

The Wave Equation

February 24, 2013

1 The time-dependent Schrödinger wave equation

Schrödinger's wave equation follows by looking at the Schrödinger equation

$$\hat{H} |\psi, t\rangle = i\hbar \frac{\partial}{\partial t} |\psi, t\rangle$$

in a position basis,

$$\langle \mathbf{x} | \hat{H} |\psi, t\rangle = i\hbar \frac{\partial}{\partial t} \langle \mathbf{x} | \psi, t\rangle$$

From the classical form of the 1-particle Hamiltonian, we infer the quantum Hamiltonian operator,

$$\begin{aligned} H &= \frac{\mathbf{P}^2}{2m} + V(\mathbf{x}) \\ \hat{H} &= \frac{\hat{\mathbf{P}}^2}{2m} + V(\hat{\mathbf{X}}) \end{aligned}$$

The potential may be immediately evaluated since we are in a position eigenbasis. Writing the wave function as

$$\psi(\mathbf{x}, t) = \langle \mathbf{x} | \psi, t\rangle$$

we have

$$\begin{aligned} \langle \mathbf{x} | V(\hat{\mathbf{X}}) |\psi, t\rangle &= \langle \mathbf{x} | V(\mathbf{x}) |\psi, t\rangle \\ &= V(\mathbf{x}) \langle \mathbf{x} | \psi, t\rangle \\ &= V(\mathbf{x}) \psi(\mathbf{x}, t) \end{aligned}$$

For the momentum term, we insert two copies of the identity and use $\langle \mathbf{x} | \hat{\mathbf{P}} | \mathbf{x}'\rangle = -i\hbar \nabla \delta^3(\mathbf{x} - \mathbf{x}')$

$$\begin{aligned} \langle \mathbf{x} | \frac{\hat{\mathbf{P}}^2}{2m} |\psi, t\rangle &= \frac{1}{2m} \int d^3x' \int d^3x'' \langle \mathbf{x} | \hat{\mathbf{P}} | \mathbf{x}'\rangle \langle \mathbf{x}' | \hat{\mathbf{P}} | \mathbf{x}''\rangle \langle \mathbf{x}'' | \psi, t\rangle \\ &= \frac{1}{2m} \int d^3x' \int d^3x'' (-i\hbar \nabla \delta^3(\mathbf{x} - \mathbf{x}')) (-i\hbar \nabla' \delta^3(\mathbf{x}' - \mathbf{x}'')) \langle \mathbf{x}'' | \psi, t\rangle \\ &= \frac{\hbar^2}{2m} \int d^3x' \int d^3x'' (\nabla' \cdot \nabla \delta^3(\mathbf{x} - \mathbf{x}')) \delta^3(\mathbf{x}' - \mathbf{x}'') \langle \mathbf{x}'' | \psi, t\rangle \\ &= \frac{\hbar^2}{2m} \int d^3x' (\nabla' \cdot \nabla \delta^3(\mathbf{x} - \mathbf{x}')) \langle \mathbf{x}' | \psi, t\rangle \\ &= -\frac{\hbar^2}{2m} \int d^3x' (\nabla' \cdot \nabla' \delta^3(\mathbf{x} - \mathbf{x}')) \langle \mathbf{x}' | \psi, t\rangle \end{aligned}$$

Now integrate by parts twice to get

$$\begin{aligned}
\langle \mathbf{x} | \frac{\hat{\mathbf{P}}^2}{2m} | \psi, t \rangle &= -\frac{\hbar^2}{2m} \int d^3 x' (\nabla' \cdot \nabla' \delta^3(\mathbf{x} - \mathbf{x}')) \langle \mathbf{x}' | \psi, t \rangle \\
&= -\frac{\hbar^2}{2m} \int d^3 x' \delta^3(\mathbf{x} - \mathbf{x}') \nabla' \cdot \nabla' \langle \mathbf{x}' | \psi, t \rangle \\
&= -\frac{\hbar^2}{2m} \nabla \cdot \nabla \langle \mathbf{x} | \psi, t \rangle \\
&= -\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{x}, t)
\end{aligned}$$

Substituting these results into the wave equation, we have the time-dependent Schrödinger equation,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{x}, t) + V(\mathbf{x}) \psi(\mathbf{x}, t) = i\hbar \frac{\partial}{\partial t} \psi(\mathbf{x}, t)$$

