unavoidable

Note: The existence of an non-zero uncertainty \( \Delta v(0) \) of the initial velocity is a purely quantum-mechanical feature; its effect on the position uncertainty at large time can be understood classically.

For a macroscopic particle of mass, say, \( m = 1 \) g, with an initial uncertainty of the position of its center of mass of order \( 10^{-13} \) cm (i.e. the size of a proton - the atomic nucleus of hydrogen) we find for the initial uncertainty of the velocity

\[
\Delta v(0) \approx \frac{\hbar}{2m \Delta} \approx 10^{-16} \frac{m}{s}
\]

For the position uncertainty to grow to 1 micron (still pretty small and only visible under a microscope) it would take 300 years! This is one of the reasons why Newtonian physics worked so well for almost 3 centuries, and why quantum mechanics was not discovered earlier.

Particle in a potential \( V(x) \)

\[
\hat{H} = \frac{\hat{p}^2}{2m} + V(x)
\]

\[
\hat{H}\left| E \right\rangle = E\left| E \right\rangle \quad \Leftrightarrow \quad \int \langle x | \frac{\hat{p}^2}{2m} + V(x) | x' \rangle \langle x' | E \rangle = E \langle x | E \rangle
\]

\[
\Rightarrow \quad -\frac{\hbar^2}{2m} \frac{d^2 \Psi_E(x)}{dx^2} + V(x) \Psi_E(x) = E \Psi_E(x)
\]

\[
\Rightarrow \quad \Psi_E''(x) + \frac{2m(E-V(x))}{\hbar^2} \Psi_E(x) = 0
\]
If \( V(x) \) is continuous, then \( \psi '' \) is continuous, and thus also (by integration) \( \psi '(x) \) and \( \psi (x) \).

But if \( V(x) \) is discontinuous, then \( \psi '' \) jumps at the discontinuity. Still, \( \psi '\) will be continuous, so will \( \psi (x) \). If \( V(x) \) jumps by an infinite amount (infinitely high wall, \( \delta \)-fct. potential), \( \psi '\) can jump, too (by infinite amount), and only \( \psi (x) \) itself remains continuous:

\[
\frac{\psi'(x+\Delta x) - \psi'(x)}{\Delta x} = -\frac{2m}{\hbar^2} [E - V(x)] \Rightarrow \psi'(x+\Delta x) = \psi'(x) + \frac{2m}{\hbar^2} \frac{\Delta x}{\Delta x} V(x) \Delta x
\]

\[
\psi(\Delta x) \rightarrow \psi(x) + \lim_{\Delta x \to 0} \frac{2m}{\hbar^2} \int x \psi(x') V(x') dx'
\]

If \( V(x) = V_0 \delta(x-x_0) \) or \( V(x') = V_0 \theta(x'-x_0) \) with \( V_0 \to \infty \),

then \( \psi'(x+\Delta x) \) and \( \psi'(x) \) can differ.

5.2 Particle in a box  

Consider \( V(x) = \begin{cases} 0 & |x| \leq \frac{L}{2} \\ \infty & |x| > \frac{L}{2} \end{cases} \)

The Schrödinger equation for this potential reads, in \( x \)-representation:

\[
\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} (E-V) \psi = 0
\]

We solve this separately in regions I, II, and III, requiring continuity of \( \psi \) at the walls.
Start with region I, and let's begin by taking the potential finite, 

\( V_0 > E \), there, taking \( V_0 \rightarrow \infty \) later:

\[
\frac{d^2 \psi_I}{dx^2} = \frac{2m}{\hbar^2} (V_0 - E) \psi_I \quad \Rightarrow \quad \psi_I = A e^{-\kappa x} + B e^{+\kappa x}
\]

where \( \kappa = \sqrt{\frac{2m}{\hbar^2} (V_0 - E)} \) is real for \( E < V_0 \).

For \( x \rightarrow -\infty \), \( A e^{-\kappa x} \) blows up, for \( \psi_I \) to be normalizable, \( \psi_I \) cannot blow up exponentially as \( x \rightarrow -\infty \). \( \Rightarrow A = 0 \)

\[ \Rightarrow \psi_I(x) = B e^{\sqrt{\frac{2m}{\hbar^2} (V_0 - E)} \cdot x} \]

\[ \begin{align*}
V_0 & \rightarrow \infty \\
& x < -\frac{L}{2} \\
\end{align*} \]

So for the box with infinitely high walls, \( \psi_I \) (and similarly \( \psi_{III} \)) vanish, \( \psi_I = \psi_{III} = 0 \)

