Other important quantum mechanics operator are:

Classical Variable	**Q.M. Operator**	**Operation**
X (*Position*)	$\hat{X}$	X (Multiply by X)
P_x(X component of Linear momentum)	$\hat{P}_x$	$- i\hbar \frac{d}{dx}$
L_z(Z component of angular momentum	$\hat{L}_z$	$- i\hbar \frac{d}{d\phi}$
t (time)	$\hat{t}$	t (multiply by t)
E (time dependent total energy)	$\hat{E}$	$- i\hbar \frac{d}{dE}$

Postulate III and IV:

3rd postulate relates results of measurement and eigenvalues of operators.

Postulate 3: In any single measurement of the observable that corresponds to the operator Â the only values that will ever be measured are the eigenvalues of that operator.

Example: Total energy of H atom determined by orbital occupied. No other values possible.

Thus If Û is an operator corresponding to an observable and Ψ is an eigenfunction of the operator Û , then the eigenvalue of the equation

Û Ψ =a Ψ will be the value of the observable.

The calculation of allowed energies of an atomic and molecular systems is a direct application of this postulate. It involves finding the wavefunction Ψ and eigenvalue E which satisfy **Schrödinger equation:**

$$\hat{H}\,\Psi = E\,\Psi \quad \text{where} \quad \text{E is the total energy}$$

$$\left(\frac{-\hbar^{2}}{2\text{m}}\nabla^{2} + V\right)\Psi = E\,\Psi$$

or

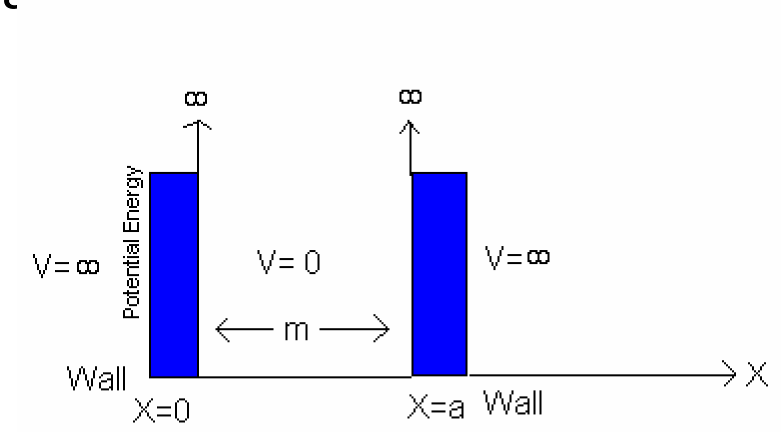
$$\frac{-\hbar^{2}}{2\text{m}}\nabla^{2}\Psi + V\,\Psi = E\,\Psi$$

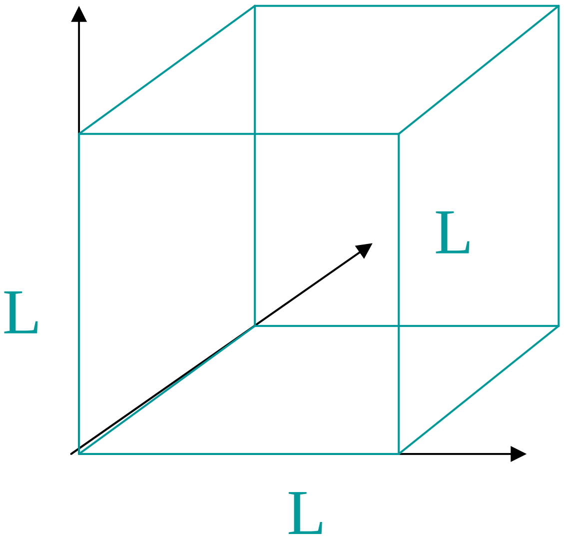
or

$$\frac{-\hbar^{2}}{2\text{m}}\nabla^{2}\Psi + (E - V)\,\Psi = 0$$

Application of the postulate to a simple system:

The particle in a box:





Consider a particle of a mass m constrained to move in one direction

(along the X-axis) inside a box of length a. Assume the potential energy V inside the box to be zero and outside the box to be infinity, i.e. no chance for the particle to go outside the box.

The observable we want to calculate is the energy of the particle. We use the Hamiltonian which is the total energy operator and solve the Schrödinger equation.

