# Application and solution of Schrödinger equation

## Transition motion

### 1- The Particle in a One-Dimensional "Box"

Imagine that a particle of mass m is free to move along the x axis between x =0 and x =L, with no change in potential (set $V = 0 \; for 0 \prec x \prec L$). At x = 0 and L and at all points beyond these limits the particle encounters an infinitely repulsive barrier ($V = \infty \; for 0 \geq x \geq L$)). The situation is illustrated in Fig. 1. Because of the shape of this potential, this problem is often referred to as a *particle in a square well* or a *particle in a box* problem. It is well to bear in mind, however, that the situation is really like that of a particle confined to movement along a finite length of wire, and the motion of electrons in chemical system such as 1, 3 butadiene and its similar.

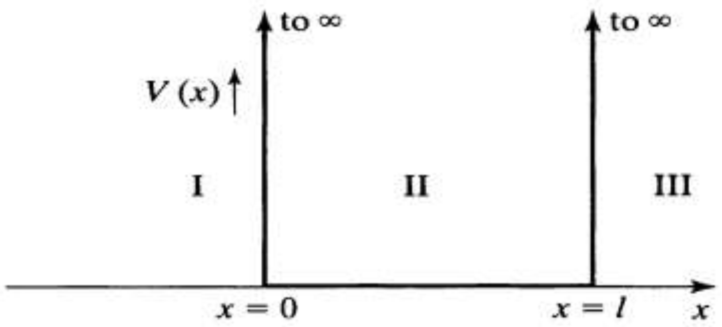



Fig 1

The independent Schrödinger equation for this system is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E_x - V_x)\psi_x = 0 \qquad (1)$$

We have two cases

A- **First**, if the particle in region I , III or at the wall i. e. $for\, 0 \geq x \geq L)$ then $V = \infty$ the Schrödinger equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (-\infty\psi_x) = 0 \qquad (2)$$

$$-\frac{h^2}{8\pi^2 m} \frac{d^2\psi}{dx^2} = -\infty\psi \qquad (3)$$

The only solution of this equation is $\psi = 0$, this means that the particle is Schrödinger equation becomes not excited in this position

B- Secondary, if the particle in region II i. e. $(0 \prec x \prec L)$ then $V_x = 0$ Schrödinger equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E_x \,\psi_x = 0 \qquad (4)$$

To solve this equation put

$$\alpha = \frac{8\pi^2 m E_x}{h^2} \; then \quad و \quad F = \frac{d\psi}{dx}$$

$$\frac{d^{2\psi}}{dx^2} = \frac{dF}{dx} = \frac{dF}{d\psi} \frac{d\psi}{dx} = F \frac{dF}{d\psi}$$

*by substituted in eqn.4 and integration*

$$F \frac{dF}{d\psi} = -\alpha\psi \quad or \int FdF = -\alpha \int \psi \, d\psi \quad (5)$$

And $$\frac{F^2}{2} = \pm\alpha \frac{\psi^2}{2} \quad \text{or} \quad F = \pm i(\alpha)^{1/2}\psi \qquad (6)$$

Then $\frac{d\psi}{dx} = \pm i(\alpha)^{1/2}\psi$ (7)

$\frac{d\psi}{\psi} = \pm i(\alpha)^{1/2} dx$ (8) and

$\ln\psi_x = \pm i(\alpha)^{1/2} x + Q$ (9)

Where Q constant

This equation can write as

$\psi_x = e^{\pm i\alpha^{1/2}x} e^{Q}$ *or* $\psi_x = Ae^{\pm i\alpha^{1/2}x}$

And then substituted by value of $\alpha$ then

$\psi_x = Ae^{\pm i(8\pi^2 mE_x/h^2)^{1/2} x}$ (10)

where $A = e^{Q}$

Equation 10 is called Euler theorem and solved as Euler rule as

$e^{\pm i\alpha x} = \cos\alpha x \pm \sin\alpha x$ (11)

Appling this rule on equation 10 under boundary condition

$at\, x = 0$ and $\psi_x = 0$ we get

$\psi_x = A\sin\alpha x + B\cos\alpha x$ (12)

So then

$A\sin\alpha x = 0$ (14) or $B\cos\alpha x = 0$ (15)

But $\cos\alpha x = 1$

then B should be equal zero $(B = 0)$ then

$\psi_x = A\sin\alpha x$

And then put the value of $\alpha$ we get

$\psi_x = A\sin(8\pi^2 mE_x/h^2)^{1/2} L = 0$ (16)

