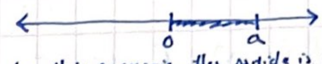
PARTICLE IN A BOX (Continued)

First, using a 3D model:

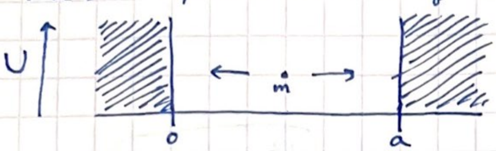
We place a particle inside a confined box from which it cannot escape. The particle is free to move, but is localized to the inside of the box.

Condense to a 1-D model (for simplicity) $\longrightarrow$



In this scenario, the particle is restricted to the range between 0 and a. There is a large energy barrier to the left of 0 and right of a to which the particle may not surpass.

$\rightarrow$ We can compare the classical and quantum interpretations of this problem.



The classical picture:

The particle of mass m would bounce from one wall to another with no limitation on momentum or energy.

For this picture, $U \begin{cases} 0 & 0 \le x \le a \quad \text{(inside)} \\ \infty & (x > a) \cup (x < 0) \quad \text{(outside)} \end{cases}$

The quantum picture:

Let us use the master recipe to describe this particle as a wave.

1) Define Hamiltonian:

$$E = K + U$$

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + \begin{Bmatrix} 0, & \text{if } 0 \le x \le a \\ \infty, & \text{if } x > a \text{ or } x < 0 \end{Bmatrix}$$

2) Write Schrödinger's Equation: We would have two separate cases due to the restriction of particle's localization.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{in} = E\psi_{in} \quad \text{for} \quad 0 \le x \le a$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{out} + U_\infty\psi_{out} = E\psi_{out} \quad \text{for } x > a \text{ or } x < 0 \longrightarrow -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{out} = (E - U_\infty)\psi_{out}$$

(Potential energy as $x \to \infty$)

Note that these two are constants.

$$\int_{-\infty}^{\infty} (PDF)\, dx = 1 \rightarrow$$

$= 1$

3) Define boundary conditions

- Wave function is normalized? Dealing with probabilities, so $\int_{-\infty}^{\infty} |\psi_{in}|^2 dx = 1$ and $\int_{-\infty}^{\infty} |\psi_{out}|^2 dx = 1$.
- Is the wave function continuous?
  - We have to make it continuous: $\psi_{out}(x=0) \rightarrow \square\, \psi_{in}(x=0)$ and $\psi_{out}(x=a) \rightarrow \square\, \psi_{in}(x=a)$
  - Aim to have $\psi_{out}(x=0) = \psi_{in}(x=0)$ and $\psi_{out}(x=a) = \psi_{in}(x=a)$
  - Therefore we consider if $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{out} = \infty\psi_{out}$ makes physical sense – which does not: probability cannot be infinitely large; $\psi_{out} \rightarrow \infty$ therefore does not make sense. ψ_{out} must converge.
  - Suppose $\psi_{out} = 0$ instead. This would make physical sense, and essentially states that probability of the particle existing for $(-\infty, 0) \cap (a, \infty) = 0$.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{out} = (E - U_\infty)\psi_{out} = 0, \text{ and only}$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{in} = E\psi_{in} \text{ remains.}$$

4) Solve Schrödinger's Equation

We have calculated $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_{in} = E\psi_{in}$ before, and found that $\psi_{\pm} = \frac{1}{\sqrt{2L}}e^{\pm ikx}$, and $\psi_{in} = \begin{cases} C_+ e^{ikx} \\ C_- e^{-ikx} \end{cases}$

However, we must still account for $\psi_{in}(x=0) = \psi_{out}(x=0)$ and $\psi_{in}(x=a) = \psi_{out}(x=a)$

We determined that $\psi_{out} = 0$, so $\psi_{in} = \begin{Bmatrix} C_+ e^{ikx} \\ C_- e^{-ikx} \end{Bmatrix} = 0$ at $x = a$ and $x = 0$.

Any linear combination of ψ_+ and ψ_- are solutions, so $\psi_{in} = x + y = 0$, $\therefore x = -y$

$$\psi_{in} = A(e^{ikx} - e^{-ikx}) \rightarrow \psi_{in} = A\underbrace{\left(\frac{e^{ikx} - e^{-ikx}}{2i}\right)}_{\sin kx} 2i = C\sin kx.$$

So we have found that

$$\psi_{in} = A\underbrace{\left(\frac{e^{ikx} - e^{-ikx}}{2i}\right)}_{\sin kx} 2i = C\sin kx.$$

Now we satisfy the limitation that $\psi_{in}(x=0) = 0$ and $\psi_{in}(x=a) = 0$.

