From LvN to Schrodinger Equation

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Abstract

In standard Quantum Mechanics approach, it is convenient to define *state vectors* and their evolution in context of Schrodinger equation. Then, taking into account the *experimental* (or as some references say, *classical*) errors and define the *density matrix* as a comprehensive quantity to describe the outcomes of desired measurements in the problems. Then, the evolution of this quantity can be produced from that of individual state vectors by Schrodinger equation which leads to Liouville-Von Neumann (LvN) equation describing the evolution of density matrices.

In this paper, I investigate the converse approach: Having known the evolution of density matrix, trying to find the evolution of a system with *pure* state (no experimental error). I'll show that this is *impossible* since evolution of density matrix doesn't imply a *unique* equation for each individual state vector. Finally, I'll show that Quantum Mechanics can be considered as treating density matrices *fundamental*, rather than state vectors.

1 Review: Purpose of Density Matrix

In Quantum Mechanics, it is known that the measurement of a physical quantity $\hat{X}$ on a quantum system described by the state vector $|\psi\rangle$ results in the probability of obtaining the outcome x_i, corresponding to the eigenvector $|x_i\rangle$ where $\hat{X}|x_i\rangle = x_i|x_i\rangle$, being given by Born's rule:

$$P(x_i) = |\langle x_i|\psi\rangle|^2 = \langle x_i|\psi\rangle\langle\psi|x_i\rangle$$

provided $|\psi\rangle$ is properly normalized to unity. If an ensemble of systems is prepared with similar state vector, the expectation value of $\hat{X}$ measurement can be obtained by:

$$\langle X\rangle = \sum_i x_i P(x_i) = \sum_i x_i \langle x_i|\psi\rangle\langle\psi|x_i\rangle = \sum_i \langle x_i|\left(\hat{X}|\psi\rangle\langle\psi|\right)|x_i\rangle$$

Since $\hat{X}$ is a physical quantity therefore Hermitian, its eigenvectors $|x_i\rangle$'s form an orthonormal basis. Hence, obtained expression is a trace of the operator inside the parentheses:

$$\langle X\rangle = \mathrm{Tr}\left[\hat{X}|\psi\rangle\langle\psi|\right] \tag{1}$$

In this approach, we were given a quantum system knowing exactly its state and we aimed to find expectation value for each outcome. Now, let's take some *experimental error* into account. We no longer know the exact state, but a set of states and their corresponding probability to occur. This error is due entirely to our *ignorance*, not to any quantum phenomena.

Consider a quantum system which is in state $|\psi_i\rangle$ with probability q_i. We aim to find the expectation value of physical quantity $\hat{X}$ with previously mentioned notation:

$$\langle X\rangle = \sum_i q_i \langle X\rangle_i$$

where $\langle X\rangle_i$ is the expectation value of X corresponding to state $|\psi_i\rangle$. It can be extended by the formula (1):

$$\langle X\rangle = \sum_i q_i \,\mathrm{Tr}\Big[\hat{X}\, |\psi_i\rangle\!\langle\psi_i|\Big] = \mathrm{Tr}\left[\hat{X} \sum_i q_i \,|\psi_i\rangle\!\langle\psi_i|\right]$$

Hence, it can be represented in term of density matrix as follows:

$$\hat{\rho} := \sum_i q_i \,|\psi_i\rangle\!\langle\psi_i| \tag{2}$$

$$\langle X\rangle = \mathrm{Tr}\Big[\hat{X}\hat{\rho}\Big] \tag{3}$$

It is worth mentioning that density matrix is defined to describe *expectation values* not the ensemble distribution. There is no guarantee that two distinct distribution result two non-equal density matrices.

2 From LvN to Schrodinger

Let's see what we get for the evolution of individual state vectors from that of density matrix. I write down the Liouville-Von Neumann equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho} = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}\right]$$

I consider a pure state (a definite state): $\hat{\rho} = |\psi\rangle\!\langle\psi|$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\,|\psi\rangle\!\langle\psi| &= -\frac{i}{\hbar}\left(\hat{H}\,|\psi\rangle\!\langle\psi| - |\psi\rangle\!\langle\psi|\,\hat{H}\right)\\ &= \left(\frac{\mathrm{d}}{\mathrm{d}t}\,|\psi\rangle\right)\langle\psi| + |\psi\rangle\left(\frac{\mathrm{d}}{\mathrm{d}t}\,\langle\psi|\right)\end{aligned}$$

