Quantum Mechanics Derivations

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Contents

3 Relation between group velocity and phase velocity

One dimensional traveling wave is given by the equation,

$$y = y_m \sin(kx - \omega t)$$

where y is the displacement at a given position x at a given time instant t. Here, k is called the wave vector and ω is the angular frequency. They are related to the wavelength λ and frequency v by,

$$k = \frac{2\pi}{\lambda} \qquad \text{and} \qquad \omega = 2\pi v$$

The wave velocity is given by, using above relations,

$$v_p = \lambda v = \frac{2\pi}{k} \frac{\omega}{2\pi} = \frac{\omega}{k}$$

This velocity of the individual monochromatic sinusoidal wave is called the *phase velocity* (v_p).

    This wave represents the matter wave corresponding to a non-relativistic particle of mass m and momentum $p = mv$ if λ is taken to be the de Broglie wavelength. A moving particle is a *wave packet* or a *wave group* resulting from adding many individual waves of the type discussed above and each with varying frequencies over a range. The velocity of such wave group is called the *group velocity* (v_g) and is usually different from the individual phase velocities of the waves that make up the wave packet. Group velocity is then given by,

$$v_g = \frac{\Delta\omega}{\Delta k} = \frac{d\omega}{dk}$$

Particle velocity v can be shown to be equal to this group velocity. Therefore,

$$v_g = v$$

With $\omega = v_p k$ group velocity can be expressed as,

$$v_g = \frac{d\omega}{dk} = \frac{d}{dk}(v_p k) = v_p + k\frac{dv_p}{dk} = v_p + k\frac{dv_p}{d\lambda}\frac{d\lambda}{dk} \qquad (1)$$

Differentiating $\lambda = 2\pi/k$ with respect to k, we have,

$$\frac{d\lambda}{dk} = \frac{d}{dk}\left(\frac{2\pi}{k}\right) = \frac{-2\pi}{k^2}$$

Substituting it in eqn. (1) we get,

$$v_g = v_p + k\frac{dv_p}{d\lambda}\left(\frac{-2\pi}{k^2}\right)$$
$$= v_p - \frac{2\pi}{k}\left(\frac{dv_p}{d\lambda}\right)$$

Substituting with $\lambda = 2\pi/k$ we get,

$$\boxed{v_g = v_p - \lambda\frac{dv_p}{d\lambda}}$$

This equation shows that v_g is less than v_p when medium is dispersive. For a light wave in vacuum, there is no dispersion. Hence $dv_p/d\lambda = 0$, so that $v_g = v_p = c$. This is true for elastic waves in a homogeneous medium.

4 Heisenberg's uncertainty principle

Heisenberg introduced the notion that it is impossible to determine simultaneously with unlimited precision the position and momentum of a particle. In words we may state the uncertainty principle as follows:

> If a measurement of position is made with precision Δx and a simultaneous measurement of momentum in the x direction is made with precision Δp_x, then the product of the two uncertainties can never be smaller than $\hbar/2$. That is,

$$\boxed{\Delta p_x \Delta x \geq \hbar/2}$$

> where $\hbar = h/(2\pi)$ with h being the Planck's constant.

According to Heisenberg's uncertainty principle, the finite lifetime Δt of the excited state means there will be an uncertainty of ΔE in the energy of the state. Hence the emitted photon energy will also have an uncertainty of ΔE in its energy and is related by,

$$\Delta E \, \Delta t \geq \hbar/2$$

Or,

$$\Delta E \geq \frac{h}{4\pi\Delta t}$$

Substituting for ΔE from (2) we get,

$$hc\frac{\Delta\lambda}{\lambda^2} \geq \frac{h}{4\pi\Delta t}$$

Or

$$\boxed{\Delta\lambda \geq \frac{1}{4\pi c}\frac{\lambda^2}{\Delta t}}$$

This shows that for a finite lifetime of the excited state, the measured value of the emitted photon wavelength will have a spread of wavelengths around the mean value λ. This demands that for a very narrow spread, the lifetime of the excited state must be very high. Such excited levels are called metastable states whose lifetimes will be of the order of 10^{-3}s. This concept is used in the production of laser light, which will be highly monochromatic due to the involvement of a metastable state.

