Notes on General Features of the Time Dependent Schrödinger Equation (TDSE)

October 12, 1995

Massachusetts Institute of Technology

Department of Physics

Physics 8.04 October 12, 1995

So far we have built up a quantum kinematic theory based on the Principle of Superposition and the interpretation of the square of quantum amplitudes in a superposition as probabilities and the first de Broglie hypothesis ($\lambda = h/p$). Upon this base we built the mathematical framework of operators, and as verification of our kinematic framework, we have seen that the Heisenberg uncertainty may be proven directly from within this framework.

We then used the principle of quantum determinism and the second de Broglie hypothesis ($\nu = E/h$) to lead us to posit the time dependent Schrödinger equation (TDSE) to describe the dynamic evolution of states. In its most general form, the TDSE reads,

$$i\hbar\partial_t|\psi(t)>= \hat{H}|\psi(t)>, \tag{1}$$

where $\hat{H}$ is the Hamiltonian (energy) operator.

For the rest of this course we will concern ourselves nearly exclusively with simple position-momentum systems of a single particle. We will also work primarily within the position representation. In these circumstances, the Hamiltonian operator in the position representation reads $\hat{H} = \frac{\hat{\vec{p}}^2}{2m} + V(\hat{\vec{x}}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x})$ in the three dimensions, so that the TDSE becomes

$$i\hbar\partial_t\psi(\vec{x},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x},t) + V(\vec{x})\psi(\vec{x},t). \tag{2}$$

In this course we will for the most part focus on system in one dimension, in which case the TDSE is just

$$i\hbar\partial_t\psi(x,t) = -\frac{\hbar^2}{2m}\partial_x^2\psi(x,t) + V(x)\psi(x,t).$$

All of what we are about to discuss is true for both one and three dimensional systems. To keep our results general, we will stick to the more general form (2) for now. The student should be able to recover the developments for the one dimensional case by simply removing the vector "$\vec{\ }$" symbols and replacing ∇ with ∂_x in all of the equations below. The rest of this note is prepared with that understanding.

The purpose of this set of notes is to explore the general features of the Schrödinger equation (2). In particular, as a check on our hypothesized dynamics, we will verify two things. We will first verify that (2) is consistent with the interpretation of $|\psi(\vec{x},t)|^2$ as a probability by showing that under (2) $\psi(\vec{x},t)$ remains normalized, that probability is *conserved.* We will then show that (2) is consistent with the correspondence principle by proving Ehrenfest's theorem, the statement that well-localized wave packets obey Newtonian dynamics, $\frac{d}{dt} < \vec{x} >=< \vec{p} > /m$ and $\frac{d}{dt} < \vec{p} >=< -\vec{\nabla} V(\vec{x}) >$. We will prove, in fact, that Ehrenfest's theorem is completely general and holds not only for well-localized wavepackets but for all quantum states.

1 Conservation of Probability

1.1 Continuity Equation

Conserved quantities in physics obey the *continuity equation.* If a quantity Q (such as charge) is conserved, neither spontaneously created or destroyed, then the time rate of change $\frac{dQ}{dt}$ of the amount of that quantity in a closed region of space V must equal the total rate S at which the quantity is pumped into or removed from the region by any sources or sinks in the region *minus* the net rate (current) I at which that quantity flows through the surface of the region,

$$\frac{dQ}{dt} = S - I.$$

We may turn this condition into an *integral* equation by defining a density field for the conserved quantity (such as charge density) $\rho(\vec{x},t)$, a sink/source density $s(\vec{x},t)$, and a current density (like the usual electric current density) $\vec{j}(\vec{x},t)$ defined so that the rate at which the conserved quantity crosses a surface element $d\vec{A}$ is $\vec{j}\cdot d\vec{A}$. Our condition for conservation in the region of space V may now be expressed as the integral condition,

$$\begin{aligned}
\frac{d}{dt}\iiint_V \rho(\vec{x},t)\,dV &= \iiint_V s(\vec{x},t)\,dV - \iint_A \vec{j}(x,t)\cdot d\vec{A} \\
\Rightarrow \iiint_V \partial_t\rho(\vec{x},t)\,dV &= \iiint_V s(\vec{x},t)\,dV - \iint_A \vec{j}(\vec{x},t)\cdot d\vec{A}.
\end{aligned}$$

