Chapter 7

A Particle in a Box

When she does not laugh...that's a par tickle....[1].

Molecules, Atoms, and Nucleii

An atom in a molecule, an electron in an atom, a nucleon in a nucleus are examples of particles confined to limited regions. Each demonstrate energy quantization while confined. Each limited region can be considered to be a "box" with "soft walls" formed by electrical or nuclear forces. We are going to take a first step toward describing such realistic system by examining a one dimensional box with the simplest possible geometry and "hard walls." The "hard walls" we use mean the potential energy function goes from zero in the region of confinement to infinity at two points at the edges. This bit of unrealism makes the mathematics most tractable while illustrating the feature of energy quantization.

Energy quantization is revealed in the form of allowed energy levels which are eigenenergies, or eigenvalues in an energy basis. These are the observable energies. The functions which correspond to the eigenenergies are eigenfunctions, or eigenstates, or eigenvectors. A wave function, or state function, may be an eigenfunction but will generally be a linear superposition of the eigenfunctions.

The differential equation approach lends itself well to this problem so we will use it. Results in three dimensions are a generalization of results in one dimension.

Solution to the One Dimensional Infinite Square Well

Figure 7.1 is a graph of energy versus position. Here

$$V(x) = \infty, \quad x \leq -a \text{ and } x \geq a,$$

$$V(x) = 0, \quad -a < x < a.$$

We divide all space into three regions. Since the "height" of the walls is infinite, the walls are impenetrable. This means the wave function must be zero in regions I and III. This is artificial because there are no "infinite" potentials. Further, there are no potentials which go from zero to infinity at a point. As indicated, these simplifications do facilitate the mathematics yet still reveal energy quantization. The general solution to the Schrodinger equation for this potential is

$$\psi(x) = \begin{cases} 0 & x \leq -a, \\ Ae^{-ikx} + Be^{ikx} & -a < x < a, \\ 0 & x \geq a, \end{cases}$$

where $k = \lambda/2\pi$ is the wave number, λ being the de Broglie wavelength. To demonstrate this is a solution, we need the second derivative of the wave function, or
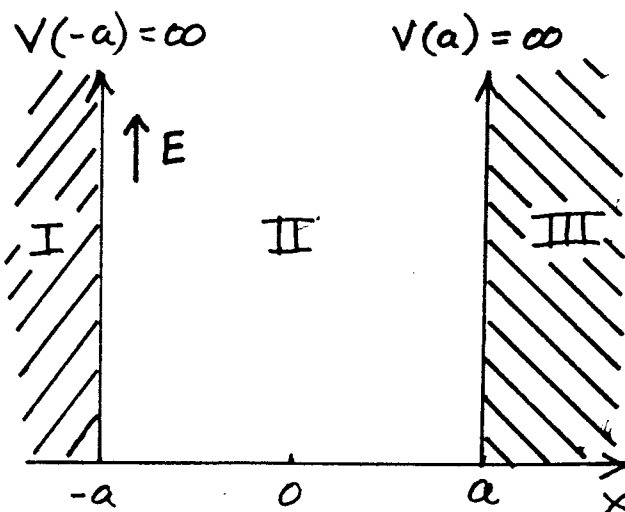

FIGURE 7-1. THE INFINITE SQUARE WELL.

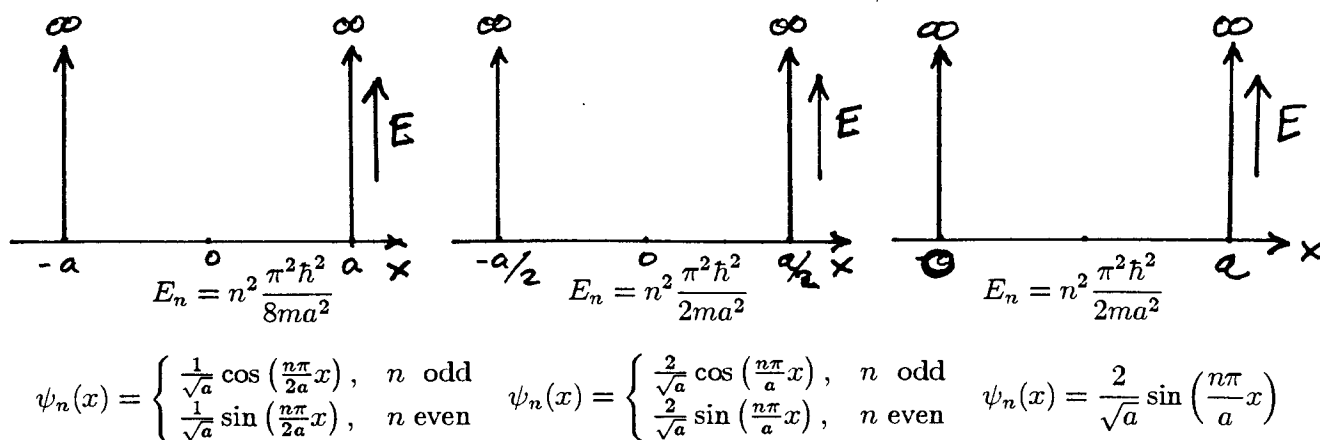
[1] Author *Title* (Publisher, Location, Year), page.