6 Time independent one dimensional Schrödinger equation

Let $\Psi(x,t)$ be the wave function for the matter wave associated with a moving particle. The corresponding wave equation is as follows,

$$\frac{\partial^2\Psi}{\partial x^2} = \frac{1}{v_p^2}\frac{\partial^2\Psi}{\partial t^2} \tag{1}$$

where v_p is the phase velocity of the associated matter waves. The solution of eq. (1) is,

$$\Psi(x, t) = \psi(x)e^{-i\omega t} \tag{2}$$

where ω is the angular frequency.

Differentiating eq. (2) partially twice with respect to t, we get,

$$\frac{\partial \Psi}{\partial t} = (-i\omega)\psi(x)e^{-i\omega t}$$

$$\frac{\partial^2 \Psi}{\partial t^2} = (-i\omega)^2 \psi(x)e^{-i\omega t} = -\omega^2 \Psi \tag{3}$$

Substituting eq. (3) in eq. 1

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{\omega^2}{v_p^2} \Psi$$

We have, for matter waves, phase velocity $v_p = \lambda v$ and angular frequency $\omega = 2\pi v$, where v is the frequency.

$$\frac{\omega^2}{v_p^2} = \left(\frac{2\pi f}{\lambda f}\right)^2 = \left(\frac{2\pi}{\lambda}\right)^2 = \frac{4\pi^2}{\lambda^2}$$

Substituting this and in the above equation we get,

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \Psi$$

Substituting Ψ from eq. (2) into it we get,

$$\frac{\partial^2 [\psi(x)e^{-i\omega t}]}{\partial x^2} = -\frac{4\pi^2}{\lambda^2}[\psi(x)e^{-i\omega t}]$$

$$e^{-i\omega t}\frac{d^2 \psi(x)}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi(x)e^{-i\omega t}$$

$$\frac{d^2 \psi(x)}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0$$

In the above equations you can note that partial differential is changed into ordinary differential because ψ is a function of x alone. Substituting de Broglie's wavelength $\lambda = h/(mv)$ for the matter waves of a particle of mass m moving with velocity v into it, we get,

$$\frac{d^2\psi(x)}{dx^2} + 4\pi^2 \frac{m^2v^2}{h^2}\psi(x) = 0 \tag{4}$$

If E is the total energy and V is the potential energy of the particle respectively, then the kinetic energy of the particle is,

$$E_k = \frac{1}{2}mv^2 = E - V$$

$$\therefore \quad m^2v^2 = 2m(E - V)$$

Substituting this into eqn. (4), we get,

$$\boxed{\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi(x) = 0} \tag{5}$$

Here ψ is a function of x alone and is independent of time. We use this equation for the cases where $V \equiv V(x)$ is a function of x alone so that the whole equation is independent of time. This equation is called one dimensional time-independent Schrödinger equation.

7 Physical significance of the wave function

The wave function $\Psi(x, t)$ is the solution of Schrödinger wave equation. It gives a quantum-mechanically complete description of the behavior of a moving particle. The wave function Ψ cannot be measured directly by any physical experiment. However, for a given Ψ, knowledge of usual dynamic variables, such as position, momentum, angular momentum, etc., of the particle can be obtained by performing suitable mathematical operations on it.

