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§13 The Density Matrix and Entropy in Quantum Mechanics.

So far the only way in which the QM nature of the world has figured in our discussion is via the sums over states being discrete and also in the interpretation of the indistinguishability of particles.

Now I want to show you how one introduces uncertainty about the quantum state of the system into the general QM formalism you have learned

[Binney & Skinner §6.3-4]

$\boxed{\text{13.1 Expectation Values}}$

Suppose we are uncertain about the quantum state of our system but think that it is one of a set of orthogonal quantum states $\{|\alpha\rangle\}$ $(\alpha = 1, \dots, \Omega)$ and our uncertainty about which one is expressed by a priori probabilities $\{p_\alpha\}$, as usual [assigned via the max. entropy procedure whose further ~~quantum~~ particulars I am about to explain]

For any observable $\hat{Q}$ (an operator! Can be, e.g., $\hat{H}$ - energy),

$$\bar{Q} = \sum_\alpha p_\alpha \underbrace{\langle \alpha | \hat{Q} | \alpha \rangle} \qquad (1)$$

exp. value

a priori probability that the system is in state $|\alpha\rangle$

exp. value of $\hat{Q}$ *if* the system is in state $|\alpha\rangle$
e.g. E_α if $\hat{Q} = \hat{H}$

$\{|\alpha\rangle\}$ is <u>not</u> necessarily the set of eigenkets of $\hat{Q}$.

Since $$\hat{Q} = \sum_\mu \underbrace{Q_\mu}_{\text{eigenvalues of } \hat{Q}} |Q_\mu\rangle\langle Q_\mu| \qquad (2)$$

$|Q_\mu\rangle$ — eigenkets of $\hat{Q}$

Then, from (1),

$$\overline{Q} = \sum_{\alpha\mu} p_\alpha Q_\mu \langle\alpha|Q_\mu\rangle\langle Q_\mu|\alpha\rangle =$$

$$= \sum_\mu Q_\mu \underbrace{\sum_\alpha \underbrace{p_\alpha}_{\substack{\text{prob.}\\ \text{to be in } |\alpha\rangle}} \underbrace{|\langle Q_\mu|\alpha\rangle|^2}_{\substack{\text{prob. to measure}\\ Q_\mu \text{ if system}\\ \text{is in } |\alpha\rangle}}}_{\text{total probability to measure } Q_\mu} \qquad (3)$$

This formula underscores that the expected outcome of a measurement is subject to two types of uncertainty:
- our uncertainty as to what state the system is in
- quantum uncertainty as to the outcome of a measurement, given a definite quantum state

13.2 Density Matrix

This construction motivates us to introduce the <u>density operator</u>

pure state: some $p_\alpha = 1$, so $\hat{\rho} = |\alpha\rangle\langle\alpha|$
impure state: $p_\alpha < 1$

$$\boxed{\hat{\rho} = \sum_\alpha p_\alpha |\alpha\rangle\langle\alpha|} \qquad (4)$$

[cf. (2), but note that $\hat{\rho}$ is <u>not</u> an observable because p_α's are subjective!]

This is useful because, knowing $\hat{\rho}$, we can ~~calculate~~ express

$$\boxed{\overline{Q} = \mathrm{Tr}\,(\hat{\rho}\hat{Q})} \equiv \sum_{\alpha'} \langle \alpha' | \hat{\rho}\hat{Q} | \alpha' \rangle = \qquad (5)$$

$$= \sum_{\alpha\alpha'} p_\alpha \underbrace{\langle \alpha' | \alpha \rangle}_{= \delta_{\alpha\alpha'}} \langle \alpha | \hat{Q} | \alpha' \rangle = \sum_{\alpha} p_\alpha \langle \alpha | \hat{Q} | \alpha \rangle$$

Same as (1) q.e.d.

