

Introduction to Quantum Mechanics 4
11/1/02
PHY 314

Particle in an infinite square well

Now let us introduce an interaction potential. The simplest, but still very interesting, example is a particle confined between two hard walls. The corresponding potential is

$$V(x) = \begin{cases} 0 & \text{if } x \text{ is in the interval } (0,a) \\ \infty & \text{otherwise} \end{cases}$$

Brethm and Mullin put the potential between $-a/2$ and $a/2$, but my choice is easier, and can be reduced to the B&M choice by a shift of $-a/2$ at the end of the calculation.

Schroedinger's time-independent equation is $\frac{-\hbar^2}{2m} \frac{d^2 y_E(x)}{dx^2} + V(x)y_E(x) = Ey_E(x)$.

In the region of the infinite potential, the only way this equation makes sense is for the wave function to vanish. In the region where the potential is zero, $V(x) = 0$, and we have (see free particle case) $y_E(x) = A \sin kx + B \cos kx$ where I have used trig functions instead of the complex exponential because it makes applying boundary conditions easier. To make the wave function continuous, set $y_E(0) = 0 = A \cos 0 + B \sin 0 = A$. At the boundary $x = a$ we have $y_E(a) = 0 = A \sin ka + 0$. Clearly A cannot be zero or else the wave function is zero everywhere. The only nontrivial solution then requires $k_n a = n\pi$ where $n = 1, 2, 3, \dots$. The subscript on k is included to distinguish among solutions of different k . This analysis is very reminiscent of our calculation of blackbody radiation. To simplify the notation, I'll set

$$y_n(x) = y_{E_n}(x) = A_n \sin k_n x = A_n \sin \frac{n\pi x}{a}.$$

I leave it to you to prove that for a properly normalized wave function, the overall constant can be taken as $A_n = \sqrt{\frac{2}{a}}$. The corresponding energy levels

$$\text{are } E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2ma^2}.$$

You should plot the first few of these wave functions and draw an energy level diagram for the corresponding states. Note in particular that each

successive energy level has one more node. This is a general result. The solution complete with time dependence is, from our general theory,

$$\Psi(x, t) = \sum_{n=1}^{\infty} C_n \mathbf{y}_n(x) e^{-iE_n t/\hbar} = \sum_{n=1}^{\infty} C_n \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} e^{-iE_n t/\hbar} .$$

We now have the full time dependence provided that we can determine C_n . As in the free particle case, if we know the wave function at $t = 0$, we should be able to determine the wave function for all time. The trick (which we will suitably generalize for all energy-level problems) is to set $t = 0$ (which makes the exponential factor equal 1) and then multiply both sides of the equation by $\mathbf{y}_{n'}(x)$ and integrate over the region $(0, a)$. The integral on the right side is easily evaluated. From the homework problem it follows that the integral vanishes unless the integers n and n' are equal. Combined with the fact that the wave function is normalized we find that

$$\int_0^a \mathbf{y}_{n'}(x) \mathbf{y}_n(x) dx = \mathbf{d}_{n'n}$$

which is known as the orthonormality (orthogonal and normalized) condition.

We now have

$$\int_0^a \mathbf{y}_{n'}(x) \Psi(x, 0) dx = \sum_{n=1}^{\infty} C_n \mathbf{d}_{n'n} = C_{n'} .$$

Simply performing the integral determines C_n for all n and hence the time dependence is now completely determined.

C_n has an interesting physical interpretation, and I will discuss it after introducing one additional postulate.

The orthonormality relation seems like magic. Was it an accident of the particular problem? No. The result was inevitable and is true for the energy eigenstates of any system (provided that a) the Hamiltonian has no explicit time dependence and b) the eigenfunctions correspond to different energies).

To prove this result and to provide some mathematics background for the final postulate of quantum mechanics, I'll must introduce a couple more mathematical topics.

Scalar product of wave functions.