The Born interpretation:

The probability that a particle will be found in the infinitesimal interval dx about the point x at time t is

$$P(x, t) = \Psi^* \Psi = |\Psi(x, t)|^2 \, dx$$

where Ψ^* is the complex conjugate of Ψ. Hence, $|\Psi(x, t)|^2$ is measurable and is just the probability per unit length, or *probability density*. The probability of finding the particle in any finite interval $a \leq x \leq b$ at time t is,

$$P = \int_a^b |\Psi(x, t)|^2 \, dx$$

Normalization of wave function:

Because, for one dimensional motion, the particle must be somewhere along the x-axis, the probabilities summed over all values of x must add to 1. That is,

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 \, dx = 1$$

Any wave function satisfying this equation is said to be *normalized.*

Expectation Value:

For a particle in state, the expectation value of position coordinate x is

$$\langle x \rangle = \int_{-\infty}^{+\infty} \Psi^* [x] \Psi \, dx = \int_{-\infty}^{+\infty} x |\Psi(x, t)|^2 \, dx$$

What exactly does this mean? It emphatically does not mean that if you measure the position of one particle over and over again, $\int x|\Psi|^2 dx$ is the average of the results you'll get. On the contrary: The first measurement (whose outcome is indeterminate) will collapse the wave function to a spike at the value actually obtained, and the subsequent measurements (if they're performed quickly) will simply repeat that same result. Rather, $\langle x \rangle$ is the average of measurements performed on particles *all in the state* Ψ, which means that either you

must find some way of returning the particle to its original state after each measurement, or else you have to prepare a whole *ensemble* of particles, each in the same state Ψ, and measure the positions of all of them: $\langle x \rangle$ is the average of these results.

In short, *the expectation value is the average of measurements on an ensemble of identically-prepared systems*, not the average of repeated measurements on one and the same system.

For the moment it will suffice to postulate that the *expectation value of the velocity is equal to the time derivative of the expectation value of position*, and it can be shown to be:

$$\langle v \rangle = \frac{d\langle x \rangle}{dt} = \int_{-\infty}^{+\infty} \Psi^* \left[\frac{-i\hbar}{m} \frac{\partial}{\partial x} \right] \Psi \, dx$$

Actually, it is customary to work with momentum ($p = mv$), rather than velocity:

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt} = \int_{-\infty}^{+\infty} \Psi^* \left[-i\hbar \frac{\partial}{\partial x} \right] \Psi \, dx$$

We say that the operator x "represents" position, and the operator $-i\hbar(\partial/\partial x)$ "represents" momentum; to calculate expectation values we "sandwich" the appropriate operator between Ψ^* and Ψ, and integrate.

An "operator" is an instruction to *do something* to the function that follows; it takes in one function, and spits out some other function. The position operator tells you to *multiply* by x; the momentum operator tells you to *differentiate* with respect to x (and multiply the result by $-i\hbar$).

That's cute, but what about other quantities? The fact is, *all* classical dynamical variables can be expressed in terms of position and momentum. Kinetic energy, for example, is

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

To calculate the expectation value of any such quantity, we simply replace every p by $-i\hbar(\partial/\partial x)$, insert the resulting operator between Ψ^* and Ψ, and integrate. For example, the expectation value of the kinetic energy is

$$\langle T \rangle = \int_{-\infty}^{+\infty} \Psi^* \left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right] \Psi \, dx$$

This is a recipe for computing the expectation value of any dynamical quantity, for a particle in state Ψ. In truth this represents such a radically new way of doing business (as compared with classical mechanics). But it can be put on a more firmer theoretical foundation. In the mean time, if you prefer to think of it as an *axiom*, that's fine with me.

Eigenfunctions and Eigenvalues

In classical mechanics, the total energy (kinetic plus potential) is called the Hamiltonian:

$$H(x, p) = \frac{p^2}{2m} + V(x)$$

The corresponding Hamiltonian operator, obtained by the canonical substitution $p \rightarrow -i\hbar(\partial/\partial x)$, is therefore

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

Thus the time-independent Schrödinger equation

$$\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi(x) = 0$$

can be rearranged and written as

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

The quantity in the parenthesis is same as the above $\hat{H}$. Therefore,

$$\hat{H}\psi = E\psi$$

This is the eigenvalue equation for the operator $\hat{H}$; ψ is an eigenfunction of $\hat{H}$, and the total energy E is the corresponding eigenvalue.

