THE SCHRODINGER EQUATION AND APPLICATION TO FREE-PARTICLE IN A BOX FOR MULTI-DIMENSIONS

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Abstract. The Schrodinger equation is a fundamental postulate of quantum mechanics that provides insight on the probabilistic density, energy, position and momentum of a particle for which classical Newtonian mechanics fails. The time-independent Schrodinger equation and its application to the one-dimensional particle in a box are discussed.

1. What is the Schrodinger Equation?

The classical mechanics of Newton fails in adequately describing the behavior of very small objects, such as an electron in an atom. There is a fundamental restriction to how well one can simultaneously measure an object's position and velocity, and this is described by the **Heisenberg Uncertainty Principle**: For a moving object confined to region Δx with uncertainty of linear momentum Δp:

$$\Delta x \Delta p_x \approx h$$

for Planck's constant $h = 6.626 \times 10^{-34} J \cdot s$ In essence, the Heisenberg Uncertainty Principle states that the position and momentum of a particle cannot be simultaneously and exactly known.

Quantum mechanics, however, provides remarkably accurate descriptions of small-scale phenomena. According to quantum mechanics, a quantum state of a particle at stationary time is a complex-valued function $\psi(x, y, z)$, defined on R^3. This complex-valued function is known as the **Schrondinger wave function**. Wave functions must be well-behaved (i.e. finite, single-valued, and continous).

The state ψ is **normalizable** if the integral of the square of the modulus of ψ over R^3 is finite and nonzero.

$$\| \psi \|^2 \equiv \int |\psi(x, y, z)|^2 dxdydz$$

ψ is said to be **normalized** when $\|\psi\|^2 = 1$. $|\psi(x, y, z)|^2$ is the **probability density** of possible positions of the particle. For a normalized state ψ, the probability the particle is in any given region A is $\int |\psi|^2 dxdydz$, a value between 0 and 1. If A is R^3, the integral is 1 and the probability must be 100% over all space (e.g. the particle is found somewhere in R^3). In addition to providing

Date: April 5, 2007.

information about probability densities, the state ψ can also be used to find energies, position and angular momentum.

A quantum state with a definite energy E (kinetic energy plus potential energy) satisfies the partial differential equation:

$$\frac{-\hbar^2}{2m}\nabla\psi + U(x)\psi = \left[\frac{-\hbar^2}{2m}\nabla + U(x)\right]\psi = E\psi$$

is known as the **Time-Independent Schrodinger equation** where m is the mass of the object, ∇ is the Laplacian Operator, and $\hbar = \frac{h}{2\pi}$.

The Schrodinger equation can be formulated as an eigenvalue problem where ψ is an eigenfunction of the Hamiltonian operator $\frac{-\hbar^2}{2m}\nabla + U(x)$, and the energy E is the associated eigenvalue.

There is a time-dependent Schrodinger equation:

$$\left[\frac{-\hbar^2}{2m}\nabla + U(x)\right]\psi(x,t) = \imath\hbar\frac{\partial\psi}{\partial t}$$

The time-dependent Schrodinger equation is a much more complicated function, and so we will discuss only the time-independent Schrodinger equation.

2. An Attempt to Derive the Schrodinger Equation

The Schrodinger equation is a fundamental postulate of quantum mechanics, and cannot be derived. However we can try to trace Schrodinger's original line of thought.

DeBroglie showed that matter has both particle and wavelike properties (duality of particle and wave). If matter possesses wavelike properties, then it should be governed by some wave equation. For simplicity, we begin with the wave equation in one-dimension:

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2}$$

We know that the wave equation can be solved by the method of separation of variables, and $u(x,t)$ can be written as the product of a function of x and a sinusoidal function of time:

$$u(x,t) = \psi(x)\cos(wt)$$

where $\psi(x)$ is the spatial factor of the amplitude $u(x,t)$. If $u(x,t)$ is substituted into the wave equation, we obtain the partial differential equation (PDE):

$$\frac{\partial^2\psi}{\partial x^2} + \frac{w^2}{v^2}\psi = 0$$

For a particle of mass m and velocity v,

$$E = KE + PE = \frac{1}{2}mv^2 + U(x) = \frac{p^2}{2m} + U(x)$$

where KE is the kinetic energy, PE is the potential energy, and momentum $p = mv$. Solving for p, we obtain: $p = [2m(E-U)]^{\frac{1}{2}}$.