In region II, \( V = 0 \), so the solutions are those for a free particle:

\[ i \sqrt{\frac{2m}{\hbar}} x \psi_I + \beta e^{i \sqrt{\frac{2m}{\hbar}} x} = A e^{i \kappa x} + B e^{-i \kappa x} \]

\( (\kappa = i \sqrt{\frac{2m}{\hbar}} x = p/\hbar) \)

Now, \( \psi \) has to be continuous, i.e., \( \psi_{II} \) must match \( \psi_I \) and \( \psi_{III} \) at \( x = \pm \frac{L}{2} \). This boundary condition selects specific allowed values for \( E \), turning the continuous energy spectrum of an unconfined free particle into a discrete spectrum:

Boundary conditions:

\[ \psi_{II}(\frac{-L}{2}) = \psi_I(-\frac{L}{2}) = 0 \]

\[ \psi_{II}(\frac{L}{2}) = \psi_{III}(\frac{L}{2}) = 0 \]
\( A e^{-ikL/2} + Be^{ikL/2} = 0 \)
\( A e^{ikL/2} + Be^{-ikL/2} = 0 \)
\[ \Rightarrow \det M = e^{-ikL} - e^{ikL} = 0 \]
\[ \Rightarrow 2i \sin(kL) = 0 \]
\[ \Rightarrow k = \frac{n\pi}{L}, \quad n = 0, \pm 1, \pm 2, \ldots \]

Energy quantization as a result of the boundary conditions!

Plugging the eigenvalues back into the boundary condition,

we get
\[ A_n e^{-in\pi/2} + B_n e^{in\pi/2} = 0 \]
\( (\text{the other B.C. giving the same!}) \)
\[ \Rightarrow A_n = -e^{in\pi} B_n = (-1)^{n+1} B_n \]
\[ \Rightarrow \] two sets of solutions (after normalization \( \int |\Psi|^2 dx = 1 \))
\[ \Psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) & \text{even, } n \neq 0 \\ \sqrt{\frac{2}{L}} \cos\left(\frac{n\pi x}{L}\right) & \text{odd} \end{cases} \]

Since \( \Psi_{-n}(x) = (-1)^{n+1} \Psi_n(x) \), negative \( n \) provide no independent solutions (they differ only by a constant phase factor)
\[ \Rightarrow \Psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \cos\left(\frac{n\pi x}{L}\right) & n = 1, 3, 5, \ldots \\ \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) & n = 2, 4, 6, \ldots \end{cases} \]

\[ \Rightarrow E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \]
energy eigenvalues increase \( \sim n^2 \)!
If $V_0$ is finite, the solutions do not vanish in regions $\text{I}$ and $\text{III}$, but decay exponentially there. In this case, the jump of $V$ is finite at $x = \pm \frac{1}{2}$, so not only $\psi(x)$, but also $\frac{d\psi(x)}{dx}$ must be continuous.

In this case, we have 4 nonzero coefficients:

$B_1, A_2, B_2, A_3$

and 4 boundary conditions:

$\psi_{\pi}(-\frac{1}{2}) = \psi_{\pi}(-\frac{1}{2})$

$\psi_{\pi}(\frac{1}{2}) = \psi_{\pi}(\frac{1}{2})$

$\psi_{\pi}(\frac{1}{2}) = \psi_{\pi}(\frac{1}{2})$

$\psi_{\pi}(\frac{1}{2}) = \psi_{\pi}(\frac{1}{2})$

It turns out that 3 of them are independent, the last coefficient must be determined from the normalization of $\psi$. The 3 independent boundary conditions will select the allowed energy eigenvalues.

Unless $E$ is very carefully chosen, the matching at $x = \frac{1}{2}$ leads to both $A_{\text{III}}$ and $B_{\text{III}}$ non-zero $\Rightarrow \psi$ not normalizable!
So why is the lowest energy eigenvalue $E_1 \neq 0$?

Let's look at the expectation value of $\hat{H}$ in any of the eigenstates:

$$\langle \hat{H} \rangle = \frac{\langle \hat{p}^2 \rangle}{2m} + \langle V(x) \rangle$$

Any bound state has $\langle \hat{p} \rangle = 0$ since for $\langle \hat{p} \rangle \neq 0$ the particle must drift on average either right or left, so it would eventually escape to infinity and wouldn't be bound.