$\sin^{-1} 0 = (8\pi^2 mE_x/h^2)^{1/2} L = 0$ (17)

But $\sin^{-1} 0 = \pi, 2\pi, 3\pi \ etc = n\pi$

Where n is an integral number and not equal zero (principal quantum number) then

$$n\,\pi = (8\pi^2 m E_x / h^2)^{1/2} L \qquad (18) \qquad \text{Or}$$

$$E_n = \frac{n^2 h^2}{8mL^2} \qquad (19)$$

Equation 10 is the eigenfunction and equation 19 is the related eigenvalue of energy

From equation 19 we concluded that

(I) The Value of $E_n$ decrease with increasing $L^2$ if the other variables are constant, So, if L is very long then $E_n$ too small then called the particle is delocalized such as $\pi$ bond in chemical compound, and if L is small then $E_n$ s high then particle is localized such as $\sigma$ bound. As you known that the excitation energy of $\pi$ bound is less than those of $\sigma$ bound for this reason.

(II) Appearance of principal quantum number (n) automatically and $E_n \alpha\, n$ this means that the energy increase with increasing value of n, and also described the number of nodes, for example n=1 no nodes and in for n = 2 only one node and n = 3 we get two nodes and so on...

(III) the energy of the system is discrete an d not continuous, E for n= 1, 2, 3 , 4 is

$$E_1 = \frac{h^2}{8mL^2} \quad , \quad E_2 = \frac{h^2}{4mL^2}$$

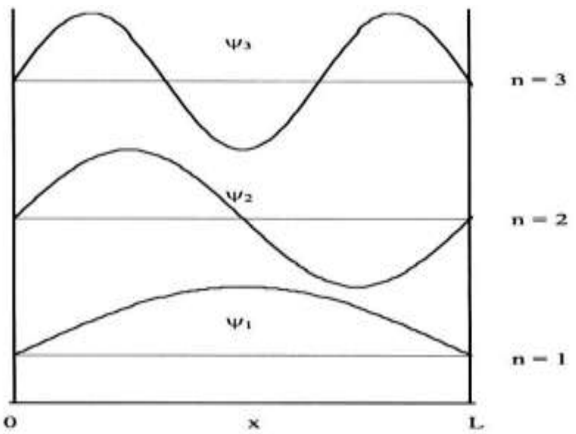
$$E_3 = \frac{9h^2}{8mL^2} \quad \quad E_4 = \frac{2h^2}{mL^2}$$

But for large particles the value Planck constant (h) is very small and the quantum rule completely falls, the particles obey the classical mechanics. If the particles move free (i. e. $L = \infty$) this chemically the electron leaves the atom, the energy level is becomes closed to each other this called also continuous spectra.

(IV) the wavefunction in region II never equal zero $(\psi \neq 0)$ them also n never equal zero( $n \neq 0$ ), this means that the ground state have energy

$$E_1 = \frac{h^2}{8mL^2} \qquad (20)$$

And this is one of difference between classical and quantum treatment.




Now we should calculate the constant A in equation 10 as

$$\psi_x = A\sin(8\pi^2 mE_x / h^2)^{1/2} x$$

$$E_x = \frac{n^2h^2}{8mL^2}$$

Then substituted the value of $E_x$ in former equation we get

$$\psi_x = A\sin[(8\pi^2 m/h^2)(n^2h^2/8mL^2)]^{1/2} x$$

$$\psi_x = A\sin(n^2 \pi^2 / L^2)^{1/2} x$$

$$\psi_x = A\sin(n\pi / L)x \qquad (21)$$

Then put $G = n\pi / L$ in equation 21 then

$$\psi_x = A\sin G_x \, x \qquad (22)$$

But the wavefunction should be normalized i. e,

$$\int \psi^2 \, dx = 1 \qquad (23)$$

With compensation by equation 21 in equation 23 we have

$$\int_o^L A^2 Sin^2 G_x dx \;= 1 = A^2 \int_0^L (1/2)(1 - \cos 2G_x) dx$$

$$\frac{A^2}{2}\int_o^L dx - \frac{A^2}{2}\int_o^L \cos 2G_x dx$$

Then by integration, we get

$$\frac{A^2 L}{2} - \frac{A^2}{4G_x} \sin 2G_x L = 1 \qquad (24)$$

and compensation of $G_x$ the equation becomes

$$\frac{A^2 L}{2} - \frac{A^2 L}{4n\pi} \sin 2n\pi = 1 \qquad (25)$$

but $\sin n\pi = 0$ then

$$\frac{A^2 L}{2} = 1 \qquad (26)$$ i. e,

$$A = \sqrt{2/L} \qquad (27)$$

Then substituted the value of constant (A) in eqn.27 to eqn. 10 the normalized wanefunction which described the motion of particles in one dimension is