8 Particle in an one-dimensional potential well of infinite depth (Particle in a box)

Suppose the potential is,

$$V(x) = \begin{cases} 0, & 0 \leq x \leq a, \\ \infty, & \text{otherwise} \end{cases}$$

A particle in this potential is completely free, except at the two ends ($x = 0$ and $x = a$), where an infinite force prevents it from escaping. A classical model would be a cart on a frictionless horizontal air track, with perfectly elastic bumpers—it just keeps bouncing back and forth forever. (This potential is artificial, of course, but I urge you to treat it with respect. Despite its simplicity—or rather, precisely because of its simplicity—it serves as a wonderfully accessible test case for all the fancy machinery that comes later.)

We begin by time independent Schrödinger equation which reads,

$$\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi(x) = 0 \tag{1}$$
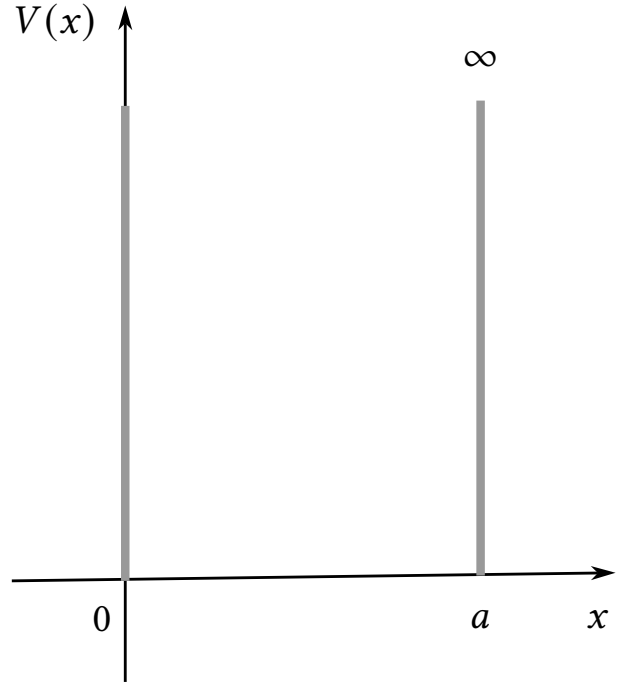
Outside the potential well ($0 \leq x \leq a$) it reads

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

This equation holds good only if $\psi(x) = 0$ for all points outside the well. The probability of finding the particle there is zero.

Inside the potential well, where $V = 0$, the time-independent Schrödinger equation (1) reads,

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

Or

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0, \qquad \text{where } k^2 = \frac{8\pi^2 m}{h^2}E \qquad (2)$$

Solution: Equation (2) is the classical *simple harmonic oscillator* equation; the general solution is,

$$\psi(x) = A\sin(kx) + B\cos(kx) \qquad (3)$$

where A and B are arbitrary constants. Typically, these constants are fixed by the *boundary conditions* of the problem.

Boundary conditions: What are the appropriate boundary conditions for $\psi(x)$? Ordinarily, both ψ and $d\psi/dx$ are continuous, but where the potential goes to infinity only the first of these applies.
  Continuity of $\psi(x)$ requires that

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

so as to join onto the solution outside the well. What does this tell us about A and B?