One dimensional case: Let $y_1(x, t)$ and $y_2(x, t)$ be any two wave functions. The scalar product of these functions is defined by

$$\langle y_2 | y_1 \rangle = \int_{-\infty}^{\infty} y_2^*(x, t) y_1(x, t) dx. \quad (\text{Notice the complex conjugate.})$$

See the PHY 301 tutorial OFFS, section 1.2 (Function spaces).

The scalar product is the “overlap” of the two functions; the contribution to the scalar product is zero in regions for which one or the other factors vanishes. For a three-dimensional system of many particles, take

$$x = (x_1, y_1, z_1, x_2, y_2, z_2, \dots, z_N) \quad \text{and} \quad dx = (dx_1 dy_1 dz_1 dx_2 \dots dz_N).$$

The scalar product has the following properties:

- i) $\langle y_1 | y_2 \rangle = \langle y_2 | y_1 \rangle^*$
- ii) If $y(x, t) = ay_1(x, t) + by_2(x, t)$ then $\langle f | y \rangle = a \langle f | y_1 \rangle + b \langle f | y_2 \rangle$ where $f(x, t)$ is any wave function and a and b are any complex constants.
- iii) For any wave function $\langle f | f \rangle \geq 0$ and if $\langle f | f \rangle = 0$ then $f(x, t) = 0$ (where I have assumed that the wave function is continuous).

If the scalar product of any two wave functions is zero, the wave functions are said to be orthogonal.

In some applications (for example a particle with only spin degrees of freedom), the wave functions are N-component column vectors with constant coefficients. If \underline{y} and \underline{f} are two such vectors, we define the scalar

product of these vectors by $\langle \underline{f} | \underline{y} \rangle = \underline{f}^T \underline{y} = \sum_{i=1}^N f_i^* y_i$ where f_i and y_i are the

components of the vectors. This result should be familiar from standard vector analysis. For example, for real vectors in three dimension, the definition reduces to the familiar $\vec{f} \cdot \vec{y} = f_x y_x + f_y y_y + f_z y_z$. (The complex conjugate are necessary when \underline{f} and \underline{y} are wave functions.)

Exercise: show that all three of the properties hold with this definition of the scalar product.

Notation. Let \hat{A} be an operator and y_1 and y_2 be wave functions. Then $\hat{A}y_1$ is also a wave function (although probably it is not normalized). The scalar product of y_2 and $\hat{A}y_1$ is obtained by multiplying y_2^* by $\hat{A}y_1$ and integrating. In our standard notation it is expressed as $\langle y_2 | \hat{A}y_1 \rangle$. It is customary to insert an additional bar “|” between to make the expression look more symmetric: $\langle y_2 | \hat{A} | y_1 \rangle$.

All about hermitian operators

The measurement of observables yields real numbers. The corresponding operator must be chosen so that its eigenvalues are all real since these are the possible values of a measurement of the observable. We will see that the class of “hermitian” operators is exactly what we need. To motivate the definition of hermitian operators, I’ll begin by studying the properties of the momentum operator.

Let y_1 and y_2 be any wave functions and take $\hat{A} = \hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$ be the

momentum operator. Then $\langle y_2 | \hat{p} | y_1 \rangle = \int y_2^* \frac{\hbar}{i} \frac{\partial y_1}{\partial x} dx$ where the integral extends over all x . Integrating by parts and assuming that the wave function vanishes at $\pm\infty$ so that the integrated part vanishes, we get

$$\langle y_2 | \hat{p} | y_1 \rangle = \int \left(-\frac{\hbar}{i} \frac{\partial y_2^*}{\partial x} \right) y_1 dx = \left(\int y_1^* \left(\frac{\hbar}{i} \frac{\partial y_2}{\partial x} \right) dx \right)^* = \langle y_1 | \hat{p} | y_2 \rangle^*$$

where I have used $i^* = -i$.

Definition:

Any operator for which $\langle y_2 | \hat{A} | y_1 \rangle = \langle y_1 | \hat{A} | y_2 \rangle^*$ for all y_1 and y_2 is said to be “hermitian.”

If you think of 1 and 2 as subscripts of a matrix, the transpose of the matrix gives its complex conjugate.