It is useful to see what this looks like in the $\{|Q_\mu\rangle\}$ representation:

$$\text{Since } |\alpha\rangle = \sum_\mu \langle Q_\mu | \alpha \rangle \, |Q_\mu\rangle , \qquad (6)$$

we have

$$\hat{\rho} = \sum_\alpha p_\alpha \sum_{\mu\nu} \langle Q_\mu | \alpha \rangle \langle \alpha | Q_\nu \rangle \, |Q_\mu\rangle\langle Q_\nu| \qquad (7)$$

$$\equiv \sum_{\mu\nu} p_{\mu\nu} \, |Q_\mu\rangle\langle Q_\nu| \, , \quad \underbrace{\boxed{p_{\mu\nu} = \sum_\alpha p_\alpha \langle Q_\mu | \alpha \rangle \langle \alpha | Q_\nu \rangle}}_{\text{Density Matrix}}$$

So, while $\hat{\rho}$ is diagonal in the "information basis" $\{|\alpha\rangle\}$, it is not in any given $\{|Q_\mu\rangle\}$ basis

(i.e. the states to which we assign a priori probabilities are not necessarily eigenstates of the observable we then wish to calculate).

We have $\mathrm{Tr}\,(\hat{\rho}\hat{Q}) = \sum_{\mu'} \langle Q_{\mu'} | \hat{\rho}\hat{Q} | Q_{\mu'} \rangle \overset{\text{use (7)}}{=}$

$$= \sum_{\mu'\mu\nu} Q_{\mu'} p_{\mu\nu} \underbrace{\langle Q_{\mu'} | Q_\mu \rangle}_{= \delta_{\mu\mu'}} \underbrace{\langle Q_\nu | Q_{\mu'} \rangle}_{= \delta_{\nu\mu'}} = \sum_\mu Q_\mu p_{\mu\mu}$$

Thus, $\boxed{\bar{Q} = \mathrm{Tr}(\hat{\rho}\hat{Q}) = \sum_\mu Q_\mu p_{\mu\mu}}$ (8)

where $p_{\mu\mu} = \sum_\alpha p_\alpha |\langle Q_\mu|\alpha\rangle|^2$ same as (3)

Thus, <u>the diagonal elements</u> of the density matrix in the $\hat{Q}$ representation are the combined quantum and a priori probabilities of the observable giving eigenvalues Q_μ as measurement outcomes.

The <u>off-diagonal elements</u> have no classical interpretation. They measure quantum correlations and come into play when, e.g., we want the expectation value of an observable other than that in whose representation we chose to write $\hat{\rho}$: for an observable $\hat{P}$,

$$\bar{P} = \mathrm{Tr}(\hat{\rho}\hat{P}) = \sum_{\mu'} \langle Q_{\mu'}| \overbrace{\sum_{\mu\nu} p_{\mu\nu} |Q_\mu\rangle\langle Q_\nu|}^{\hat{\rho}} \hat{P} |Q_{\mu'}\rangle$$

$$= \sum_{\mu\nu} p_{\mu\nu} \langle Q_\nu|\hat{P}|Q_\mu\rangle \qquad (9).$$

13.3 Quantum Entropy

The generalisation of Gibbs entropy in this formalism is the <u>Von-Neumann Entropy</u>:

definition of $\ln\hat{\rho}$

$$\boxed{S_{VN} = -\mathrm{Tr}(\hat{\rho}\ln\hat{\rho}) =} \qquad (10)$$

$$= -\sum_\alpha \langle\alpha| \left(\sum_\mu p_\mu |\mu\rangle\langle\mu|\right) \overbrace{\left(\sum_\nu \ln p_\nu |\nu\rangle\langle\nu|\right)} |\alpha\rangle$$

$$= -\sum_{\alpha\mu\nu} p_\mu \ln p_\nu \underbrace{\langle\alpha|\mu\rangle}_{\delta_{\alpha\mu}} \underbrace{\langle\mu|\nu\rangle}_{\delta_{\mu\nu}} \underbrace{\langle\nu|\alpha\rangle}_{\delta_{\nu\alpha}} =$$

$$= -\sum_\alpha p_\alpha \ln p_\alpha \quad \text{same as Gibbs entropy}$$

As always, we find p_α's by maximising this subject to constraints imposed by the information we possess, often in the form of exp. values – eq. (3).