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

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}+V\right)\Psi = E\Psi$$

Since inside the box V = 0

$$\therefore \frac{-\hbar^2}{2\mathrm{m}}\frac{d^2\Psi}{dx^2} = E\Psi$$

Re*arranging*

$$\frac{d^2\Psi}{dx^2} = \frac{-2mE}{\hbar^2}\Psi$$

This is a second order differential equation whose Solutions are functions that when differentiated twice Will give the same function back multiplied by a constant. Based upon the previous discussed topics Concerning the type of functions (finding the eigenfunction and eigenvalue equations). Therefore, the second order differentiated equation perhaps of the type e^n , sin(n) or cos(n). A very general solution is:

Ψ= Asinαx + Bcosαx

Where A, B and α are constants.

If we differentiate Ψ twice , we get:

$$\frac{d\Psi}{dx} = A\alpha\cos\alpha x - B\alpha\sin\alpha x$$

$$\frac{d^2\Psi}{dx^2} = -A\alpha^2\sin\alpha x - B\alpha^2\cos\alpha x$$

$$= -\alpha^2\left(\mathrm{A}\sin\alpha\mathrm{x} + \mathrm{B}\cos\alpha\mathrm{x}\right)$$

$$= -\alpha^2\Psi \qquad \therefore \frac{-\,2\mathrm{mE}}{\hbar^2} = -\alpha^2 \text{ and } \mathrm{E} = \frac{\alpha^2\hbar^2}{2\mathrm{m}}$$

Now we apply the **boundary conditions:**

- At the edge of the box, i.e. at X=0 and X=a the value of Ψ=0. This is the result of the requirement that must be single value, because just outside the box Ψ=0). Therefore, when we consider a particle trapped in a 1D-box bouncing back and forth between the walls. Since there is zero probability of finding the particle outside, ψ(x)=0 outside the box; and since the wave-function must be continuous, ψ(x)=0 at the walls too.

The general solution was:

Ψ= Asinαx + Bcosαx

(i) Substituting x=0 in the above equation of Ψ we get:

Ψ= Asinα(0) + Bcosα(0)

Ψ= 0 + B

$\therefore$For Ψ to be zero at x=0, B must be zero

$\therefore$ Ψ =Asinαx only

(ii) Substituting x=a we get: Ψ =Asinαa

For Ψ to be zero at x=a, αa must be equal to nπ where n is an integer.

$$\alpha\,\mathrm{a} = \mathrm{n}\pi \qquad \text{or} \qquad \alpha = \frac{\mathrm{n}\pi}{\mathrm{a}}$$

$$E = \frac{n^2\hbar^2\pi^2}{2ma^2}$$

$$E = n^2\left(\frac{h^2}{8ma^2}\right) \quad n = 1,2,3,.....$$

Thus the position of boundary conditions leads to discrete values of energy.

To complete the solution, we must normalize the wavefunction .The normalize condition in the case is:

$$\int_{all\ space} \Psi^* \Psi dx = 1$$

$$\int_0^a \left(A \sin \frac{n\pi x}{a} \right)^2 dx = 1$$

$$A^2 \int_0^a \sin^2 \frac{n\pi x}{a} dx = 1$$

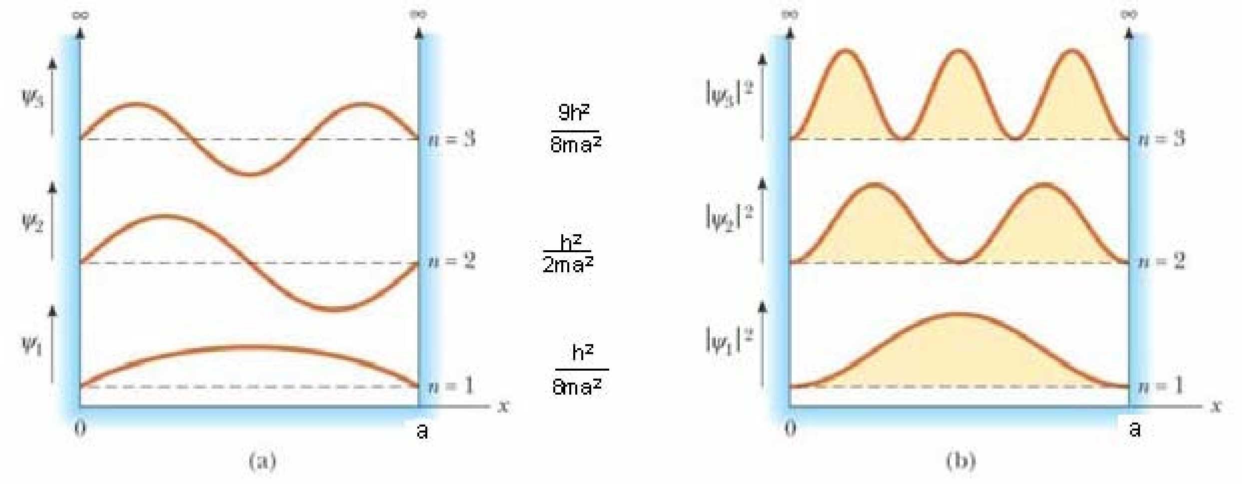
$$\frac{A^2 a}{2} = 1 \qquad \therefore \mathrm{A}^2 = \frac{2}{\mathrm{a}} \qquad \therefore \mathrm{A} = \left(\frac{2}{a} \right)^{\frac{1}{2}}$$

