CHM 502 – Module 11 – Density Matrices & Dephasing

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So far, we've discussed the time-dependent behavior of quantum mechanical systems that can be described neatly by a wavefunction, with perfectly coherent behavior. In the real world, however, we are usually dealing with messy ensembles of quantum systems which exhibit disorder and decoherence. In order to describe these ensembles, we will need to introduce *statistical mixtures* of species in well-defined quantum states.

The density matrix (or density operator) $\hat{\rho}$ is critical infrastructure to treat statistical mixtures of quantum systems. We'll start by reviewing this formalism. The treatment we follow here borrows heavily from Peter Hamm's pamphlet "Mukamel for Dummies" as well as from Andrei Tokmakoff's notes on time-dependent quantum mechanics – both recommended reads for more details.

1 The density matrix of a pure state

The density matrix of a pure quantum state $|\psi\rangle$ is defined as the outer product of the wavefunction with its conjugate transpose:

$$\hat{\rho} \equiv |\psi\rangle \langle\psi| \tag{1}$$

Note that we define a "pure state" here as any quantum where we can write down the wavefunction – it could be an energy eigenstate, or some superposition state.

We can expand $|\psi\rangle$ in the basis of energy eigenstates $|n\rangle$ as:

$$|\psi\rangle = \sum_n c_n |n\rangle \quad \text{and} \quad \langle\psi| = \sum_n c_n^* \langle n| \tag{2}$$

The density matrix can therefore be expressed as

$$\hat{\rho} = \left[\sum_n c_n |n\rangle\right]\left[\sum_m c_m^* \langle m|\right] = \sum_{n,m} c_n c_m^* |n\rangle \langle m| \tag{3}$$

or by its matrix elements

$$\rho_{nm} \equiv \langle n|\hat{\rho}|m\rangle = c_n c_m^* \tag{4}$$

The diagonal matrix elements $\langle n|\hat{\rho}|n\rangle = |c_n|^2$ represent the probability that we find the system in state $|n\rangle$, hence the term "density matrix," since $\hat{\rho}$ describes the quantum probability density of the system.

The density operator has many convenient properties which we will see shortly. One convenient property is a new means of expressing expectation values:

$$\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle = \left[\sum_m c_m^* \langle m | \right] \hat{A} \left[\sum_n c_n | n \rangle \right] \tag{5}$$

$$= \sum_{n,m} c_m^* c_n \langle m | \hat{A} | n \rangle = \sum_{n,m} c_m^* c_n A_{mn} \tag{6}$$

$$= \sum_{n,m} \rho_{nm} \cdot A_{mn} = \boxed{\mathrm{Tr}(\hat{\rho}\hat{A})} \tag{7}$$

where in the last step we've used a definition for the trace of the product of two matrices.

The time-evolution of the density operator is given by the Liouville-Von Neumann equation, which can be derived from the time-dependent Schrödinger equation:

$$\frac{d}{dt}\hat{\rho} \quad = \quad \frac{d}{dt}\Big[|\psi\rangle \langle \psi| \Big] \quad = \quad \left[\frac{d}{dt} |\psi\rangle \right] \langle \psi| + |\psi\rangle \left[\frac{d}{dt} \langle \psi| \right] \tag{8}$$

$$= -\frac{i}{\hbar} \hat{H} |\psi\rangle \langle \psi| + \frac{i}{\hbar} |\psi\rangle \langle \psi| \hat{H} = \boxed{-\frac{i}{\hbar} \Big[\hat{H}, \hat{\rho} \Big]} \tag{9}$$

It turns out that the Liouville-Von Neumann equation gives you the same the time dependence of $\hat{\rho}(t)$ as you would find within the Heisenberg picture:

$$\hat{\rho}(t) = |\psi(t)\rangle \langle \psi(t)| = \hat{U} |\psi(0)\rangle \langle \psi(0)| \hat{U}^\dagger = \hat{U} \hat{\rho}(0) \hat{U}^\dagger \tag{10}$$

The time dependence of the matrix elements of $\hat{\rho}(t)$ are also useful to inspect:

$$\rho_{nm}(t) = \langle n | \hat{\rho}(t) | m \rangle = \langle n | \hat{U} \hat{\rho}(0) \hat{U}^\dagger | m \rangle \tag{11}$$

$$= \langle n | e^{-iE_n t/\hbar} \hat{\rho}(0) e^{+iE_m t/\hbar} | m \rangle \tag{12}$$

$$= e^{-i\omega_{nm} t} \rho_{nm}(0) \qquad \text{where} \quad \omega_{nm} = (E_n - E_m)/\hbar \tag{13}$$

We can see here that the diagonal elements $\rho_{nn}(t) = \rho_{nn}(0)$, since the probabilities of being in an energy eigenstate $|n\rangle$ are time-invariant. Meanwhile, the off-diagonal elements $\rho_{nm}(t)$ represent coherences between pairs of states present in a superposition, which oscillate at the energy splitting ω_{nm}.

