

Quantum Mechanics: Particles in Potentials

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I. Applications of the Postulates of Quantum Mechanics

Now that some of the machinery of quantum mechanics has been assembled, one can begin to apply the concepts of wavefunctions, superposition, eigenfunctions, operators, eigenvalues, observables, etc. to derive wavefunctions for several model systems. These will afford insight in to some fundamental ideas to be extended later in the context of more complicated systems.

The first system will be a free particle, i.e., a particle with no external potential acting on it. The second system will be a particle in a one-dimensional box with a defined external potential, $V(x)$.

1. Free Particle

Consider a *free* particle, i.e., one that does not have an external potential acting upon it. In the development of the time-independent Schrodinger equation discussed earlier, the *total* energy of a quantum mechanical state is taken to be composed of a Kinetic and a Potential component. In this first example, consider the potential is constant everywhere; in this case, there is no spatial dependence of the potential. Moreover, since the potential is everywhere equal, we can allow it to be null everywhere.

Thus, the time-independent Schrodinger equation becomes,

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

Rearranging, we have:

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

Solutions to this equation are of the form:

$$\psi^+(x) = A_+ e^{+i\sqrt{2mE/\hbar^2}x} = A_+ e^{+ikx}$$

$$\psi^-(x) = A_- e^{-i\sqrt{2mE/\hbar^2}x} = A_- e^{-ikx}$$

Here the relation $k = 2\pi/\lambda = \sqrt{2mE/\hbar^2}$ has been used. To obtain the time-dependent wavefunction, one can multiply the spatially-dependent function by the time dependent $e^{-i\omega t}$.

Note: Solutions are plane waves (moving in $+x$ and $-x$ directions)

Note: This result is analogous to the classical solution to a free particle moving in zero external field with **constant velocity**. This results from the fact that the wavevector, $k = 2\pi/\lambda = \sqrt{2mE/\hbar^2} = mv/\hbar$ is constant. Thus, the velocity of the wavefunction has to be constant and equal to the initial specified velocity.

Note: The Energy can take on all values (k is continuous). Thus, the quantum mechanical free particle can take on a continuous spectrum of energies. **Keep in mind that for the free particle, we have NOT imposed any BOUNDARY conditions or restrictions on the behavior of the wavefunction, apart from the requirement that it satisfy a second-order differential equation.**

Note: The free particle wavefunction is **not localized in space**. Thus it cannot be normalized over the range $-\infty$ to ∞ . It is a **plane wave**. One can show that the probability of finding the particle in an interval, dx about x is when the range of valid x is restricted to the interval $-L$ to L :

$$P(x) = \frac{1}{2L}$$

The probability is simply dependent on the inverse of the length of the region over which the wavefunction is normalized. This demonstrates that $P(x)$ is simply the inverse of the spatial distance over which the wavefunction is relevant. All positions are equally likely to be "harboring" the particle. **The particle is equally likely to be everywhere.**

Note: The notion that the particle has equal probability of being anywhere tells us nothing with certainty of where the particle is. We do know, however, the momentum of the particle since we know the wavevector, k . This is a prelude to the uncertainty conditions.

II. Particle in a One-Dimensional Box

Consider a particle confined in the x -direction to a region from $x=0$ to $x=a$ (a = the box length). At the points $x=0$ and $x=a$, there is a wall, modelled as an **infinite** potential. Thus, the potential is described mathematically:

$$\begin{aligned} V(x) &= 0 && \text{for } 0 < x < a \\ V(x) &= \infty && \text{for } x \geq a, \quad x \leq 0 \end{aligned}$$

What are the corresponding eigenfunctions and eigenvalues for this potential (recall that in the free particle case, the potential was pre-set to be zero everywhere in space)?

The time-independent Schrodinger equation is written as:

$$\frac{\partial^2 \psi(x)}{\partial x^2} = \frac{2m}{\hbar^2} [V(x) - E] \psi(x)$$

Consider: 1. The wavefunction must be zero outside of the box; the second derivative cannot be ∞ as would be the case for ∞ potential.