The canonical distribution has the following density matrix, in energy representation:

$$\left.\begin{aligned} \hat\rho &= \sum_\alpha \frac{e^{-\beta E_\alpha}}{Z} \underset{\uparrow \text{ eigenkets of } \hat H}{|\alpha\rangle\langle\alpha|} = \frac{1}{Z} e^{-\beta \hat H} \\ \text{where } Z &= \sum_\alpha e^{-\beta E_\alpha} = \mathrm{Tr}\, e^{-\beta \hat H} \end{aligned}\right\} \quad (11)$$

13.4 Time Evolution

If we know $\hat\rho$ at some time, we can easily find it at any later time:

$$\frac{d\hat\rho}{dt} = \sum_\alpha p_\alpha \left(\frac{\partial|\alpha\rangle}{\partial t}\langle\alpha| + |\alpha\rangle \frac{\partial\langle\alpha|}{\partial t}\right)$$

probabilities do not change: if system was in state $|\alpha(0)\rangle$ initially, it'll be in its descendant state $|\alpha(t)\rangle$ at later time t

$$= \frac{1}{i\hbar}\sum_\alpha p_\alpha \left(\hat H|\alpha\rangle\langle\alpha| - |\alpha\rangle\langle\alpha|\hat H\right) = \frac{\hat H\hat\rho - \hat\rho\hat H}{i\hbar}$$

$$\text{or } \quad i\hbar\frac{d\hat\rho}{dt} = [\hat H, \hat\rho] \quad (12)$$

Time-dependent Schrödinger equation

So we may envision a situation where we are uncertain about a system's initial conditions, work out $\hat{\rho}(t=0)$ via the max. ent. principle (constrained by some measurements) and then evolve it forever if we know the Hamiltonian precisely.

Since p_λ's do not change, the Gibbs (= von Neumann) entropy of the system stays the same during this time evolution — the only uncertainty was in the initial conditions.

What if we do not know the Hamiltonian? (or choose to forget) This was discussed in § 12.6: then, at some later time, we may make another measurement and ~~again~~ construct the new density matrix $\hat{\rho}_{new}(t)$ via the max. entropy principle.

Same as the argument in § 12.6

Both $\hat{\rho}_{new}(t)$ and $\hat{\rho}_{old}(t)$ – our $\hat{\rho}(0)$ evolved via (12) with the (unknown) precise $\hat{H}$ are consistent with the new measurement. But $\hat{\rho}_{new}(t)$ corresponds to the max. possible value of Gibbs entropy consistent with this measurement while $\hat{\rho}_{old}(t)$ has the same entropy as $\hat{\rho}(0)$ did at $t=0$.

Therefore, $S_{new}(t) > S_{old}(0)$ 2nd law.

13.5 How Information is lost

In practice, for the purposes of physical measurement, the world can be thought of as consisting of two parts:

- the system to be measured
- the rest of the world: the environment, including the measurement apparatus (sometimes only it if the experiment is "isolated")

The observables we have and so the info we will use for statistical inference will pertain to the system, while the environment will remain mysterious.

For example, imagine we measured the energy of the system at some initial time. For lack of better knowledge, it is natural to make stat. inferences about the microstates of the world in the following form:

$$\underbrace{|\alpha\alpha', 0\rangle}_{\text{time } 0} = \underbrace{|E_\alpha^{(s)}(0)\rangle}_{\text{energy states of the system}} \underbrace{|E_{\alpha'}^{(e)}(0)\rangle}_{\text{energy state of the environment (unknown!)}} \qquad (13)$$

So,

$$\hat{\rho}(0) = \sum_{\alpha\alpha'} \underbrace{p_{\alpha\alpha'}}_{\text{probabilities of } |E_\alpha^{(s)}(0)\rangle \text{, indifferent to } |E_{\alpha'}^{(e)}(0)\rangle} |\alpha\alpha', 0\rangle\langle\alpha\alpha', 0| \qquad (14)$$

Now evolve this density matrix according to TDSE (12): $p'_{\alpha\alpha}$s will stay the same, while

$$|\alpha\alpha',0\rangle \to |\alpha\alpha',t\rangle \neq |E^{(s)}_{\alpha}(t)\rangle |E^{(e)}_{\alpha'}(t)\rangle$$

The descendants of the old states will not in general be superpositions of the energy states of the system and the environment

This is because the system and the environment get entangled. Formally speaking,

$|E^{(s)}_{\alpha}\rangle$ are eigenstates of $\hat{H}^{(s)}$ - Hamiltonian of the system