We can finally note a few relevant properties of the density matrix:

- The density matrix is Hermitian, since $\Big[|\psi\rangle \langle \psi| \Big]^\dagger = |\psi\rangle \langle \psi|$ and $\rho_{nm} = \rho_{mn}^*$
- The diagonal elements of $\hat{\rho}$ are non-negative: $\rho_{nn} \geq 0$, and ρ_{nn} can be viewed as the probability of the system to be found in state $|n\rangle$.
- $\mathrm{Tr}(\hat{\rho}) = \sum_n |c_n|^2 = 1$, assuming the wavefunction is correctly normalized.
- $\hat{\rho}^2 = |\psi\rangle \langle \psi|\psi\rangle \langle \psi| = |\psi\rangle \langle \psi| = \hat{\rho}$. We therefore also have $\mathrm{Tr}(\hat{\rho}^2) = 1$ for a pure quantum state.

2 Example: Density matrices of two-level systems

Let's consider a two-level system with Hamiltonian $\hat{H}$ and energy eigenstates $|1\rangle$ and $|2\rangle$. We can write down the density matrices for various wavefunctions:

$$|\psi\rangle = |1\rangle \quad \rightarrow \quad \hat{\rho} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \tag{14}$$

$$|\psi\rangle = |2\rangle \quad \rightarrow \quad \hat{\rho} = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \tag{15}$$

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left[|1\rangle + |2\rangle\right] \quad \rightarrow \quad \hat{\rho} = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{bmatrix} \tag{16}$$

We can explicitly solve the Liouville-Von Neumann equation for this system. If we have Hamiltonian

$$\hat{H} = \hbar \begin{bmatrix} \omega_1 & 0 \\ 0 & \omega_2 \end{bmatrix} \tag{17}$$

We therefore have:

$$\frac{d}{dt}\hat{\rho} = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}\right] \tag{18}$$

$$\frac{d}{dt}\begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} = -i\left(\begin{bmatrix} \omega_1 & 0 \\ 0 & \omega_2 \end{bmatrix}\begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} - \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix}\begin{bmatrix} \omega_1 & 0 \\ 0 & \omega_2 \end{bmatrix}\right) \tag{19}$$

$$= -i\begin{bmatrix} 0 & \omega_{12}\,\rho_{12} \\ \omega_{21}\,\rho_{21} & 0 \end{bmatrix} \tag{20}$$

And therefore:

$$\dot{\rho}_{11} = 0 \quad \rightarrow \quad \rho_{11}(t) = \rho_{11}(0) \tag{21}$$

$$\dot{\rho}_{22} = 0 \quad \rightarrow \quad \rho_{22}(t) = \rho_{22}(0) \tag{22}$$

$$\dot{\rho}_{12} = -i\omega_{12}\,\rho_{12} \quad \rightarrow \quad \rho_{12}(t) = e^{-i\omega_{12}t}\rho_{12}(0) \tag{23}$$

$$\dot{\rho}_{21} = -i\omega_{21}\,\rho_{21} \quad \rightarrow \quad \rho_{21}(t) = e^{+i\omega_{12}t}\rho_{21}(0) \tag{24}$$

The diagonal elements are independent of time, while the off-diagonal elements oscillate with the frequency splitting $\omega_{12} = \omega_1 - \omega_2$.

3 Density matrices of mixed states

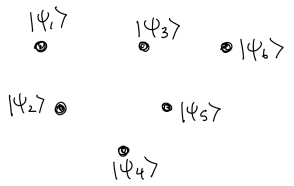
So far we have defined the density matrix of a pure quantum state, $\hat{\rho} = |\psi\rangle\langle\psi|$. We have written out the equations for this formalism, but we haven't introduced any new physics yet. We could just as well work with the wavefunction directly. For example, the equations governing time dynamics:

$$\frac{d}{dt}|\psi\rangle = -\frac{i}{\hbar}\hat{H}|\psi\rangle \quad \leftrightarrow \quad \frac{d}{dt}\hat{\rho} = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}\right] \tag{25}$$

can be used interchangeably provided that $\hat{\rho}$ is the density matrix of a pure quantum state.

However, in most real physical systems, we deal with statistical ensembles (or "mixed states") rather than pure states. There is no way to write down the wavefunction of a statistical ensemble – but we can easily write down the density matrix!