Condition 1: At $x = 0$, $\psi = 0$
  Substituting it in equation (3), we get

$$\psi(0) = A\sin 0 + B\cos 0 = B$$

so $B = 0$ as $\psi(0) = 0$, and hence equation (3) will become,

$$\psi(x) = A\sin(kx) \qquad (4)$$

Condition 2: At $x = a$, $\psi = 0$
  Substituting it in equation 4, we get

$$\psi(a) = A\sin(ka)$$

Since $\psi(a) = 0$,

$$A \sin(ka) = 0$$

so either $A = 0$ (in which case we're left with the trivial—non-normalizable—solution $\psi(x) = 0$), or else $\sin(ka) = 0$ which means that

$$ka = 0, \ \pm\pi, \ \pm 2\pi \ \pm 3\pi, \ \ldots$$

But $k = 0$ is no good (again, that would imply $\psi(x) = 0$, which means the particle is not inside the well), and the negative solutions give nothing new, since $\sin(-\theta) = -\sin(\theta)$ and we can absorb the minus sign into A. So the *distinct* solutions are

$$k = \frac{n\pi}{a}, \qquad \text{with } n = 1, 2, 3, \ldots \tag{5}$$

Curiously, the boundary condition at $x = a$ does not determine the constant A, but rather the constant k, and hence the possible values of E by substituting k^2 into equation (2). We get,

$$\frac{n^2\pi^2}{a^2} = \frac{8\pi^2 m}{h^2} E$$

or

$$\boxed{E = \frac{n^2 h^2}{8ma^2}} \qquad \text{with } n = 1, 2, 3, \ldots \tag{6}$$

In radical contrast to the classical case, a quantum particle in the infinite square well cannot have just any old energy—it has to be one of these special ("allowed") values.

The equation (6) gives energy (also called the energy eigenvalue) of the particle in the well. The lowest value of n is 1. The lowest energy corresponds to $n = 1$ and is called the *zero-point energy* or *ground state energy.*

$$E_{\text{zero-point}} = \frac{h^2}{8ma^2}$$

All the other states with $n > 1$ are called excited states.

Normalization of wave function: Actually, it's the wave function $\Psi(x, t)$ that must be normalized, but in view of $\Psi(x, t) = \psi(x)e^{-i\omega t}$ we will get $\Psi^*\Psi = \psi^*\psi$. This entails the normalization of $\psi(x)$.

To find A, we normalize ψ from equation 4 with normalization condition:

$$\int_{-\infty}^{+\infty} \psi^*\psi \, dx = \int_{-\infty}^{+\infty} |\psi(x)|^2 \, dx = 1$$

Since $\psi(x) = 0$ outside the well, it is sufficient to integrate between 0 to a. With $\psi(x) = A\sin(kx)$ inside the well we have,

$$\int_0^a |\psi(x)|^2 \, dx = \int_0^a |A|^2 \sin^2(kx) \, dx = 1$$

With the identity, $\sin^2\theta = (1 - \cos(2\theta))/2$ the above integral can be written as,

$$\frac{|A|^2}{2} \int_0^a [1 - \cos(2kx)] \, dx = 1$$

$$\text{or,} \quad \frac{|A|^2}{2} \left[x - \frac{1}{2k}\sin(2kx) \right]_0^a = 1$$

By substituting limits and k from equation (5) we get,

$$\frac{|A|^2}{2} \left[a - \frac{a}{2n\pi}\cancel{\sin(2n\pi)} \right]_{}^{0} = 1$$

$$\therefore \quad |A|^2 = \frac{2}{a}$$

This only determines the magnitude of A, but it is simplest to pick the positive real root and the phase of A carries no physical significance anyway. Hence,

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

Inside the well, then, the normalized solutions (also called eigenfunctions) are,

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x \right)}$$

The eigenfunctions for $n = 1, 2, 3$ are as follows.

$$\psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right)$$

$$\psi_2 = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi}{a}x\right)$$

$$\psi_3 = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi}{a}x\right)$$

Wave functions and probability densities: The above obtained solutions represents *stationary states*. Although the wave function itself,

$$\Psi(x, t) = \psi(x)e^{-i\omega t}$$

does (obviously) depend on t, the *probability density*,

$$|\Psi(x, t)|^2 = \Psi^*\Psi = \psi^* e^{+i\omega t}\psi e^{-i\omega t} = \psi^*\psi = |\psi(x)|^2$$

does *not* depend on time — the time-dependence cancels out. The same thing happens in calculating the expectation value of any dynamical variable. Every expectation value is constant in time.