$$\psi_x = \sqrt{\frac{2}{L}} \sin \frac{\pi n x}{L} \qquad (28)$$

and for a system with constant mass and volume of box, the energy

$$E_n = k \quad n^2 \qquad (29)$$

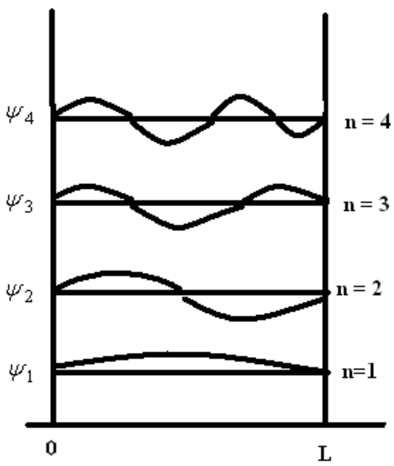
Where k is constant and equal

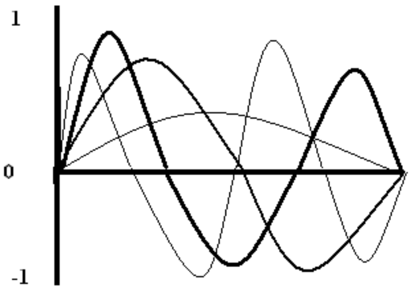
$$k = \frac{h^2}{8mL^2}$$

Also from equation 28 the conditions for formation of nodes is

$$\frac{n\pi x}{L} = 0, \pi, 2\pi, 3\pi, 4\pi \; Or \qquad x = 0, \frac{L}{n}, \frac{2L}{n}, \frac{3L}{n} \qquad (30)$$

Which the condition gives $\psi$ always equal zero (see next figure), example for $n=1 \; then \; \psi_1$ have two nodes at $x = 0 \; and \; x = L$ but for wavefunction $\psi_2 and \, n = 2$ have a three nodes at $x = 0, x = L/2 \; and \; x = L$ and so on






C- Eigen Value for momentum: the momentum of particles moves a long x axis can be write as

$$P_x^2 = 2mE_x = 2m\frac{n^2\pi^2h^2}{8\pi^2 mL^2} = \frac{n^2\pi^2h^2}{4L^2}$$

$$P_x = \pm\frac{nh}{2L} \qquad (31)$$

D- Probability density for position of particle in box: From the meaning of probability equal

$$p(x) = |\psi_x(x)|^2 \qquad \text{Then} \qquad p(x) = \frac{2}{L}\sin^2\frac{n\pi x}{L} \qquad (32)$$

From equation 32, the maximum probability density at angles equal or distance

$$\frac{n\pi x}{L} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}, \frac{7\pi}{2} \; Or$$

$$x = \frac{L}{2n},, \frac{3L}{2n}, \frac{5L}{2n}, \frac{7L}{2n}$$

Under this condition the value of $|\psi_x(x)|^2 = \frac{L}{2n}$ always , next table show that

| | | | | | |
|---|---|---|---|---|---|
| | $\frac{L}{2n}$ | $\frac{3L}{2n}$ | $\frac{5L}{2n}$ | $\frac{7L}{2n}$ | $\frac{9L}{2n}$ |

| | | | | |
|---|---|---|---|---|
| $\|\psi_1\|^2$ | $\frac{L}{2}$ | | | |
| $\|\psi_2\|^2$ | $\frac{L}{4}$ | $\frac{3L}{4}$ | | |
| $\|\psi_3\|^2$ | $\frac{L}{6}$ | $\frac{3L}{6}$ | $\frac{5L}{6}$ | |
| $\|\psi_4\|^2$ | $\frac{L}{8}$ | $\frac{3L}{8}$ | $\frac{5L}{8}$ | $\frac{7L}{8}$ |

From this table, at $n=1$the most probable find particle at $x=\frac{1}{2}L$

i. e. at the medal of the box, and $n=2$ the most probable find

particle at $x=\frac{1}{4}L \, and \, \frac{3}{4}L$

and so on, and by increasing the value of n number of probability increases and thatched (closed together ) and the probability of find the particle is equal at any point in box, and then the wave property is fail and becomes a macroscopic object, i. e. classical particles.

