

6-27-2006

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Recommended Citation

David, Carl W., "The Particle in a Box (and in a Circular Box)" (2006). *Chemistry Education Materials*. 12.
http://digitalcommons.uconn.edu/chem_educ/12

The Particle in a Box (and in a Circular Box)

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(Dated: June 27, 2006)

I. SYNOPSIS

The particle in a box is the simplest problem in elementary quantum mechanics, and as such is useful in more places than one can easily enumerate. For instance, the molecular orbital theory is explained easily in terms of particle in a box wavefunctions, easier than using standard atomic orbitals. Hence, the attention to this particular problem.

II. INTRODUCTION

We start with a choice of coordinate systems, which, by the way, influences the form of the solutions we are going to get, but not the substance. Here, we choose to use $0 < x < L$ for the region on the x-axis where the particle is said to exist. For regions $x < 0$, i.e., the negative x-axis, we say the particle is forbidden, and mathematically, we do this by stating that $V(x) = \infty$, $\psi(x) = 0$ in this region. We say exactly the same thing in the region $x > L$, i.e., the potential energy is infinite, and the wave function vanishes.

In the domain $0 < x < L$, we expect the wave function to exist and have a value different from zero, but at the boundaries, we declare $\psi(0) = 0$, $\psi(L) = 0$.

Then, the Schrodinger Equation (inside the domain) becomes

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

where m is the mass of the particle, \hbar is, of course, Planck's constant divided by 2π , and E is the energy, the eigenvalue, the allowed value of the energy that this particle can have. We know the solution to this differential equation from elementary calculus, since there are very few functions which resurrect themselves after being differentiated twice. One of these is the exponential, and the other is the (sine/cosine) combination (which are really forms of the exponential). Assume the sines and cosines form, we have

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

where A , B , and ω are unknown (to be determined) constants. Taking the first derivative of this solution, we have

$$\frac{d\psi(x)}{dx} = -A\omega \sin(\omega x) + B\omega \cos(\omega x)$$

and, taking the second derivative, we have

$$\frac{d^2\psi(x)}{dx^2} = -A\omega^2 \cos(\omega x) - B\omega^2 \sin(\omega x)$$

which is, of course,

$$-\omega^2\psi(x)$$

This means that

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

or, said in the most straightforward manner, E is related to ω i.e.,

$$\omega^2 = \frac{2mE}{\hbar^2}$$

. Later, we will obtain values for ω and thereby obtain values of E . They will turn out to be $E_n = \frac{n^2\hbar^2\pi^2}{2mL^2}$, a very famous result.

To obtain this result, we note the boundary conditions, that the wave function vanish on the left and right boundaries. The left boundary condition, $x=0$ says $\psi(0) = A \cos(0) + B \sin(0) = A \cos(0) = A$ i.e., A must be chosen to be zero (as $\cos 0$ equals 1).

The right boundary condition now reads $\psi(L) = B \cos(\omega L)$ and it is a famous argument that if B is not to be zero, then the cosine must. This can only occur if ω has values such that the argument ωL equates to $\pi, 2\pi, 3\pi, \dots$ i.e. $n\pi$. This is the infamous quantization which takes place to force discrete values of E , the energy. Every text book says this better than I do, so you are referred to standard texts for alternative presentations of this material.

The various wave functions, now indexed with "n", are orthogonal to each other, i.e., "perpendicular" in function space. We see that this is just a Fourier discussion in mufti. Thus, we have

$$\int_0^L \psi_1(x)\psi_2(x)dx = 0$$

And we can change 1 to 17, and 2 to 43, and the same holds. Formally,

$$\int_0^L \psi_n(x)\psi_m(x)dx = 0$$

if $n \neq m$. Of course, when $n=m$, we have the normalization integral

$$\int_0^L \psi_n^2(x) dx \neq 0$$

i.e., something other than zero. This last condition is used to choose the (so far) arbitrary constant, A, to force the integral to have a value of 1, in accord with the probabilistic interpretation of the wave function. Since these are, in the case of the particle in a box, integrals of products of sines, we have

$$\int_0^L \left(A \frac{e^{i \frac{n\pi}{L} x} - e^{-i \frac{n\pi}{L} x}}{2i} \right)^2 dx$$

which are trivial. A turns out to be $\sqrt{\frac{2}{L}}$ if we force the integral to be 1. Again, this is explained in every text book. Of course, the orthogonality integrals may also be evaluated using DeMoivre's theorem. All of this turns out to be extraordinarily elementary.