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

$$\psi_n(x) = \begin{cases} \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi}{2a}x\right), & n \text{ odd} \\ \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi}{2a}x\right), & n \text{ even} \end{cases} \qquad \psi_n(x) = \begin{cases} \frac{2}{\sqrt{a}} \cos\left(\frac{n\pi}{a}x\right), & n \text{ odd} \\ \frac{2}{\sqrt{a}} \sin\left(\frac{n\pi}{a}x\right), & n \text{ even} \end{cases} \qquad \psi_n(x) = \frac{2}{\sqrt{a}} \sin\left(\frac{n\pi}{a}x\right)$$

Figure 7 − 2. Alternate Choices of Coordinate

Our convention generalizes easily to descriptions using radius. The second generalizes well to descriptions using diameter. The last is used in introductory texts because it can be derived without the use of exponentials with complex arguments, i.e., completely in terms of sines and cosines. The last is also simplest, in that there is one expression for all n.

While on the subject of conventions, notice the particle in a box problem uses $n = 1$ as the lowest energy state, or the **ground state**. In contrast, the simple harmonic oscillator, addressed in the chapter 8 uses $n = 0$ for the lowest energy state, or the ground state.

Example 7–1: A typical atomic radius is on the order of one half of one Angstrom. What is the ground state energy of an electron in an infinite square well of "radius" one half Angstrom?

Using equation (7–6) for $n = 1$, which corresponds to the ground state energy,

$$E_n = n^2 \frac{\pi^2 \hbar^2}{8ma^2} \quad \Rightarrow \quad E_1 = \frac{\pi^2 \hbar^2}{8ma^2} = \frac{\pi^2 h^2}{(2\pi)^2 8ma^2} = \frac{h^2 c^2}{(4)8mc^2 a^2}$$

$$= \frac{(1.24 \times 10^4 \, eV \cdot \text{Å})^2}{32 \left(0.511 \times 10^6 \, \frac{eV}{c^2}\right) c^2 (0.5 \, \text{Å})^2} = \frac{1.54 \times 10^8 \, eV^2 \cdot \text{Å}^2}{4.09 \times 10^6 \, eV \cdot \text{Å}^2} = 37.65 \, eV.$$

Notice that we use the constant hc and the electron mass is in units of eV/c^2, consistent with calculations in chapter 1. Converting quantities from CGS or MKS units is inconvenient by comparison.

Example 7–2: Find the eigenenergies of the first three excited states for the infinite square well described in example 7–1.

Notice the eigenenergies are proportional to n^2. For a given particle in a given infinite square well, the only thing that changes is the quantum number. This makes it convenient to describe the energy of excited states, those eigenenergies which are described by quantum numbers other than $n = 1$, in terms of the ground state energy. If E_g is ground state energy, all eigenenergies are described by $n^2 E_g$. Since we have the ground state energy from example 7–1, the energies of the first three excited states are

