Pure and Mixed States in Quantum Mechanics

Review of the Basic Formalism and Pure States

• *Definition:* A pure quantum state is a vector $\Psi = |\psi\rangle$ in a Hilbert space $\mathcal{H}$, a complex vector space with an inner product $\langle\phi|\psi\rangle$. This defines a norm in the space, $\|\psi\| := \langle\psi|\psi\rangle^{1/2}$, and we will usually assume that all vectors are normalized, so that $\|\psi\| = 1$. For a particle moving in a region R of space these vectors are commonly taken to be square-integrable functions $\psi(\mathbf{r}) = \langle\mathbf{r}|\psi\rangle$ in $\mathcal{H} = \mathrm{L}^2(R, \mathrm{d}^3x)$, with inner product

$$\langle\phi|\psi\rangle := \int_R \mathrm{d}^3r\, \phi^*(\mathbf{r})\, \psi(\mathbf{r}) .$$

• *Choice of basis and interpretation:* Any state can be written as a linear combination $|\psi\rangle = \sum_\alpha c_\alpha\, |\phi_\alpha\rangle$ of elements of a complete orthonormal set (c.o.n.s.) $\{|\phi_\alpha\rangle \mid \langle\phi_\alpha|\phi_{\alpha'}\rangle = \delta_{\alpha\alpha'}\}$ (for example $\phi_\mathbf{k}(\mathbf{r}) = \mathrm{e}^{\mathrm{i}\,\mathbf{k}\cdot\mathbf{r}}/\sqrt{V}$), where the coefficients $c_\alpha = |c_\alpha|\, \mathrm{e}^{\mathrm{i}\theta_\alpha}$ can be calculated from $c_\alpha = \langle\phi_\alpha|\psi\rangle$ and are interpreted as the probability amplitudes for the system to be found in the corresponding states.

• *Observables:* A quantum observable is an operator $\hat{A} : \mathcal{H} \to \mathcal{H}$ that is self-adjoint (if the corresponding classical observable is real). The possible outcomes of a measurement of $\hat{A}$ are its eigenvalues λ_α, satisfying $\hat{A}\,|\phi_\alpha\rangle = \lambda_\alpha|\phi_\alpha\rangle$, where $|\phi_\alpha\rangle$ are its eigenvectors. The expectation value of $\hat{A}$ in a given state Ψ is

$$\langle\hat{A}\rangle_\psi = \langle\psi|\hat{A}|\psi\rangle = \int \mathrm{d}^3q_1 ... \mathrm{d}^3q_N\, \psi^*(q)\, \hat{A}\, \psi(q) = \sum\nolimits_{\alpha,\alpha'} c^*_\alpha c_{\alpha'}\, A_{\alpha\alpha'} .$$

• *Time evolution:* It is governed by the Hamiltonian operator $\hat{H}$. If $\{\phi_\alpha\}$ is a basis of eigenfunctions of the Hamiltonian, with $\hat{H}|\phi_\alpha\rangle = E_\alpha\, |\phi_\alpha\rangle$, the Schrödinger equation and the time evolution of $|\psi\rangle$ are given by

$$\frac{\partial\psi(x,t)}{\partial t} = -\frac{\mathrm{i}}{\hbar}\, \hat{H}\psi(x,t) , \qquad \psi(x,t) = \hat{U}(t,t_0)\, \psi(x,t_0) = \mathrm{e}^{-\mathrm{i}\int \hat{H}\mathrm{d}t/\hbar}\, \psi(x,t_0) = \sum\nolimits_\alpha c_\alpha\phi_\alpha(x)\, \mathrm{e}^{-\mathrm{i}E_\alpha t/\hbar} .$$

• *Matrix notation:* Given any state Ψ, we can define an operator $\rho = |\psi\rangle\,\langle\psi|$. If the vector Ψ is normalized this operator satisfies $\rho^2 = \rho$, $\rho^\dagger = \rho$ (it is a projection operator), and $\mathrm{tr}\,\rho = 1$, and we can rewrite expectation values as $\langle\hat{A}\rangle_\psi = \mathrm{tr}\,\rho\hat{A}$. Then, if $\Psi = \sum_\alpha c_\alpha\, \Phi_\alpha$, in terms of a c.o.n.s. ρ can be written as a matrix,

$$\rho = \sum\nolimits_{\alpha\alpha'} \rho_{\alpha\alpha'}\, |\phi_\alpha\rangle\langle\phi_{\alpha'}| , \quad \text{with} \quad \rho_{\alpha\alpha'} = c_\alpha c^*_{\alpha'} ,$$