If we express this relation on a per unit volume basis and take the limit as the volume of the region vanished $V \to 0$, we find a differential equation describing conservation, the *continuity equation*,

$$\begin{aligned}
\lim_{V\to 0}\frac{1}{V}\iiint_V \partial_t\rho(\vec{x},t)\,dV &= \lim_{V\to 0}\frac{1}{V}\iiint_V s(\vec{x},t)\,dV - \lim_{V\to 0}\frac{1}{V}\iint_A \vec{j}(\vec{x},t)\cdot d\vec{A} \\
\partial_t\rho(\vec{x},t) &= s(\vec{x},t) - \vec{\nabla}\cdot\vec{j}(\vec{x},t).
\end{aligned}$$

The continuity equation is most often written in the form,

$$\partial_t\rho(\vec{x},t) + \vec{\nabla}\cdot\vec{j}(\vec{x},t) = s(\vec{x},t) \tag{3}$$

1.2 Global Conservation

With this very general mathematical result, we may now demonstrate the simple idea that without the introduction or removal of a conserved quantity ($s(\vec{x},t) = 0$), the integral over all of space of the density of the quantity remains fixed. This may shown directly from (3),

$$\begin{aligned}
\frac{d}{dt}\iiint \rho(\vec{x},t)\,dV &= \iiint \partial_t\rho(\vec{x},t)\,dV \\
&= -\iiint \vec{\nabla}\cdot\vec{j}(\vec{x},t)\,dV \quad \text{; from (3) with } s(\vec{x},t) = 0 \\
&= -\iint \vec{j}(\vec{x},t)\cdot d\vec{A} \quad \text{; divergence theorem} \\
&\longrightarrow 0.
\end{aligned}$$

In the final step, we use the fact that for any finite system, there is no current density at infinite distances, $\vec{j}(\vec{x},t)_{\vec{x}\to\infty} \to 0$ and so the final surface integral at infinity vanishes.

1.3 Probability Currents

We will now use a very general procedure to show that probability is conserved under the dynamics given by the TDSE. By conservation of probability we mean the requirement that the integral of $\mathcal{P}$ will remain properly normalized $\int \mathcal{P}(\vec{x},t)\,dV = 1$ for all time $t > 0$. The procedure we are about to use is very general. It is used, for instance, to show that energy and momentum are conserved in electrodynamics under Maxwell's equations and that mass and momentum are conserved under the equations of Newtonian fluid flow.

As we saw in the previous section the mathematical condition that $\mathcal{P} = |\psi(\vec{x},t)|^2$ be conserved is that it obey the continuity equation with no source term ($s(\vec{x},t) = 0$) as $\psi(\vec{x},t)$ evolves according to the TDSE. To demonstrate conservation all that we must now do is identify a *probability current* density $\vec{j}(\vec{x},t)$ so that $\partial_t \mathcal{P}(\vec{x},t) + \vec{\nabla}\cdot\vec{j}(\vec{x},t) = 0$.

To identify this current density, we begin with the time derivative in the equation of continuity (3) and then employ our knowledge of the time derivatives of ψ through the TDSE (2),