2. The wavefunction must be continuous in the box (and at the edges). Thus, $\psi(0) = \psi(a) = 0$.

The **boundary conditions** for this problem are thus:

$$\psi(0) = \psi(a) = 0$$

IIa. Wavefunctions for a Particle in a Box: 1-Dimensional

Since the potential within the box is zero, we can treat the particle with wavefunction forms analogous to the free particle case:

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

Applying the boundary condition just mentioned, we obtain:

$$\psi(0) = 0 + B = 0$$

Thus, $B = 0$ in order to conform to this boundary condition!

$$\psi(a) = A\sin(ka) + B = 0$$

We note that A cannot be zero (wouldn't have a wavefunction then). The second equality is fulfilled for certain combinations of ka .

$$ka = n(\pi) \quad n = 1, 2, 3, \dots, \infty$$

Thus, the wavefunction is of the form:

$$\psi(x) = A\sin\left(\frac{n\pi x}{a}\right)$$

The complete set of eigenfunctions for this case is thus:

$$\psi_n(x) = A\sin\left(\frac{n\pi x}{a}\right) \quad n = 1, 2, 3, \dots, \infty$$

Each value of n corresponds to a different eigenfunction of $\hat{H}_{(particle\ in\ a\ box)}$. This is the **infinite set of eigenfunctions** of the total energy operator, i.e. Hamiltonian, for the potential energy function corresponding to infinite, impenetrable walls at the edges of a one-dimensional box.

IIb1. Normalizing the Wavefunction: The particle has to be there

There is now only the constant A to worry about. This can be determined by recalling that, as postulated, the norm of the wavefunction corresponds

to the probability of finding the particle in a certain interval of space. This has to be unity since we have defined the particle to be in the box. Thus, normalizing the wavefunctions as derived above:

$$\int_0^a \psi_n^*(x) \psi_n(x) dx = 1$$

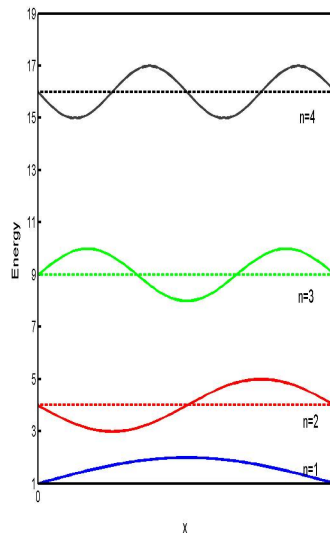
$$A^* A \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$$

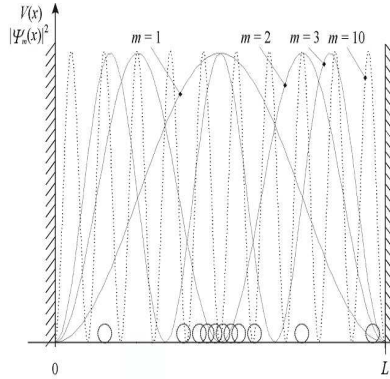
Using standard Table of integrals:

$$A = \sqrt{2/a}$$

The final wavefunction form is thus:

$$\psi_n(x) = \sqrt{2/a} \sin\left(\frac{n\pi x}{a}\right) \quad n = 1, 2, 3, \dots, \infty$$





IIB2. The Eigenvalues

The eigenvalues are determined by substituting the general solution back into the eigenvalue equation; this yields:

$$E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{a} \right)^2 = \frac{\hbar^2 n^2}{8ma^2} \quad n = 1, 2, 3, \dots, \infty$$

Note: The energy values obtained from possible measurements on this system are now **discretized** or **quantized** in contrast to the case of the free particle for which the energies available were continuous.

This arises due to the boundary condition imposed $ka = n\pi$. Since k is the wavevector related to the energy as follows:

$$k = \frac{2\pi}{\lambda}$$

$$k = \frac{p}{\hbar}$$

$$k = \frac{\sqrt{2mE}}{\hbar} \quad \text{free particle inside box}$$

Thus, the boundary condition $ka = n\pi$ becomes,

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

Rearranging the last equation to solve for E gives the above-derived equation for the quantized energy levels for the 1-D particle in a box.

Note: The number, n , is a **quantum number**.

Note: The lowest energy allowable is **not zero**; this lowest energy corresponds to the **zero-point energy** of the system.