We can simplify the $\frac{w^2}{v^2}$ term in the above to:

$$\frac{\omega^2}{\upsilon^2} = \frac{4\pi^2}{\lambda^2} = 4\pi^2 \frac{p^2}{h^2} = \frac{2m\left(E-U\right)}{\hbar^2}$$

where the angular frequency $\omega = 2\pi\nu$, velocity $\upsilon = \nu\lambda$, and the DeBroglie wavelength $\lambda = \frac{h}{p}$.

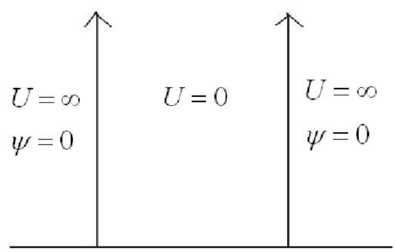
Substituting these values into the PDE above, we obtain:

$$\frac{\partial^2\psi}{\partial x^2} + \left[\frac{2m}{\hbar^2}\left(E-U\right)\right]\psi = 0$$

Rearrangement of this equation gives the time-independent Schrodinger equation in one-dimension:

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + U\psi = E\psi$$

3. Application: One-Dimensional Free Particle in a Box



$DE : \frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + U\psi = E\psi$

$BC : \psi(0) = 0, \psi(a) = 0$

Outside the box: $U = \infty$ and $\psi = 0$

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + \infty\psi = E\psi$$

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = -\infty\psi$$

$$\therefore \psi = \frac{1}{\infty}\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = 0$$

(i.e. $\psi = 0$ when $U(x) = \infty$ and the particle is never found outside the box)

Inside the box: $U = 0$

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + 0\psi = E\psi$$

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} - E\psi = 0$$

Let a=$\frac{-\hbar^2}{2m}$.

$$a\frac{\partial^2\psi}{\partial x^2} - E\psi = 0$$

Let $\psi = e^r$.

$$\begin{aligned}
a(r^2 e^r) - Ee^r &= 0 \\
ar^2 - E &= 0 \\
r = \pm\frac{\sqrt{4aE}}{2a} &= \pm\sqrt{\frac{c}{a}} \\
\therefore r = \pm\sqrt{\frac{E}{\frac{-\hbar^2}{2m}}} &= \pm\sqrt{\frac{-2mE}{\hbar^2}} = \pm\iota\sqrt{\frac{2mE}{\hbar^2}} \\
\psi &= A\cos(kx) + B\sin(kx)
\end{aligned}$$

where $k = \sqrt{\frac{2mE}{\hbar^2}}$ and constants A, B.

To find the constants A and B, we apply the boundary conditions of the problem.

$$\psi(0) = A\cos(k0) + B\sin(k0) = A + B \cdot 0 = A = 0.$$

$$\therefore A = 0$$

$\psi(a) = 0\cos(ka) + B\sin(ka) = B\sin(ka) = 0$ only if $ka = n\pi$.

If B=0, we would get the trivial solution.

$$\therefore k = \frac{n\pi}{a}, \psi = B\sin\left(\frac{n\pi x}{a}\right)$$

for $n = 1, 2, 3, \ldots$

Since ψ must be normalizable, we can find the value of the constant B.

$$\begin{aligned}
\int_0^a \psi^\star\psi dx &= \int_0^a B^2(sin\left(\frac{n\pi x}{a}\right))^2 dx \\
&= B^2\int_0^a (\sin\left(\frac{n\pi x}{a}\right)^2 dx \\
&= B^2\int_0^a \left[\frac{1}{2} - \frac{1}{2}\cos\left(\frac{2n\pi x}{a}\right)\right] dx \\
&= B^2\left[\frac{x}{2} - \frac{a}{4n\pi x}\sin\left(\frac{2n\pi x}{a}\right)\right]_0^a \\
&= B^2\left[\frac{x}{2}\right]_0^a = \frac{aB^2}{2} = 1 \\
\implies B &= \sqrt{\frac{2}{a}}
\end{aligned}$$

Hence, $\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$ for $n = 1, 2, 3, \ldots$.

The energy eigenvalue E can be found by equating the values for k as defined earlier:

$$k = \frac{n\pi}{a} = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\implies \left(\frac{n\pi}{a}\right)^2 = \frac{2mE}{\hbar^2}$$

Solving for E, we obtain for $n = 1, 2, 3, \ldots$

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{n^2h^2}{8ma^2}$$

i.e. the energy of a particle in a box is quantized and discrete energy levels exist.