I use a simpler notation for convenience:

$$|\partial_t\psi\rangle\!\langle\psi| + |\psi\rangle\!\langle\partial_t\psi| = -\frac{i}{\hbar}\left(\hat{H}\,|\psi\rangle\!\langle\psi| - |\psi\rangle\!\langle\psi|\,\hat{H}\right)$$

by plugging a $|\psi\rangle$ from right assuming the state vector to be properly normalized:

$$|\partial_t\psi\rangle + |\psi\rangle\langle\partial_t\psi|\psi\rangle = -\frac{i}{\hbar}\left(\hat{H}|\psi\rangle - |\psi\rangle\langle\psi|\hat{H}|\psi\rangle\right)$$

rearranging the expression:

$$|\partial_t\psi\rangle + \frac{i}{\hbar}\hat{H}|\psi\rangle = \frac{i}{\hbar}|\psi\rangle\langle\psi|\hat{H}|\psi\rangle - |\psi\rangle\langle\partial_t\psi|\psi\rangle$$

$$|\partial_t\psi\rangle + \frac{i}{\hbar}\hat{H}|\psi\rangle = -|\psi\rangle\left(\langle\partial_t\psi| - \frac{i}{\hbar}\langle\psi|\hat{H}\right)|\psi\rangle \tag{4}$$

It's all LvN tells us. It's sufficient to determine density matrix $|\psi\rangle\langle\psi|$ but it doesn't itself suffice to obtain $|\psi\rangle$ uniquely. Indeed, LvN equation doesn't preserve the norm of state vector (in contrast to Schrodinger equation). Let's attempt to "plug" the normalization of $|\psi\rangle$ at all instants:

$$\langle\partial_t\psi|\psi\rangle = -\langle\psi|\partial_t\psi\rangle$$

Therefore:

$$|\partial_t\psi\rangle + \frac{i}{\hbar}\hat{H}|\psi\rangle = \frac{i}{\hbar}|\psi\rangle\langle\psi|\hat{H}|\psi\rangle + |\psi\rangle\langle\psi||\partial_t\psi\rangle$$

$$(1 - |\psi\rangle\langle\psi|)\left(|\partial_t\psi\rangle + \frac{i}{\hbar}\hat{H}|\psi\rangle\right) = 0$$

which is possible only if:

$$|\partial_t\psi\rangle + \frac{i}{\hbar}\hat{H}|\psi\rangle = \alpha(t)|\psi\rangle$$

where $\alpha(t)$ is a time-dependent complex-valued scalar. It follows then:

$$\langle\psi|\partial_t\psi\rangle + \frac{i}{\hbar}\langle\psi|\hat{H}|\psi\rangle = \alpha(t)$$

$$\langle\partial_t\psi|\psi\rangle - \frac{i}{\hbar}\langle\psi|\hat{H}|\psi\rangle = \alpha^*(t)$$

It is now obvious that the normalization condition implies that:

$$\alpha + \alpha^* = 0$$

which means that α is a pure imaginary number:

$$\alpha = ir,\ r \in \mathbb{R}$$

Therefore, the most general formula for evolution of an individual state vector which obeys LvN and preserves the normalization is found:

$$\frac{\mathrm{d}}{\mathrm{d}t}|\psi\rangle + \frac{i}{\hbar}\hat{H}|\psi\rangle = ir|\psi\rangle \tag{5}$$

with r an arbitrary real-valued number.

I now, show that the RHS term of (5) can be properly removed just by a phase:

$$|\Phi\rangle := e^{-i\phi}|\psi\rangle\,,\ \phi \in \mathbb{R}$$

$$e^{i\phi}\frac{\mathrm{d}}{\mathrm{d}t}|\Phi\rangle + i\frac{\mathrm{d}\phi}{\mathrm{d}t}|\psi\rangle + \frac{i}{\hbar}e^{i\phi}\hat{H}|\Phi\rangle = ir|\psi\rangle$$

So, choosing $\phi(t) = rt$ leads to the common Schrodinger equation for $|\Phi\rangle$:

$$\frac{\mathrm{d}}{\mathrm{d}t}|\Phi\rangle + \frac{i}{\hbar}\hat{H}|\Phi\rangle = 0 \tag{6}$$

3 Density Matrix as Fundamental

In my approach, I chose state vectors to be *fundamental* rather than density matrix. It made the usage of normalization, kind of "out of nowhere" to me. However, this approach can be revised by beginning the QM postulates with density matrix as follows.