2 Stationary state Schrödinger equation

We use separation of variables to remove the time dependence. Writing the wave function as

$$\psi(\mathbf{x}, t) = \psi(\mathbf{x}) f(t)$$

substituting into the Schrödinger equation, and dividing by $\psi(\mathbf{x}, t)$,

$$\begin{aligned}
-\frac{\hbar^2}{2m} f(t) \nabla^2 \psi(\mathbf{x}) + V(\mathbf{x}) \psi(\mathbf{x}) f(t) &= i\hbar \psi(\mathbf{x}) \frac{\partial}{\partial t} f(t) \\
\frac{1}{\psi(\mathbf{x})} \left(-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{x}) + V(\mathbf{x}) \right) &= i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t)
\end{aligned}$$

Since the left side depends only on position and the right on only time, each must be equal to some constant, E . Therefore,

$$\begin{aligned}
-\frac{1}{\psi(\mathbf{x})} \frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{x}) + V(\mathbf{x}) &= E \\
i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t) &= E
\end{aligned}$$

The second of these integrates immediately to give

$$f(t) = e^{-\frac{i}{\hbar} E t}$$

while the first is the time-independent (or stationary state) Schrödinger equation,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{x}) + V(\mathbf{x}) \psi(\mathbf{x}) = E \psi(\mathbf{x})$$

If the energy spectrum is non-degenerate, a complete solution is found by solving this for arbitrary energy, E , then summing the resulting $\psi(E, \mathbf{x})$ over an arbitrary superposition of the resulting eigenstates. For bound states, the boundary conditions lead to a discrete energy spectrum, so we sum,

$$\psi(\mathbf{x}, t) = \sum_{n=0} \alpha_n \psi(E_n, \mathbf{x}) e^{-\frac{i}{\hbar} E_n t}$$

For unbound states, we may have a continuum spectrum of energies, so the general superposition is an integral,

$$\psi(\mathbf{x}, t) = \int dE \alpha(E) \psi(E, \mathbf{x}) e^{-\frac{i}{\hbar} E t}$$

More generally, there is degeneracy among the energy eigenstates. For example, a free particle will have energy E as long as $\mathbf{p}^2 = 2mE$. In this case we expand in momentum eigenstates, with a constraint giving the energy,

$$\psi(\mathbf{x}, t) = \int d^3p \alpha(\mathbf{p}) \psi_{\mathbf{p}}(\mathbf{x}) \delta\left(E - \frac{\mathbf{p}^2}{2m}\right) e^{-\frac{i}{\hbar}Et}$$

There may also be angular momentum eigenstates. In general, we find the most complete set of states we can, and allow for an arbitrary superposition of them for the general state.

3 Boundary conditions

The stationary state Schrödinger equation is a linear differential equation, and we may find boundary conditions by integrating an infinitesimal distance across a boundary. Looking in one dimension only, we have

$$-\frac{\hbar}{2m}\psi''(x) + V\psi(x) = E\psi(x)$$

and integrate across the boundary at x_0 , from $x_0 - \varepsilon$ to a final value of x within the interval $x \in (x_0 - \varepsilon, x_0 + \varepsilon)$

$$-\frac{\hbar}{2m}(\psi'(x) - \psi'(x_0 - \varepsilon)) + (x - x_0 + \varepsilon)V(x_0)\psi(x_0) = (x - x_0 + \varepsilon)E\psi(x_0)$$

where the first term on the left integrates immediately and the other two may be approximated for sufficiently small ε by

$$\int_{x_0 - \varepsilon}^{x_0 + \varepsilon} f(x) dx \approx f(x_0)2\varepsilon$$

This becomes exact in the limit as $\varepsilon \rightarrow 0$. If we carry this integral all the way to $x = x_0 + \varepsilon$, then take the limit as $\varepsilon \rightarrow 0$, we have

$$\begin{aligned} \lim_{\varepsilon \rightarrow 0} \left[-\frac{\hbar}{2m}(\psi'(x_0 + \varepsilon) - \psi'(x_0 - \varepsilon)) + 2\varepsilon V(x_0)\psi(x_0) \right] &= \lim_{\varepsilon \rightarrow 0} [2\varepsilon E\psi(x_0)] \\ \lim_{\varepsilon \rightarrow 0} \left[-\frac{\hbar}{2m}(\psi'(x_0 + \varepsilon) - \psi'(x_0 - \varepsilon)) \right] &= 0 \end{aligned}$$

so that the derivative of ψ must be continuous across the boundary. Defining

$$\begin{aligned} \psi_- &= \lim_{\varepsilon \rightarrow 0} \psi(-\varepsilon) \\ \psi_+ &= \lim_{\varepsilon \rightarrow 0} \psi(+\varepsilon) \end{aligned}$$