**Example 4**

What the probability to fine the particle moves in box in one direction from $x=0 \; to \;\; x= \; L/10$, for levels $n$=1, 2, 3?

**Solution**

The wavefunction of this particle is $\psi_x=\sqrt{\frac{2}{L}}\sin\frac{\pi n x}{L}$

And the probability is $P=\int_0^{L/10}\psi^2 dx=\int_0^{L/10}\left(\sqrt{\frac{2}{L}}\sin\frac{\pi n x}{L}\right)^2 dx$

$P=\frac{2}{L}\int_0^{L/10}\sin^2\left(\frac{\pi n x}{L}\right) \; dx$ To integrate this equation you obey

$$\int \sin^2(cx)dx = \frac{x}{2} - \frac{1}{4c}\sin 2cx$$

In former example

$x = L/10$ , $c = \frac{n\pi}{L}$ then

$$P_n = \frac{2}{L}\left[\frac{L}{20} - \left(\frac{L}{4n\pi}\right)\sin\left(\frac{2n\pi}{10}\right)\right] = \left[\frac{1}{10} - \frac{1}{2n\pi}\sin\frac{n\pi}{5}\right] \text{ then}$$

$$P_1 = \left[\frac{1}{10} - \frac{1}{2\pi}\sin\frac{\pi}{5}\right] = 0.0064$$

$$P_2 = \left[\frac{1}{10} - \frac{1}{3\pi}\sin\frac{2\pi}{5}\right] = 0.024$$

$$P_3 = \left[\frac{1}{10} - \frac{1}{6\pi}\sin\frac{3\pi}{5}\right] = 0.5$$

# 2-Particle in three dimensional box:

Schrödinger equation for this system becomes

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}E_{x,y,z} = 0 \qquad (29)$$

to solve this equation you first separate the variables for one variable only as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}E_x = 0 \qquad (30)$$

$$\frac{d^2\psi}{dy^2} + \frac{8\pi^2 m}{h^2}E_y = 0 \qquad (31)$$

$$\frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}E_z = 0 \qquad (32)$$

this three equation like motion in one dimension as we solve before then the solution of them is

$$\psi_x = A\sin\frac{\pi n x}{L_x} \qquad (33)$$

$$\psi_y = B\sin\frac{\pi n y}{L_y} \qquad (34)$$

$$\psi_z = C\sin\frac{\pi n z}{L_z} \qquad (35)$$

and the constants (A- B – C) is

$$A = \sqrt{\frac{2}{L_x}} \;,\; B = \sqrt{\frac{2}{L_y}} \;,\; C = \sqrt{\frac{2}{L_z}} \qquad (36)$$

Finally the wavefunction in three dimension is

$$\psi_{x,y,z} = \left[\frac{2}{L_x}\frac{2}{L_y}\frac{2}{L_z}\right]^{1/2} \sin\frac{n_{x\pi}}{L_x}\sin\frac{n_{y\pi}}{L_y}\sin\frac{n_{z\pi}}{L_z} \qquad (37)$$

The eigenfunction for this system is

$$E_{x,y,z} = \frac{n_x^2 h^2}{8mL_x^2} + \frac{n_y^2 h^2}{8mL_y^2} + \frac{n_z^2 h^2}{8mL_z^2}$$

$$E_{x,y,z} = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right] \qquad (38)$$

and for cubic box where $L_x^2 = L_y^2 = L_z^2 = L$ becomes

$$E_{x,y,z} = \frac{h^2}{8mL^2}\left[n_x^2 + n_y^2 + n_z^2\right]$$

**Example:** 5

The energy level for particle in cube for levels 1, 2, 3 is [n may be]

$(n_x = 1,\ n_y = 1,\ n_z = 2)\, or\, (n_x = 2,\ n_y = 1, n_z = 1)$
$or\, (n_x = 1,\ n_y = 2, n_z = 1)$ then

$$E_{112} = \frac{h^2}{8m}\left[\frac{1}{L^2} + \frac{1}{L^2} + \frac{4}{L^2}\right] = \frac{4h^2}{8mL^2}$$

$$E_{211} = \frac{h^2}{8m}\left[\frac{4}{L^2} + \frac{1}{L^2} + \frac{1}{L^2}\right] = \frac{4h^2}{8mL^2}$$

$$E_{121} = \frac{h^2}{8m}\left[\frac{1}{L^2} + \frac{4}{L^2} + \frac{1}{L^2}\right] = \frac{4h^2}{8mL^2}$$

