THE SCHRÖDINGER EQUATION

De Broglie's ideas led directly to Schrödinger's wave equation. This is not the only form of quantum mechanics, but it is the simplest, and by far the most used. Schrödinger looked for an equation something like the classical wave equation which could be used to solve for the various physical properties of a particle. There are many plausibility arguments in such texts as Eisberg & Resnick, *Quantum Mechanics of Atoms, Molecules, Solids, Nuclei, and Particles or* Tipler, *Modern Physics.*

The equation should be consistent with the de Broglie relations:

$$p = h/\lambda \qquad\qquad E = h\nu$$

or, using the wave number and angular frequency,

$$p = \hbar k \qquad\qquad E = \hbar \omega$$

It must also be consistent with the conservation of energy:

$$E = \sqrt{(mc^2)^2 + (pc)^2} + U(\vec{r}) \;\rightarrow\; mc^2 + \frac{p^2}{2m} + U(\vec{r}) \quad \text{for } \frac{v^2}{c^2} \ll$$

Schrödinger dropped the constant mc^2 since the zero of energy is arbitrary.

The equation must also be linear, in order to satisfy the superposition principle for amplitudes, giving interference patterns in energy transported. [See Feynman, R., *The Feynman Lectures on Physics,* v. 3].

We will start out working in one dimension. For a free particle $U(x) = 0$, and we expect a sine wave of the form

$$\Psi(x,t) = \text{const } \sin(kx - \omega t) \text{ or } \cos(kx - \omega t)$$

Note that differentiating twice with respect to x will bring out a factor $-k^2$, while differentiating once with respect to time can produce a multiplicative factor $-\omega$, provided we use the form

$$e^{i(kx - \omega t)} = \cos(kx - \omega t) + i \sin(kx - \omega t)$$

This suggests [if you are as brilliant as Schrödinger or have great hindsight] an equation of the form

$$\alpha \frac{\partial^2 \Psi}{\partial x^2} + U(x)\,\Psi = \beta \frac{\partial \Psi}{\partial t}$$

which is consistent with

$$\frac{\hbar^2 k^2}{2m} + U(x) = \hbar\omega.$$

The solution is

$$\alpha = -\frac{\hbar^2}{2m} \qquad\qquad \beta = i\hbar .$$

Actually the only honest thing to do is to **postulate**

$$p_x \rightarrow \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x} \qquad\qquad E \rightarrow i\hbar\frac{\partial}{\partial t}$$

and substitute into the energy equation

$$\frac{p^2}{2m} + U(x) = E$$

to obtain the one-dimensional Schrödinger equation:

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + U(x)\Psi = i\hbar\frac{\partial\Psi}{\partial t}}$$

One can then justify it by the only means that any scientific theory is justified by: it works! Note that for a constant potential $U(x) = U_0$, which corresponds to no force in classical mechanics,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + U_0\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad\qquad \frac{\hbar^2 k^2}{2m} + U_0 = \hbar\omega$$

with $\qquad \Psi(x,t) = Ae^{i(kx-\omega t)}$

It was Max Born who explained the significance of the wave function $\Psi(x,t)$ as the *probability amplitude* of finding a particle. Thus, if there is one particle, the probability of finding it between x and $x + dx$ at time t is

$$P(x,t)\,dx = |\Psi(x,t)|^2\,dx$$

Since the total probability of finding the particle somewhere must be one, we obtain the normalization condition:

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,dx = 1$$

Think of the amplitude as like the amplitude of a water or light wave. Amplitudes add; where they add to zero, there is destructive interference. The squares of amplitudes represent energy transported by a water or light wave, or particles by a de Broglie wave.