The wave function for the first few states are plotted in figure 1 [3]:

Ground state ($n = 1$)

$$\psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right), E_1 = \frac{h^2}{8ma^2}$$

First excited state ($n = 2$)

$$\psi_2 = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right), E_2 = \frac{4h^2}{8ma^2}$$

Second excited state ($n = 3$)

$$\psi_3 = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi x}{a}\right), E_3 = \frac{9h^2}{8ma^2}$$

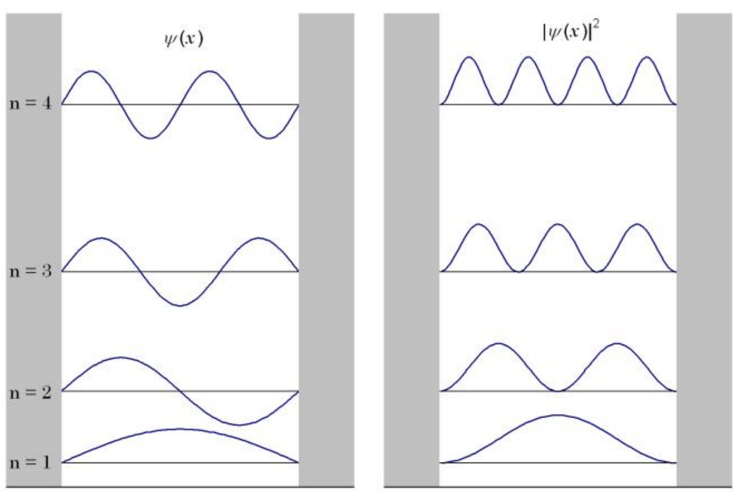
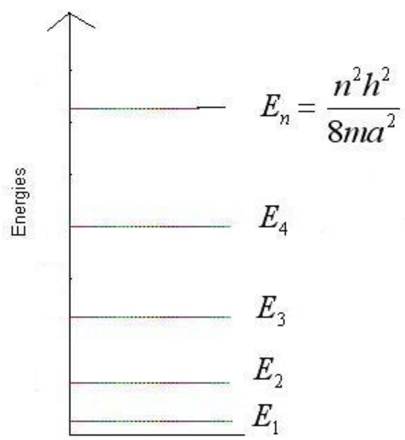


FIGURE 1. The particle-in-a-box wavefunctions (left) and probability densities (right) for $n = 1, 2, 3, 4$.

Recall, $|\psi(x,y,z)|^2$ is the probability density. When $|\psi(x,y,z)|^2 = 0$, it is called a NODE. The number of nodes in this system is $n-1$. The second derivative describes curvature. Wavefunctions with higher curvature indicate a higher kinetic energy of the particle.

The energy diagram in figure 2 shows that the system has discrete energy levels. E decreases as a increases. $\Delta E = E_n - E_{n-1}$ increases with n, but decreases as a increases.



4. Higher dimensions of Free Particle in a Box

The same technique can be applied to higher dimensions (e.g. 2-D, 3-D box) with the method of separation of variables.

For the two-dimensional particle in a box, let $\psi = XY$. Then the PDE becomes:

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)XY = EXY$$

Divide through by XY to separate variables:

$$\left(\frac{-\hbar^2}{2m}\frac{1}{x}\frac{\partial^2}{\partial x^2}\right) + \left(\frac{-\hbar^2}{2m}\frac{1}{y}\frac{\partial^2}{\partial y^2}\right) = E_x + E_y = E$$

Applying the same techniques as above, we obtain for the 2-D case:

$$X = \sqrt{\frac{2}{a}}\sin\frac{n_x \pi x}{a}, Y = \sqrt{\frac{2}{b}}\sin\frac{n_y \pi y}{b}$$

$$\therefore \psi = XY = \sqrt{\frac{4}{ab}}\sin\frac{n_x \pi x}{a}\sin\frac{n_y \pi y}{b}$$

$$E = E_x + E_y = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$

In general,

$$Hamiltonian\ Operator = \frac{-\hbar^2}{2m}\nabla^2$$

$$\psi = \prod_i \psi_i$$

$$E = \sum_i E_i$$

References

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