Exercise: show that the Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$ is a hermitian operator assuming that $V(x)$ is real for all real x . (You will need to integrate by parts twice on the kinetic-energy term.)

Properties of Hermitian operators

Let \hat{A} be an arbitrary hermitian operator.

a) If $\mathbf{y}_1 = \mathbf{y}_2 \equiv \mathbf{y}$, then $\langle \mathbf{y} | \hat{A} | \mathbf{y} \rangle = \langle \mathbf{y} | \hat{A} | \mathbf{y} \rangle^*$, so the expectation value of a hermitian operator is real.

b) Let $\hat{A}\mathbf{y}_1 = a_1\mathbf{y}_1$ and $\hat{A}\mathbf{y}_2 = a_2\mathbf{y}_2$ define two eigenfunctions and the corresponding eigenvalues of a hermitian operator \hat{A} . Evaluate the scalar product of the first equation with \mathbf{y}_2 and the scalar product of the second equation with \mathbf{y}_1 . The resulting equations are

$$\begin{aligned}\langle \mathbf{y}_2 | \hat{A} | \mathbf{y}_1 \rangle &= a_1 \langle \mathbf{y}_2 | \mathbf{y}_1 \rangle \quad (\text{equation a}) \\ \langle \mathbf{y}_1 | \hat{A} | \mathbf{y}_2 \rangle &= a_2 \langle \mathbf{y}_1 | \mathbf{y}_2 \rangle\end{aligned}$$

Using the definition of hermitian and the first property of the scalar product, the second of these equations becomes

$$\langle \mathbf{y}_2 | \hat{A} | \mathbf{y}_1 \rangle^* = a_2 \langle \mathbf{y}_2 | \mathbf{y}_1 \rangle^*.$$

The complex conjugate of this equation is simply

$$\langle \mathbf{y}_2 | \hat{A} | \mathbf{y}_1 \rangle = a_2^* \langle \mathbf{y}_2 | \mathbf{y}_1 \rangle \quad (\text{equation b})$$

There are two applications of equations “a” and “b”. First set $\mathbf{y}_1 = \mathbf{y}_2$ (and so $a_1 = a_2$). Then equation a implies that $\langle \mathbf{y}_1 | \hat{A} | \mathbf{y}_1 \rangle = a_1 \langle \mathbf{y}_1 | \mathbf{y}_1 \rangle$ and equation b implies that $\langle \mathbf{y}_1 | \hat{A} | \mathbf{y}_1 \rangle = a_1^* \langle \mathbf{y}_1 | \mathbf{y}_1 \rangle$. Comparing these implies that a_1 is real. The conclusion is that **the eigenvalues of any hermitian operator are real numbers**. This is reason that all observables are represented by hermitian operators.

The second application uses $\mathbf{y}_1 \neq \mathbf{y}_2$ and $a_1 \neq a_2$. Subtracting equations a and b gives

$$0 = (a_2 - a_1) \langle \mathbf{y}_2 | \mathbf{y}_1 \rangle$$

Since $a_1 \neq a_2$ we can cancel the first factor and so it follows that $\langle \mathbf{y}_2 | \mathbf{y}_1 \rangle = 0$.

Conclusion: Eigenfunctions of a hermitian operator corresponding to different eigenvalues are orthogonal. The orthogonality of the energy eigenstates of the particle in a rigid box simply had to turn out orthogonal. It was no accident.

Now let's put the scalar product to further use. With postulate 4, we nearly complete the foundations of quantum mechanics. (The last step will come later when we take into account the Pauli exclusion principle.)

Postulate 4. A system is in state defined by the wave function \mathbf{y}_i . The probability that a measurement will find the system wave function \mathbf{y}_f is $|\langle \mathbf{y}_f | \mathbf{y}_i \rangle|^2$ where it is assumed that $\langle \mathbf{y}_i | \mathbf{y}_i \rangle = \langle \mathbf{y}_f | \mathbf{y}_f \rangle = 1$.