If the potential energy does not depend on time, the Schrödinger equation may be solved by separation of variables, and reduced to separate differential equations in space and time:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + U(x)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Try $\Psi(x,t) = f(t)\psi(x)$. Then $\frac{\partial^2\Psi}{\partial x^2} = f(t)\psi''(x)$ and $\frac{\partial\Psi}{\partial t} = f'(t)\psi(x)$ and, substituting into the d.e. and dividing both sides by $\Psi = f\psi$, we obtain

$$-\frac{\hbar^2}{2m}\frac{\psi''(x)}{\psi(x)} + U(x) = i\hbar\frac{f'(t)}{f(t)} = C$$

The time equation is easily solved:

$$\frac{df}{dt} = \frac{C}{i\hbar}f \qquad f(t) = Ae^{-iCt/\hbar} = Ae^{-i\omega t}$$

If this is to agree with the de Broglie relation, the separation constant must be the total energy:

$$C = E = \hbar\omega$$

We now have the **time-independent Schrödinger equation:**

$$\boxed{\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi(x) = E\psi(x)}$$

Note that our starting point is the energy equation, the statement that the sum of potential and kinetic energies is constant. This works much more often with quantum systems than with classical ones, since there is no friction in the microscopic world. It does not work in all cases, however. The assumption is made that the forces are not changing with time. This is not true, for example, in the presence of oscillating electromagnetic fields, where the force changes with time. Where all forces are conservative, we start out with the conservation law:

$$\frac{p^2}{2m} + U(x) = E = \text{constant}$$

Compare the classical case. Quantum mechanics must reduce to classical mechanics in the limit where $\hbar$ is negligibly small compared to the parameters in the problem. We could develop the classical mechanics of a particle in a conservative force field by postulating this same equation. Then differentiate both sides with respect to time and

$$\frac{p}{m}\frac{dp}{dt} + \frac{dU}{dx}\frac{dx}{dt} = 0$$

but momentum is defined by $p = m\, dx/dt$ (neglecting relativistic effects). Thus the above equation becomes

$$\frac{dp}{dt} + \frac{dU}{dx} = 0 \;\Rightarrow\; \frac{dp}{dt} = -\frac{dU}{dx} \equiv F(x)$$

The most common way to develop classical mechanics is to postulate this last equation and, going in the reverse order, to derive the conservation of energy law. Actually, they are completely equivalent; either can be derived from the other.

Note that the Schrödinger equation is linear. Any linear combination of solutions is also a solution. Note also that if there is only one energy, the probability distribution is independent of time:

$$P(x,t) = |\Psi(x,t)|^2 = \left(\psi(x)e^{-iEt/\hbar}\right)^*\left(\psi(x)e^{-iEt/\hbar}\right) = \psi^*(x)\psi(x) = P(x)$$

Schrödinger-type quantum mechanics, also known as *wave mechanics,* can be built from the following postulates:

A particle is described by a wave function $\Psi(x,t)$. This function is not directly observable, indeed it is usually complex. It is obtained by solving the Schrödinger equation with the appropriate potential energy and boundary conditions. Among the boundary conditions are the requirements that the wave function be single-valued and continuous and [except where potentials $\to \infty$] that the spatial derivatives of the wave function be continuous.

Physically observable quantities are represented by *operators* which operate on wave functions. Examples include

$$p_{x,op} = \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad x_{op} = x \qquad E_{op} = i\hbar\frac{\partial}{\partial t}$$

The probability of finding the particle between x and $x + dx$ at time t is

$$P(x,t)\,dx = \Psi^*(x,t)\Psi(x,t)\,dx = |\Psi(x,t)|^2\,dx$$

Thus $P(x,t) = |\Psi(x,t)|^2$ is called the *probability density*. Since the total probability of the particle being somewhere is unity, we have the *normalization condition:*

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,dx = 1$$

If we know the wave function of a particle, we can calculate the *expectation value* of a measurable quantity:

$$\langle A\rangle = \int \Psi^*(x,t)A_{op}\Psi(x,t)\,dx$$

e.g., $$\langle p_x \rangle = \int \Psi^*(x,t)\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi(x,t)\, dx$$

The expectation value would be the average value obtained if we could make a very large number of identical measurements on identical systems.