This three wavefunction with one value of energy this called degenerate or three degenerates, and chemically means three levels with the same energy

# 3- Free particle:

In this system the particle move along $L = \infty$ or the volume of box is finite then the wavefunction $\psi \to 0$ and also the probability $\psi^2 \to 0$ in any position in box. The Schrödinger equation for this system becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E_x)\psi_x = 0$$

$$\psi_x = Ae^{\pm i(8\pi^2 mE_x / h^2)^{1/2} x}$$

$$\int_{-\infty}^{+\infty} \psi_x \psi_x^* dx = 1$$

Then the integration of this case in finite if the $\psi \neq 0$ and then the probability to fined the particle in any place is equal (or the same) this means we can't determine the position of particle.

**Example 6**

A particle with mass m move in cube with length L and have [2-3-4] quantum numbers, fined the degree of degenerate and the energy values?

**Solution**

Now the $n_x, n_y, n_z$ may be taken this values

$234 - 243 - 324 - 342 - 432 - 423$

But

$$E = \frac{h^2}{8mL^2}[n_x^2 + n_y^2 + n_z^2]$$

$$E_{234} = \frac{h^2}{8mL^2}[4+9+16] = \frac{29h^2}{8mL^2}, \quad E_{243} = \frac{h^2}{8mL^2}[4+9+16] = \frac{29h^2}{8mL^2}$$

$$E_{324} = \frac{h^2}{8mL^2}[4+9+16] = \frac{29h^2}{8mL^2}, \quad E_{342} = \frac{h^2}{8mL^2}[4+9+16] = \frac{29h^2}{8mL^2}$$

$$E_{432} = \frac{h^2}{8mL^2}[4+9+16] = \frac{29h^2}{8mL^2}, \quad E_{423} = \frac{h^2}{8mL^2}[4+9+16] = \frac{29h^2}{8mL^2}$$

So a 6 function have the same energy then called six degenerates

**Example 7**

1-3 butadiene's can be considered as a particle move in box, which contains a two $\pi$ electron bond, this like a particle move in cube, you can make approximate which move in one dimensional (linear),[ but actually the compound in cis and trans forms], under this condition calculate the ground energy and the energy required to transition to next level and compare this result with ethylene and propene? [Length of $C-C$ ,$C=C$ is 0.148, 0.134 nm respectively, $M_e$ =9.1x $10^{-31}$kg and c=

$2.998x10^{8}$ m/s and $h=6.626x10^{-34}$J $s^{-1}$and $Js^{-1}$=kg m $s^{-1}$] comment in your results?

**Solution**

**In 1-butadiene**: contains $2\pi\, bonds + 1\sigma\, bound$ then the distance available for electrons move is $L = 2x0.134 + 0,148 = 0.416\, nm$

The energy of first state is $E_1 = \frac{n^2h^2}{8mL^2}$

$$E_1 = \frac{1(6.62x10^{-34})^2}{8x9.11x10^{-31}(0.416\,x10^{-9})^2} = 3.476x10^{-19}\,J$$

The energy of second state (n =2)

$E_2 = 4E_1 = 4x3,476x10^{-19} = 13.904x10^{-19}\,J$

The energy difference $\Delta E = E_2 - E_1 = 10.428x10^{-19}\,J$

**In propene**: contains $\pi\, bonds + 1\sigma\, bound$ then the distance available for electrons move is $L = 0.134 + 0,148 = 0.282\, nm$

The energy of first state is $E_1 = \frac{n^2h^2}{8mL^2}$

$$= \frac{1(6.62x10^{-34})^2}{8x9.11x10^{-31}(0.282\,x10^{-9})^2} = 7.562x10^{-19}\,J$$

The energy of second state (n =2)

$E_2 = 4E_1 = 4x7.562x10^{-19} = 30.248x10^{-19}\,J$

The energy difference

$\Delta E = E_2 - E_1 = 22.686x10^{-19}\,J$

**In ethylene:** contains only $\pi\, bonds$ then the distance available for electrons move is $L = 0.134\,nm$

The energy of first state is

$$E_1 = \frac{n^2h^2}{8mL^2}$$
$$= \frac{1(6.62x10^{-34})^2}{8x9.11x10^{-31}(0.134x10^{-9})^2} = 33.001x10^{-19}\,J$$