we have

$$\psi'_+(x_0) = \psi'_-(x_0)$$

Integrating our first result a second time over the same integral gives

$$\begin{aligned} 0 &= -\frac{\hbar}{2m}(\psi(x_0 + \varepsilon) - \psi(x_0 - \varepsilon) - 2\varepsilon\psi'(x_0 - \varepsilon)) \\ &\quad + V(x_0)\psi(x_0) \int_{x_0 - \varepsilon}^{x_0 + \varepsilon} (x - x_0 + \varepsilon) dx - E\psi(x_0) \int_{x_0 - \varepsilon}^{x_0 + \varepsilon} (x - x_0 + \varepsilon) dx \\ 0 &= -\frac{\hbar}{2m}(\psi(x_0 + \varepsilon) - \psi(x_0 - \varepsilon) - 2\varepsilon\psi'(x_0 - \varepsilon)) \\ &\quad + V(x_0)\psi(x_0) \left[(x_0 + \varepsilon - x_0 + \varepsilon)^2 - (x_0 - \varepsilon - x_0 + \varepsilon)^2 \right] \\ &\quad - \frac{1}{2}E\psi(x_0) \left[(x_0 + \varepsilon - x_0 + \varepsilon)^2 - (x_0 - \varepsilon - x_0 + \varepsilon)^2 \right] \\ 0 &= -\frac{\hbar}{2m}(\psi(x_0 + \varepsilon) - \psi(x_0 - \varepsilon) - 2\varepsilon\psi'(x_0 - \varepsilon)) + 2V(x_0)\psi(x_0)\varepsilon^2 - 2E\psi(x_0)\varepsilon^2 \end{aligned}$$

Taking this limit, the second two integrals vanish provided E and V remain finite, so defining

$$\begin{aligned}\psi_- &= \lim_{\varepsilon \rightarrow 0} \psi(-\varepsilon) \\ \psi_+ &= \lim_{\varepsilon \rightarrow 0} \psi(+\varepsilon)\end{aligned}$$

we are left with the continuity of ψ across the boundary,

$$\psi_- = \psi_+$$

This condition is altered for infinite potentials. See if you can justify the boundary conditions used for the infinite square well.

In conclusion, unless we are dealing with changes in the potential, the wave function and its first derivative must be continuous at any boundary.

4 Interpretation

We can use the Schrödinger equation to derive a conservation law. Multiply the full time-dependent equation by $\psi^\dagger = \psi^*$,

$$-\frac{\hbar^2}{2m} \psi^* \nabla^2 \psi + V(\mathbf{x}) \psi^* \psi = i\hbar \psi^* \frac{\partial}{\partial t} \psi$$

Take the conjugate of this equation

$$-\frac{\hbar^2}{2m} \psi \nabla^2 \psi^* + V(\mathbf{x}) \psi^* \psi = -i\hbar \psi \frac{\partial}{\partial t} \psi^*$$

then subtract the two and rewrite the derivatives,

$$\begin{aligned}\frac{\hbar^2}{2m} \psi \nabla^2 \psi^* - \frac{\hbar^2}{2m} \psi^* \nabla^2 \psi &= i\hbar \psi^* \frac{\partial}{\partial t} \psi + i\hbar \psi \frac{\partial}{\partial t} \psi^* \\ \frac{\hbar^2}{2m} \nabla \cdot (\psi \nabla \psi^* - \psi^* \nabla \psi) &= i\hbar \frac{\partial}{\partial t} (\psi^* \psi)\end{aligned}$$

Then,

$$\frac{\partial}{\partial t} (\psi^* \psi) + \nabla \cdot \frac{i\hbar}{2m} (\psi \nabla \psi^* - \psi^* \nabla \psi) = 0$$

If we define a real-valued density and real-valued current,

$$\begin{aligned}\rho &= \psi^* \psi \\ \mathbf{J} &= \frac{i\hbar}{2m} (\psi \nabla \psi^* - \psi^* \nabla \psi)\end{aligned}$$

this is just the continuity equation,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = 0$$

The continuity equation always describes some conserved quantity, given by the spatial integral of the density. Define the integral over some volume V to be a “charge” Q ,

$$Q(V) = \int_V d^3x \rho(\mathbf{x}, t)$$

Then

$$\begin{aligned}
\frac{dQ}{dt} &= \int_V d^3x \frac{\partial}{\partial t} \rho(\mathbf{x}, t) \\
&= - \int_V d^3x \nabla \cdot \mathbf{J} \\
&= - \int_S d^2x \mathbf{n} \cdot \mathbf{J}
\end{aligned}$$

where S is the boundary of V and \mathbf{n} is the outward unit normal. This says that any rate of change of Q is due to current that flows across the boundary. If we take the boundary to infinity where the wave function vanishes, then \mathbf{J} vanishes on all of S and the total Q is conserved

$$\frac{dQ}{dt} = 0$$

The question is, what does Q represent?