III. A RECTANGULAR BOX

When we talk about rectangular and square boxes in two dimensional particle in a box problems, we are getting set up to discuss degeneracy. The wave equation itself offers no hint of the complexity that is coming, but the boundary conditions, which are inextricably bound to the solutions of the Schrödinger Equation, are the key here.

Assuming we are working in the x-y space (2 dimensions), so $\psi(x, y)$ is what is being sought, we have

$$-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \right) = E\psi \quad (3.1)$$

where x and y are the standard Cartesian coordinates. The solution to this variable separable differential equation is discussed in all texts, and has the form

$$X(x)Y(y) = N_{\ell_x, \ell_y} \sin \frac{n_x \pi x}{\ell_x} \sin \frac{n_y \pi y}{\ell_y}$$

where n_x and n_y are integer quantum numbers, ranging from 1 to ∞ . The box is rectangular if $\ell_x \neq \ell_y$. N_{ℓ_x, ℓ_y} is the normalization factor, which has the form

$$N_{\ell_x, \ell_y} = \sqrt{\frac{2}{\ell_x}} \sqrt{\frac{2}{\ell_y}}$$

Once substituted into the original Schrödinger Equation, the solution suggests that the energy is given by the formula:

$$E_{n_x, n_y} = \frac{\hbar^2 \pi^2}{2\mu} \left(\left(\frac{n_x}{\ell_x} \right)^2 + \left(\frac{n_y}{\ell_y} \right)^2 \right) \quad (3.2)$$

(a well known result).

The degeneracy appears when we allow the length of the two sides of the "box" to become equal. At that point, we can factor the common $\ell = \ell_x = \ell_y$ out of this formula to obtain

$$E_{n_x, n_y} = \frac{\hbar^2 \pi^2}{2\mu \ell^2} (n_x^2 + n_y^2)$$

It is clear that the sum of two squares can add up to the same value, e.g., $5^2 + 2^2 = 2^2 + 5^2$, i.e., $n_x^2 + n_y^2 = reverse$. We are seeing a double degeneracy emerging. (In three dimensions, we would have a three fold degeneracy developing, when the box became cubical.) Notice that when $n_x = n_y$, we have a loss of degeneracy.

IV. A CIRCULAR BOX

Squares are nice, but we learn more from circles. Consider a two dimensional particle in a circular box. The particle is restricted to be within $r=R$, where R is a constant. This is a polar coordinate problem, since the boundary condition will be that $\psi(R, \theta) = 0 \forall \theta$, i.e., the wave function will be required to vanish at the edge of the disk region.

The first thing we have to do is transform the Schrödinger Equation from Cartesian to polar coordinates. We are going from $(x, y) \rightarrow (r, \theta)$. The transformation equations are

$$\begin{aligned} x &= r \cos \theta \\ y &= r \sin \theta \end{aligned} \quad (4.1)$$

which says, given r and θ , we can compute x and y. The reverse equations are

$$\begin{aligned} r &= \sqrt{x^2 + y^2} \\ \theta &= \tan^{-1} \frac{y}{x} \end{aligned} \quad (4.2)$$

which says the reverse, i.e., given x and y, we can compute r and θ .

First we need to express $\frac{\partial}{\partial x}$ in terms of partial derivatives with respect to r and θ . From the chain rule we have

$$\left(\frac{\partial}{\partial x} \right)_y = \left(\frac{\partial r}{\partial x} \right)_y \left(\frac{\partial}{\partial r} \right)_\theta + \left(\frac{\partial \theta}{\partial x} \right)_y \left(\frac{\partial}{\partial \theta} \right)_r$$

where we are carefully attempting to indicate what is constant during each partial differentiation. We find that

$$\left(\frac{\partial r}{\partial x} \right)_y = \left(\frac{\partial \sqrt{x^2 + y^2}}{\partial x} \right)_y = \frac{1}{2} \frac{2x}{r} = \cos \theta$$

and

$$\left(\frac{\partial \theta}{\partial x} \right)_y = \left(\frac{\partial \tan^{-1} \frac{y}{x}}{\partial x} \right)_y$$