$$E_2 = 2^2 E_g = 4(37.65 \, eV) = 150.60 \, eV,$$

$$E_3 = 3^2 E_g = 9(37.65 \, eV) = 338.85 \, eV,$$

$$E_4 = 4^2 E_g = 16(37.65 \, eV) = 602.40 \, eV.$$

Graphical Representations

Figure 7–3a shows the eigenenergies of an infinite square well for $n = 1, 2, 3$ and 4. The vertical axis is energy and the horizontal axis is position. Figure 7–3b shows the wave functions and the eigenenergies. The vertical axis is both energy and amplitude of the wave function. The wave functions *should* all be located on the horizontal axis. They have the value of zero at the boundaries, and if the vertical axis represents amplitude, a zero amplitude would be on the horizontal axis. Nevertheless, it is conventional to locate them at the level of the corresponding energy. It would be difficult to tell which wave function corresponded to which energy if all wave functions were superimposed on the horizontal axis. Figure 7–3b then, represents a number of graphs with amplitude of the wave functions being zero at boundaries, but shown at the level of the corresponding eigenenergy. When you see these sorts of graphs, and this is just the first of many, realize what you are looking at and what it is telling you.
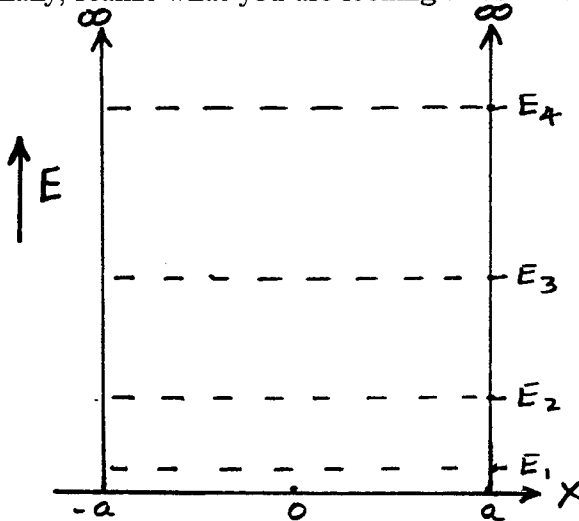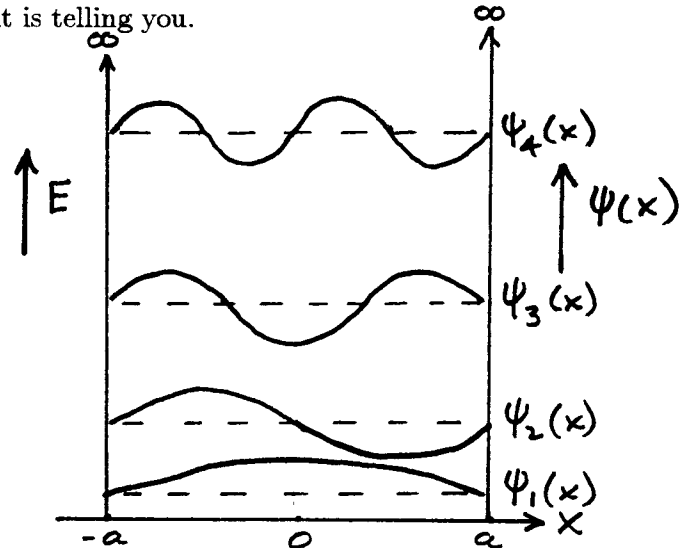
Figure 7 − 3a. Eigenenergies   Figure 7 − 3b. Eigenergies and Wave Functions

Consistent with example 7–2, the eigenenergies are proportional to n^2. Notice the vertical separation of the eigenenergies goes as n^2 in Figure 7–3. The vertical separation between eigenenergies increases as n increases. The vertical separation of other systems we will examine will differ. For instance, in the next chapter we will find the vertical separation between eigenenergies of the quantum mechanical simple harmonic oscillator are steps of equal energy.

The next step is to graph **probability density**, as shown in Figure 7–4. Remember probability is

$$|\psi(x)|^2 \, dx$$

so probability density is

$$|\psi(x)|^2$$

which has the units of $1/\sqrt{\text{length}}$. This also uses the convention of placing the corresponding quantity at the level of the eigenenergy, vice trying to superimpose many of them on the horizontal axis.
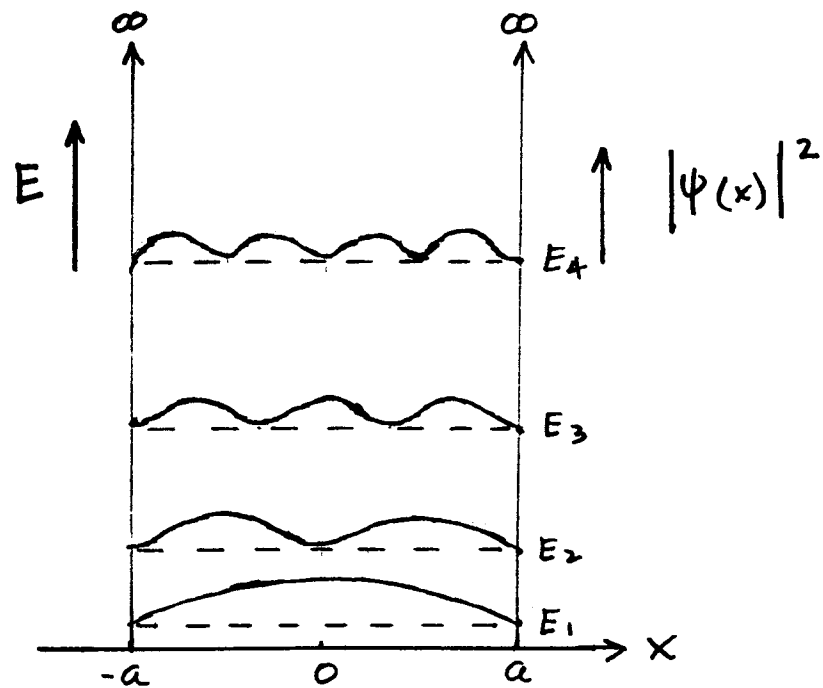
6