The most natural answer is that ψ is some field, say, the electron field, and $\psi^*\psi$ is the density of that field. The problem is that we could then measure the amount of Q in some region and that would have to be some fraction of an electron. However, we either measure all of the electron or none at all. This leads us to a better interpretation: $Q(V)$ is the *probability* of finding the electron in the volume V . Since the probability of finding the electron somewhere is 1, we require the integral of ρ over all space to be 1, normalizing the wave function:

$$\iiint_{-\infty}^{\infty} d^3x \rho(\mathbf{x}, t) = \iiint_{-\infty}^{\infty} d^3x \psi^*(\mathbf{x}, t) \psi(\mathbf{x}, t) = 1$$

The interpretation of \mathbf{J} is therefore a probability flux, and it is directly related to the momentum of the particle, since

$$\begin{aligned}
\iiint_{-\infty}^{\infty} d^3x \mathbf{J} &= \frac{1}{2m} \iiint_{-\infty}^{\infty} d^3x (\psi i\hbar \nabla \psi^* - \psi^* i\hbar \nabla \psi) \\
&= \frac{1}{2m} \iiint_{-\infty}^{\infty} d^3x (2\psi^* (-i\hbar \nabla) \psi) \\
&= \frac{1}{m} \iiint_{-\infty}^{\infty} d^3x \psi^* \hat{\mathbf{P}} \psi \\
&= \frac{1}{m} \langle \hat{\mathbf{P}} \rangle
\end{aligned}$$

5 Classical limit

Returning to the Schrödinger equation,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{x}) \psi = i\hbar \frac{\partial}{\partial t} \psi$$

consider the wave function written in polar form,

$$\begin{aligned}
\psi &= \sqrt{\psi^* \psi} e^{\frac{i}{\hbar} S(\mathbf{x}, t)} \\
\psi &= \sqrt{\rho(\mathbf{x}, t)} e^{\frac{i}{\hbar} S(\mathbf{x}, t)}
\end{aligned}$$

Substituting into the equation,

$$\begin{aligned}
i\hbar \frac{\partial}{\partial t} \left(\sqrt{\rho} e^{\frac{i}{\hbar} S} \right) &= -\frac{\hbar^2}{2m} \nabla^2 \left(\sqrt{\rho} e^{\frac{i}{\hbar} S} \right) + V(\mathbf{x}) \sqrt{\rho} e^{\frac{i}{\hbar} S} \\
i\hbar \left(\frac{1}{2\sqrt{\rho}} \frac{\partial \rho}{\partial t} + \sqrt{\rho} \frac{i}{\hbar} \frac{\partial S}{\partial t} \right) e^{\frac{i}{\hbar} S} &= -\frac{\hbar^2}{2m} \nabla \cdot \left(\frac{1}{2\sqrt{\rho}} e^{\frac{i}{\hbar} S} \nabla \rho + \frac{i}{\hbar} \sqrt{\rho} e^{\frac{i}{\hbar} S} \nabla S \right) + V(\mathbf{x}) \sqrt{\rho} e^{\frac{i}{\hbar} S} \\
\left(\frac{i\hbar}{2\rho} \frac{\partial \rho}{\partial t} - \frac{\partial S}{\partial t} \right) \sqrt{\rho} e^{\frac{i}{\hbar} S} &= -\frac{\hbar^2}{2m} \left(-\frac{1}{4\rho^{3/2}} e^{\frac{i}{\hbar} S} \nabla \rho \cdot \nabla \rho + \frac{i}{\hbar} \frac{1}{2\sqrt{\rho}} e^{\frac{i}{\hbar} S} \nabla S \cdot \nabla \rho + \frac{1}{2\sqrt{\rho}} e^{\frac{i}{\hbar} S} \nabla^2 \rho \right) \\
&\quad -\frac{\hbar^2}{2m} \left(\frac{i}{\hbar} \frac{1}{2\sqrt{\rho}} e^{\frac{i}{\hbar} S} \nabla \rho \cdot \nabla S - \frac{1}{\hbar^2} \sqrt{\rho} e^{\frac{i}{\hbar} S} \nabla S \cdot \nabla S + \frac{i}{\hbar} \sqrt{\rho} e^{\frac{i}{\hbar} S} \nabla^2 S \right) \\
&\quad + V(\mathbf{x}) \sqrt{\rho} e^{\frac{i}{\hbar} S}
\end{aligned}$$

so extracting a factor of ψ ,

$$\begin{aligned}
\frac{i\hbar}{2\rho} \frac{\partial \rho}{\partial t} - \frac{\partial S}{\partial t} &= \frac{\hbar^2}{8m\rho^2} \nabla \rho \cdot \nabla \rho - \frac{\hbar^2}{4m\rho} \nabla^2 \rho \\
&\quad - \frac{i\hbar}{2m} \left(\nabla^2 S + \frac{1}{\rho} \nabla S \cdot \nabla \rho \right) \\
&\quad + \frac{1}{2m} \nabla S \cdot \nabla S + V(\mathbf{x})
\end{aligned}$$