Let's plot the first three stationary states of the infinite square well. As you go up in energy, each successive state has one more node (zero-crossing): ψ_1 has none (the end points don't count), ψ_2 has one, ψ_3 has two, and so on.

1. For $n = 1$ (ground state): The energy eigenvalue, eigenfunction and the probability density for this state are,
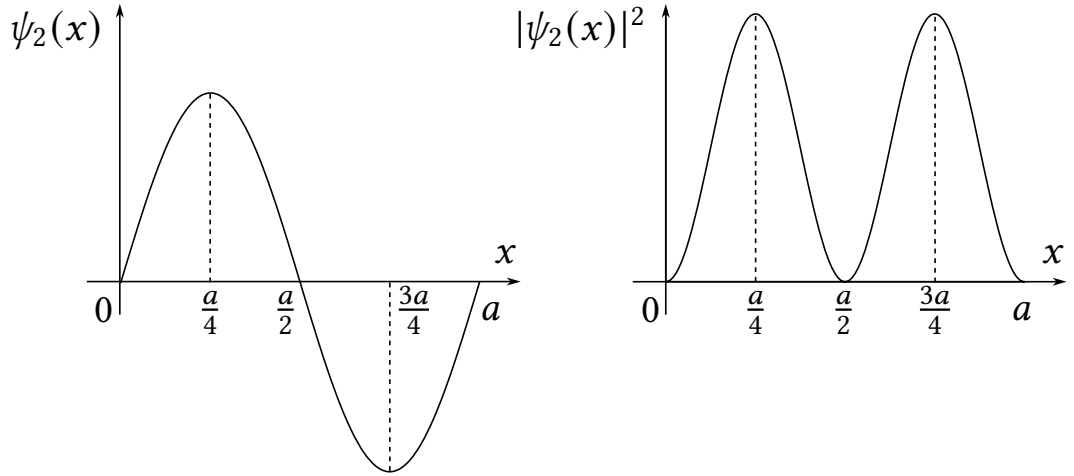
$$E_1 = \frac{h^2}{8ma^2}, \quad \psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right) \quad \text{and} \quad |\psi_1|^2 = \frac{2}{a} \sin^2\left(\frac{\pi}{a}x\right)$$
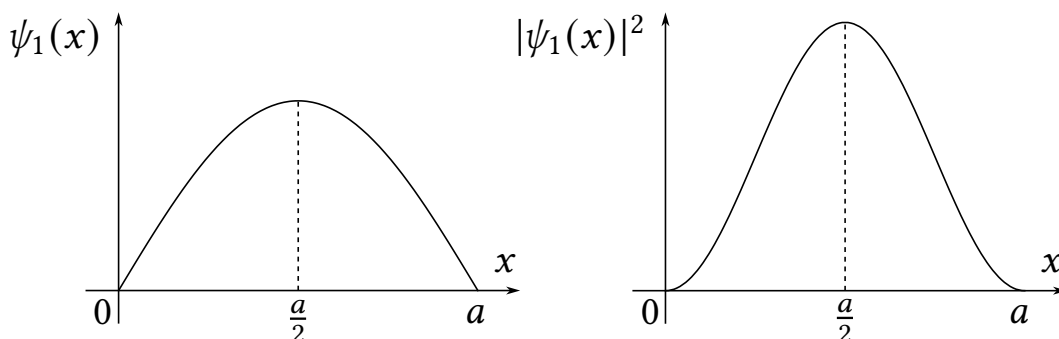
(a) $\psi_1 = 0$ for $x = 0, a$.

(b) ψ_1 reaches maximum value of $\sqrt{2/a}$ for $x = a/2$.

(c) $|\psi_1|^2 = 0$ for $x = 0, a$.