An operator has certain functions, called *eigenfunctions* Ψ_n for which

$$A_{op}\Psi_n = A_n\Psi_n$$

where A_n is a constant called an *eigenvalue*. For example, consider the momentum operator:

$$p_{op} = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

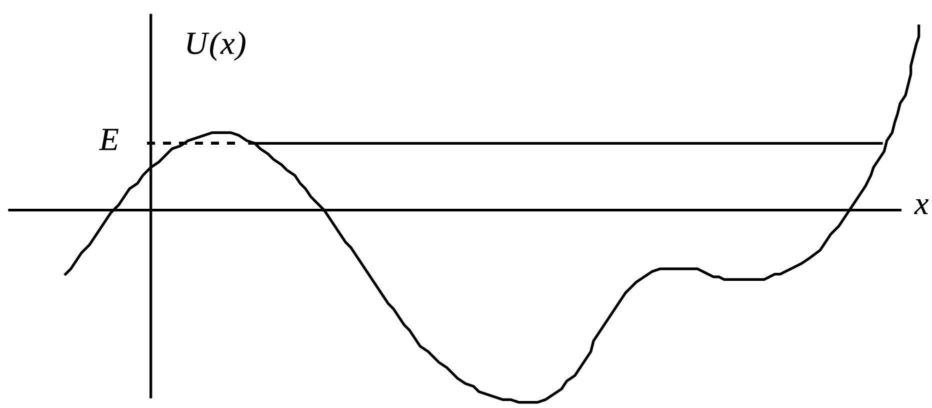
Its eigenfunctions are $\psi_k(x) = Ae^{ikx}$ and the associated eigenvalues are $\hbar k$. The allowed values of k depend on the boundary conditions.

Before attempting some problems with the Schrödinger equation, let us review some classical mechanics. Recall that the conservation of energy equation is completely equivalent to Newton's law of motion (conservative forces only):

$$E = \frac{p^2}{2m} + U(x) \qquad\qquad \frac{dp}{dt} = -\frac{dV}{dx}$$

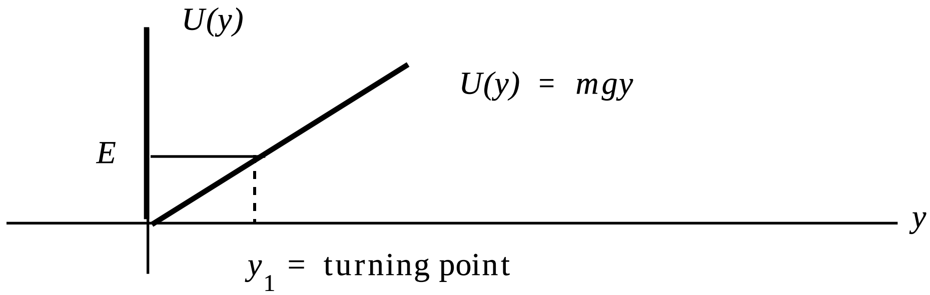
In general, the interactions of the particle with the rest of the universe may be represented by a potential energy function. It is useful to keep in mind a frictionless roller coaster, for which the potential energy is

$$U(x) = mgy(x)$$



The increase in kinetic energy as the particle moves into a region of lower potential energy is obvious for the roller coaster rider. The statement that the force on the particle at any location is the negative of the gradient of the potential energy

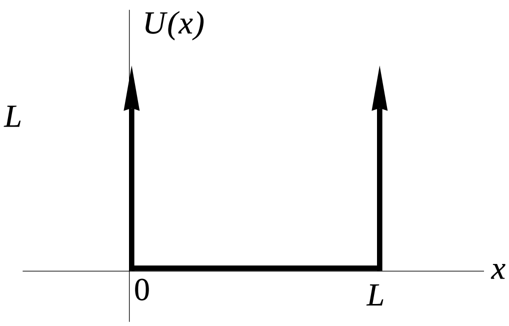
$F = -\dfrac{dU}{dx}$ is familiar as the phenomenon that objects accelerate down hill. The classical turning points are the points where the kinetic energy reaches zero. For example, this can be the maximum altitude of a projectile fired straight upward:



Here y is the height above the ground. The representation of the potential as becoming very large at $y = 0$ implies a very hard surface, off which the projectile will bounce. Thus the projectile bounces back and forth between $y_{min} = 0$ and $y_{max} = y_1 = E/mg$. If the projectile is initially fired from $y = 0$, then $E = \frac{1}{2} m v_0^2$.