In the limit as $\hbar \rightarrow 0$, we have the Hamilton-Jacobi equation,

$$\frac{1}{2m} \nabla S \cdot \nabla S + V(\mathbf{x}) = -\frac{\partial S}{\partial t}$$

where S is Hamilton's principal function. This limit establishes a strong connection to classical mechanics, and is closely related to the path integral method of quantization.

If we include the rest of the expansion, with the linear and quadratic terms in Planck's constant, we can develop a perturbation theory around the classical action. It is this perturbation theory that is made concrete with the path integral.

Another approach to this equation is to:

1. Assume that quantum mechanic may be described by two real fields, ρ and S
2. Assume that this equation is solved order by order in Planck's constant.

Each of these assumptions is problematic. The first would suggest that both ρ and S should be measurable quantities, but they cannot be since the wave function is not entirely measurable – there always remains an undetermined phase. The second assumption is a simplification, since it is possible that, for example, the solution to the zeroth order for S has corrections of higher order in \hbar , $S = S_0 + \hbar S_1 + \dots$. Then S_0 would satisfy the Hamilton-Jacobi equation, but new terms would appear in the first and second order equations.

Nonetheless, it is amusing to see that tidy equations emerge from these assumptions. Assuming the equation is solved order by order we have,

$$\begin{aligned}
\frac{i\hbar}{2\rho} \frac{\partial \rho}{\partial t} &= -\frac{i\hbar}{2m} \left(\nabla^2 S + \frac{1}{\rho} \nabla S \cdot \nabla \rho \right) \\
\frac{\hbar^2}{8m\rho^2} \nabla \rho \cdot \nabla \rho - \frac{\hbar^2}{4m\rho} \nabla^2 \rho &= 0
\end{aligned}$$

Simplifying these, the equation linear in \hbar becomes

$$\begin{aligned}
\frac{1}{\rho} \frac{\partial \rho}{\partial t} &= -\frac{1}{m} \left(\nabla^2 S + \frac{1}{\rho} \nabla S \cdot \nabla \rho \right) \\
\frac{\partial \rho}{\partial t} &= -\nabla \cdot \left(\frac{1}{m} \rho \nabla S \right)
\end{aligned}$$

If we define

$$\mathbf{j} = \frac{1}{m}\rho\nabla S$$

this becomes a continuity equation,

$$\frac{\partial\rho}{\partial t} + \nabla \cdot \mathbf{j} = 0$$

while the terms quadratic in \hbar reduce to

$$\begin{aligned} \frac{1}{2}\nabla\rho \cdot \nabla\rho - \rho\nabla \cdot \nabla\rho &= 0 \\ \nabla \cdot \left(\frac{1}{\sqrt{\rho}}\nabla\rho \right) &= -\frac{1}{2}\frac{1}{\rho^{-3/2}}\nabla\rho \cdot \nabla\rho + \frac{1}{\sqrt{\rho}}\nabla \cdot \nabla\rho \\ &= -\frac{1}{\rho^{-3/2}}\left(\frac{1}{2}\nabla\rho \cdot \nabla\rho - \rho\nabla^2\rho \right) \\ &= 0 \end{aligned}$$

But

$$\frac{1}{\sqrt{\rho}}\nabla\rho = 2\nabla\sqrt{\rho}$$

so we can write all three orders as

$$\begin{aligned} \frac{1}{2m}\nabla S \cdot \nabla S + V(\mathbf{x}) &= -\frac{\partial S}{\partial t} \\ \frac{\partial\rho}{\partial t} + \nabla \cdot \mathbf{j} &= 0 \\ \nabla^2\sqrt{\rho} &= 0 \end{aligned}$$

where $\mathbf{j} = \frac{1}{m}\rho\nabla S$. This gives a familiar set of equations to solve for S and ρ , and any S and ρ satisfying these equations does lead to a solution to the Schrödinger equation. However, as mentioned above, it is not a complete solution to the problem.