This latter differential is a little more difficult than the former one was, and we attack it in a special manner, guaranteed to bring a smile of recognition to weary readers. Specifically, we use implicit differentiation. Thus

$$\tan \theta = \frac{y}{x}$$

so

$$d \tan \theta = \frac{dy}{x} - \frac{y dx}{x^2} = d \frac{\sin \theta}{\cos \theta} = d\theta + \frac{\sin^2 \theta}{\cos^2 \theta} d\theta$$

which is

$$\frac{dy}{x} - \frac{y dx}{x^2} = \left(1 + \frac{\sin^2 \theta}{\cos^2 \theta}\right) d\theta = \left(\frac{\cos^2 \theta + \sin^2 \theta}{\cos^2 \theta}\right) d\theta = \left(\frac{1}{\cos^2 \theta}\right) d\theta$$

so, holding y constant, one has

$$\left(\frac{1}{\cos^2 \theta}\right) d\theta = -\frac{y dx}{x^2} \rightarrow \frac{d\theta}{dx} = -\frac{y}{\left(\frac{1}{\cos^2 \theta}\right) x^2} \rightarrow -\frac{y \cos^2 \theta}{x^2} \left(\frac{1}{\cos^2 \theta}\right) d\theta = -\frac{y dx}{x^2} \rightarrow \frac{d\theta}{dx} = -\frac{y}{\left(\frac{1}{\cos^2 \theta}\right) x^2} \rightarrow -\frac{y \cos^2 \theta}{x^2}$$

$$\frac{d\theta}{dx} = -\frac{\tan \theta \cos^2 \theta}{K}$$

so

$$\left(\frac{d\theta}{dx}\right)_y = -\frac{\tan \theta \cos^2 \theta}{r \cos \theta} = -\frac{\sin \theta}{r}$$

$$\left(\frac{\partial}{\partial x}\right)_y = \cos \theta \left(\frac{\partial}{\partial r}\right)_\theta - \frac{\sin \theta}{r} \left(\frac{\partial}{\partial \theta}\right)_r$$

Going the other way i.e., holding x constant, we have

$$\frac{dy}{x} = \frac{d\theta}{\cos^2 \theta}$$

$$\left(\frac{\partial}{\partial y}\right)_x = \sin \theta \left(\frac{\partial}{\partial r}\right)_\theta + \frac{\cos \theta}{r} \left(\frac{\partial}{\partial \theta}\right)_r$$

so

$$\frac{\cos^2 \theta}{x} = \left(\frac{\partial \theta}{\partial y}\right)_x$$

The second partial derivatives then must be

$$\left(\frac{\partial^2}{\partial x^2}\right)_y = \frac{\partial (\cos \theta (\frac{\partial}{\partial r})_\theta - \frac{\sin \theta}{r} (\frac{\partial}{\partial \theta})_r)}{\partial x} \quad (4.3)$$

$$\frac{\cos^2 \theta}{r \cos \theta} = \left(\frac{\partial \theta}{\partial y}\right)_x$$

$$\left(\frac{\partial^2}{\partial y^2}\right)_x = \frac{\partial (\sin \theta (\frac{\partial}{\partial r})_\theta + \frac{\cos \theta}{r} (\frac{\partial}{\partial \theta})_r)}{\partial y} \quad (4.4)$$

$$\frac{\cos \theta}{r} = \left(\frac{\partial \theta}{\partial y}\right)_x$$

Equation 4.3 expands to become

$$\left(\frac{\partial^2}{\partial x^2}\right)_y = \cos \theta \left(\frac{\partial (\cos \theta (\frac{\partial}{\partial r})_\theta - \frac{\sin \theta}{r} (\frac{\partial}{\partial \theta})_r)}{\partial r}\right) - \frac{\sin \theta}{r} \left(\frac{\partial (\cos \theta (\frac{\partial}{\partial r})_\theta - \frac{\sin \theta}{r} (\frac{\partial}{\partial \theta})_r)}{\partial \theta}\right)$$

i.e.,

$$\begin{aligned} \left(\frac{\partial^2}{\partial x^2}\right)_y &= \cos^2 \theta \frac{\partial^2}{\partial r^2} + \frac{\sin \theta \cos \theta}{r^2} \frac{\partial}{\partial \theta} - \frac{\sin \theta \cos \theta}{r} \frac{\partial^2}{\partial r \partial \theta} \\ &+ \frac{\sin^2 \theta}{r} \frac{\partial}{\partial r} - \frac{\sin \theta \cos \theta}{r} \frac{\partial^2}{\partial r \partial \theta} + \frac{\sin \theta \cos \theta}{r^2} \frac{\partial}{\partial \theta} + \frac{\sin^2 \theta}{r^2} \frac{\partial^2}{\partial \theta^2} \end{aligned} \quad (4.5)$$

