$) and expand the state vector for each member of the ensemble in this orthonormal set:

$$|\Psi^{(\alpha)}\rangle = \sum_k C_k^{(\alpha)} |\phi_k\rangle$$

The expectation value of an observable, averaged over the ensemble of systems is given by the average of the expectation value of the observable computed with respect to each member of the ensemble:

$$\langle A \rangle = \frac{1}{Z} \sum_{\alpha=1}^{Z} \langle \Psi^{(\alpha)} | A | \Psi^{(\alpha)} \rangle$$

Substituting in the expansion for $|\Psi^{(\alpha)}\rangle$, we obtain

$$\begin{aligned}\langle A \rangle &= \frac{1}{Z} \sum_{k,l} C_k^{(\alpha)^*} C_l^{(\alpha)} \langle \phi_k | A | \phi_l \rangle \\ &= \sum_{k,l} \left(\frac{1}{Z} \sum_{\alpha=1}^{Z} C_l^{(\alpha)} C_k^{(\alpha)^*} \right) \langle \phi_k | A | \phi_l \rangle\end{aligned}$$

Let us define a matrix

$$\rho_{lk} = \sum_{\alpha=1}^{Z} C_l^{(\alpha)} C_k^{(\alpha)^*}$$

and a similar matrix

$$\tilde{\rho}_{lk} = \frac{1}{Z} \sum_{\alpha=1}^{Z} C_l^{(\alpha)} C_k^{(\alpha)^*}$$

Thus, ρ_{lk} is a sum over the ensemble members of a product of expansion coefficients, while ρ_{lk} is an average over the ensemble of this product. Also, let $A_{kl} = \langle \phi_k | A | \phi_l \rangle$. Then, the expectation value can be written as follows:

$$\langle A \rangle = \frac{1}{Z} \sum_{k,l} \rho_{lk} A_{kl} = \frac{1}{Z} \sum_k (\rho A)_{kk} = \frac{1}{Z} \mathrm{Tr}(\rho A) = \mathrm{Tr}(\tilde{\rho} A)$$

where ρ and A represent the matrices with elements ρ_{lk} and A_{kl} in the basis of vectors $\{|\phi_k\rangle\}$. The matrix ρ_{lk} is known as the **density matrix**. There is an abstract operator corresponding to this matrix that is basis-independent. It can be seen that the operator

$$\rho = \sum_{\alpha=1}^{Z} |\Psi^{(\alpha)}\rangle \langle \Psi^{(\alpha)}|$$

and similarly

$$\tilde{\rho} = \frac{1}{Z} \sum_{\alpha=1}^{Z} |\Psi^{(\alpha)}\rangle \langle \Psi^{(\alpha)}|$$

have matrix elements ρ_{lk} when evaluated in the basis set of vectors $\{|\phi_k\rangle\}$.

$$
\begin{aligned}
\langle \phi_l|\rho|\phi_k\rangle &= \sum_{\alpha=1}^{Z}\langle \phi_l|\Psi^{(\alpha)}\rangle\langle\Psi^{(\alpha)}|\phi_k\rangle \\
&= \sum_{\alpha=1}^{Z} C_l^{(\alpha)} C_k^{(\alpha)^*} \\
&= \rho_{lk}
\end{aligned}
$$

Note that ρ is a hermitian operator

$$\rho^\dagger = \rho$$

so that its eigenvectors form a complete orthonormal set of vectors that span the Hilbert space. If w_k and $|w_k\rangle$ represent the eigenvalues and eigenvectors of the operator $\tilde{\rho}$, respectively, then several important properties they must satisfy can be deduced.