Mixed Quantum States

• *Idea:* To represent the available information about a system in statistical mechanics, we need more general *mixed states*, giving the probabilities $|c_\alpha|^2$ of finding the system in any of the $|\phi_\alpha\rangle$, but not necessarily any information on the phases θ_α. This can be done using operators $\rho : \mathcal{H} \to \mathcal{H}$ satisfying $\rho^\dagger = \rho$ and $\mathrm{tr}\,\rho = 1$ but in general with $\rho^2 \neq \rho$, called *density matrices.* The space of density matrices is *Liouville space.*

• *Observables:* Generalizing the expression for expectation values obtained for pure states in the matrix notation, we define $\langle\hat{A}\rangle_\rho := \mathrm{tr}\,\rho\hat{A}$. In particular, if we use as c.o.n.s. $\{|\phi_\alpha\rangle\}$ one whose elements are eigenvectors of $\hat{A}$, then $A_{\alpha\alpha'} = \lambda_\alpha\delta_{\alpha\alpha'}$ and $\langle\hat{A}\rangle_\rho = \mathrm{tr}\,\rho\hat{A} = \sum_\alpha \rho_{\alpha\alpha}\lambda_\alpha$. This means that for any mixed state ρ, $\rho_{\alpha\alpha} = \langle\psi_\alpha|\,\rho\,|\phi_\alpha\rangle = |c_\alpha|^2$ is the probability of finding the system in eigenstate α, as with a pure state.

• *Mixed states from averaged-out phase information:* In quantum statistical mechanics mixed states often arise as follows. If the probabilities $|a_\alpha|^2$ that a quantum system will be found in each of the $|\phi_\alpha\rangle$s are known while the phases θ_α are not, assume that all values are equally likely and average the matrix elements $\rho_{\alpha\alpha'} = c^*_\alpha c_{\alpha'}$ over $0 < \theta_\alpha < 2\pi$. The off-diagonal entries in $\rho_{\alpha\alpha'}$ will average to zero, while the diagonal entries will give $\rho_{\alpha\alpha} = |c_\alpha|^2$. The new density matrix ρ in general no longer satisfies $\rho^2 = \rho$.

• *Additional comments:* (1) The Hilbert space for a system consisting of two subsystems A and B is $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$, and from any state $\rho_{A,B}$ a mixed state for A can be obtained by tracing over subsystem B, $\rho_A = \mathrm{tr}_B\,\rho_{A,B}$. (2) As a measure of the mixedness of a quantum state ρ one can use its $n = 2$ Rényi entropy.

Example: Mixed State for the Spin of an Electron

• *Density matrix:* Suppose that an electron has a 50% probability of S_z being $+\frac{\hbar}{2}$, and 50% of being $-\frac{\hbar}{2}$. A pure state, its corresponding density matrix, and a mixed state which give these values are, respectively,

$$|\psi\rangle = \tfrac{1}{\sqrt{2}}\,(|\!\uparrow\rangle + \mathrm{e}^{\mathrm{i}\theta}|\!\downarrow\rangle) \quad \text{or} \quad \rho_{\text{pure}} = |\psi\rangle\langle\psi| = \tfrac{1}{2}\begin{pmatrix} 1 & \mathrm{e}^{-\mathrm{i}\theta} \\ \mathrm{e}^{\mathrm{i}\theta} & 1 \end{pmatrix}, \qquad \rho_{\text{mixed}} = \tfrac{1}{2}\begin{pmatrix} 1 & a \\ a^* & 1 \end{pmatrix}.$$

• *Mean value and fluctuation of spin:* Check that the mean value of S_z vanishes in both states and calculate the mean value of S_x in both states; why is the result reasonable? Calculate their variances $(\Delta S_z)^2$ and $(\Delta S_x)^2$, and compare the results for the pure state and the mixed state; comment on the results.

State Evolution

• *Evolution equation:* Working in the Schrödinger picture, we start by obtaining the time evolution of a ρ corresponding to a pure state, $\rho = |\psi\rangle\langle\psi|$, by taking a time derivative of $\rho(x,x') = \psi(x)\,\psi^*(x')$,

$$\frac{\partial}{\partial t}\,\rho(x,x') = \Big(\frac{\partial\psi^*(x)}{\partial t}\,\psi(x') + \psi^*(x)\,\frac{\partial\psi(x')}{\partial t}\Big) = \frac{1}{\mathrm{i}\hbar}\,[\hat H,\rho\,]\,.$$

By linearity we can then extend the validity of the expression $(1/\mathrm{i}\hbar)\,[\hat H,\rho\,]$ for the time derivative to all density matrices ρ. This is the Liouville-von Neumann equation, and the operator $\hat{\mathcal{L}} = (\mathrm{i}\hbar)^{-1}[\hat H,\,\cdot\,]$ is sometimes called the Liouvillian. Alternatively, $\rho(t) = \hat U(t,t_0)\,\rho(t_0)\,\hat U(t,t_0)^\dagger$, with $\hat U(t,t_0) = \exp\{-\mathrm{i}\int \hat H \mathrm{d}t/\hbar\}$.