FIG 7-4. PROBABILITY DENSITIES AT EIGENENERGIES.

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the maxima than an equal interval near the minima from the probability density graphs, and that qualitative picture is the focal point in drawing graphs like those in Figure 7–4.

Graphical Representations in Energy and Momentum Space

To this point, graphs have all been in position space and you will see these in many quantum mechanics texts. What you will not often see is the same graphs in energy and momentum space. Being able to qualitatively picture systems in different bases is very helpful, and being able to think in other than the position basis is essential. We present these in this simple system to improve your ability of being able to "think in other bases." It is a skill essential for detailed examination of more complex systems.

In energy space, the energy wave functions, $\widetilde{\psi}(E)$, are discontinuous spikes because only eigenvalues of energy are possible. In momentum space, $\widehat{\psi}(p)$ versus wave number, the wave functions will be variations of sinc functions. Because energy is related to momentum, $E = p^2/2m = \hbar^2 k^2/2m$, energy in the form of the wave number is on the horizontal axis. The effect is the spikes in energy space are "spread" in momentum space at the wave number which corresponds to the eigenenergy. The following three figures picture the wave function in position space, the energy space wave function versus energy, and finally the momentum space wave function versus wave number. We will illustrate $n = 1$, $n = 2$, and $n = \text{many}$.
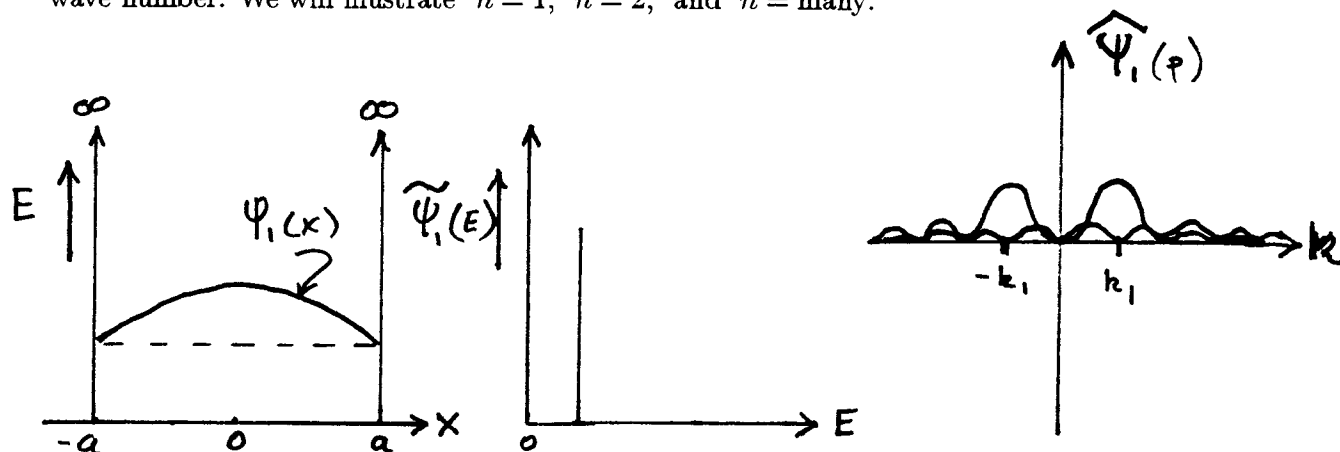