$|E^{(e)}_{\alpha}\rangle$ " " of $\hat{H}^{(e)}$ - " of the environment

but $|E^{(s)}_{\alpha}\rangle |E^{(e)}_{\alpha}\rangle$ are not eigenstates of the world's Hamiltonian:

$$\hat{H} = \hat{H}^{(s)} + \hat{H}^{(e)} + \underbrace{\hat{H}^{(int)}}_{\text{interaction!}}$$

If now, at time t, we wish to measure the energy of the system again, we will have to make stat. inferences about superposed eigenstates:

$$|\mu\mu', \text{new}\rangle = |E^{(s)}_{\mu}(t)\rangle |E^{(e)}_{\mu'}(t)\rangle \neq |\alpha\alpha',t\rangle \quad (15)$$

In this representation, our old density matrix is not diagonal:

$$\hat{\rho}^{(old)}(t) = \sum_{\alpha\alpha'} P^{(old)}_{\alpha\alpha'} |\alpha\alpha', t\rangle\langle\alpha\alpha', t| =$$

$$= \sum_{\alpha\alpha'} P^{(old)}_{\alpha\alpha'} \sum_{\mu\mu'} \sum_{\nu\nu'} \langle\mu\mu', new|\alpha\alpha', t\rangle\langle\alpha\alpha', t|\nu\nu', new\rangle \cdot |\mu\mu', new\rangle\langle\nu\nu', new|$$

$$= \sum_{\mu\mu'} \sum_{\nu\nu'} P^{(old)}_{\mu\mu'\nu\nu'}(t) |\mu\mu', new\rangle\langle\nu\nu', new|, \qquad (16)$$

where $P^{(old)}_{\mu\mu'\nu\nu'}(t) = \sum_{\alpha\alpha'} P^{(old)}_{\alpha\alpha'} \langle\mu\mu', new|\alpha\alpha', t\rangle\langle\alpha\alpha', t|\nu\nu', new\rangle$

[see eq. (7)].

But the measured energy of the system at time t only depends on ~~the diagonal elements~~ the diagonal ~~elements~~ elements:

$$U = \mathrm{Tr}\left[\hat{\rho}^{(old)}(t)\, \hat{H}^{(s)}(t)\right] =$$

$$= \sum_{\alpha\alpha'} \sum_{\mu\mu'} \sum_{\nu\nu'} P^{(old)}_{\mu\mu'\nu\nu'}(t) E^{(s)}_{\nu}(t) \langle\alpha\alpha', new|\mu\mu', new\rangle \langle\nu\nu', new|\alpha\alpha', new\rangle$$

$$= \sum_{\alpha\alpha'} E^{(s)}_{\alpha}(t)\, \underbrace{P^{(old)}_{\alpha\alpha'\alpha\alpha'}(t)}_{\text{diagonal elements}} \qquad (17)$$

<u>All information about correlations between the system and the environment is lost in this measurement.</u>

When we maximize entropy and thus make a new statistical inference about the system, the new entropy will be higher than the old for two reasons:

1) All off-diagonal elements from the old density matrix are lost

2) The diagonal elements $p^{(old)}_{\alpha\alpha'\alpha\alpha'}(t)$ are in general not the ones that maximise entropy, $p^{(new)}_{\alpha\alpha'}$ — same argument as in §12.6.

Thus,

$$\hat{\rho}^{(new)} = \sum_{\alpha\alpha'} p^{(new)}_{\alpha\alpha'} |\alpha\alpha', new\rangle\langle\alpha\alpha', new| \qquad (18)$$

will have

$$S^{(new)}_{VN} = -\mathrm{Tr}\left[\hat{\rho}^{(new)} \ln \hat{\rho}^{(new)}\right] > S^{(old)}_{VN}(t) = -\mathrm{Tr}\left[\hat{\rho}^{(old)}(t) \ln \hat{\rho}^{(old)}(t)\right]$$

(19)
$$= S^{(old)}_{VN}(0) = -\mathrm{Tr}\left[\hat{\rho}(0) \ln \hat{\rho}(0)\right]$$

old entropy did not change because $p_{\alpha\alpha'}$'s did not change.

Thus, information is lost and we move forward to ever more boring world... (which is a very interesting fact!) So don't despair!

[You might think of what has happened as ~~the~~ our total ignorance about the environment having polluted our knowledge about the system as a result of the former getting entangled with the latter.]