Traditional QM problems: wave-functions $\psi(\vec{r},t)$ used to describe the evolution of the system

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$$

Normally, we identify the complete orthonormal set of eigenfunctions $\{u_n(\vec{r},t)\}$ Such that $\hat{H}|u_n\rangle = E_n|u_n\rangle$ and solve for $\psi(\vec{r},t)$ as a linear combination of u_n

$$|\psi\rangle = \sum_n a_n(t)|u_n\rangle \qquad \langle u_m|\psi\rangle = \sum_n a_n \overbrace{\langle u_m|u_n\rangle}^{\delta_{mn}}$$

$$\langle \psi|\psi\rangle = \sum_n |a_n(t)|^2 \qquad\qquad = a_m$$

At the same time, the wavefunction is not physically measurable entity; in reality we measure probability of being in a particular state $P_n = |a_n|^2$.
Also, we often need to find the expectation value of an operator: $\hat{Q}$

$$\langle Q\rangle = \langle \psi|\hat{Q}|\psi\rangle = \sum_{n,m} a_m^* a_n \underbrace{\langle u_m|\hat{Q}|u_n\rangle}_{Q_{mn}}$$

matrix element

Density matrix operator $\hat{\rho} = |\psi\rangle\langle\psi|$

$$\rho_{mn} = \langle u_m|\hat{\rho}|u_n\rangle = \langle u_m|\psi\rangle\langle\psi|u_n\rangle = a_m a_n^*$$

then $P_n = \rho_{nn}$

$$\langle Q\rangle = \sum_{n,m} \rho_{nm} Q_{mn} = \sum_n [\hat{\rho}\hat{Q}]_{nn} = \text{Tr}[\hat{\rho}\hat{Q}]$$

Just as we can follow the dynamics of the system using a wave function, we can do it using a density matrix

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

$$= \frac{1}{i\hbar}\hat{H}|\psi\rangle\langle\psi| + \frac{1}{-i\hbar}|\psi\rangle\langle\psi|\hat{H} = \frac{1}{i\hbar}\left[\hat{H}\hat{\rho} - \hat{\rho}\hat{H}\right] =$$

$$i\hbar\frac{d}{dt}\hat{\rho} = \{\hat{H}, \hat{\rho}\}$$

Density matrix elements have no phase ambiguity

$$|\tilde{\psi}\rangle - = e^{i\varphi}|\psi\rangle$$

$$\hat{\rho} \cdots = e^{i\varphi}|\psi\rangle\langle\psi|e^{-i\varphi} = |\psi\rangle\langle\psi| = \rho$$

$$\rho^2 = \rho \qquad \text{(idempotent operator)}$$

$$\rho_{nn} \geq 0 \qquad \text{since} \qquad \rho_{nn} = |a_n|^2$$

For a pure state there is no difference b/w using $|\psi\rangle$ or $\hat{\rho}$ — why bother?

The state must be pure and continuously evolving to be described by the wave function.
Density matrix can handle mixed state

Statistical mixture

A system can be in the state $|\psi_i\rangle$ with a probability p_i ($\sum_i p_i = 1$)
This is different from a superposition

$$|\psi\rangle = \sqrt{p_1}\,|\psi_1\rangle + \sqrt{p_2}\,|\psi_2\rangle + \ldots$$

We are forced to use the statistical description when we lack full information about the evolution of the system.

How we can describe the state of the system now?

For example, if we need to find the expectation value of an operator, for each of the states $\langle Q \rangle_i = \langle \psi_i | \hat{Q} | \psi_i \rangle =$

$$= Tr\left(\hat{\rho}_i \hat{Q} \right)$$

and $\langle Q \rangle = \sum_i p_i \langle Q \rangle_i = \sum_i p_i \, Tr\left(\hat{\rho}_i \hat{Q} \right) =$

$$= Tr\left(\left[\sum_i p_i \hat{\rho}_i \right] \hat{Q} \right) = Tr\left(\hat{\rho} \hat{Q} \right)$$

where $\hat{\rho} = \sum_i p_i \hat{\rho}_i$ "average" of the density matrix operators over the ensemble

Similarly $i\hbar \dfrac{\partial \hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}]$

but $\hat{\rho}^2 = \hat{\rho}$ for non-pure state.

Why we have to use density matrix formalism when we talk about atom-light interaction? To account for spontaneous emission!

$|\psi\rangle = c_1|1\rangle + c_2|2\rangle$

——— $|2\rangle$

$|\psi(t)\rangle = c_1(t)e^{-i\omega_1 t}|1\rangle + c_2(t)e^{-i\omega_2 t}|2\rangle$

Light - atom interaction

$\hat{V} = -\hat{\vec{d}}\,\vec{E} = -e\hat{\vec{r}}\,\vec{E}(t)$

——— $|1\rangle$

$V_{11} = V_{22} = 0$

$V_{12} = V_{21}^* = \langle 1|-e\hat{\vec{r}}|2\rangle \cdot \vec{E} = \rho_{12}\,E(t)$

$\qquad\qquad = \rho_{12}\,E_0 \sin\omega t$

$\dfrac{\partial|\psi\rangle}{\partial t} = (\hat{H}_0 + \hat{V})|\psi\rangle$

↑ describes an atom   ↑ interaction

For $\omega = \omega_2 - \omega_1$ (resonance) and $c_2 \Rightarrow c_2 e^{-i\omega t}$

$\dot{c}_1 = i\dfrac{\rho_{12}E_0}{2\hbar}c_2$

$\dot{c}_2 = i\dfrac{\rho_{12}E_0}{2\hbar}c_1$

$\Rightarrow \ddot{c}_1 + \left(\dfrac{\rho_{12}E_0}{2\hbar}\right)^2 c_1 = 0$

$c_1 = \cos\Omega t$

where $\Omega = \rho_{12}E_0/2\hbar$ Rabi freq.