Here's how we do this: say we have a collection of quantum systems in a statistical mixture of states. Let's assume that these systems all have identical Hamiltonians, and each has probability P_k of being found in pure quantum state $|\psi_k\rangle$ (where $|\psi_k\rangle$ need not be an energy eigenstate!).



We can define a density matrix for this collection of systems as a weighted sum over the various relevant pure-state density matrices, $\hat{\rho}_k \equiv |\psi_k\rangle\langle\psi_k|$:

$$\hat{\rho} = \sum_k P_k \, |\psi_k\rangle\langle\psi_k| = \sum_k P_k \, \hat{\rho}_k \tag{26}$$

$$\text{with} \quad 0 \le P_k \le 1, \;\; \sum_k P_k = 1 \tag{27}$$

This mixed-state density matrix therefore has matrix elements:

$$\rho_{nm} = \langle n| \left[\sum_k P_k \, |\psi_k\rangle\langle\psi_k| \right] |m\rangle \tag{28}$$

$$= \sum_k P_k \langle n|\psi_k\rangle\langle\psi_k|m\rangle \tag{29}$$

$$= \sum_k P_k \, [\rho_k]_{nm} \tag{30}$$

It's also instructive to inspect the time-dependence of this mixed-state density matrix:

$$\frac{d\hat{\rho}}{dt} = \sum_k \frac{dP_k}{dt}\hat{\rho}_k + \sum_k P_k \frac{d}{dt}\hat{\rho}_k \tag{31}$$

$$= \underbrace{\sum_k \frac{dP_k}{dt}\hat{\rho}_k}_{\text{population relaxation}} - \underbrace{\frac{i}{\hbar}\sum_k P_k \left[\hat{H}, \hat{\rho}_k\right]}_{\text{quantum oscillations}} \tag{32}$$

where in the last step we substituted in the Liouville-Von Neumann equation.

Finally, we can jot down a few general properties of $\hat{\rho}$ that hold even for statistical mixtures:

- $\hat{\rho}$ is still Hermitian, since it arises from a linear combination of Hermitian density matrices of pure states
- $\mathrm{Tr}(\hat{\rho}) = 1$, since the diagonal elements still represent probabilities.
- $\mathrm{Tr}(\hat{\rho}^2) \leq 1$, and indeed is only equal to 1 for a pure state
- Since all our work is linear in $\hat{\rho}$ thus far, the Liouville-Von Neumann equation still holds, and we still have $\langle A \rangle = \mathrm{Tr}(\hat{\rho}\hat{A})$.

4 Example: Mixed states of a two-level system

For a two-level system in a statistical mixture of states $|1\rangle$ and $|2\rangle$ with $P_1 = P_2 = \frac{1}{2}$ we would find:

$$\hat{\rho} = \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{bmatrix} \tag{33}$$

Note that there is no wavefunction $|\psi\rangle$ that would give $\hat{\rho} = |\psi\rangle\langle\psi|$ in Eqn. 33! Instead, the best way to think of the system that gives rise to this density matrix is two non-interacting molecules, one in pure state $|1\rangle$ and one in pure state $|2\rangle$.

It's worth stating explicitly that the density matrix in Eqn. 16 above *does not* correspond to:

$$|\psi\rangle \neq \frac{1}{\sqrt{2}}\Big[\,|1\rangle + |2\rangle\,\Big] \qquad \rightarrow \qquad \hat{\rho} = |\psi\rangle\langle\psi| = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{bmatrix} \tag{34}$$

This $\hat{\rho}$ has off-diagonal elements describing the coherence of the superposition state.

This treatment allows us to consider the decay of coherent pure states into mixed states. Consider a system with initial density matrix:

$$\rho(0) = \begin{bmatrix} \rho_{11}(0) & \rho_{12}(0) \\ \rho_{21}(0) & \rho_{22}(0) \end{bmatrix} \tag{35}$$

Let's see what happens if we let the off-diagonal elements of $\hat{\rho}$ decay in time, obeying:

$$\frac{d}{dt}\rho_{12} = -i\omega_{12}\,\rho_{12} - \Gamma\rho_{12} \quad \rightarrow \quad \rho_{12}(t) = e^{-i\omega_{12}t}\,e^{-\Gamma t}\,\rho_{12}(0) \tag{36}$$

$$\frac{d}{dt}\rho_{21} = -i\omega_{21}\rho_{21} - \Gamma\rho_{21} \quad \rightarrow \quad \rho_{21}(t) = e^{+i\omega_{12}t}\,e^{-\Gamma t}\,\rho_{21}(0) \tag{37}$$

This phenomenologically captures the exponential decay of the coherent off-diagonal elements of $\hat{\rho}$ to 0 as $t \rightarrow \infty$, taking the system from a coherent superposition state to a statistical mixture:

$$\begin{bmatrix} \rho_{11}(0) & \rho_{12}(0) \\ \rho_{21}(0) & \rho_{22}(0) \end{bmatrix} \quad \rightarrow \quad \begin{bmatrix} \rho_{11}(0) & 0 \\ 0 & \rho_{22}(0) \end{bmatrix} \tag{38}$$

This takes us, for instance, from Eqn. 16 to Eqn. 33.