And so the allowed wavefunctions and energies for a particle in one-dimensional (1-D) box are:

$$\Psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \qquad\qquad En = \frac{n^2 h^2}{8ma^2}$$

Units: h in Js, m in Kg , a in m, E in Joules (system I.N)

h in ergs, mass in g, a in cm,   E in ergs



Schematic drawing of E_n , Ψ_n and Ψ_n^2 for the case of a particle moving in 1-D box. Note that Ψ_n changes sign at each node while Ψ_n^2 always remains positive or zero. Also note that the energy spacing between levels diverges as n increase.

Features of the solution:

1- Quantization of energy levels arise from the constrained of the motion of the particle to a certain region of space i.e. to boundary conditions.

2- For the same value of the quantum number n , the energy is inversely proportional to the mass of the particle and the length of the box. As n and a become large energy levels become more closely spaced.

Thus, as the particle becomes heavier and the box larger, the energy levels become more closely spaced. It is only when the quantity ma^2 is of the same order as h^2 that quantized energy levels become important in experimental measurements. When dealing with dimension of 1g and 1cm, the energy levels become so closely spaced that they seem to us to be continuous. The quantum mechanical formula, therefore, gives the classical result for systems with dimensions such that $ma^2 >> h^2$. This is an illustration of the "**correspondence principle**" that states that the quantum mechanical results must become identical with the classical one in the limit where the quantum numbers describing the system become very large.

3- As the energy increasing the number of nodes increases, a node is a point where the value of Ψ is zero, excluding the edges.