3.1 Postulates

- **Postulate 1: States.** The state of a quantum system is given by a normalized, positive semi-definite, Hermitian operator called *density matrix* $\hat{\rho}$ on a Hilbert space. Normalization condition of the operator is given by:

$$\mathrm{Tr}[\hat{\rho}] = 1$$

- **Postulate 2: Evolution.** The evolution of density matrix is given by a unitary operator called *time-evolution operator* $\hat{U}(t, t_0)$ given by:

$$\hat{\rho}(t) = \hat{U}(t, t_0)\hat{\rho}(t_0)\hat{U}^{\dagger}(t, t_0)$$

- **Postulate 3: Measurement.**

  i Any measurement corresponds to a Hermitian operator $\hat{A}$ on Hilbert space. The set of possible outcomes is the set of eigenvalues of this operator.

  ii Density matrix of the system after measurement is given by:

  $$\hat{\rho}_{\text{after}} = \sum_i |a_i\rangle\langle a_i|\,\hat{\rho}_{\text{prior}}\,|a_i\rangle\langle a_i|$$

  where $|a_i\rangle$ is the i'th eigenvector of $\hat{A}$ normalized by unity.

  iii The probability of the outcome to be a_i is given by:

  $$P(a_i) = \sum_g \sum_i \langle a_i, g|\,\hat{\rho}\,|a_i, g\rangle$$

  where g counts the basis in degenerate subspace.

- **Postulate 4: Composite systems.** The Hilbert space of a system composed of some subsystem is given by the *tensor product* of the Hilbert space of each.

3.2 First Postulate Revised

The first postulate seems weird because of many non-trivial constraints it sets for density matrix; those which were proven in standard approach from a conceivable definition of density matrix. In fact, this postulate can be revised by the following more ”sensing” conditions with aid of third postulate:

- Probabilities are real. (Therefore, $\hat{\rho}$ is Hermitian.)
- Expectation value for square of an observable is semi-positive. (Therefore, $\hat{\rho}$ is positive semi-definite.)
- Expectation value of identity $\hat{\mathbb{1}}$ is 1. (Therefore, $\mathrm{Tr}[\hat{\rho}] = 1$)

The last two conclusions is simply obtained if I express the expectation value of an observable from third postulate:

$$\langle A\rangle = \sum_i a_i P(a_i) = \sum_i a_i \langle a_i|\,\hat{\rho}\,|a_i\rangle = \sum_i \langle a_i|\,\hat{A}\hat{\rho}\,|a_i\rangle = \mathrm{Tr}\Big[\hat{A}\hat{\rho}\Big]$$

where i counts also the degenerate subspace basis.

3.3 Derivation of LvN From Second Postulate

Also, the differential equation governing density matrix (LvN) can be derived from this postulate as follows (I denote, for clarity, $\hat{\rho}(t_0)$ as $\hat{\rho}_0$ and $\hat{U}(t, t_0)$ as $\hat{U}$):

$$\dot{\hat{\rho}} = \dot{\hat{U}}\hat{\rho}_0\hat{U}^\dagger + \hat{U}\hat{\rho}_0\dot{\hat{U}}^\dagger$$

It is known that $\hat{U}$ is unitary. Therefore:

$$\dot{\hat{U}}^\dagger\hat{U} = -\hat{U}^\dagger\dot{\hat{U}}$$

$$\dot{\hat{U}}^\dagger = -\hat{U}^\dagger\dot{\hat{U}}\hat{U}^\dagger$$

The evolution equation becomes:

$$\dot{\hat{\rho}} = \dot{\hat{U}}\hat{\rho}_0\hat{U}^\dagger - \hat{U}\hat{\rho}_0\hat{U}^\dagger\dot{\hat{U}}\hat{U}^\dagger$$

Since $\hat{\mathbb{1}} = \hat{U}^\dagger\hat{U}$, it becomes:

$$\dot{\hat{\rho}} = \dot{\hat{U}}\hat{U}^\dagger\hat{U}\hat{\rho}_0\hat{U}^\dagger - \hat{U}\hat{\rho}_0\hat{U}^\dagger\dot{\hat{U}}\hat{U}^\dagger$$

I define the Hermitian operator $\hat{H}$ called *Hamiltonian* as:

$$\hat{H} := i\hbar\dot{\hat{U}}\hat{U}^\dagger$$

Then, LvN is obtained by replacing $\hat{U}\hat{\rho}_0\hat{U}^\dagger$ by $\hat{\rho}$ from the postulate:

$$\dot{\hat{\rho}} = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}\right]$$

Here, I never claimed that $\hat{H}$ is exactly the classical Hamiltonian; just similar to "standard" approach (beginning from Schrodinger equation). It's a fact that must be verified *experimentally* in both approaches.

References

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