$\psi_{in}(x=a) = C\sin ka = 0$. When $ka = n\cdot\pi$, $\psi_{in}(x=a) = 0$, where $\underbrace{n=0,1,2,3,\dots}_{\text{quantization in space!}}$

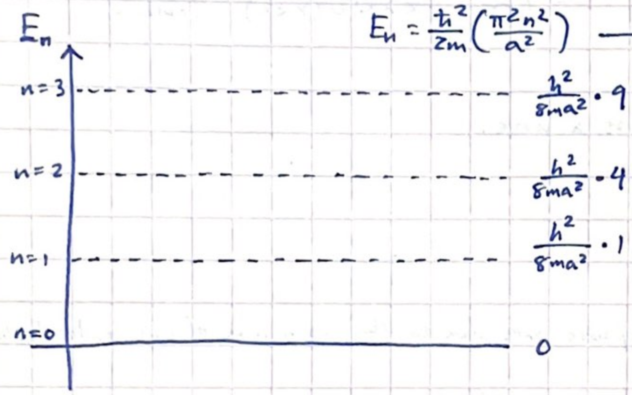
Relevance: We can now relate this to the particle's energy:

$$ka = n\pi, \quad \therefore\ k = \frac{n\pi}{a} \qquad k = \sqrt{\frac{2mE}{\hbar^2}}$$

$$E_n = \frac{k^2\hbar^2}{2m}$$

$$E_n = \frac{\hbar^2}{2m}\left(\frac{\pi^2 n^2}{a^2}\right) \longrightarrow \frac{h^2}{\cancel{4\pi^2}}\left(\frac{1}{2m}\right)\left(\frac{\cancel{\pi^2} n^2}{a^2}\right) = \boxed{\frac{h^2}{8ma^2}n^2 = E_n}$$

where $n = 0, 1, 2, 3 \dots$



We should consider if the statement $n=0$ makes sense:

If $n=0$, then $\psi=0$, meaning that there is 0 probability to find the particle everywhere: The particle does not exist: WTF

Notice that the larger the range, the smaller the energy difference between quanta. The smaller the ~~differen~~ range, the large the energy difference between each quanta.

As $a \to \infty$, the particle will more closely resemble a free particle.

Relating what we have found back to the wave function, $\psi_n = C\sin\left(\frac{\pi n x}{a}\right)$ as $k = \frac{n\pi}{a}$.

We now have the wave function. The next step is to normalize it, using probability density:

$$\int_{-\infty}^{\infty}(\text{PDF})\,dx = \underbrace{\cancel{\int_{-\infty}^{0}|\psi_{out}|^2dx}}_{0} + \int_0^a|\psi_{in}|^2dx + \underbrace{\cancel{\int_a^{\infty}|\psi_{out}|^2dx}}_{0} = 1$$

$$\therefore \int_{-\infty}^{\infty}(\text{PDF})\,dx = \int_0^a|\tilde{\psi}_{in}|^2dx = 1 \quad \text{to be normalized.}$$

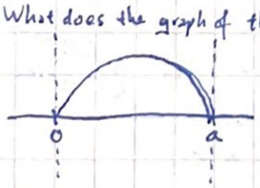
$\psi_{in} = C\sin\left(\frac{\pi n x}{a}\right)$,

$|\psi_{in}|^2 = C^2\sin^2\left(\frac{\pi n x}{a}\right)$. $\quad C^2\int_0^a \sin^2\left(\frac{\pi n x}{a}\right)dx \xrightarrow[\left(\sin^2 a = \frac{1}{2}(1-\cos 2a)\right)]{} \frac{C^2}{2}\int_0^a\left(1-\cos\left(\frac{2\pi n x}{a}\right)\right)dx$