• *Quantum equilibrium density matrix:* An equilibrium density matrix is one which is time-independent or, given the form of the evolution equation for ρ, one satisfying $[\hat H,\rho\,] = 0$. So, ρ must be a function of some set of $3N$ commuting operators including $\hat H$, and be diagonal in the corresponding basis of eigenstates.

The Quantum Microcanonical Density Matrix

• *Density matrix:* To describe a system with energy $E_n \in (E-\Delta/2, E+\Delta/2)$ in an incoherent superposition of states, start with a coherent sum over such states, $\psi = \sum_n |a_n|\,\mathrm{e}^{\mathrm{i}\theta_n}\,\phi_n$, and write ρ as an average $\langle|\psi\rangle\langle\psi|\rangle$ over all phase angles θ_n. The assumption of equal a priori probabilities implies that all $|a_n|$ for states in this energy range are equal; if we also assume a priori uniformly random phases, we get

$$\rho_{\alpha\alpha'} = \big\langle |a_\alpha|\,|a'_\alpha|\,\mathrm{e}^{\mathrm{i}(\theta'_\alpha-\theta_\alpha)}\big\rangle = \frac{1}{\Gamma(N,V,E;\Delta)}\,\delta_{\alpha\alpha'} \quad \text{for } E_\alpha \in (E-\Delta/2, E+\Delta/2)\ ,\ 0 \text{ otherwise}\ ,$$

where $\Gamma(N,V,E;\Delta)$ is the number of states in this energy range.

The Quantum (Grand) Canonical Density Matrix

• *Density matrix:* If we can partition the system into two parts, each of which is similar to the whole system so that its ρ is the same function of the constants of motion, with little interaction between them, then as in the classical case $H \approx H_1 + H_2$ and $\rho_{\alpha\alpha} = \rho^{(1)}_{\alpha_1\alpha_1}\,\rho^{(2)}_{\alpha_2\alpha_2}$, so $\ln\rho_{\alpha\alpha} = \ln\rho^{(1)}_{\alpha_1\alpha_1} + \ln\rho^{(2)}_{\alpha_2\alpha_2}$. This means that $\ln\rho_{\alpha\alpha}$ must be an additive constant of the motion, or neglecting a possible overall $\vec p$ or $\vec L$ and in a basis of eigenstates of $\hat H$ and $\hat N$,

$$\rho_{\alpha\alpha'} = \mathrm{e}^{c-\beta E_\alpha+\beta\mu N_\alpha}\,\delta_{\alpha\alpha'}\ .$$

Then, in an arbitrary basis and calling $\mathrm{e}^c =: Z^{-1}$ ($K := H - \mu N$ is sometimes called the grand Hamiltonian),

$$\rho = \frac{1}{Z}\,\mathrm{e}^{-\beta(\hat H-\mu\hat N)}\ , \qquad Z := \mathrm{tr}\ \mathrm{e}^{-\beta(\hat H-\mu\hat N)}\ .$$

• *Example:* A spin-$\frac{1}{2}$ particle in a magnetic field $\vec B = B\,\hat{\mathbf{z}}$, with Hamiltonian $H = -\vec\mu\cdot\vec B = -\mu\,\vec\sigma\cdot\vec B$, where the σ_i are the Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & \mathrm{i} \\ -\mathrm{i} & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Then $\rho = \big[2\cosh(\beta\mu B)\big]^{-1}\,\mathrm{diag}(\mathrm{e}^{\beta\mu B}, \mathrm{e}^{-\beta\mu B})$ and one gets, for example, $\langle\mu_z\rangle = \mu\tanh(\beta\mu B)$.

Reading

• *Textbooks:* Kennett does not discuss this material; Pathria & Beale, Chapter 5.

• *Other references:* Part of this material is covered in Plischke & Bergersen (§ 2.4), Halley (the first half of Ch 2) and Schwabl (§§ 1.3-1.4). An extended treatment is in J A Gyamfi, arXiv:2003.11472 (2020).