Note that there is no way to describe such a dephasing process within the wavefunction picture! A wavefunction cannot be written down for a statistical mixture, and we could never write a differential equation for our wavefunction like:

$$\frac{d}{dt}\,|\psi\rangle \neq -\frac{i}{\hbar}H\,|\psi\rangle - \Gamma\,|\psi\rangle \tag{39}$$

5 Bloch vectors & dephasing

In statistical ensembles, molecules may undergo dephasing and population relaxation processes. They may also have heterogeneous oscillation frequencies that destructively interfere. One can better understand these processes using the framework of Bloch vectors.

Imagine we have a coherent superposition state of a single two-level system:

$$|\psi(t)\rangle = c_1\, e^{-iE_1 t/\hbar}\,|1\rangle + c_2(t)\, e^{-iE_2 t/\hbar}\,|2\rangle \tag{40}$$

$$\equiv \cos(\theta/2)\, e^{-iE_1 t/\hbar}\,|1\rangle + e^{i\phi}\sin(\theta/2)\, e^{-iE_2 t/\hbar}\,|2\rangle \tag{41}$$

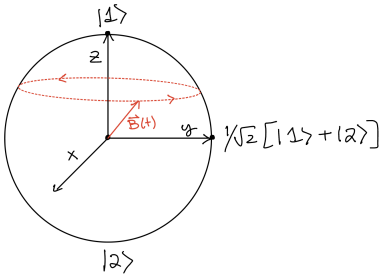
where θ and ϕ are determined by the initial conditions of the system.

We define the Bloch vector $\underline{B} = [B_x, B_y, B_z]$ with:

$$B_z(t) \equiv |c_1(t)|^2 - |c_2(t)|^2 = \cos(\theta) = \rho_{11}(t) - \rho_{22}(t) \tag{42}$$

$$B_x(t) \equiv i\,[c_1(t)\,c_2^*(t) - c_1^*(t)\,c_2(t)] = \sin(\theta)\sin(\omega_{12}t + \phi) = i\,[\rho_{12}(t) - \rho_{21}(t)] \tag{43}$$

$$B_y(t) \equiv c_1(t)\cdot c_2^*(t) + c_1^*(t)\cdot c_2(t) = \sin(\theta)\cos(\omega_{12}t + \phi) = \rho_{12}(t) + \rho_{21}(t) \tag{44}$$



A few observations:

- By construction, the length of the Bloch vector is 1 for a pure quantum state, which maps the space of pure-state vectors onto the surface of the "Bloch sphere."
- The $|\psi\rangle = |1\rangle$ state is represented by a Bloch vector pointing along the $+z$ axis, while the $|\psi\rangle = |2\rangle$ state points along $-z$. A coherent, equally weighted superposition state will precess around the "equator" of the Bloch sphere in the x-y plane with angular frequency ω_{12}. Unequal superposition states will precess around the z axis at different "latitudes," but with the same angular frequency.
- The connection to the elements of the density matrix elements is key here. The B_z component of the Bloch vector is defined by the difference in the diagonal elements of $\hat{\rho}$, which arises purely from *populations* in different states, while the off-diagonal elements of $\hat{\rho}$ are the source of quantum *coherences* that cause the Bloch vector to rotate in the x-y plane.

If we were just describing the wavefunction of a single molecule, we don't really need the Bloch vector to understand the time dynamics. This framework does become useful, for instance, if we have a statistical mixture of molecules whose coherences oscillate at different frequencies (heterogeneity) or accrue random phase jumps (dephasing). In this case, we can use the mixed state density matrix to calculate the *average* Bloch vector of the ensemble and watch how it loses coherence.