(d) $|\psi_1|^2$ reaches maximum value of $2/a$ for $x = a/2$.

2. For $n = 2$ (first excited state): The energy eigenvalue, eigenfunction and the probability density for this state are,
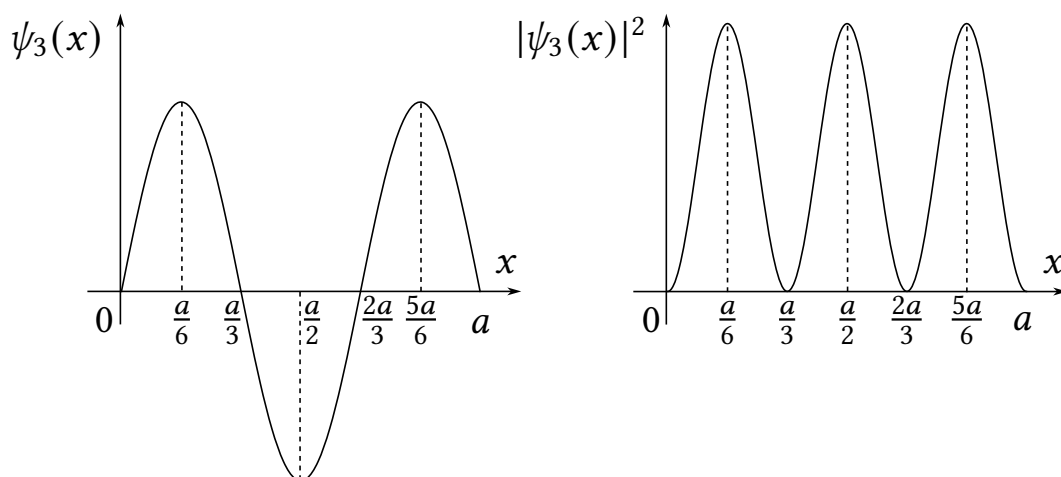
$$E_2 = \frac{4h^2}{8ma^2} = 4E_1, \quad \psi_2 = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi}{a}x\right) \quad \text{and} \quad |\psi_2|^2 = \frac{2}{a}\sin^2\left(\frac{2\pi}{a}x\right)$$

(a) $\psi_2 = 0$ for $x = 0, a/2, a$.

(b) ψ_2 reaches maximum value of $\sqrt{2/a}$ for $x = a/4$.

(c) ψ_2 reaches minimum value of $-\sqrt{2/a}$ for $x = 3a/4$.

(d) $|\psi_2|^2 = 0$ for $x = 0, a/2, a$.

(e) $|\psi_2|^2$ reaches maximum value of $2/a$ for $x = a/4, 3a/4$.

3. For $n = 3$ (second excited state): The energy eigenvalue, eigenfunction and the probability density for this state are,

$$E_3 = \frac{9h^2}{8ma^2} = 9E_1, \quad \psi_3 = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi}{a}x\right) \quad \text{and} \quad |\psi_3|^2 = \frac{2}{a}\sin^2\left(\frac{3\pi}{a}x\right)$$

(a) $\psi_3 = 0$ for $x = 0, a/3, 2a/3, a$.

(b) ψ_3 reaches maximum value of $\sqrt{2/a}$ for $x = a/6, 5a/6$.

(c) ψ_3 reaches minimum value of $-\sqrt{2/a}$ for $x = a/2$.

(d) $|\psi_3|^2 = 0$ for $x = 0, a/3, 2a/3, a$.

(e) $|\psi_3|^2$ reaches maximum value of $2/a$ for $x = a/6, a/2, 5a/6$.

References

[1] *Modern Physics*, Raymond A Serway, Clement J Moses and Curt A Moyer, 3rd edition, Thomson Learning, Inc.

[2] Introduction to Quantum Mechanics, David J Griffiths and Darrell F Schroeter, 3rd edition, Cambridge University Press.