For the y term we have

$$\left(\frac{\partial^2}{\partial y^2}\right)_x = \sin\theta \left(\frac{\partial(\sin\theta \frac{\partial}{\partial r} + \frac{\cos\theta}{r} \frac{\partial}{\partial\theta})}{\partial r}\right) + \frac{\cos\theta}{r} \left(\frac{\partial(\sin\theta \frac{\partial}{\partial r} + \frac{\cos\theta}{r} \frac{\partial}{\partial\theta})}{\partial\theta}\right) \quad (4.6)$$

i.e.,

$$\begin{aligned} \left(\frac{\partial^2}{\partial y^2}\right)_x &= \sin^2\theta \frac{\partial^2}{\partial r^2} - \frac{\cos\theta \sin\theta}{r^2} \frac{\partial}{\partial\theta} + \frac{\sin\theta \cos\theta}{r} \frac{\partial^2}{\partial r \partial\theta} \\ &+ \frac{\cos^2\theta}{r} \frac{\partial}{\partial r} + \frac{\cos\theta \sin\theta}{r} \frac{\partial^2}{\partial r \partial\theta} - \frac{\cos\theta \sin\theta}{r^2} \frac{\partial}{\partial\theta} + \frac{\cos^2\theta}{r^2} \frac{\partial^2}{\partial\theta^2} \end{aligned} \quad (4.7)$$

so, adding the two relevant results we have

$$\begin{aligned} \left(\frac{\partial^2}{\partial y^2}\right)_x + \left(\frac{\partial^2}{\partial x^2}\right)_y &= \frac{\partial^2}{\partial r^2} + \underbrace{\frac{\sin\theta \cos\theta}{r^2} \frac{\partial}{\partial\theta}}_{\text{cross term}} - \overbrace{\frac{\sin\theta \cos\theta}{r} \frac{\partial^2}{\partial\theta \partial r}}^{\text{cross term}} \\ &+ \frac{\sin^2\theta}{r} \frac{\partial}{\partial r} - \overbrace{\frac{\sin\theta \cos\theta}{r} \frac{\partial^2}{\partial r \partial\theta}}^{\text{cross term}} + \underbrace{\frac{\sin\theta \cos\theta}{r^2} \frac{\partial}{\partial\theta}}_{\text{cross term}} + \frac{\sin^2\theta}{r^2} \frac{\partial^2}{\partial\theta^2} \\ &\quad - \underbrace{\frac{\cos\theta \sin\theta}{r^2} \frac{\partial}{\partial\theta}}_{\text{cross term}} + \overbrace{\frac{\sin\theta \cos\theta}{r} \frac{\partial^2}{\partial r \partial\theta}}^{\text{cross term}} \\ &+ \frac{\cos^2\theta}{r} \frac{\partial}{\partial r} + \overbrace{\frac{\cos\theta \sin\theta}{r} \frac{\partial^2}{\partial r \partial\theta}}^{\text{cross term}} - \underbrace{\frac{\cos\theta \sin\theta}{r^2} \frac{\partial}{\partial\theta}}_{\text{cross term}} + \frac{\cos^2\theta}{r^2} \frac{\partial^2}{\partial\theta^2} \end{aligned} \quad (4.8)$$

which becomes

$$\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial\theta^2}$$

V. NOW, THE QUANTUM MECHANICS

The Schrödinger Equation now becomes

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2\psi}{\partial r^2} + \frac{1}{r} \frac{\partial\psi}{\partial r} + \frac{1}{r^2} \frac{\partial^2\psi}{\partial\theta^2}\right) + \text{zero} \times \psi = E\psi$$

(why zero? because a particle in a box just feels its boundaries, i.e., the model is of a particle free to roam (linearly) until it hits a wall.) which is going to be related to Bessel's equation. We know this equation is variable separable, between r and θ , so we will write the solution as

$$\psi = R_{m_\ell}(r) e^{\pm m_\ell i \theta}$$

which, when we substitute this into the Schrödinger Equation, gives us

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 R_{m_\ell}(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R_{m_\ell}(r)}{\partial r} - \frac{m_\ell^2}{r^2} R_{m_\ell}(r)\right) = E R_{m_\ell}(r)$$

which is

$$r^2 R''(r) + r R'(r) + (\epsilon r^2 - \frac{2m}{\hbar^2} m_\ell^2) R(r) = 0$$

where $\epsilon = 2mE/\hbar^2$.

