Density Matrices I

(See CTDL pp. 252-263, 295-307**, 153-163, 199-202, 290-294)

Last time: Variational Method

[Linear variation: $0 = |\mathbf{H} - \varepsilon \mathbf{S}| \Rightarrow 0 = \left|\tilde{\tilde{\mathrm{H}}} - \varepsilon \mathbf{1}\right|$

$$\psi = \sum_n c_n \phi_n \qquad \frac{d\varepsilon}{dc_n} = 0$$

[Variation vs. pert. theory

TODAY

ψ phase ambiguity – but for all observables each state always appears as a bra and a ket.

what is needed to encode motion in the probability density? A superposition of eigenstates belonging to several different values of E.

coherent superposition vs. statistical mixture: think about polarized light

$\boldsymbol{\rho}$ no phase ambiguity

"**coherences**" in off-diagonal position

"**populations**" along diagonal

$$\langle \mathbf{A} \rangle = \mathrm{Tr}(\boldsymbol{\rho}\mathbf{A}) = \mathrm{Tr}(\mathbf{A}\boldsymbol{\rho})$$

Quantum Beats

prepared state $\rightarrow \boldsymbol{\rho}$

detection $\rightarrow \mathbf{D}$ (detect or destroy coherences)

$\boldsymbol{\rho}(t)$

$\langle \mathbf{A} \rangle_t$

$$\frac{d}{dt}\langle \mathbf{A} \rangle = \frac{i}{\hbar}\langle [\mathbf{H}, \mathbf{A}] \rangle + \left\langle \frac{\partial \mathbf{A}}{\partial t} \right\rangle$$

$$ih\frac{d\boldsymbol{\rho}}{dt} = [\mathbf{H}(t), \boldsymbol{\rho}]$$

* state: $\boldsymbol{\rho}$
* evolution: $\mathbf{H}$
* detection: $\mathbf{D}$

Let us define a quantity called "Density Matrix"

$$\boldsymbol{\rho} \equiv |\psi\rangle\langle\psi| \qquad \text{a pure state}$$

$\boldsymbol{\psi}$ can be any sort of QM wavefunction

* eigenstate of **H**
* coherent superposition of several eigenstates of **H**

but $\boldsymbol{\psi}$ cannot represent a statistical (i.e. incoherent) mixture of several different $\boldsymbol{\psi}$'s

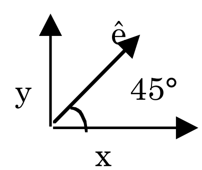
However, $\boldsymbol{\rho}$ can represent a statistical (i.e. equilibrium) mixture of states

$$\boldsymbol{\rho} \equiv \sum_k p_k |\psi_k\rangle\langle\psi_k| = \sum_k p_k \boldsymbol{\rho}_k$$

$$\boxed{\sum p_k = 1}$$

Example

* one beam of linarly polarized light, with the polarization axis (ε-field)



$$\hat{e} = 2^{-1/2}\left(\hat{e}_x + \hat{e}_y\right)$$

* two beams of linearly polarized light, 50% along $\hat{e}_x$, 50% along $\hat{e}_y$.

These 2 cases seem to be identical if you make 2 measurements with analyzer polarizers along $\hat{e}_x$ then $\hat{e}_y$. But they are different with respect to 2 measurements with analyzer polarizers along $2^{-1/2}\left(\hat{e}_x + \hat{e}_y\right)$ then $2^{-1/2}\left(\hat{e}_x - \hat{e}_y\right)$.
In the statistical mixture, it does not matter how the analyzer is oriented.

What are the properties of $\boldsymbol{\rho}$?

1. $\boldsymbol{\rho}$ for a pure state is Hermitian with positive elements along diagonal and other elements off-diagonal.

$$\rho_{nm} = \langle n|\psi\rangle\langle\psi|m\rangle$$

$\langle n|\psi\rangle \rightarrow c_n$, $\langle\psi|m\rangle \rightarrow c_m^*$

$$|\psi\rangle = \sum c_n|n\rangle$$

can expand $|\psi\rangle$ in any basis set but **H** eigenbasis is most useful.