The scalar product $\langle \mathbf{y}_f | \mathbf{y}_i \rangle$ is sometimes known as the probability amplitude for the transition from state i to state f . As an example, return to the problem of a particle in a rigid box. If the initial state of the particle is described by the wave function $\Psi(x, t)$ then the probability that a measurement of the energy of the system will find it in energy level E_n is $P_n = |\langle \mathbf{y}_n | \Psi \rangle|^2 = |C_n|^2$. This gives the physical meaning of the expansion coefficient that we found earlier.

Finally, here is an unpleasant but necessary complication. Postulate 4 needs to be amended in the cases in which one or both of the wave functions can not be normalized to 1. I'll show you how to do this for the two most important examples, a coordinate measurement and a momentum measurement. The basic idea is that in this case $|\langle \mathbf{y}_f | \mathbf{y}_i \rangle|^2$ is not the probability, but is rather the probability *density* for the transition. To get the probability, we must multiply $|\langle \mathbf{y}_f | \mathbf{y}_i \rangle|^2$ by df , where df is dx in the case of a position measurement and is $dp/2p\hbar$ in the case of a momentum measurement. The factor of $2p\hbar$ is required by our choice of normalization.

The generalization to 3D replaces df to d^3r for a position measurement and $d^3p/(2\pi\hbar)^3$ for a momentum measurement.

Position measurement:

At a given time, make a measurement of the position of the particle. If the final state corresponds to the particle being at position $x = x_0$, then

$\mathbf{y}_f(x) = \mathbf{y}_{x_0}(x) = \mathbf{d}(x - x_0)$. Then $\langle \mathbf{y}_f | \mathbf{y}_i \rangle = \int \mathbf{d}(x - x_0) \mathbf{y}_i(x, t_0) dx = \mathbf{y}_i(x_0, t_0)$. This is just the original wave function! Its absolute square is the probability density $|\langle \mathbf{y}_f | \mathbf{y}_i \rangle|^2 = |\mathbf{y}_i(x_0, t_0)|^2 = P(x_0, t_0)$. The probability that a position measurement finds the particle in the interval $(x, x + dx)$ is obtained by multiplying the probability density by dx .

Momentum measurement:

At a given time, make a measurement of the momentum of the particle. If the final state corresponds to the particle having momentum $p = p_0$, then $\mathbf{y}_f(x) = e^{ip_0x/\hbar}$. Then the scalar product is $\langle \mathbf{y}_f | \mathbf{y}_i \rangle = \int e^{-ip_0x/\hbar} \mathbf{y}_i(x, t_0) dx = \tilde{\mathbf{y}}(p_0, t_0)$ which is the *Fourier transform* of the initial wave function. $\tilde{\mathbf{y}}(p, t_0)$ is also known as the momentum-space wave function. The probability density for the system being found with momentum p is then $|\tilde{\mathbf{y}}(p, t_0)|^2$. The probability that the particle is found in the interval $(p, p + dp)$ is obtained by multiplying the probability density by $\frac{dp}{2\pi\hbar}$. Why is that factor of $2\pi\hbar$ present? Integrate over all p , and we should end up with 1. Check that it works:

$$\int \frac{dp}{2\pi\hbar} |\tilde{\mathbf{y}}(p, t)|^2 = \int \frac{dp}{2\pi\hbar} \int dx' \int dx e^{ipx'/\hbar} \mathbf{y}^*(x', t) e^{-ipx/\hbar} \mathbf{y}(x, t)$$

First integrate over p and recall that

$$\int e^{ip(x-x')/\hbar} \frac{dp}{2\pi\hbar} = \mathbf{d}(x - x')$$

Combining, we have

$$\int \frac{dp}{2\pi\hbar} |\tilde{\mathbf{y}}(p, t)|^2 = \int dx' \int dx \mathbf{d}(x - x') \mathbf{y}^*(x', t) \mathbf{y}(x, t) = \int dx |\mathbf{y}(x, t)|^2 = 1$$

This verifies that the factor $2\pi\hbar$ (which is really just h) is required to assure that $\tilde{\mathbf{y}}(p, t)$ is the correct momentum-space wave function.