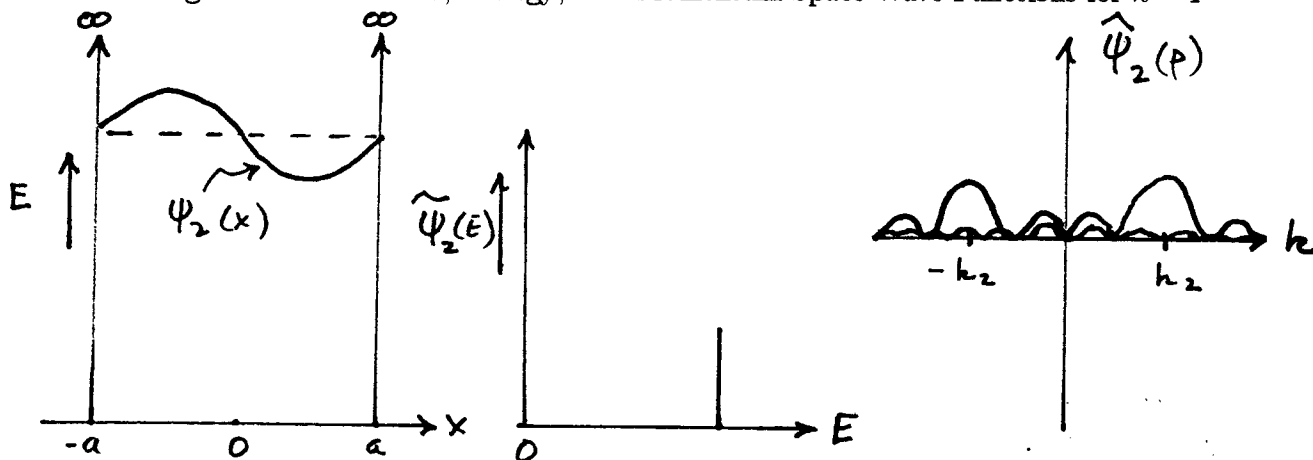Figure 7 – 5. Position, Energy, and Momentum Space Wave Functions for $n = 1$

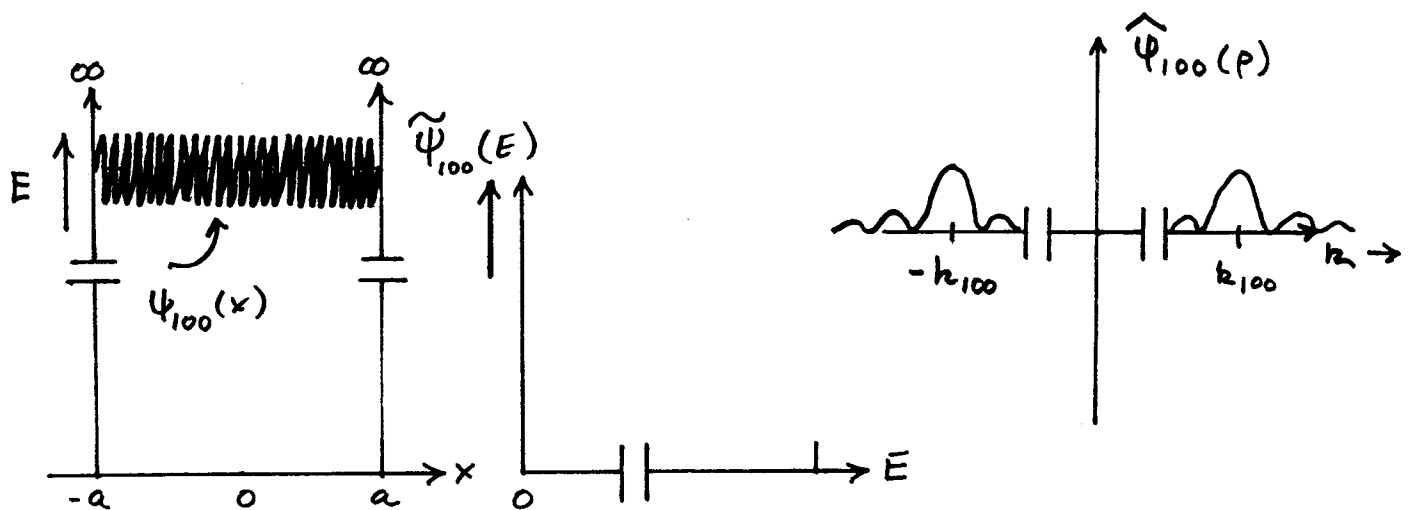Figure 7 – 6. Position, Energy, and Momentum Space Wave Functions for $n = 2$

8

FIGURE 7-7. POSITION, ENERGY, AND MOMENTUM SPACE WAVE FUNCTIONS FOR n = MANY.