$$\rho_{nm} = c_n c_m^*$$

$$\text{but } \left(\boldsymbol{\rho}^\dagger\right)_{nm} = \rho_{mn}^* = \left[\langle m|\psi\rangle\langle\psi|n\rangle\right]^*$$

$$= \langle\psi|m\rangle\langle n|\psi\rangle = \langle n|\psi\rangle\langle\psi|m\rangle = \rho_{nm}$$

$$\therefore\ \boldsymbol{\rho}^\dagger = \boldsymbol{\rho}$$

$$\rho_{nn} = \langle n|\psi\rangle\langle\psi|n\rangle = c_n c_n^* = |c_n|^2 \geq 0$$

positive along diagonal

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2. <u>2 × 2 Example</u> <u>Coherent Superposition</u> vs. <u>Statistical Mixture</u>

$$|\psi\rangle = 2^{-1/2}\begin{pmatrix}1\\ \pm 1\end{pmatrix}$$

$$\boldsymbol{\rho}_{cs} = \frac{1}{2}\begin{pmatrix}1\\ \pm 1\end{pmatrix}\begin{pmatrix}1 & \pm 1\end{pmatrix} = \frac{1}{2}\begin{pmatrix}1 & \pm 1\\ \pm 1 & 1\end{pmatrix}$$

Trace $\boldsymbol{\rho} = 1$

Now consider a statistical mixture state.

$$\boldsymbol{\rho}_{\text{sm}} = \frac{1}{2}\begin{pmatrix}1\\0\end{pmatrix}(1\ \ 0) + \frac{1}{2}\begin{pmatrix}0\\1\end{pmatrix}(0\ \ 1)$$
$$= \frac{1}{2}\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix} \qquad \text{trace } \boldsymbol{\rho} = 1$$

The difference is in the off-diagonal positions of $\boldsymbol{\rho}$

diagonal elements → "populations"
off-diagonal elements → "coherences"

(statistical mixture states have strictly diagonal $\boldsymbol{\rho}$)

Expectation values of $\hat{\mathbf{A}}$ in terms of $\boldsymbol{\rho}$

$$\langle \mathbf{A} \rangle = \langle \psi | \mathbf{A} | \psi \rangle = \sum_{j,k} \langle \psi | k \rangle \langle k | \mathbf{A} | j \rangle \langle j | \psi \rangle$$
$$= \sum_{j,k} \underbrace{\langle j | \psi \rangle \langle \psi | k \rangle}_{\rho_{jk}} \mathbf{A}_{kj}$$
$$= \sum_{j} (\boldsymbol{\rho}\mathbf{A})_{jj} \equiv \text{Trace}(\boldsymbol{\rho}\mathbf{A})$$

[Could have arranged the factors $\sum_{j,k} \mathbf{A}_{kj} \langle j | \psi \rangle \langle \psi | k \rangle = \sum_{k} (\mathbf{A}\boldsymbol{\rho})_{kk} = \text{Trace}(\mathbf{A}\boldsymbol{\rho})$]

$$\langle \mathbf{A} \rangle = \text{Trace}(\mathbf{A}\boldsymbol{\rho}) = \text{Trace}(\boldsymbol{\rho}\mathbf{A})$$

So $\boldsymbol{\rho}$ describes state of system, $\boldsymbol{A}$ describes a measurement to be made on the system

simple prescription for calculating $\langle \mathbf{A} \rangle$

The separation between initial preparation, evolution, and measurement of a specific observable is very convenient and instructive.

Example: Quantum Beats

Preparation, evolution, detection

magically prepare some coherent superposition state $\Psi(t)$

$$\Psi(t) = N \sum_n \underbrace{a_n \psi_n}_{\text{Several eigenstates of H. Evolve freely without any time-dependent intervention}} e^{-iE_n t/\hbar}$$

$$N = \left[\sum_n |a_n|^2 \right]^{-1/2}$$

normalization

$$\boldsymbol{\rho}(t) = |\Psi(t)\rangle\langle\Psi(t)|$$

Case (1): Detection: only one of the eigenstates, ψ_1, in the superposition is capable of giving fluorescence that our detector can "see".