Number of Nodes = n-1

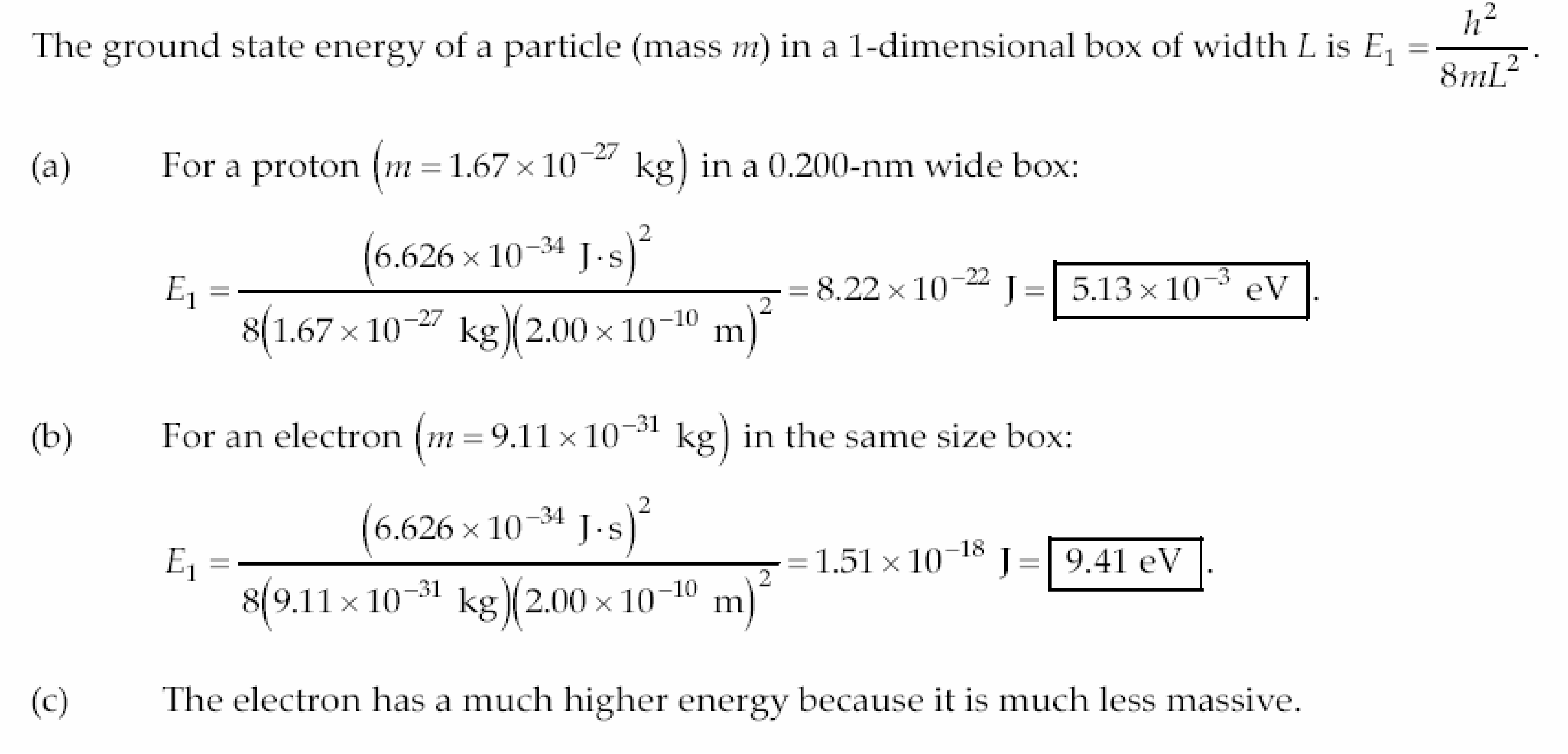
The greater the number of nodes, the shorter is the wavelength and therefore the larger is the energy and momentum.

Problem1: What is the separation between energy levels n=2 and n=1 for electron in the box of length L=10 cm? $\Delta E21 \cong 10^{-16}$ eV (tiny)

Problem2: What is the separation between energy levels n=2 and n=1 for electron in the box with length L=1Å? $\Delta E21 \cong 100$ eV

Examples:

1. A proton is confined to move in a one-dimensional box of length 0.200 nm .(a) Find the lowest possible energy of the proton. (b) **What If?** What is the lowest possible energy of an electron confined to the same box? (c) How do you account for the great difference in your results for (a) and (b)?



The ground state energy of a particle (mass m) in a 1-dimensional box of width L is $E_1 = \frac{h^2}{8mL^2}$.

(a) For a proton $\left(m = 1.67 \times 10^{-27}\ \text{kg}\right)$ in a 0.200-nm wide box:

$$E_1 = \frac{\left(6.626 \times 10^{-34}\ \text{J} \cdot \text{s}\right)^2}{8\left(1.67 \times 10^{-27}\ \text{kg}\right)\left(2.00 \times 10^{-10}\ \text{m}\right)^2} = 8.22 \times 10^{-22}\ \text{J} = \boxed{5.13 \times 10^{-3}\ \text{eV}}.$$

(b) For an electron $\left(m = 9.11 \times 10^{-31}\ \text{kg}\right)$ in the same size box:

$$E_1 = \frac{\left(6.626 \times 10^{-34}\ \text{J} \cdot \text{s}\right)^2}{8\left(9.11 \times 10^{-31}\ \text{kg}\right)\left(2.00 \times 10^{-10}\ \text{m}\right)^2} = 1.51 \times 10^{-18}\ \text{J} = \boxed{9.41\ \text{eV}}.$$

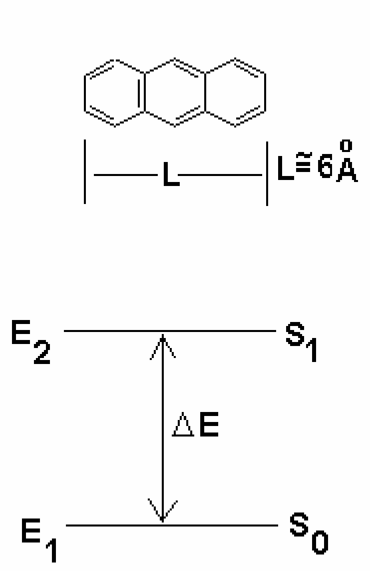
(c) The electron has a much higher energy because it is much less massive.