$$\begin{aligned}
-\vec{\nabla}\cdot\vec{j}(\vec{x},t) &= \partial_t \mathcal{P}(\vec{x},t) \\
&= \partial_t \left(\psi^*(\vec{x},t)\psi(\vec{x},t)\right) \\
&= \left(\partial_t\psi(\vec{x},t)\right)^* \psi(\vec{x},t) + \psi^*(\vec{x},t)\left(\partial_t\psi(x,t)\right) \\
&= \left(\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x},t) + V(\vec{x})\psi(\vec{x},t)\right)\right)^* \psi(\vec{x},t) + \\
&\qquad \psi^*(\vec{x},t)\left(\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x},t) + V(\vec{x})\psi(\vec{x},t)\right)\right) \quad ;\ \text{TDSE} \\
&= -\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x},t) + V(\vec{x})\psi(\vec{x},t)\right)^* \psi(\vec{x},t) + \\
&\qquad \frac{1}{i\hbar}\psi^*(\vec{x},t)\left(-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x},t) + V(\vec{x})\psi(\vec{x},t)\right) \\
&= \frac{1}{i\hbar}\left(\frac{\hbar^2}{2m}(\nabla^2\psi^*(\vec{x},t))\psi(\vec{x},t) - \psi^*(\vec{x},t)(\nabla^2\psi(\vec{x},t))\right) - \\
&\qquad \frac{1}{i\hbar}\left(V^*(\vec{x},t) - V(\vec{x},t)\right)\psi^*(\vec{x},t)\psi(\vec{x},t) \\
&= \frac{\hbar}{2im}\left((\nabla^2\psi^*)\psi - \psi^*(\nabla^2\psi)\right) \quad ;\ V \text{ is real}
\end{aligned}$$

To complete the identification of $\vec{j}$, express the hand side of the above expression as the divergence of some quantity. This we do by noting the following identity of vector calculus, which amounts to integration by parts,

$$\begin{aligned}
\vec{\nabla}\cdot\left((\vec{\nabla}\psi^*)\psi - \psi^*(\vec{\nabla}\psi)\right) &= \left(\left((\nabla^2\psi^*)\psi + \vec{\nabla}\psi^*\cdot\vec{\nabla}\psi - \vec{\nabla}\psi^*\cdot\vec{\nabla}\psi - \psi^*\nabla^2\psi\right)\right) \\
&= (\nabla^2\psi^*)\psi - \psi^*(\nabla^2\psi).
\end{aligned}$$

Inserting this into our previous result gives

$$-\vec{\nabla}\cdot\vec{j}(\vec{x},t) = \frac{\hbar}{2im}\vec{\nabla}\cdot\left((\vec{\nabla}\psi^*)\psi - \psi^*(\vec{\nabla}\psi)\right). \tag{4}$$

Thus, our final form for the probability current density is

$$\vec{j}(\vec{x},t) = \frac{\hbar}{2im}\left(\psi^*(\vec{x},t)(\vec{\nabla}\psi(\vec{x},t)) - (\vec{\nabla}\psi^*(\vec{x},t))\psi(\vec{x},t)\right). \tag{5}$$

For $\psi(\vec{x},t)$ developing under the Schrödinger equation, this $\vec{j}$ satisfies the continuity equation with no source term,

$$\partial_t|\psi(\vec{x},t)|^2 + \vec{\nabla}\cdot\vec{j}(\vec{x},t) = 0. \tag{6}$$

Thus, probability is conserved and the rate of change of probability in a region V balances the total flux leaving the region,

$$\frac{d}{dt}\iiint_V |\psi(\vec{x},t)|^2\, dV + \iint_A \vec{j}(\vec{x},t)\cdot d\vec{A} = 0, \tag{7}$$

and the total probability in all of space is conserved,

$$\frac{d}{dt}\iiint |\psi(\vec{x},t)|^2\, dV = 0. \tag{8}$$

1.4 Supplemental note on the uniqueness of $\vec{j}$.

One subtle point in our development is that (4) only determines $\vec{\nabla}\cdot\vec{j}$, it does not determine $\vec{j}$ completely. For instance we may add the curl of any vector field $\vec{C}$ to our form,

$$\vec{j} = \frac{\hbar}{2im}\left(\psi^*(\vec{x},t)(\vec{\nabla}\psi(\vec{x},t)) - (\vec{\nabla}\psi^*(\vec{x},t))\psi(\vec{x},t)\right) + \vec{\nabla}\times\vec{C},$$