Thus $$\mathbf{D} = |\psi_1\rangle\langle\psi_1| = \begin{pmatrix} 1 & 0 & \cdots \\ 0 & 0 & 0 \\ \vdots & 0 & 0 \end{pmatrix}$$

a projection operator (designed to project out only $|\psi_1\rangle$ part of state vector or ρ_{11} part of $\boldsymbol{\rho}$.

$$\boldsymbol{\rho} = N^2 \begin{pmatrix} |a_1|^2 & a_1 a_2^* e^{-(E_1 - E_2)t/\hbar} & & \cdots \\ & |a_2|^2 & & \\ & & |a_3|^2 & \\ & & & \ddots \end{pmatrix}$$

$$\rho_{12} = \langle 1|\Psi\rangle\langle\Psi|2\rangle$$

$$\rho_{12} = N^2 a_1 e^{-E_1 t/\hbar} a_2^* e^{+iE_2 t/\hbar}$$

D picks out only 1st row of $\boldsymbol{\rho}$.

$$\langle \mathbf{D} \rangle_t = \text{Trace}(\mathbf{D}\boldsymbol{\rho}) = N^2 \,\text{Trace} \begin{pmatrix} |a_1|^2 & a_1 a_2^* e^{-i\omega_{12} t} & \text{stuff} & \cdots \\ 0 & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}$$

$$= N^2 |a_1|^2$$

no time dependence!

case (2): a particular linear combination of eigenstates is bright: the initial state $2^{-1/2}(\psi_1 + \psi_2)$ has $\langle \mathbf{D} \rangle = 1$.

$$\mathbf{D} = \frac{1}{2}\left(|\psi_1\rangle + |\psi_2\rangle\right)\left(\langle\psi_1| + \langle\psi_2|\right)$$

a projection operator. How much of the original state is present in the evolved state?

$$= \frac{1}{2}\left[|\psi_1\rangle\langle\psi_1| + |\psi_2\rangle\langle\psi_2| + |\psi_1\rangle\langle\psi_2| + |\psi_2\rangle\langle\psi_1|\right]$$

$$= \frac{1}{2}\left[\begin{pmatrix} 1 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & \cdots \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 1 & 0 & \cdots \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & \cdots \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix}\right]$$

$$= \frac{1}{2}\begin{pmatrix} 1 & 1 & 0 & \cdots \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix}$$

[if the bright state had been $2^{-1/2}(\psi_1 - \psi_2)$, then $\mathbf{D} = \frac{1}{2}\begin{pmatrix} 1 & -1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$]

$$\text{Trace}(\mathbf{D}\boldsymbol{\rho}) = \frac{1}{2}N^2 \ \ \text{Trace}\begin{pmatrix} \ \ \end{pmatrix}$$

why do we need to look at only the 1,2 block of $\boldsymbol{\rho}$?

$$(\mathbf{D}\boldsymbol{\rho})_{11} = \frac{1}{2}N^2\left[|a_1|^2 + a_1^* a_2 e^{+i(E_1 - E_2)t/\hbar}\right]$$

$$(\mathbf{D}\boldsymbol{\rho})_{22} = \frac{1}{2}N^2\left[|a_2|^2 + a_1 a_2^* e^{-i(E_1 - E_2)t/\hbar}\right]$$

$$\text{Trace}(\mathbf{D}\boldsymbol{\rho}) = \frac{1}{2}N^2\left[|a_1|^2 + |a_2|^2 + 2\,\text{Re}\left[a_1^* a_2 e^{+i\omega_{12}t}\right]\right]$$

↑ beat note at ω_{12}

[if the bright state had been $2^{-1/2}(\psi_1 - \psi_2)$, then $\text{Tr}(\mathbf{D}\rho)$ would be the same except for $-2\text{Re}[\quad]$]

If $|a_1|^2 = |a_2|^2$ (and a_1, a_2 real), $\text{Trace}(\mathbf{D}\rho) = N^2 |a_1|^2 [1 \pm \cos\omega_{12} t]$ $(N^2 = 1/2)$

QUANTUM BEAT! 100% modulation!

So we see that the same $\Psi(x,t)$ or $\boldsymbol{\rho}(t)$ can look simple or complicated depending on the nature of the measurement operator! The measurement operator is designed to be sensitive only to specific coherences (i.e. locations in $\boldsymbol{\rho}$) which oscillate at ω_{ij}.
THIS IS THE REASON WHY WE SEPARATE PREPARATION AND OBSERVATION SO CLEANLY.