Firstly, let A be the identity operator I. Then, since $\langle I\rangle = 1$, it follows that

$$1 = \frac{1}{Z}\mathrm{Tr}(\rho) = \mathrm{Tr}(\tilde{\rho}) = \sum_k w_k$$

Thus, the eigenvalues of $\tilde{\rho}$ must sum to 1. Next, let A be a projector onto an eigenstate of $\tilde{\rho}$, $A = |w_k\rangle\langle w_k| \equiv P_k$. Then

$$\langle P_k\rangle = \mathrm{Tr}(\tilde{\rho}|w_k\rangle\langle w_k|)$$

But, since $\tilde{\rho}$ can be expressed as

$$\tilde{\rho} = \sum_k w_k|w_k\rangle\langle w_k|$$

and the trace, being basis set independent, can be therefore be evaluated in the basis of eigenvectors of $\tilde{\rho}$, the expectation value becomes

$$
\begin{aligned}
\langle P_k\rangle &= \sum_j \langle w_j|\sum_i w_i|w_i\rangle\langle w_i|w_k\rangle\langle w_k|w_j\rangle \\
&= \sum_{i,j} w_i\delta_{ij}\delta_{ik}\delta_{kj} \\
&= w_k
\end{aligned}
$$

However,

$$
\begin{aligned}
\langle P_k\rangle &= \frac{1}{Z}\sum_{\alpha=1}^{Z}\langle\Psi^{(\alpha)}|w_k\rangle\langle w_k|\Psi^{(\alpha)}\rangle \\
&= \frac{1}{Z}\sum_{\alpha=1}^{Z}|\langle\Psi^{(\alpha)}|w_k\rangle|^2 \geq 0
\end{aligned}
$$

Thus, $w_k \geq 0$. Combining these two results, we see that, since $\sum_k w_k = 1$ and $w_k \geq 0$, $0 \leq w_k \leq 1$, so that w_k satisfy the properties of probabilities.

With this in mind, we can develop a physical meaning for the density matrix. Let us now consider the expectation value of a projector $|a_i\rangle\langle a_i| \equiv \mathcal{P}_{a_i}$ onto one of the eigenstates of the operator A. The expectation value of this operator is given by

$$\begin{aligned}\langle \mathcal{P}_{a_i} \rangle &= \frac{1}{Z}\sum_{\alpha=1}^{Z} \langle \Psi^{(\alpha)} | P_{a_i} | \Psi^{(\alpha)} \rangle \\ &= \frac{1}{Z}\sum_{\alpha=1}^{Z} \langle \Psi^{(\alpha)} | a_i \rangle \langle a_i | \Psi^{(\alpha)} \rangle \\ &= \frac{1}{Z}\sum_{\alpha=1}^{Z} |\langle a_i | \Psi^{(\alpha)} \rangle|^2 \end{aligned}$$

But $|\langle a_i|\Psi^{(\alpha)}\rangle|^2 \equiv P_{a_i}^{(\alpha)}$ is just probability that a measurement of the operator A in the α th member of the ensemble will yield the result a_i. Thus,

$$\langle \mathcal{P}_{a_i} \rangle = \frac{1}{Z}\sum_{\alpha=1}^{P} P_{a_i}^{(\alpha)}$$

or the expectation value of P_{a_i} is just the ensemble averaged probability of obtaining the value a_i in each member of the ensemble. However, note that the expectation value of P_{a_i} can also be written as

$$\begin{aligned}\langle \mathcal{P}_{a_i} \rangle &= \mathrm{Tr}(\tilde{\rho}\mathcal{P}_{a_i}) \\ &= \mathrm{Tr}(\sum_k w_k |w_k\rangle\langle w_k|a_i\rangle\langle a_i|) \\ &= \sum_{k,l} \langle w_l|w_k|w_k|w_k\rangle\langle w_k|a_i\rangle\langle a_i|w_l\rangle \\ &= \sum_{k,l} w_k \delta_{kl} \langle w_k a_i\rangle\langle a_i w_l\rangle \\ &= \sum_k w_k |\langle a_i|w_k\rangle|^2 \end{aligned}$$

Equating the two expressions gives

$$\frac{1}{Z}\sum_{\alpha=1}^{Z} \langle P_{a_i}^{(\alpha)} \rangle = \sum_k w_k |\langle a_i|w_k\rangle|^2$$

The interpretation of this equation is that the ensemble averaged probability of obtaining the value a_i if A is measured is equal to the probability of obtaining the value a_i in a measurement of A if the state of the system under consideration were the state $|w_k\rangle$, weighted by the average probability w_k that the system in the ensemble is in that state. Therefore, the **density operator** ρ (or ρ) plays the same role in quantum systems that the phase space distribution function $f(\mathbf{\Gamma})$ plays in classical systems.