Recall that the density matrix for a mixed state is essentially a weighted ensemble average over pure state density matrices:

$$\hat{\rho} = \sum_k P_k \left|\psi_k\right\rangle \left\langle\psi_k\right| \tag{45}$$

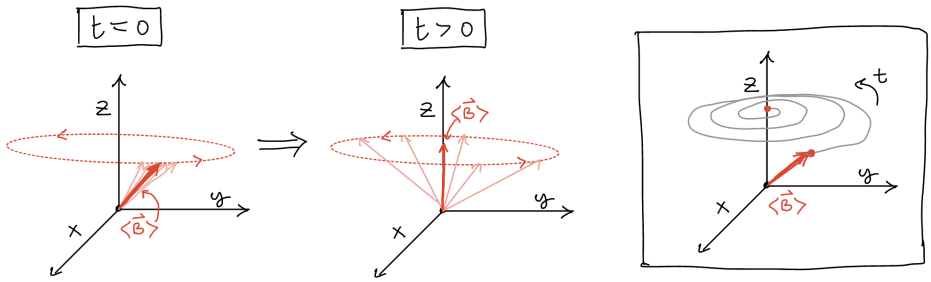
Thus, we can use this mixed state density matrix to calculate the average Bloch vector:

$$\langle B_z(t)\rangle = \rho_{11}(t) - \rho_{22}(t) \tag{46}$$
$$\langle B_x(t)\rangle = i\left[\rho_{12}(t) - \rho_{21}(t)\right] \tag{47}$$
$$\langle B_y(t)\rangle = \rho_{12}(t) + \rho_{21}(t) \tag{48}$$

Note that now that our system is in a mixed state, the magnitude of $\underline{B}$ may be less than 1!

Let's now consider what can happen to $\langle \underline{B} \rangle$ in a statistical ensemble. We can easily treat two processes that limit the lifetime of coherences: destructive interference and population relaxation.

We first discuss destructive interference: at $t = 0$ all members of the ensemble have similar Bloch vectors. But if each individual vector precesses with a slightly different frequency (e.g. due to sample inhomogeneity) or experiences dynamic fluctuations in phase (e.g. due to homogeneous dephasing from collisions), then the Bloch vectors spread out over time and destructively interfere. Both homogeneous and inhomogeneous broadening processes result in the decay of the off-diagonal matrix elements of $\hat{\rho}$ which give rise to $\langle B_x \rangle$ and $\langle B_y \rangle$, causing $\langle \underline{B} \rangle$ to spiral towards the z axis. The timescale associated with destructive interference of coherence due purely to homogeneous environmental fluctuations is usually referred to as the *pure dephasing time*, T_2^*.



We must also consider population relaxation: the fact that the excited state of our two-level system has a finite lifetime due to radiative and non-radiative relaxation processes. We'll call this the *population lifetime* T_1. Here $\frac{1}{T_1} = \frac{1}{t_1} + \frac{1}{t_2} + \ldots$ where the t_n are all the contributing relaxation timescales which add inversely, as their rates. In terms of Bloch vectors, T_1 decay adds an exponential decay of the z component of $\langle \underline{B} \rangle$ back to $\langle B_z \rangle = 1$, indicating that all population returns to the ground state at long times.

Our phenomenological description of the decay of quantum coherences lets us motivate the way that elements of $\hat{\rho}(t)$ decay. It is straightforward to write down the diagonal "population" matrix elements:

$$\rho_{22}(t) = \rho_{22}(0) \cdot e^{-t/T_1} \tag{49}$$
$$\rho_{11}(t) = 1 - \rho_{22}(t) \tag{50}$$

Meanwhile the coherent, off-diagonal elements of $\hat{\rho}(t)$ decay due to both population relaxation and dephasing:

$$\rho_{12}(t) = \rho_{12}(0) \cdot e^{+i\omega_{12}t} \cdot e^{-t/2T_1} \cdot e^{-t/T_2^*} \equiv \rho_{12}(0) \cdot e^{+i\omega_{12}t} \cdot e^{-t/T_2} \quad (51)$$

$$\rho_{21}(t) = \rho_{21}(0) \cdot e^{-i\omega_{12}t} \cdot e^{-t/2T_1} \cdot e^{-t/T_2^*} \equiv \rho_{21}(0) \cdot e^{-i\omega_{12}t} \cdot e^{-t/T_2} \quad (52)$$

where we define the total homogeneous dephasing time as $\frac{1}{T_2} \equiv \frac{1}{T_2^*} + \frac{1}{2T_1}$. Note that the off-diagonal elements decay as $2T_1$ rather than T_1. This is because $\rho_{22}(t) = \rho_{22}(0) \cdot e^{-t/T_1} \propto |c_2(t)|^2$, so $c_2(t) \propto \left[e^{-t/T_1}\right]^{1/2}$. Therefore, e.g. $\rho_{21}(t) \propto c_1^*(t)c_2(t) \propto e^{-t/2T_1}$.