If $|1\rangle$ and $|2\rangle$ are stationary states, the system oscillates b/w them with Rabi frequency

$\rho_{11} = |c_1|^2 = \cos^2\Omega t$

$\rho_{22} = |c_2|^2 = \sin^2\Omega t$

$\rho_{12} = c_1 c_2^* = i\cos\Omega t \sin\Omega t$

↑ coherence b/w the two states

$\hat{\rho} = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix}$

$$i\hbar \frac{\partial \hat{S}}{\partial t} = \{\hat{H}, \hat{S}\}$$

$$\hat{H} = \hat{H}_0 + \hat{V} = \begin{pmatrix} \hbar\omega_1 & p_{12} E \cos\omega t \\ p_{12} E \cos\omega t & \hbar\omega_2 \end{pmatrix}$$

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} = \begin{pmatrix} \hbar\omega_1 & p_{12} E \cos\omega t \\ p_{12} E \cos\omega t & \hbar\omega_2 \end{pmatrix} \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} -$$

$$- \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} \hbar\omega_1 & p_{12} E \cos\omega t \\ p_{12} E \cos\omega t & \hbar\omega_2 \end{pmatrix}$$

$$i\hbar \frac{\partial S_{11}}{\partial t} = \hbar\omega_1 S_{11} + p_{12} E \cos\omega t \, S_{21} - \hbar\omega_1 S_{11} - p_{12} E \cos\omega t \, S_{12}$$

$$i\hbar \frac{\partial S_{12}}{\partial t} = \hbar\omega_1 S_{12} + p_{12} E \cos\omega t \, S_{22} - S_{11} E \cos\omega t \, S_{11} - \hbar\omega_2 S_{12}$$

$$i\hbar \frac{\partial S_{12}}{\partial t} = \hbar(\omega_1 - \omega_2) S_{12} + p_{12} E \cos\omega t \, (S_{22} - S_{11})$$

$$S_{12} = \tilde{S}_{12} e^{i\omega t}$$

$$-\hbar\omega \tilde{S}_{12} e^{-i\omega t} + i\hbar e^{-i\omega t} \frac{\partial \tilde{S}_{12}}{\partial t} = \hbar(\omega_1 - \omega_2) \tilde{S}_{12} e^{i\omega t} +$$
$$+ p_{12} E \cdot \tfrac{1}{2} (e^{i\omega t} + e^{-i\omega t})(S_{22} - S_{11})$$

for $\omega = \omega_2 - \omega_1$ and neglecting $\sim e^{-2i\omega t}$

$$i\hbar \frac{\partial \tilde{S}_{12}}{\partial t} = \tfrac{1}{2} p_{12} E \, (S_{22} - S_{11})$$

$$i\hbar \frac{\partial S_{11}}{\partial t} = \tfrac{1}{2} p_{12} E \, (\tilde{S}_{21} - \tilde{S}_{12})$$

Solving this will give us the same solution

Spontaneous emission arises from interaction of atoms in the excited states with an e-m vacuum (thing the ground state of a SHO). Can we use wavefunctions to describe the process — yes! <u>if</u> the vacuum modes are a part of our system. However, we can avoid it using the density matrix.

later
$$\begin{bmatrix} \dfrac{\partial \rho_{11}}{\partial t} = +\gamma \rho_{22} - i\dfrac{\rho_{12}E}{2\hbar}(\rho_{21} - \rho_{12}) \\[4mm] \underbrace{\dfrac{\partial \rho_{22}}{\partial t} = -\gamma \rho_{22}}_{\text{spontaneous decay}} + i\dfrac{\rho_{12}E}{2\hbar}(\rho_{21} - \rho_{12}) \end{bmatrix}$$

Forget about the interaction with light, how do we discribe the system where n_1 atoms are in state $|1\rangle$, and n_2 atoms are in state $|2\rangle$

$$P_1 = {n_1}/{n_1 + n_2} \qquad P_2 = {n_2}/{n_1 + n_2}$$

$$\hat{\rho} = \begin{pmatrix} P_1 & 0 \\ 0 & P_2 \end{pmatrix} \qquad \text{no off-diagonal terms}$$

If there is a decay from the state $|2\rangle$ to the state $|1\rangle$

$$\frac{dP_2}{dt} = -\gamma P_2 \; , \quad \frac{dP_1}{dt} = \gamma P_2$$

$$P_2(t) = P_1(0)\, e^{-\gamma t}$$
$$P_1(t) = 1 - P_2(t)$$

$$\frac{d\rho_{22}}{dt} = -\gamma \rho_{22} \qquad \frac{\partial \rho_{11}}{\partial t} = \gamma \rho_{22}$$

For the coherences the decay rate

$$\Gamma_{12} = \frac{1}{2}(\gamma_1 + \gamma_2) = \frac{\gamma}{2}$$

$$\frac{\partial \rho_{12}}{\partial t} = -\frac{\gamma}{2}\rho_{12} - i\frac{\rho_{12}\mathcal{E}}{2\hbar}(\rho_{22} - \rho_{11})$$