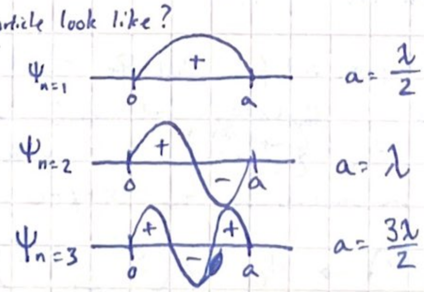
$$\frac{C^2}{2}\int_0^a\left(1-\cos\left(\frac{2\pi n x}{a}\right)\right)dx = \frac{C^2}{2}\left[\int_0^a dx - \int_0^a\cos\left(\frac{2\pi n x}{a}\right)dx\right] = \left[\frac{C^2}{2}a - \frac{C^2}{2}\left(\frac{a}{2\pi n}\right)\sin\left(\frac{2\pi n x}{a}\right)\right]_0^a$$

Substituting a and 0, we end up with $\frac{C^2}{2}a = 1$, and that $C = \sqrt{2/a}$. Therefore $\boxed{\tilde{\psi}_{in} = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi n x}{a}\right)}$

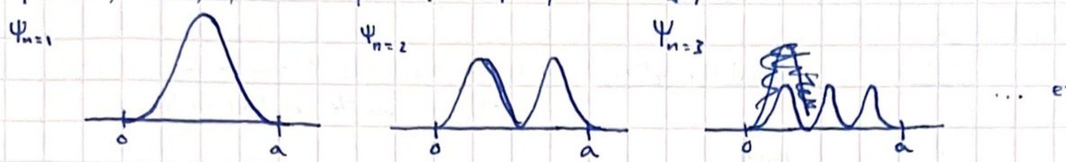
What does the graph of this particle look like?



The box restricts the wavelengths possible for the particle.



The probability density of the wave function, $|\Psi|^2$, may also be graphed:



Note that the sum of all these distributions are still 1. There are points inside the box in which the probability of the particle existing at the point is 0, known as nodes, occurring due to destructive interference:

$$\Psi_n(x,t) = \Psi_n(x)e^{-i/\hbar Et} = \sqrt{\frac{2}{a}}\frac{1}{2i}\left(e^{-i(\omega t - kx)} - e^{-i(\omega t + kx)}\right)$$

$\downarrow$ Travels right $\quad$ $\downarrow$ Travels left

= Destructive interference

An aside ... Wave functions cannot be reconstructed from a particle in the superposition state.

For example,

$\Psi = 3e^{i5x} + 2e^{-i3x} - 2ie^{ix}$ is a particle in superposition.

What are the corresponding momenta for each part of the wave function?

Recall that $\hat{p}(e^{ikx}) = \hbar k$:

Then
$$\left.\begin{aligned}\hat{p}(3e^{i5x}) &= 5\hbar \\ \hat{p}(2e^{-i3x}) &= -3\hbar \\ \hat{p}(-2ie^{ix}) &= \hbar\end{aligned}\right\} \text{Eigenvalues for momentum}$$

Experimentally, we determine if a particle is in a pure state if there is only one outcome of the measurement among many.

What are the probabilities of each state?

~~Two ways to~~ determine using probability ~~or integral form of expected value equation~~:

Probability:

$$P_1 = \frac{3^2}{3^2+2^2+2^2} = 9/17, \quad P_2 = \frac{2^2}{3^2+2^2+2^2} = 4/17, \quad P_3 = \frac{2^2}{3^2+2^2+2^2} = 4/17$$

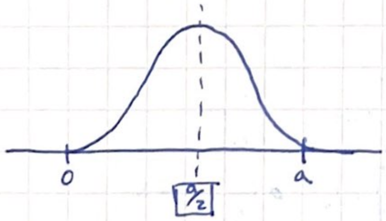
What is the expected value of momentum?

Apply eigenvalues with probabilities:

$$\langle p \rangle = 5\hbar\left(\frac{3^2}{3^2+2^2+2^2}\right) - 3\hbar\left(\frac{2^2}{3^2+2^2+2^2}\right) + \hbar\left(\frac{2^2}{3^2+2^2+2^2}\right)$$

The expected value of a wave function (where we would expect the particle to be) is always halfway in the range of the particle ($a/2$). Let us prove this using the expected value method:

$$\langle A \rangle = \frac{\int \Psi^* \hat{A}(\Psi)\,dx}{\int |\Psi|^2 dx}$$, so drawing upon $\Psi_n = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi n x}{a}\right)$, we get:



$$\langle x \rangle = \frac{2}{a}\int_0^a \sin\left(\frac{\pi n x}{a}\right)\cdot \sin\left(\frac{\pi n x}{a}\right)\cdot x\,dx$$

$$\left(\text{Since } E(x) = \int_{-\infty}^{\infty} x f(x)\,dx \text{ probabilistically, } E(\Psi) = \int_{-\infty}^{\infty} x|\Psi|^2 dx\right)$$