This is one of the forms of the Bessel differential equation. To bring it to standard form, we change variables from r to $k\rho = r$, so

$$\frac{\partial\rho}{\partial r} \frac{\partial}{\partial\rho} = \frac{\partial}{\partial r} = \frac{1}{k} \frac{\partial}{\partial\rho}$$

so, choosing

$$k^2 \epsilon = 1$$

we have

$$k = \sqrt{\frac{1}{\epsilon}}$$

and we have

$$\rho^2 R''(\rho) + \rho R'(\rho)' + (\rho^2 - m_\ell^2) R(\rho) = 0$$

It is traditional to solve this equation separately for different values of m, and in fact, it is rare to see solutions for $m_\ell > 0$ anywhere, since the problem, from the point of view of quantum mechanics, is quite silly.

For $m_\ell = 0$ we have

$$\rho^2 R''(\rho) + \rho R'(\rho)' + \rho^2 R(\rho) = 0$$

and we start the solution by assuming an *Ansatz*

$$R(\rho) = \sum_{i=0} a_i \rho^i$$

leaving the question of the indicial equation to more advanced study. We then have

$$R'(\rho) = \sum_{i=1} i a_i \rho^{i-1}$$

and

$$R''(\rho) = \sum_{i=2} (i)(i-1) a_i \rho^{i-2}$$

$$\begin{aligned} \rho^2 R''(\rho) &\rightarrow \sum_{i=2} (i)(i-1) a_i \rho^i \rightarrow 2a_2 \rho^2 + (3)(2) a_3 \rho^3 + (4)(3) a_4 \rho^4 + \dots \\ + \rho R'(\rho)' &\rightarrow \sum_{i=1} i a_i \rho^i \rightarrow a_1 \rho + 2a_2 \rho^2 + 3a_3 \rho^3 + \dots \\ + (\rho^2) R(\rho) &\rightarrow \sum_{i=0} a_i \rho^{i+2} \rightarrow a_0 \rho^2 + a_1 \rho^3 + a_2 \rho^4 + \dots \\ &= 0 \end{aligned}$$

Gathering terms in the standard manner, we have

$$\begin{aligned} a_2 &= -a_0/2 \\ ((3)(2) + 3) a_3 &= a_1 \\ ((4)(3) + 4) a_4 &= -a_2 = \frac{a_0/2}{((4)(3) + 4)} \end{aligned}$$

It is fairly obvious that, contrary to other Frobenius Schemes in standard Quantum Chemistry, this one does not lead to quantization through truncation of a power series into a polynomial.

Instead, this Bessel Function's expansion never terminates, is never truncated, i.e., remains an infinite power series.

The quantization occurs when the boundary condition that the wave function vanish when we are at the rim of the enclosure is invoked.

The requirement that the function be zero at the boundary ($r=R$), results in requiring that the Bessel function have a zero, call it ρ_0 . This can be found in tables of the Bessel Function. For instance, the first root, $J_0(\rho_0)$ occurs at $\rho_0 = 2.4048$ (and 5.5207, 8.6537, 11.7915, etc., E. Kreyszig, "Advanced Engineering Math-

ematics", John Wiley and Sons. New York, 1962, page 548). So

$$\rho_0 = \frac{R}{k} = \frac{R}{\sqrt{\frac{1}{\epsilon}}}$$

i.e.,

$$\left(\frac{\rho_0}{R}\right)^2 = \epsilon = \frac{2mE}{\hbar^2}$$

or,

$$E_0 = \frac{\hbar^2}{2m} \left(\frac{\rho_0}{R}\right)^2 = \frac{\hbar^2}{2m} \left(\frac{2.4048}{R}\right)^2$$

where you have specified the value of R when setting up the problem.

The zero's of the Bessel function act to quantize the energy via the boundary conditions, in a slightly different mode than what we are used to, but never the less, we obtain a result which is quite comfortable inside the context of standard quantum mechanical constructs.