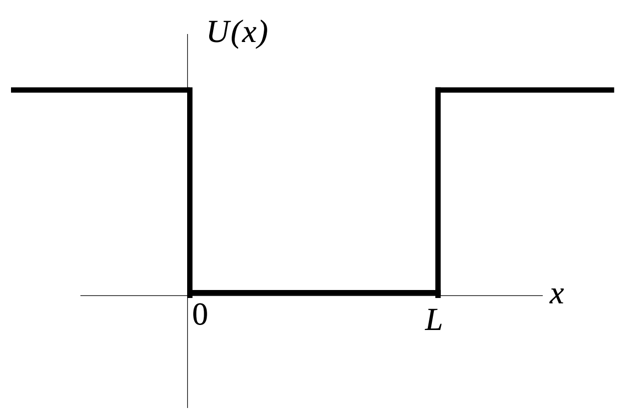
It is convenient to represent an impenetrable barrier by an infinite potential. Thus a particle enclosed in a one-dimensional box of length L is described by the potential:

$$U(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$



This is called the *infinite square well*. It does not exist in nature, since it implies that even a particle with arbitrarily large kinetic energy cannot penetrate it. It is a good representation for cases where the particle would have to have much more energy than it actually has to penetrate. It is also easier to solve than the *finite* square well which is more realistic:

$$U(x) = \begin{cases} 0 & 0 < x < L \\ U_0 & \text{otherwise} \end{cases}$$



For the infinite square well the Schrödinger equation is easy to solve:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \qquad 0 < x < L$$
$$\psi = 0 \quad \text{otherwise}$$

The boundary conditions which restrict the solutions are that ψ be continuous everywhere, in particular at $x = 0$ and at $x = L$. Normally, we require that $d\psi/dx$ be continuous as well, but this condition is not required when $U(x) \to \infty$

Where $U(x) \to \infty$ the wave function can only be zero for the Schrödinger equation to be satisfied.

Inside the "well" the differential equation can be written

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \text{ where } \frac{d^2\psi}{dx^2} + k^2\psi = 0 \text{ where } k^2 = \frac{2mE}{\hbar^2}.$$

The d.e. is satisfied by sin kx and by cos kx or by any linear combination, but only sin kx satisfies the continuity condition at $x = 0$ where ψ must = 0. In order to satisfy continuity at the other end, i.e., to have $\psi = 0$ at $x = L$, we must restrict the values of k

$$k = k_n = \frac{n\pi}{L} \text{ with } n = 1, 2, 3, \cdots$$

Thus we obtain restrictions on the energy:

$$E = E_n = \frac{\hbar^2 k_n^2}{2m} = n^2\frac{\pi^2\hbar^2}{2mL^2} \text{ with } n = 1, 2, 3, \cdots$$