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

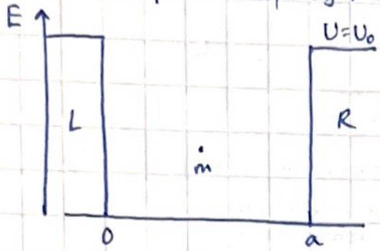
$$= \boxed{\int_0^a x\,dx + \cancel{\int_0^a x\cos\left(\frac{2\pi n x}{a}\right)dx}}$$

0 $\quad$ $\hookrightarrow$ (Integrate by parts)

$$\hookrightarrow \frac{1}{2}x^2\Big|_0^a = \frac{a^2}{2}$$

$$\frac{a}{2} = \frac{1}{a}\left(\frac{a^2}{2}\right)$$

So far, we have dealt with the case of an infinitely high wall enclosing the particle. However, what happens if the wall enclosing the particle is of height U_0?



Classical description: When $E \leq U_0$, the particle stays in the box.
When $E \geq U_0$, the particle can leave the box.

Inside:
$$p = \pm\sqrt{2mE}$$ → This momentum will be larger (and the particle will be faster) inside the box.

Outside:
$$p = \pm\sqrt{2m(E-U_0)}$$ → The particle is slower outside the box.

The Quantum Model: When $E \leq U_0$, the particle behaves as a particle in a 1D box.
When $E \geq U_0$, the particle behaves as a wave which is proportionalized to λ.

$$\hat{H}_{in} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$ Is used for when the particle is inside the box.

$$\hat{H}_{out} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U_0$$ Is used for when the particle is outside the box, either left or right.

Compare both using TISE:

$$\hat{H}_{in}\Psi_{in} = E\Psi_{in}, \quad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi_{in} = E\Psi_{in}$$

$$\hat{H}_{out}\Psi_{out} = E\Psi_{out}, \quad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi_{out} = (E-U_0)\Psi_{out}$$, for both left and right sides.

Boundary conditions:
$$\int P\,dx = 1, \text{ so } \int_0^a |\Psi|^2\,dx = 1.$$

Additionally, $\frac{d}{dx}\Psi$ must be continuous, so $\Psi_{in}(x\to 0) = \Psi_{out}(x\to 0)$, and $\Psi_{in}(x\to a) = \Psi_{out}(x\to a)$.

The general solutions to the equations are

$$k_{in} = \pm\sqrt{\frac{2mE}{\hbar}}, \quad k_{out} = \sqrt{\frac{2m(E-U_0)}{\hbar}}$$

Resulting in the expressions $\Psi_{in} = Ae^{ikx} + Be^{-ikx}$ $\quad \Psi_{out,L} = Ce^{ikx} + De^{-ikx}$ $\quad \Psi_{out,R} = Fe^{ikx} + Ge^{-ikx}$

Note that for the expressions determined, the k is different, and depends on where the particle is measured.
Seven unknown variables: A, B, C, D, E (energy), F, and G.
↳ When $E > U_0$, there will be more unknown variables than equations, and therefore no quantization in space since there is no restriction on what values energy can take on.

Probability density restriction:

$$P_{out,L} = \Psi_{out,L}^2 = \cancel{C^2e^{-2kx}} + D^2e^{2kx} = D^2e^{2kx}, \quad \therefore P(x<0) = \int_{-\infty}^{0} P\,dx = \frac{D^2}{2k}e$$

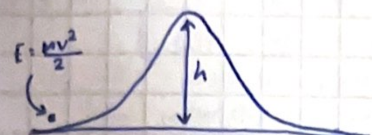
$$P_{out,R} = \Psi_{out,R}^2 = F^2e^{-2kx} + \cancel{G^2e^{2kx}} = F^2e^{-2kx} \quad \therefore P(x>a) = \int_a^{\infty} P\,dx = \frac{F^2}{2k}e^{-2ka}$$

- The penetration depth is defined as $\Delta x = \frac{1}{k}$:
- Reason for the tunneling effect in SEM, applications in proton exchange for chemical reactions
- Typically observed for small particles:

$$k = \frac{\sqrt{2m(U_0-E)}}{\hbar}$$

More on penetration depth

Valence electrons have longer penetration lengths = the electrons are spread out more, so when two atoms are close to each other, the valence electrons are the first to interact with each other.



