Density Matrices I

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

Last time: Variational Method

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

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

[Variational method vs. perturbation theory]

TODAY

ψ phase ambiguity – but for every observable 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.

ρ no phase ambiguity in density matrix, $|\psi\rangle\langle\psi|$, an N × N matrix
- “**coherences**” in off-diagonal position
- “**populations**” along diagonal

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

Quantum Beats

prepared state → ρ
detection → $\mathbf{D}$ (detect or destroy coherences)

$\rho(t)$

$\langle \mathbf{A} \rangle_t$ equations of motion

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

expectation value
each element of $\boldsymbol{\rho}$ encodes important information

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

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

Let us define a quantity called "Density Matrix"

$$\rho \equiv |\psi\rangle\langle\psi|$$

ψ can be any sort of QM wavefunction

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

but ψ cannot represent a statistical (i.e. incoherent) mixture of several different ψ' s

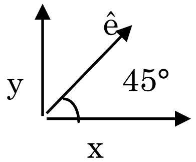
However, ρ can represent a statistical (i.e. equilibrium) mixture of states!

$$\rho \equiv \sum_k p_k |\psi_k\rangle\langle\psi_k| = \sum_k \underset{\uparrow}{p_k} \rho_k$$

$$\sum p_k = 1$$ probability of each contributing term to $\boldsymbol{\rho}$

Example

* *one* beam of linearly polarized light, with its polarization axis at 45° (ε -field)



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

* *two* superimposed beams of linearly polarized light, 50% along $\hat{e}_x$, 50% along $\hat{e}_y$. Call this a statistical mixture state.

These 2 cases seem to be identical if you make 2 measurements with analyzer polarizers along $\hat{e}_x$ then $\hat{e}_y$. But the 2 cases are different with respect to 2 measurements with analyzer polarizers along $2^{-1/2}\left(\hat{e}_x + \hat{e}_y\right)$ and then along $2^{-1/2}\left(\hat{e}_x - \hat{e}_y\right)$.

In the statistical mixture, it does not matter how the analyzer is oriented.

What are the properties of ρ?

1. ρ for a pure state is Hermitian with positive elements along the diagonal and other elements off-diagonal. $\rho \equiv |\psi\rangle\langle\psi|$ so evaluate matrix elements of ρ

$$\rho_{nm} = \underbrace{\langle n|\psi\rangle}_{c_n}\underbrace{\langle\psi|m\rangle}_{c_m^*}$$

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

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

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

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

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

$\therefore$ ρ passes the Hermiticity test that all observable quantities must pass! So if ρ is observable, what does it tell us?

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

positive along diagonal

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

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

$$\rho_{cs} = \frac{1}{2}\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}\begin{pmatrix} 1 & \pm 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & \pm 1 \\ \pm 1 & 1 \end{pmatrix}$$

Trace $\rho = 1$

$$\rho^2 = \frac{1}{4}\begin{pmatrix} 2 & \pm 2 \\ \pm 2 & 2 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & \pm 1 \\ \pm 1 & 1 \end{pmatrix}$$

$$\rho^2 = \rho$$

Now consider a statistical mixture state.

$$\rho_{\text{sm}} = \frac{1}{2}\begin{pmatrix}1\\0\end{pmatrix}(1\ 0) + \frac{1}{2}\begin{pmatrix}0\\1\end{pmatrix}(0\ 1)$$

$$= \frac{1}{2}\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix} \qquad \text{trace } \rho = 1$$

The difference is in the off-diagonal positions of ρ

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

(statistical mixture states have strictly diagonal ρ)

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

$$\langle \mathbf{A}\rangle = \langle\psi|\mathbf{A}|\psi\rangle = \sum_{j,k}\langle\psi\,\overbrace{\underline{|\,k\rangle\langle k|\mathbf{A}|\,j\rangle\langle j\,|}}^{\text{completeness}}\,\psi\rangle$$

these are three simple numbers and can be rearranged in any order.

$$= \sum_{j,k}\underbrace{\langle j|\psi\rangle\langle\psi|k\rangle}_{\rho_{jk}}\mathbf{A}_{kj}$$

$$= \sum_{j}(\rho\mathbf{A})_{jj} \equiv \mathit{Trace}(\rho\mathbf{A})$$

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

a fantastic labor saving and insight generating result!

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

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

So ρ describes the state of system, **A** describes a measurement to be made on the system

simple prescription for calculating ⟨**A**⟩

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

Example: Quantum Beats

<u>Preparation</u>, <u>evolution</u>, <u>detection</u>

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

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

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

normalization

$$\rho(t) = |\Psi(t)\rangle\langle\Psi(t)|$$

Case (1): Detection: only one of the eigenstates, ψ_1, in the superposition is capable of giving fluorescence that our detector can "see". (Build a detector matrix out of the same form as the selected bright state in $\boldsymbol{\rho}$.)

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

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

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

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

$$\rho_{12} = N^2 a_1 e^{-iE_1 t/\hbar} a_2^* e^{+iE_2 t/\hbar}$$

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

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

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

no time dependence!

You do not need to work out the full $\mathbf{D}\rho$ matrix product!

case (2): a particular linear combination of eigenstates is bright: the initial (i.e. at t = 0) 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?

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

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

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

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

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

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

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

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

The 1,2 block is the only part of **D** that picks out something that can appear along the diagonal of **Dρ**

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

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 –2Re[ ]]

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

QUANTUM BEAT! 100% modulation! Either $2\mathrm{N}^2|a_1|^2$ at t = 0 or 0 at t = 0.

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 (can detect or "destroy" a particular coherence) only to specific coherences (i.e. locations in $\boldsymbol{\rho}$) which oscillate at ω_{ij}. THIS IS THE REASON WHY WE CAN SEPARATE PREPARATION AND OBSERVATION SO CLEANLY.

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

Start with the time-dependent Schrödinger equation:

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

Hermitian conjugate.

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

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

$$\rho(t) = |\Psi(t)\rangle\langle\Psi(t)|$$

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

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

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

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

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

Heisenberg Equation of Motion

Note that nothing has been assumed here about the time-dependence of **H**. This is a simple prescription for calculating the motion of ⟨A⟩. One observable quantity.

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 $i\hbar \frac{\partial \rho}{\partial t} = [\mathbf{H}(t), \rho]$, which describes evolution of ρ under **H**(t).

If **H** is time dependent

This is a matrix equation. It specifies the time dependence of each element of $\boldsymbol{\rho}$. Usually has the form of many <u>coupled</u> first-order differential equations.

<u>Summarize</u>

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

info about quantity being measured

info about state on which measurement is to be made

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

time evolution

state

$$\left.\begin{array}{ll} \text{initial state : } & \boldsymbol{\rho} \\ \text{time evolution of } \rho\text{: } & \mathbf{H} \\ \text{observable quantity : } & \mathbf{A} \end{array}\right\}$$

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

NMR pulse gymnastics

<u>statistical mixture states</u> - use the same machinery BUT add the independent $\boldsymbol{\rho}_k$ matrices with weights p_k that correspond to their fractional populations [populations have no phase].

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

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