So we can write

$$\langle \hat{H} \rangle = \frac{\langle (\hat{p} - \langle \hat{p} \rangle)^2 \rangle}{2m} + \langle V \rangle = \frac{(\Delta p)^2}{2m} + \langle V \rangle$$

If we use the uncertainty relation (see chapter 9 for proof)

$$\Delta p \cdot \Delta x \geq \frac{\hbar}{2}$$

This gives

$$\langle \hat{H} \rangle \geq \frac{\hbar^2}{8m(\Delta x)^2} + \langle V \rangle$$

In our case $x$ is strictly constrained to $|x| \leq \frac{L}{2}$ where $\hat{V} = 0 \Rightarrow \Delta x \leq \frac{L}{2} \Rightarrow \langle \hat{H} \rangle \geq \frac{\hbar^2}{2mL^2}$

In an energy eigenstate $\langle \hat{H} \rangle = E_n \Rightarrow E_n \geq \frac{\hbar^2}{2mL^2}$

So $E_n$ cannot be zero. In fact, $E_1$ is $\pi^2$ times this lower bound, showing that in the ground state $\Delta x$ is smaller than $\frac{L}{2}$. 
The propagator for a particle in a box:

$$\hat{U}(t) = \sum_{n=1}^{\infty} |n\rangle \langle n| e^{-i \frac{n^2 x^2 + n^2 y^2 + n^2 z^2}{2mL^2} t / \hbar} = \hat{U}(t,0)$$

In the x-basis:

$$\langle x' | \hat{U}(t,0) | x \rangle = U(x_t; x', 0) = \sum_{n=1}^{\infty} \Psi_n(x) \Psi^*_n(x') e^{-i \frac{n^2 x^2}{2mL^2} t}$$

with $\Psi_n = \left\{ \begin{array}{ll} \sin(n\pi x / L) & n \text{ even} \\ \cos(n\pi x / L) & n \text{ odd} \end{array} \right.$

5.3 The Continuity Equation

We have already discussed that the quantum mechanical time evolution is unitary, such that the norm of the state of the system (i.e. the total probability to find the particle in any eigenstate of some observable) is conserved:

$$\langle \psi(t) | \psi(t) \rangle = \langle \psi(0) | \hat{U}^*(t) \hat{U}(t) | \psi(0) \rangle = \langle \psi(0) | \psi(0) \rangle = 1$$

$$\Rightarrow \int dxdydz \langle \psi(t) | x, y, z \rangle \langle x, y, z | \psi(t) \rangle = \int d^3r |\psi(r,t)|^2 = \int d^3r \frac{dP(r,t)}{d^3r} = 4 \pi \text{ constant.}$$

This is like charge conservation in E&M: $Q = const = \int P(r,t) d^3r$ independent of time.

Let us study this a bit further. We start from the Schrödinger equation and its complex conjugate:

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

$$-i\hbar \frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi^* + V\psi^* \quad (V \text{ is real}) \quad \mid \psi \psi^*$$

subtract
Multiply the first by $\psi^*$, the second by $\psi$, subtract:

$$i\hbar \frac{\partial}{\partial t} (\psi^* \psi) = -\frac{\hbar^2}{2m} \left( \psi^* \nabla^2 \psi - \psi \nabla^2 \psi^* \right)$$

$$\psi \frac{\partial \psi}{\partial t} = -\frac{\hbar}{2mi} \nabla \cdot \left( \psi^* \nabla \psi - \psi \nabla \psi^* \right) = -\nabla \cdot \mathbf{j}$$

where

$$\mathbf{j} = \frac{\hbar}{2mi} \left( \psi^* \nabla \psi - \psi \nabla \psi^* \right)$$

**continuity equation**

The continuity equation \( \frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0 \) is a local form of the law of conservation of probability:

$$\int d^3r \frac{\partial \rho}{\partial t} (r, t) = \frac{d}{dt} \int \rho (r, t) d^3r = \frac{dP}{dt} = -\int d^3r \nabla \cdot \mathbf{j}$$

= (divergence theorem) \(-\oint_{\partial S} \mathbf{j} \cdot d\mathbf{a} = 0\)

where \(d\mathbf{a}\) is a surface normal vector on a surface that encloses all of \(\rho (r, t)\)

For any wave function that is square integrable one can show that \(\rho \to 0\) as \(r \to \infty\) (otherwise \(\psi^* \psi d^3r d\mathbf{a}\) is not bounded) such that \(\mathbf{j}\) vanishes on \(S_\infty\), \(\oint_{S_\infty} \mathbf{j} \cdot d\mathbf{a} = 0\).

\[\Rightarrow P = \text{constant} \quad (\text{probability is conserved})\]

An analogous equation holds in \(\mathbb{E}^3\), with \(\rho = \text{charge density and } \mathbf{j} = \text{electric current}\).