(INSERT AFTER PAGE 8, CHAPTER 7)

From (8) and (9), we get:

$$\Delta P_n = \sqrt{\langle P^2 \rangle_n - \langle P \rangle_n^2} = \frac{n\pi\hbar}{a} \tag{10}$$

The root-mean-square deviation therefore increases linearly with n.

b.   DISCUSSION

Let us trace, for different values of n, the curves which give the probability density $\overline{\mathscr{P}}_n(p)$. To do this, let us begin by studying the function inside brackets in expression (6). For the ground state $(n = 1)$, it is the sum of two functions F, the centers of these two diffraction curves being separated by half their width (fig. 1-a). For the first excited level $(n = 2)$, the distance between these centers is twice as large, and in this case, moreover, the difference of two functions F must be taken (fig. 2-a). Finally, for an excited level corresponding to a large value of n, the centers of the two diffraction curves are separated by a distance much greater than their width.
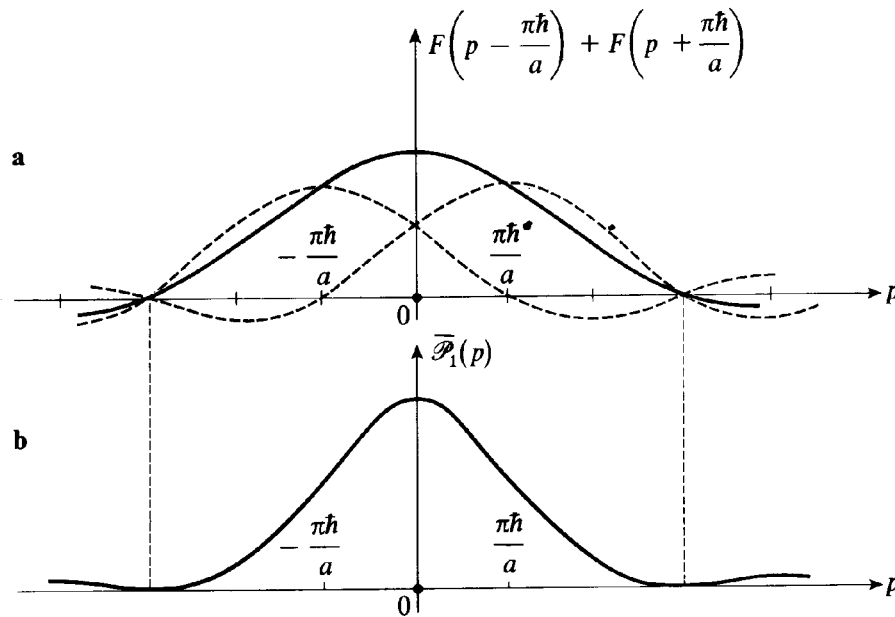

FIGURE 1

The wave function $\overline{\varphi}_1(p)$, associated in the $\{ \,|\, p \,\rangle \,\}$ representation with the ground state of a particle in a infinite well, is obtained by adding two diffraction functions F (curves in dashed lines in figure a). Since the centers of these two functions F are separated by half their width, their sum has the shape represented by the solid-line curve in figure a. Squaring this sum, one obtains the probability density $\overline{\mathscr{P}}_1(p)$ associated with a measurement of the momentum of the particle (fig. b).

Squaring these functions, one obtains the probability density $\overline{\mathscr{P}}_n(p)$ ($cf.$ fig. 1-b and 2-b). Note that for large n the interference term between $F\left(p - \dfrac{n\pi\hbar}{a}\right)$ and
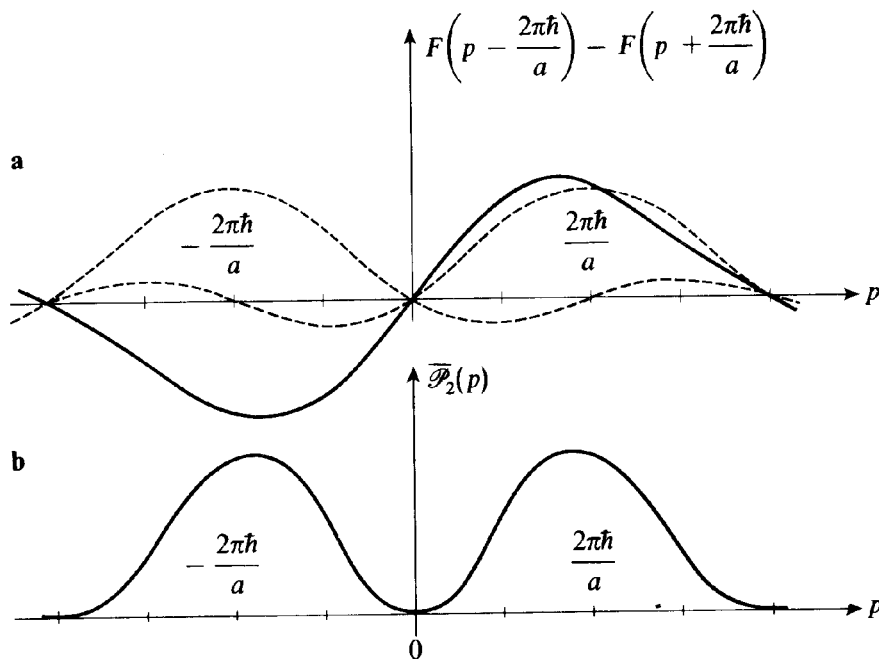
FIGURE 2