III. On the Nature of the Wavefunctions for a Particle in a 1-Dimensional Box

1. The wavefunction is a stationary state (problem initially defined with two nodes at $x=0$ and $x=a$).
2. Energy of eigenstates is quantized. Each eigenstate (eigenfunction) adds $1/2$ wavelength and increases number of nodes by 1.
3. Probability of finding a particle in a finite interval dx in the box.

As the quantum number increases to large values, probability of particle position approaches uniform distribution in the region $[0,a]$. This is the classical limit. Quantum mechanics approaches classical mechanics in the limit of large quantum numbers.

As the quantum number increases to large values, the relative spacing between energy levels (eigenstates) becomes infinitesimally small; the energy spectrum appears *continuous* as for the classical free particle (discussed above). This is the classical limit. Quantum mechanics approaches classical mechanics in the limit of large quantum numbers.

A more concrete description of this is shown in Example 15.1 of Engel and Reid (page 325). If one considers the relative energy spacing between levels as given by:

$$\frac{E_{n+1} - E_n}{E_n} = \frac{h^2[(n+1)^2 - n^2]/8ma^2}{h^2n^2/8ma^2}$$

$$\frac{E_{n+1} - E_n}{E_n} = \frac{2n+1}{n^2}$$

IV. Particle in 2 and 3 Dimensional Boxes

Consider a 3-dimensional box of side lengths a , b , c . As in the case of a one-dimensional box, the regions outside of the box are defined to have an infinite potential. Thus

$$V(x, y, z) = 0 \quad \text{for } 0 < x < a, 0 < y < b, 0 < z < c$$

$$V(x, y, z) = \infty \quad \text{everywhere else}$$

The eigenvalue equation for the 3-D case becomes (note, the wavefunction is now $\psi(x, y, z)$):

$$\frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) = E\psi(x, y, z)$$

Since the potential in the box is independent of (x, y, z) , one assumes that the wavefunction is a product of **three independent functions**:

$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

This results straightforwardly in the following **three** eigenvalue equations for each dimension:

$$\frac{-\hbar^2}{2m} \frac{\partial^2 E(x)}{\partial x^2} = E_x X(x)$$

$$\frac{-\hbar^2}{2m} \frac{\partial^2 E(y)}{\partial y^2} = E_y Y(y)$$

$$\frac{-\hbar^2}{2m} \frac{\partial^2 E(z)}{\partial z^2} = E_z Z(z)$$

By analogy to the one-dimensional case:

$$\psi(x, y, z) = \psi_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

The total energy can be written as a sum of the independent terms corresponding to different wavefunctions (degrees of freedom), $\mathbf{E} = \mathbf{E}_x + \mathbf{E}_y + \mathbf{E}_z$.

The eigenvalues become:

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad n_x, n_y, n_z = 1, 2, 3, \dots, \infty$$

Note: Since the energy depends on three quantum numbers, the concept of degeneracy arises naturally. For instance, an energy of 14 (in reduced units) can be obtained for a cubic box ($a=b=c$) in the following ways: $(n_x^2 = 9, n_y^2 = 4, n_z^2 = 1)$, $(n_x^2 = 9, n_y^2 = 1, n_z^2 = 4)$, $(n_x^2 = 1, n_y^2 = 4, n_z^2 = 9)$, $(n_x^2 = 1, n_y^2 = 9, n_z^2 = 4)$, $(n_x^2 = 4, n_y^2 = 1, n_z^2 = 9)$, $(n_x^2 = 4, n_y^2 = 9, n_z^2 = 1)$, etc.... Thus, the number of ways in which the same energy is realized is the **degeneracy**. Equivalently, the degeneracy gives the number of states with the same energy.

A simple table for a 3-D particle in a **cubic** box of dimensions $\mathbf{a} = \mathbf{b} = \mathbf{c}$:

State	n_x	n_y	n_z	$n = (n_x^2 + n_y^2 + n_z^2)$	Energy in units of $\frac{h^2}{8ma^2}$
Lowest	1	0	0	1	1
Lowest	0	1	0	1	1
Lowest	0	0	1	1	1
First Excited	1	1	0	2	2
First Excited	1	0	1	2	2
First Excited	0	1	1	2	2
Second Excited	1	1	1	3	3