The energy of second state (n =2)

$$E_2 = 4E_1 = 4x33.001x10^{-19} = 132.004x10^{-19}\,J$$

The energy differences $\Delta E = E_2 - E_1 = 99.003x10^{-19}\,J$

It possible to convert this energy by means of wave length using this relation $\lambda = hc/E$

| compound | $E_1$ x $10^{-19}$ J | $E_2$ x $10^{-19}$ J | Δ E x $10^{-19}$ J |
|---|---|---|---|
| ethylene | 33.001 | 132.004 | 99.003 |
| Propene | 7.562 | 30.248 | 22.686 |
| ethylene | 3.476 | 1.904 | 10.428 |

From these results we concluded that the excitation energy decrease as the distance of motion increase by other meaning the 1-3 butadienes is less localized

**Example: 8**

When the particle is in ground state (n = 1). What is the probability of finding it in the left quarter of the wall, between $0 \prec x \succ (1/4)L$? what is the probability of finding the particle between? $1/4)L \prec x \succ (3/4)$?

**Solution:**

$$p=\int_0^{(L/4)}\psi^2dx=\frac{2}{L}\int_0^{L/4}\sin^2\left(\frac{\pi x}{L}\right)dx=\frac{2}{L}\int_0^{L/4)}\frac{1}{2}[1-\cos\left(\frac{2\pi x}{L}\right)dx$$

$$=\frac{1}{L}\left[x-\frac{L}{2\pi}\sin\left(\frac{2\pi x}{L}\right)\right]_0^{L/4}=\frac{1}{L}\left(\frac{L}{4}-\frac{L}{2\pi}\right)=0.09$$

Where as we expected is 0.25 classically. By symmetry the probability of finding the particle between $(3/4)L \prec x \succ L?$ is also 0.09, so the probability of finding between $(1/4)L \prec x \succ (3/4)?$ is p = 1-22(0.09) = 0.82

**Example: 9**

An electron is confined in a finite square well. In the ground state 1s energy is 1eV. What is the width of the well? How much energy is required to excite the electron from ground state to the second excited state (n = 3)?

**Solution**

$$E_n=\frac{n^2h^2}{8mL^2},\ \therefore L^2=\frac{n^2h^2}{8mE}$$

$$=\frac{1(6.63x10^{-34}J.s)^2}{8(9.11x10^{-31}kg)(1eVx1{,}6x10^{-19}J/eV)}=3.8x10^{-19}m$$

$$L-=0.614\,nm,\ E_3=E_1n^2=1x9=9eV$$

The lowest energy for a particle in an infinite is $E_1=h^2/8mL^2$. This is called zero point energy, and is not zero. This means that even that at absolute zero of temperature, a particle confined a finite region of space can never be rest, contrary to the classical idea of absolute zero. Further, such a particle can not travel at any possible speed, but rather it can have only the speeds determined by $E_n = (1/2)mu^2$. It is hard to understand this intuitively, since none of us has ever seen such strange behavior firsthand.

**Example 10**

A microscopic dust particle of mass 2 x $10^{-8}$ kg is confined to a box of width 1 mm. What is the minimum speed it can be have? If the speed of the particle is 0.1 mm/s, what state is it in?

Solution

$$E_1 = (1/2)mu^2 = h^2/8mL^2$$

$$u = \frac{h}{2mL} = \frac{6.63x10^{-34}\,J.s}{2(2x10^{-8})kg(0.001)m} = 1.66x10^{-23}\,m/s$$

You can see that for all particle purposes, even a particle as small as a speck of dust is at rest in its ground state. In the nth state

$$E_n = (1/2)mu^2 = n^2h^2/8mL^2 \; or \; n = \frac{2mlu}{h}$$

$$n = \frac{2(2x10^{-8}kg)(10^{-3}m)(10^{-4}m/s)}{6.63x10^{-34}} = 6x10^{18}$$

At such high quantum number, transition from a state n +1 to n is not observable on macroscopic scale. Further the wave function goes through so many oscillations in the width of the well that the probability density is essentially constant across the well, in agreement with what we expect classically. This is an example of Bohr's correspondence principle, which states that quantum mechanical behavior must agree with classical theory in the limit of very high quantum number.