For the first excited level, the function $\bar{\varphi}_2(p)$ is obtained by taking the difference between two functions F, which have the same width as in figure 1-a but are now more widely separated (dashed-line curve in figure a). The curve obtained is the solid line in figure a. The probability density $\bar{\mathcal{P}}_2(p)$ then has two maxima located in the neighborhood of $p = \pm\ 2\pi\hbar/a$ (fig. b).

$F\left(p + \dfrac{n\pi\hbar}{a}\right)$ is negligible (because of the separation of the centers of the two curves):

$$\bar{\mathcal{P}}_n(p) = \frac{a}{4\pi\hbar}\left[F\left(p - \frac{n\pi\hbar}{a}\right) + (-1)^{n+1}F\left(p + \frac{n\pi\hbar}{a}\right)\right]^2$$

$$\simeq \frac{a}{4\pi\hbar}\left[F^2\left(p - \frac{n\pi\hbar}{a}\right) + F^2\left(p + \frac{n\pi\hbar}{a}\right)\right] \tag{11}$$

The function $\bar{\mathcal{P}}_n(p)$ then has the shape shown in figure 3.

It can be seen that when n is large, the probability density has two symmetrical peaks, of width $\dfrac{4\pi\hbar}{a}$, centered at $p = \pm\ \dfrac{n\pi\hbar}{a}$. It is then possible to predict with almost complete certainty the results of a measurement of the momentum of the particle in the state $|\ \varphi_n\ \rangle$: the value found will be nearly equal to $+\dfrac{n\pi\hbar}{a}$ or

$-\dfrac{n\pi\hbar}{a}$, the relative accuracy* improving as n increases (the two opposite

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* The absolute accuracy is independent of n, since the width of the curves is always $\dfrac{4\pi\hbar}{a}$.

values $\pm \dfrac{n\pi\hbar}{a}$ being equally probable). This is simple to understand: for large n, the function $\varphi_n(x)$, which varies sinusoidally, performs numerous oscillations inside the well; it can then be considered to be practically the sum of two progressive waves corresponding to opposite momenta $p = \pm \dfrac{n\pi\hbar}{a}$.
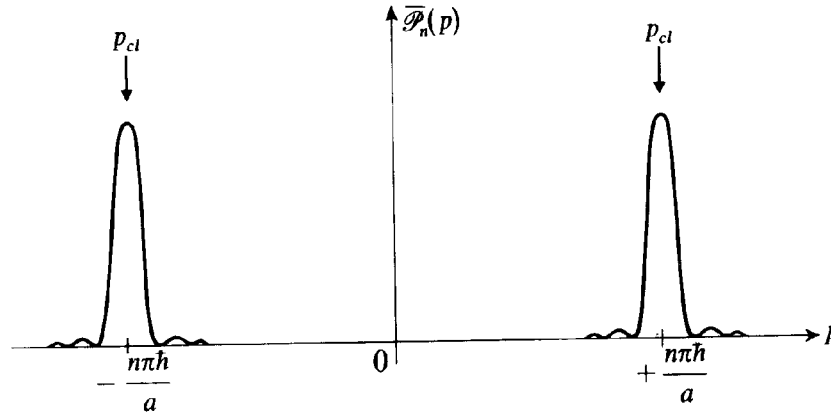

FIGURE 3

When n is large (a very excited level), the probability density has two pronounced peaks, centered at the values $p = \pm\ n\pi\hbar/a$, which are the momenta associated with the classical motion at the same energy.