without affecting (4) because $\vec{\nabla}\cdot\vec{\nabla}\times\vec{C} = 0$ for all vector fields $\vec{C}$. Fortunately, the freedom involved in this choice has no physical consequences because when integrating the flux over any closed surface, the term $\vec{\nabla}\times\vec{C}$ has no effect, $\iint_A(\vec{\nabla}\times\vec{C})\cdot d\vec{A} = 0$. In writing (5) we did make a particular choice, however. We made the conventional choice of the $\vec{j}$ consistent with (4) which minimizes the total magnitude of the flow $\iiint |\vec{j}(\vec{x},t)|^2\, dV$. This minimization condition is equivalent to insisting $\vec{\nabla}\times\vec{j} = 0$. A quick calculation (keeping in mind that $\vec{\nabla}\times\vec{\nabla}\phi = 0$ for any scalar field ϕ) verifies that our form (5) meets this condition,

$$\begin{aligned}
\vec{\nabla}\times\frac{\hbar}{2im}\left(\psi^*(\vec{\nabla}\psi) - (\vec{\nabla}\psi^*)\psi\right) &= \frac{\hbar}{2im}\vec{\nabla}\times\left(\psi^*(\vec{\nabla}\psi) - (\vec{\nabla}\psi^*)\psi\right) \\
&= \frac{\hbar}{2im}\left((\vec{\nabla}\psi^*)\times(\vec{\nabla}\psi) - (\vec{\nabla}\psi^*)\times(\vec{\nabla}\psi)\right) \\
&= 0
\end{aligned}$$

2 Ehrenfest's Theorem

By the correspondence principle, the dynamics we have introduced via equation (2) must ensure that we recover Newtonian behavior for well-localized wave packets,

$$m\frac{d^2}{dt^2} < \vec{x} > = < -\vec{\nabla}V(\vec{x}) > \equiv < \vec{F} > . \tag{9}$$

That this is true follows directly from Ehrenfest's theorem. Ehrenfest's theorem is a much stronger statement which holds exactly true for the time development of all quantum states (not just well-localized wave packets). Ehrenfest's theorem states

$$\frac{d}{dt} < \vec{x} > \quad = \quad < \vec{p} > /m \tag{10}$$

and

$$\frac{d}{dt} < \vec{p} > \quad = \quad < -\vec{\nabla}V(\vec{x}) >, \tag{11}$$

from which follows immediately the usual second order Newtonian equation of motion (9),

$$m\frac{d^2}{dt^2} < \vec{x} > = m\frac{d}{dt}\left(\frac{d}{dt} < \vec{x} >\right) = m\frac{d}{dt}\left(\frac{< \vec{p} >}{m}\right) = \frac{d}{dt} < \vec{p} > = < -\vec{\nabla}V(\vec{x}) > = < \vec{F} > .$$

2.1 General result for the time derivative of any operator

The proof of Ehrenfest's theorem proceeds directly and in a similar manner to the proof of the continuity equation: we begin with the time derivatives in the statement we wish to prove and then replace the time derivatives using the TDSE. The first part of the proof of Ehrenfest's Theorem is very general. It applies to the time derivative of the average of any physical observable and depends only on the TDSE and the fact that the Hamiltonian operator, being associated with the observable E, is always Hermitian. We will give the general result for an arbitrary operator $\hat{\mathcal{O}}$ first and then apply this result to prove Ehrenfest's theorem.