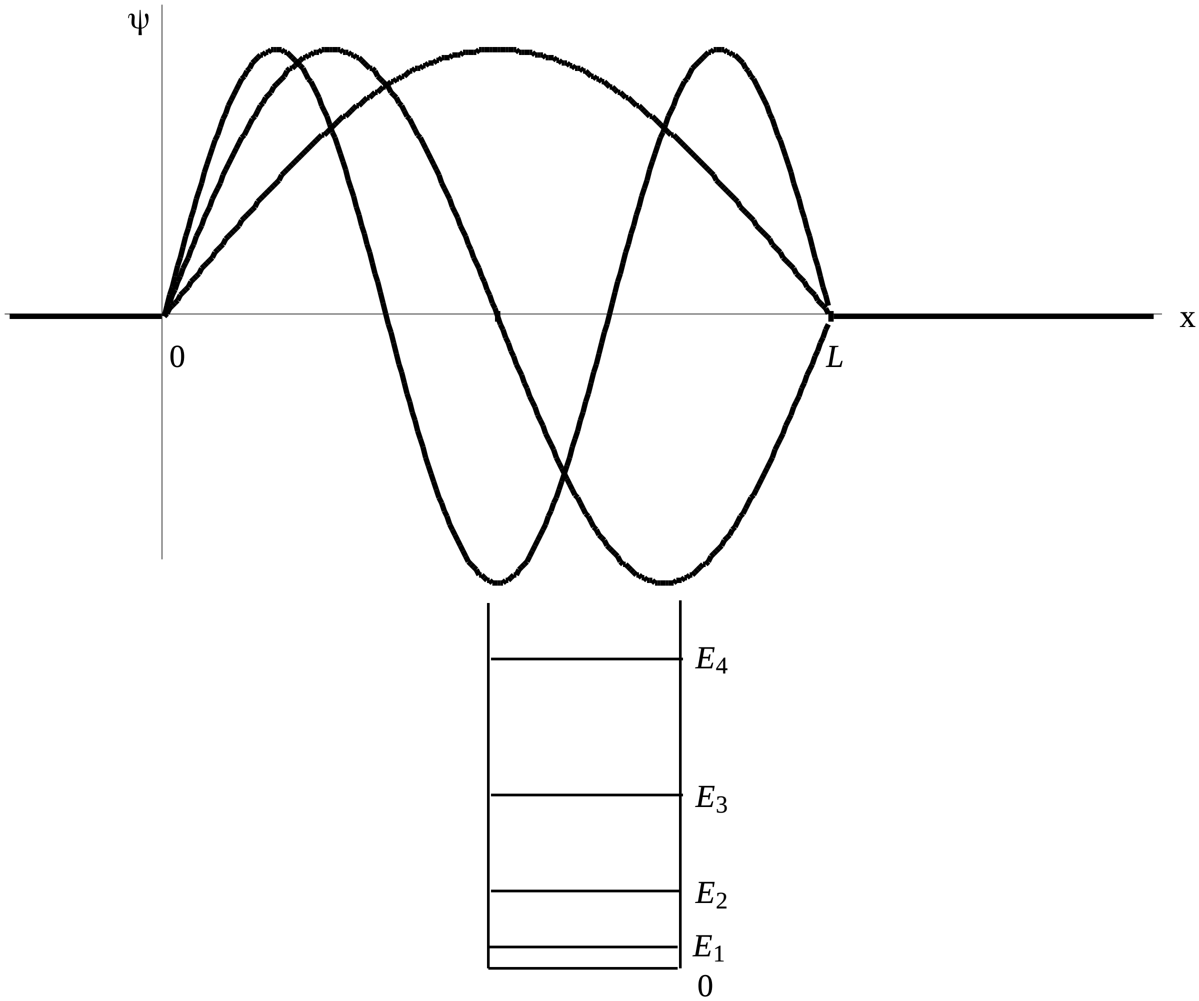
We can normalize the wave functions:

$$1 = \int_{-\infty}^{\infty} |\psi_n(x)|^2\, dx = \int_0^L |A_n|^2 \sin^2\!\left(\frac{n\pi x}{L}\right) dx = |A_n|^2\frac{L}{2} \qquad |A_n| = \sqrt{\frac{2}{L}}$$

Thus we conclude that the solutions to the infinite square well problem, with the potential $U(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{otherwise} \end{cases}$

are the eigenfunctions with the associated eigenvalues

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} & 0 < x < L \\ 0 & \text{otherwise} \end{cases} \qquad E_n = n^2\frac{\pi^2\hbar^2}{2mL^2} \text{ with } n = 1, 2, 3, \cdots$$



Note that the minimum energy possible is not zero. If the particle had zero energy, we could know both position and momentum exactly, and the uncertainty principle would be violated. According to the uncertainty principle

$$\Delta x = L \qquad \Delta p = \frac{\hbar}{L} \qquad \left\langle p^2 \right\rangle_{\min} = (\Delta p)^2 = \left(\frac{\hbar}{L}\right)^2$$

$$E_{\min} = \frac{\left\langle p^2 \right\rangle_{\min}}{2m} = \frac{\hbar^2}{2mL^2} = \frac{1}{\pi^2} E_1 \qquad \frac{1}{10} \mathrm{E}_1$$

As is often the case, estimates based on the uncertainty principle give the ground state energy to within an order of magnitude, but not exactly.