When n decreases, the relative accuracy with which one can predict the possible values of the momentum diminishes. We see, for example, in figure 2-b, that when $n = 2$, the function $\overline{\mathscr{P}}_n(p)$ has two peaks whose widths are comparable to their distance from the origin. In this case, the wave function undergoes only one oscillation inside the well. It is not surprising that, for this sinusoid "truncated" at $x = 0$ and $x = a$, the wavelength (and therefore, the momentum of the particle) is poorly defined. Finally, for the ground state, the wave function is represented by half a sinusoidal arc: the relative values of the wavelength and momentum of the particle are then very poorly known (fig. 1-b).

COMMENTS:

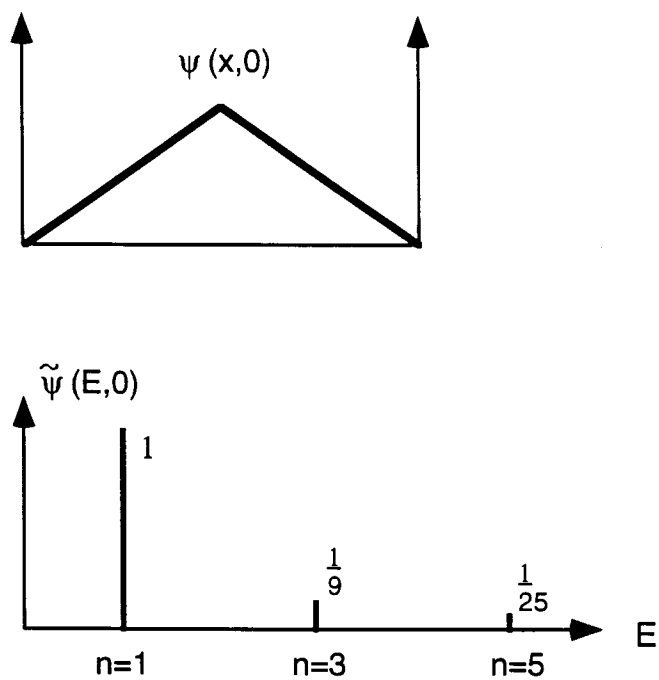(i) Let us calculate the momentum of a classical particle of energy E_n given in (1); we have:

$$\frac{p_{cl}^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{12}$$
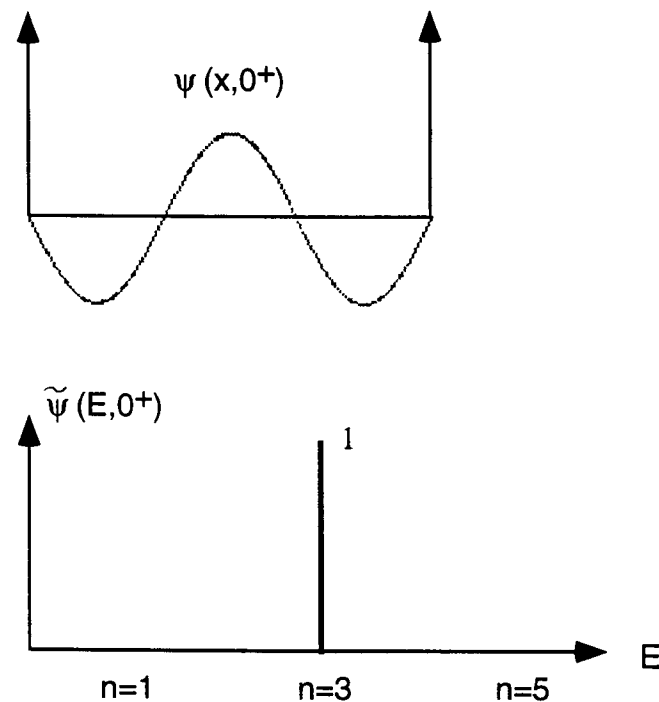
that is:

$$p_{cl} = \pm \frac{n\pi\hbar}{a} \tag{13}$$

When n is large, the two peaks of $\overline{\mathscr{P}}_n(p)$ therefore correspond to the classical values of the momentum.

Immediately before the measurement, the two wavefunctions look like this

$\psi\,(x,0)$

$\widetilde{\psi}\,(E,0)$

1

$\frac{1}{9}$

$\frac{1}{25}$

E

n=1   n=3   n=5

And immediately after the measurement, the two wavefunctions look like this

$\psi\,(x,0^+)$

$\widetilde{\psi}\,(E,0^+)$

1

E

n=1   n=3   n=5

Remember, however that these two wavefunctions are just different representations of exactly the same state vectors—they are just $|\,\psi(0^-)>$ and $|\,\psi(0^+)>$ in two different bases!

24