The time derivative of the average of an observable $\mathcal{O}$ will always obey

$$\begin{aligned}
\frac{d}{dt} < \mathcal{O} > &\equiv \partial_t(\psi(\vec{x},t), \hat{\mathcal{O}}\psi(\vec{x},t)) \\
&= (\partial_t\psi(\vec{x},t), \hat{\mathcal{O}}\psi(\vec{x},t)) + (\psi(\vec{x},t), \hat{\mathcal{O}}\partial_t\psi(\vec{x},t)) \quad \text{; product rule for derivatives} \\
&= (\frac{1}{i\hbar}\hat{H}\psi(\vec{x},t), \hat{\mathcal{O}}\psi(\vec{x},t)) + (\psi(\vec{x},t), \hat{\mathcal{O}}\frac{1}{i\hbar}\hat{H}\psi(\vec{x},t)) \quad \text{; TDSE} \\
&= -\frac{1}{i\hbar}(\hat{H}\psi(\vec{x},t), \hat{\mathcal{O}}\psi(\vec{x},t)) + \frac{1}{i\hbar}(\psi(\vec{x},t), \hat{\mathcal{O}}\hat{H}\psi(\vec{x},t)) \\
&\qquad \text{; linearity properties of Hermitian inner product} \\
&= -\frac{1}{i\hbar}\Big((\hat{H}\psi(\vec{x},t), \hat{\mathcal{O}}\psi(\vec{x},t)) - (\psi(\vec{x},t), \hat{\mathcal{O}}\hat{H}\psi(\vec{x},t))\Big) \\
&= \frac{i}{\hbar}\Big((\hat{H}\psi(\vec{x},t), \hat{\mathcal{O}}\psi(\vec{x},t)) - (\psi(\vec{x},t), \hat{\mathcal{O}}\hat{H}\psi(\vec{x},t))\Big) \\
&= \frac{i}{\hbar}\Big((\psi(\vec{x},t), \hat{H}\hat{\mathcal{O}}\psi(\vec{x},t)) - (\psi(\vec{x},t), \hat{\mathcal{O}}\hat{H}\psi(\vec{x},t))\Big) \quad \text{; Hermitianness of } \hat{H} \\
&= \frac{i}{\hbar}(\psi(\vec{x},t), (\hat{H}\hat{\mathcal{O}} - \hat{\mathcal{O}}\hat{H})\psi(\vec{x},t)) \quad \text{; linearity of Hermitian inner product} \\
&= (\psi(\vec{x},t), \frac{i}{\hbar}[\hat{H},\hat{\mathcal{O}}]\psi(\vec{x},t)). \\
\Rightarrow \frac{d}{dt} < \mathcal{O} > &= < \frac{i}{\hbar}[\hat{H},\hat{\mathcal{O}}] >, \qquad (12)
\end{aligned}$$

where by the average of an operator $< \hat{\mathcal{O}} >$ in a state ψ we just mean the inner product $(\psi, \hat{\mathcal{O}}\psi)$. Note that our development of (12) is completely general and has used nothing other than the dynamics $\partial_t\psi(\vec{x},t) = \frac{1}{i\hbar}\hat{H}\psi(\vec{x},t)$ from the Schrödinger equation and the fact that the Hamiltonian, being physical, is a Hermitian operator.

2.2 Proof of Ehrenfest's Theorem

To apply our general result (12) to prove Ehrenfest's theorem, we must now compute the commutator $[\hat{H}, \hat{\mathcal{O}}]$ using the specific forms of the operator $\hat{H}$, and the operators $\hat{\vec{x}}$ and $\hat{\vec{p}}$. We will begin with the position operator $\hat{\vec{x}}$,

$$\begin{aligned}
[\hat{H}, \vec{x}]\psi(\vec{x},t) &= \hat{H}(\vec{x}\psi(\vec{x},t)) - \vec{x}(\hat{H}\psi(\vec{x},t)) \\
&= (-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x}))(\vec{x}\psi(\vec{x},t)) - \vec{x}(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x}))(\psi(\vec{x},t)) \\
&= -\frac{\hbar^2}{2m}\left(\nabla^2(\vec{x}\psi(\vec{x},t))\right) + \vec{x}V(\vec{x})\psi(\vec{x},t) + \frac{\hbar^2}{2m}\vec{x}\nabla^2\psi(\vec{x},t) - \vec{x}V(\vec{x})\psi(\vec{x},t) \\
&= -\frac{\hbar^2}{2m}\left(2\vec{\nabla}\psi(\vec{x},t) + \vec{x}\nabla^2\psi(\vec{x},t)\right) + \frac{\hbar^2}{2m}\vec{x}\nabla^2\psi(\vec{x},t) \\
&= -\frac{\hbar^2}{m}\vec{\nabla}\psi(\vec{x},t) \\
&= \frac{\hbar}{i}(-i\hbar\vec{\nabla})\psi(\vec{x},t)
\end{aligned}$$