$U = mgh$

If we assume $m = 50\,kg$

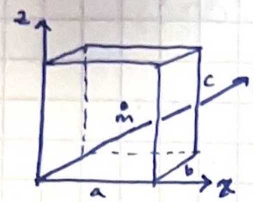
$h = 2m$

and $v = 2m/s$,

What is k and the penetration depth?

So far, we have only dealt with the case of a particle in a 1-Dimensional box. How should we go from 1D→2D→3D?

Mostly the same: Imagine a cube with side lengths of a, b, and c:



Conditions:

$U = 0$ inside

$U = U_\infty$ outside

We can consider the movement of the particle of mass m to be independent in the x, y, and z directions. As such, we define the kinetic energy to be:

$$E = KE = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \text{ inside the box.}$$

→Since the 1-D model involves a wave propogating in 1 dimension, the quantum mechanical model translates this to waves propogating in 2 dimensions, and likewise in 3 dimensions.

The mathematical proof for this argument:

Defining hamiltonian:

$$\hat{H}\Psi(x,y,z) = \underbrace{-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi}_{\boxed{\text{What is the solution to this differential equation?}}} + \begin{cases} 0 & \text{if inside} \\ U_\infty & \text{if outside} \end{cases}$$

Taking the differential by its components, we find that $\frac{\partial^2}{\partial x^2}\Psi \Rightarrow \frac{d^2}{dx^2} X \cdot Y \cdot Z$

$= \underbrace{YZ}_{\text{constant}}\frac{d}{dx}X$

Similarly, $\frac{\partial^2}{\partial y^2}\Psi$ & $\frac{\partial^2}{\partial z^2}\Psi$ result in similar results.

We have three parts:

$X_{(x)} \cdot Y_{(y)} \cdot Z_{(z)}$

Notice how in all the differentials, there is no crossing of variables: no $\frac{\partial^2}{\partial x \partial y}$. Therefore we can split this as:

- $X_{(x)}$ is the part of the wave function which only depends on X
- $Y_{(y)}$ is the part of the wave function which only depends on Y
- $Z_{(z)}$ is " on Z.

If we use this function in the Schrödinger equation,

$$\hat{H}\Psi(x,y,z) = \begin{Bmatrix} E \\ (E - U_\infty) \end{Bmatrix}\Psi(x,y,z)$$

As established in the previous part,

$$\left.\begin{aligned} \frac{\partial^2}{\partial x^2}\Psi &= Y \cdot Z\frac{d^2}{dx^2}X \\ \frac{\partial^2}{\partial y^2}\Psi &= XZ\frac{d^2}{dy^2}Y \\ \frac{\partial^2}{\partial z^2}\Psi &= XY\frac{d^2}{dz^2}Z \end{aligned}\right\} \longrightarrow -\frac{\hbar^2}{2m}\left[YZ\frac{d^2}{dx^2}X + XZ\frac{d^2}{dy^2}Y + XY\frac{d^2}{dz^2}Z\right] = \hat{H}\Psi(x,y,z),$$

and therefore $-\frac{\hbar^2}{2m}\left[YZ\frac{d^2}{dx^2}X + XZ\frac{d^2}{dy^2}Y + XY\frac{d^2}{dz^2}Z\right] = E(XYZ)$

through algebraic manipulation (divide by XYZ to isolate E), we find

$$-\frac{\hbar^2}{2m}\left[\frac{\frac{d^2}{dx^2}X}{X} + \frac{\frac{d^2}{dy^2}Y}{Y} + \frac{\frac{d^2}{dz^2}Z}{Z}\right] = E \longleftarrow$$

Remember that E is constant: In order for this system to be described by the equation, each term must be separate and constant.

We can simplify further ~~using~~ by defining

$$E_x X = -\frac{\hbar^2}{2m}\left(\frac{d^2X}{dx^2}\right)$$
$$E_y Y = -\frac{\hbar^2}{2m}\left(\frac{d^2Y}{dy^2}\right)$$
$$E_z Z = -\frac{\hbar^2}{2m}\left(\frac{d^2Z}{dz^2}\right)$$

$$-\frac{\hbar^2}{2m}\left(\frac{\frac{d^2}{dx^2}X}{X} + \frac{\frac{d^2}{dy^2}Y}{Y} + \frac{\frac{d^2}{dz^2}Z}{Z}\right) \longrightarrow \frac{E_xX}{X} + \frac{E_yY}{Y} + \frac{E_zZ}{Z} = E = E_x + E_y + E_z$$

Compare this result to $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)$ in one dimension: We see that this expression is a combination of 1-D motions in 3-D.