What you should learn from this lecture

1. For the particle in a box You should remember the dependence of the energy on the quantum number n and the box length l. You should also note the lower limit ($n = 1$) for n and the consequence it has for the minimum energy (zero point energy).

2 You should also know roughly the form of the state functions Ψ_n Especially, you should note that Ψn nodes.

Particle in a Box Simple model of molecular energy levels.



Anthracene molecule

π electrons – consider “free” in box of length L.

Ignore all coulomb interactions. Calculate wavelength of absorption of light. Form particle in box energy level formula.

$$\Delta E = hv$$
$$v = \frac{\Delta E}{h} = 7.64 \times 10^{14}\,Hz$$
$$h = \frac{c}{v} = 393nm \ \text{ blue - violet}$$
$$\text{Experiment} \Rightarrow 400\ \text{nm}$$

$$m = me = 9 \times 10^{-31}\,Kg$$
$$L = 6\,\text{Å} = 6 \times 10^{-10}\,m$$
$$h = 6.6 \times 10^{-34}\,Js$$
$$\Delta E = 5.04 \times 10^{-19}\,J$$

Anthracene particularly good agreement. Other molecules, naphthalene, benzene, agreement much worse. Important point

Confine a particle with “size” of electron to box size of a molecule

Get energy level separation, light absorption, in visible and UV.

Molecular structure, realistic potential give accurate calculation, but

It is the mass and size alone that set scale.

Big molecules ⟶ **absorb in red.**

Small molecules ⟶ **absorb in UV.**

Postulate V: (expectation value)

If Û is an operator corresponding to an observable and Ψ is a function describing the system. Furthermore if Ψ is not an eigenfunction of Û then a series of measurements of the observable will not give the same results but a distribution of results. The average or mean or "**expectation value**" of the observable will be given by:

$$\langle P \rangle = \frac{\int_{all\ space} \Psi^* \hat{U} \Psi d\tau}{\int_{all\ space} \Psi^* \Psi d\tau}$$

Where <P> is the expectation value of the observable.

Ex1: Calculate the momentum along the x-axis for the particle in a box. It is required to calculate P_x and therefore the operator to be used is $-i\hbar\frac{d}{dx}$

For the particle in a box Ψ is $\Psi = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$

It is clear that is not an eigenfunction of the momentum operator. So we can only calculate the mean or expectation value of P_x

$$\left\langle p\right\rangle = \frac{\int\limits_{all\,space} \Psi^{*} P\overset{\wedge}{\Psi} d\tau}{\int\limits_{all\,space} \Psi^{*} P\overset{\wedge}{\Psi} d\tau}$$

$$\left\langle p\right\rangle = \frac{\int_{0}^{a} \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}\left(-i\hbar\frac{d}{dx}\right)\sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}\, dx}{\int_{0}^{a} \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}.\sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}\, dx}$$

$$\left\langle p\right\rangle = \frac{\left(\frac{2}{a}\right)\int_{0}^{a} \sin\frac{n\pi x}{a}\left(-i\hbar\frac{d}{dx}\right)\sin\frac{n\pi x}{a}\, dx}{1}$$

$$\left\langle p\right\rangle = \frac{-2i\hbar}{a}\int_{0}^{a} \sin\frac{n\pi x}{a}\frac{d}{dx}\sin\frac{n\pi x}{a}\, dx$$

$$\left\langle p\right\rangle = \frac{-2i\hbar}{a}\int_{0}^{a} \sin\frac{n\pi x}{a}.\cos\frac{n\pi x}{a}.\left(\frac{n\pi}{a}\right)dx$$

$$\left\langle p\right\rangle = \frac{-2i\hbar}{a}\left[Sin^{2}\frac{n\pi x}{a}\right]_{0}^{a}$$

$$\left\langle p\right\rangle = \frac{-i\hbar}{a}\left[(0)-(0)\right] = Zero$$