$$
\begin{aligned}
&= \frac{\hbar}{i}\frac{\hat{\vec{p}}}{m}\psi(\vec{x},t) \\
\Rightarrow [\hat{H},\vec{x}] &= \frac{\hbar}{i}\frac{\hat{\vec{p}}}{m}
\end{aligned}
$$

Inserting this into (12) completes the proof of the first part of Ehrenfest's Theorem,

$$
\begin{aligned}
\frac{d}{dt} < \vec{x} > &= < \frac{i}{\hbar}[\hat{H},\vec{x}] > \quad ; \text{Equation (12)} \\
&= < \frac{i}{\hbar} \cdot \frac{\hbar}{i}\frac{\hat{\vec{p}}}{m} > \\
&= < \vec{p} > /m \\
\Rightarrow \frac{d}{dt} < \vec{x} > &= < \vec{p} > /m
\end{aligned}
$$

The proof of the second part of Ehrenfest's theorem proceeds in the precisely the same way, but now we must compute the commutator $[\hat{H},\hat{\vec{p}}]$,

$$
\begin{aligned}
[\hat{H},\hat{\vec{p}}]\psi(\vec{x},t) &= \hat{H}(\hat{\vec{p}}\psi(\vec{x},t)) - \hat{\vec{p}}(\hat{H}\psi(\vec{x},t)) \\
&= (-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x}))(\frac{\hbar}{i}\vec{\nabla}\psi(\vec{x},t)) - \frac{\hbar}{i}\vec{\nabla}(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x}))(\psi(\vec{x},t)) \\
&= -\frac{\hbar^2}{2m}\nabla^2(\frac{\hbar}{i}\vec{\nabla}\psi(\vec{x},t)) + V(\vec{x})\frac{\hbar}{i}\vec{\nabla}\psi(\vec{x},t) + \frac{\hbar^2}{2m}\frac{\hbar}{i}\vec{\nabla}\nabla^2\psi(\vec{x},t) - \frac{\hbar}{i}\vec{\nabla}\,(V(\vec{x})\psi(\vec{x},t)) \\
&= -\frac{\hbar^2}{2m}\frac{\hbar}{i}\left(\nabla^2\vec{\nabla}\psi(\vec{x},t) - \vec{\nabla}\nabla^2\psi(\vec{x},t)\right) + \frac{\hbar}{i}\left(V(\vec{x})\vec{\nabla}\psi(\vec{x},t) - \vec{\nabla}(V(\vec{x})\psi(\vec{x},t))\right) \\
&= \frac{\hbar}{i}\left(V(\vec{x})\vec{\nabla}\psi(\vec{x},t) - (\vec{\nabla}V(\vec{x}))\psi(\vec{x},t) - V(\vec{x})\vec{\nabla}\psi(\vec{x},t)\right) \\
&= -\frac{\hbar}{i}(\vec{\nabla}V(\vec{x}))\psi(\vec{x},t) \\
\Rightarrow [\hat{H},\hat{\vec{p}}] &= -\frac{\hbar}{i}(\vec{\nabla}V(\vec{x}))
\end{aligned}
$$

Inserting this into (12) completes the proof of second part of Ehrenfest's Theorem,

$$
\begin{aligned}
\frac{d}{dt} < \vec{p} > &= < \frac{i}{\hbar}[\hat{H},\hat{\vec{p}}] > \\
&= < \frac{i}{\hbar} \cdot (-\frac{\hbar}{i}\vec{\nabla}V(\vec{x})) > \\
&= < -\vec{\nabla}V(\vec{x}) > .
\end{aligned}
$$