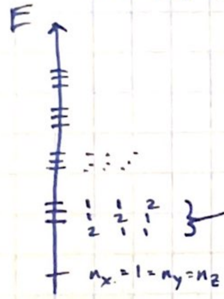
Now, we have 3 quantum numbers describing the system, for each independent motion in the system.
Note also that each X, Y, and Z as well as their corresponding energy values are quantized, similarly to the 1-D case:

$$X = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi n_x x}{a}\right) \qquad Y = \sqrt{\frac{2}{b}}\sin\left(\frac{\pi n_y x}{b}\right) \qquad Z = \sqrt{\frac{2}{c}}\sin\left(\frac{\pi n_z x}{c}\right)$$

$$E_x = \frac{h^2}{8ma^2}n_x^2 \qquad E_y = \frac{h^2}{8mb^2}n_y^2 \qquad E_z = \frac{h^2}{8mc^2}n_z^2$$

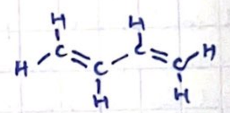
$n_x = 1, 2, 3\ldots$ $\quad n_y = 1, 2, 3\ldots$ $\quad n_z = 1, 2, 3\ldots$

Note that the normalization factor depends on the lengths of the box in that direction.



If there is more than one state corresponding to the same level of energy, that is, if $a = b$, or $b = c$, this is known as degeneracy.

Applications to chemistry: Conjugated Polyenes



Butadiene, C_4H_6

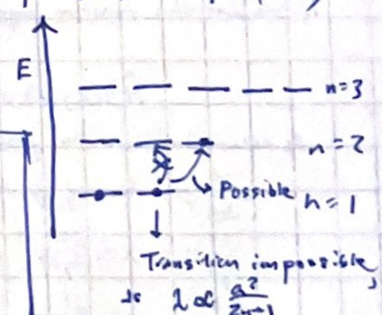
- The pi-electrons are delocalized in the structure, and are free to move along the molecule in a manner similar to e^- moving along in a 1-D box.
- The movement of electrons across the structure creates color: e^- transferring through the structure's energy can be described as:

$$\Delta E = E_{n+1} - E_n = \frac{h^2}{8ma^2}(2n+1) = h\nu = h\frac{c}{\lambda}.$$

$\therefore \lambda \propto a^2$ – More conjugation (increase in a) results in increase of λ.

where n: # of $\frac{\pi\ e^-}{2}$

Applying pauli's exclusion principle, more specifically, $\lambda \propto \frac{a^2}{2n+1}$.



as $\lambda \propto \frac{a^2}{2n+1}$

Heisenberg's Uncertainty Principle:

Suppose $\psi = b_1\phi_1 + b_2\phi_2$, in superposition

Possible measurements: $a_1 \quad a_2$ → If we measure either of these eigenvalues, the wave function collapses and exists in a pure state $\psi = \phi_1$, for example (if a_1 is measured)

→ How can we accurately measure something?
Question of precision, NOT accuracy:

$$A_{measured} = \langle A\rangle \pm \delta A \qquad (\text{like } \bar{x} \pm \sigma_{\bar{x}})$$

We know from statistics that $P(\delta A)$ is normally or gaussian distributed:

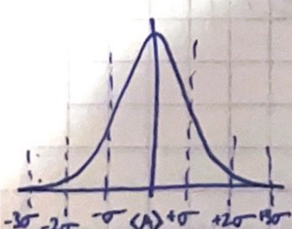
Where the gaussian is $\frac{1}{\sigma\sqrt{2\pi}}e^{-\frac{\delta A^2}{2\sigma^2}}$ in this case

We know variance is

$$\sigma^2 = \frac{\sum(A - \langle A\rangle)^2}{N} = \frac{\sum \langle A^2\rangle - \langle A\rangle^2}{N}$$

And standard deviation is

$$\sigma = \Delta A = \left|\sqrt{\langle A^2\rangle - \langle A\rangle^2}\right|$$



With this statistical background, we can apply this to quantum measurements, where

$$A = \hat{A}\psi$$

– Must know $\hat{A}$ and ψ.