The *finite square well* is a more realistic approach to the problem of a particle confined to a finite region of space by “hard” walls. It is often used [in 3 dimensions] to represent a neutron or proton confined to an atomic nucleus. The solution of the Schrödinger equation is slightly more difficult than the problem of the infinite square well. The graph of the potential is two pages back. The problem is to solve

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi(x) = E\,\psi(x$$

with the potential

$$U(x) = \begin{cases} U_0 & x < 0 \\ 0 & 0 < x < L \\ U_0 & x > L \end{cases}$$

We can simplify this to

for $x < 0$ $\quad \psi'' = \alpha^2\psi \quad$ with $\alpha^2 \equiv \frac{2m}{\hbar^2}(U_0 - E)$

for $0 < x < L$ $\quad \psi'' = -k^2\psi \quad$ with $k^2 \equiv \frac{2mE}{\hbar^2}$

for $x > L$ $\quad \psi'' = \alpha^2\psi \quad$ with $\alpha^2 \equiv \frac{2m}{\hbar^2}(U_0 - E)$

One family of solutions exists for $0 < E < U_0$. These are the *bound states.* In this case both α^2 and k^2 are positive, and therefore both α and k are real. No generality is lost by taking them both positive. In each of the three regions there are two independent solutions to the differential equation, but in the regions outside the well we are forced by the boundary conditions (see postulates) to reject one.

For x < 0 $\quad \psi = e^{\alpha x}$ and $\psi = e^{-\alpha x}$ satisfy the d.e. The most general solution is any linear combination. However, the boundary conditions require that ψ be normalizable, i.e., that $\int |\psi|^2 dx$ be finite; therefore the solution $\psi = e^{-\alpha x}$ must be rejected, as it $\rightarrow \infty$ as $x \rightarrow 0$.

For x > L $\quad \psi = e^{\alpha x}$ and $\psi = e^{-\alpha x}$ satisfy the d.e. Here we must reject the solution $\psi = e^{\alpha x}$ for the same reason.

For $0 < x < L$ the two independent solutions to the d.e. are $\psi = \sin kx$ and $\psi = \cos kx$. Neither can be rejected. Now we must consider two other boundary conditions, continuity of ψ and of ψ' at $x = 0$ and at $x = L$. This leads to four algebraic equations which can be solved for four unknowns: the constants in front of three of the solutions and the wave number k. In order to do this it is much simpler if we take advantage of the symmetry of the potential and put the origin at the center. It is convenient to let $L = 2a$. The potential then becomes

$$U(x) = \begin{cases} U_0 & x < -a \\ 0 & -a < x < a \\ U_0 & x > a \end{cases}$$

[Actually, most physicists prefer this symmetrical form for the infinite square well also, in which case the solutions are alternately cosines and sines.] With the symmetrical potential, i.e., with $U(-x) = U(x)$, the solutions are alternately even and odd functions of x.

For example, if we choose $\psi_{\text{even}}(x) = \begin{cases} Ae^{\alpha x} & x < -a \\ B\cos kx & -a < x < a \\ Ae^{-\alpha x} & x > a \end{cases}$

then the requirement that ψ be continuous at $x = \pm a$ yields the equation

$$Ae^{-\alpha a} = B\cos ka$$

and the requirement that ψ' be continuous at $x = \pm a$ yields

$$\alpha Ae^{-\alpha a} = kB\sin ka$$

Simultaneous solution (it must be done numerically or graphically; no analytic solutions exist) yield two quantities, one of which is B/A. The other may be taken to be k or α or E. Recall that these last three are related by the definitions of k and α. The value of A may be determined from the normalization condition, while the allowed values of E are the quantized energy levels of the bound states. The number of bound states may be one, two, or any finite number, depending only on the value of the dimensionless number $\sqrt{2mU_0L^2/\hbar^2}$. [Recall that $L = 2a$ is the width of the well.] If this quantity is less than 2π there is one bound state, if it is between 2π and 4π there are two, etc.