Time evolution of ρ_{nm} and $\langle \mathbf{A} \rangle$

Start with the time-dependent Schrödinger equation:

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t} \qquad \begin{cases} H|\Psi\rangle = i\hbar \dfrac{\partial}{\partial t}|\Psi\rangle \\ \langle\Psi|H = -i\hbar \dfrac{\partial}{\partial t}\langle\Psi| \end{cases}$$

for time-independent $\mathbf{H}$ we know $\Psi(t) = \sum_n a_n \psi_n e^{-iE_n t/\hbar}$

1. $\boldsymbol{\rho}(t)$

$$\boldsymbol{\rho}(t) = |\Psi(t)\rangle\langle\Psi(t)|$$

$$\rho_{nn}(t) = \langle n|\Psi(t)\rangle\langle\Psi(t)|n\rangle = |a_n|^2$$

a time independent "**population**" in state *n*.

$$\rho_{nm}(t) = a_n a_m^* e^{-i(E_n - E_m)t/\hbar} = a_n a_m^* e^{-i\omega_{nm} t}$$

a "**coherence**" which oscillates at ω_{nm} (eigenstate energy differences $/\hbar$)

2. $\langle \mathbf{A} \rangle_t$

Recall $i\hbar \frac{\partial \Psi}{\partial t} = \mathbf{H}\Psi$

$$\frac{\partial}{\partial t}\langle \mathbf{A} \rangle = \left[\frac{\partial}{\partial t}\langle\Psi|\right]\mathbf{A}|\Psi\rangle + \left\langle\Psi\left|\frac{\partial \mathbf{A}}{\partial t}\right|\Psi\right\rangle + \langle\Psi|\mathbf{A}\left[\frac{\partial}{\partial t}|\Psi\rangle\right]$$

$$= \frac{-1}{i\hbar}\left[\langle\Psi|\mathbf{H}\right]\mathbf{A}|\Psi\rangle + \left\langle\frac{\partial \mathbf{A}}{\partial t}\right\rangle + \langle\Psi|\mathbf{A}\left[\frac{1}{i\hbar}\mathbf{H}|\Psi\rangle\right]$$

$$= \frac{i}{\hbar}\langle[\mathbf{H},\mathbf{A}]\rangle + \left\langle\frac{\partial \mathbf{A}}{\partial t}\right\rangle$$

Heisenberg Equation of Motion

Note that nothing has been assumed about the time-dependence of $\mathbf{H}$.

If **A** commutes with **H** (regardless of whether **H** is time-dependent), there is no dynamics as far as observable **A** is concerned. However, if **A** does not commute with **H**, there can be dynamics of $\langle \mathbf{A} \rangle$ even if both **A** and **H** are time-independent.

Similarly can derive $i\hbar \frac{\partial \boldsymbol{\rho}}{\partial t} = [\mathbf{H}(t), \boldsymbol{\rho}]$ evolution of $\boldsymbol{\rho}$ under $\mathbf{H}(t)$. This is a matrix equation. It specifies the time dependence of each element of $\boldsymbol{\rho}$.

(If **H** is time dependent)

<u>Summarize</u>

$$\langle \mathbf{A} \rangle = \mathrm{Tr}(\boldsymbol{\rho}\mathbf{A}) = \mathrm{Tr}(\mathbf{A}\boldsymbol{\rho})$$

A: info about quantity being measured

$\boldsymbol{\rho}$: info about state on which measurement is to be made

$$i\hbar \frac{\partial \boldsymbol{\rho}}{\partial t} = [\mathbf{H}, \boldsymbol{\rho}]$$

H: time evolution

$\boldsymbol{\rho}$: state

initial state: $\boldsymbol{\rho}$
time evolution of $\boldsymbol{\rho}$: **H**
observable quantity: **A**

each expressed independently in the form of matrices which can be easily read (or designed!).

NMR pulse gymnastics

<u>statistical mixture states</u> - use same machinery BUT add the independent $\boldsymbol{\rho}_k$ matrices with weights p_k that correspond to their fractional populations.

$\boldsymbol{\rho}$ is Hermitian so can be diagonalized by $\mathbf{T}^\dagger\boldsymbol{\rho}\mathbf{T}$. However, if $\boldsymbol{\rho}$ is time-dependent, **T** would have to be time-dependent. This transformation gives a representation without any coherences in $\hat{\boldsymbol{\rho}}$ even if we started with a coherent superposition state. No problem because this transformation will undiagonalize **H**, thereby reintroducing time dependencies.