

The Quantum Theory of Atoms and Molecules

Particles in boxes and applications

Dr Grant Ritchie

The free particle

What is the appropriate form of the time independent Schrödinger equation?

$V = 0$, so that TISE is:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$$

Solutions are of the form: $\psi = Ae^{ikx} + Be^{-ikx}$ **Eigenfunctions** (A, B are constants)

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

Eigenvalues

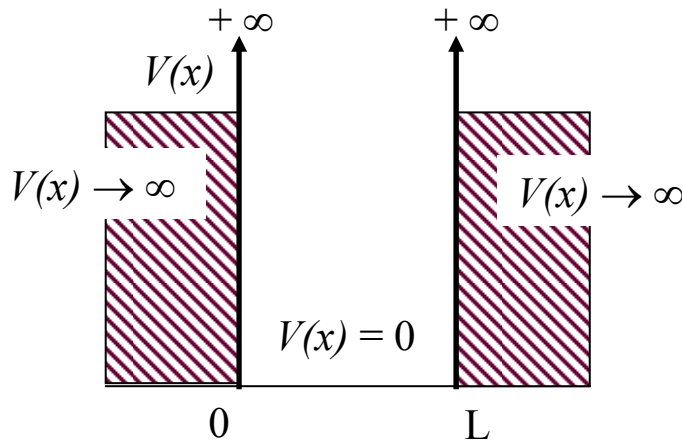
There is **no** restriction on k or allowed energies \Rightarrow **energy is continuous!**

Probability density example: Suppose that $B = 0$, then $\psi(x) = A e^{ikx}$. Where is the particle? $\psi^* \psi = (A e^{ikx})^* (A e^{ikx}) = (A^* e^{-ikx})(A e^{ikx}) = |A|^2$. This is **independent of x** , in other words, we **cannot predict where we will find the particle**.

N.B. $k = 2\pi/\lambda$ and as k is known exactly then so is p . cf. $\Delta x \Delta p_x \geq \hbar / 2$.

Particle in a 1-d box (or infinite square well!)

What are the wavefunctions (eigenfunctions) and energies (eigenstates/eigenvalues) of a particle confined in a very deep potential well?



Inside the box: $V = 0$, so that SE is:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$$

$$\psi = Ae^{ikx} + Be^{-ikx} = C \cos kx + D \sin kx$$

Outside the box: $V = \infty$, so that outside the box $\psi = 0$, and because ψ is continuous, ψ must also be 0 at the edges of the box, i.e. $\psi(0) = 0$ and $\psi(L) = 0$.

For $\psi(0) = 0$ then $C = 0$, and so $\psi(x) = D \sin(kx)$.

For $\psi(L) = 0$ then either $D = 0$ (SILLY!) or $\psi(L) = D \sin(kL) = 0$.

$\sin(n\pi) = 0$ where $n = 1, 2, 3, \dots$ and so k is now **restricted** as follows: $k = \frac{n\pi}{L}$

Quantisation of energy

Boundary conditions lead to wavefunctions (eigenfunctions) of the form $\psi(x) = D \sin kx$ with *quantised* values of k ($= n\pi/L$) and results in *quantised* values for the energy E :

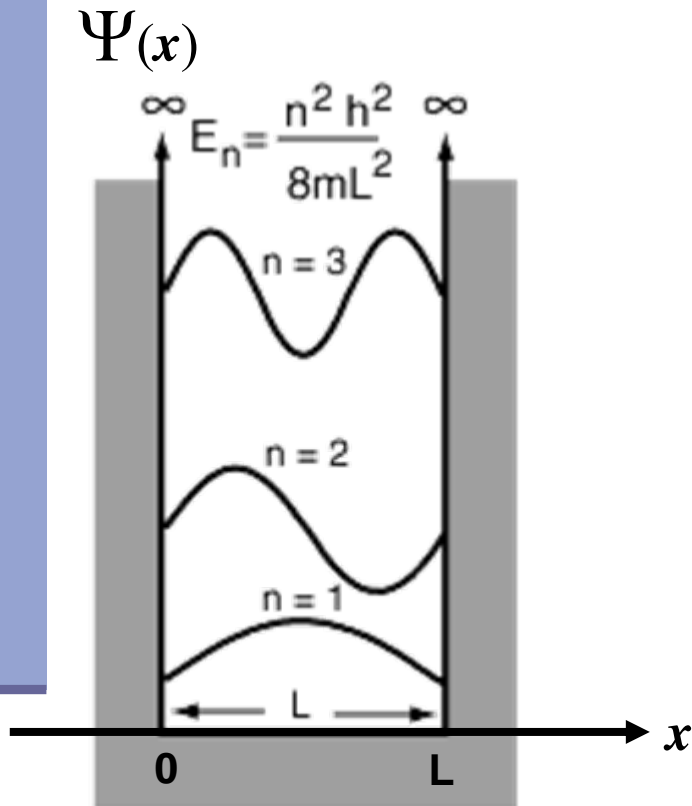
Eigenvalues:
$$E = \frac{k^2 \hbar^2}{2m} = \frac{n^2 h^2}{8mL^2} \quad n = 1, 2, 3, \dots$$

To completely specify the eigenfunctions we need to *normalise* them:

$$\int_0^L \psi^* \psi \, dx = D^2 \int_0^L \sin^2 kx \, dx = 1 \quad \Rightarrow \quad D = \sqrt{\frac{2}{L}} \quad .$$

Eigenfunctions:
$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad n = 1, 2, \dots$$

Particle in box properties



1. Increasing n indicates increasing K.E. (increasing curvature of the wavefunction).
2. Lowest energy: $E_1 = h^2/8mL^2 > 0$; **ZERO POINT ENERGY**. If $E \rightarrow 0$, then $p, \delta p \rightarrow 0$ and requires $\delta x \rightarrow \infty$ (Heisenberg)
3. Difference between adjacent energy levels:

$$\Delta E = E_{n+1} - E_n = (2n + 1) h^2/8mL^2 = (2n + 1) E_1$$
4. The more the particle is confined, i.e. L gets smaller, the greater ΔE and the K.E. – hard to compress matter!
5. If $L \rightarrow \infty$, $\Delta E \rightarrow 0$, continuous: translational energy is not quantised. **Back to classical physics!**

Consistent with De Broglie: The longest wavelength is $\lambda = 2L$ and the higher modes have wavelengths given by $\lambda = 2L/n$ ($n = 1, 2, \dots$). Therefore the De Broglie relationship yields momentum $p = \pm (nh/2L) = \pm h/\lambda$.

Orthogonality

Often we are interested in integrating products of wavefunctions. If the integral turns out to be zero then the functions, ψ_n and ψ_m are said to be *orthogonal*:

$$\int_{-\infty}^{\infty} \psi_n^*(x) \psi_m(x) dx = \frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx = 1 \quad \text{if } n = m$$
$$= 0 \quad \text{if } n \neq m$$

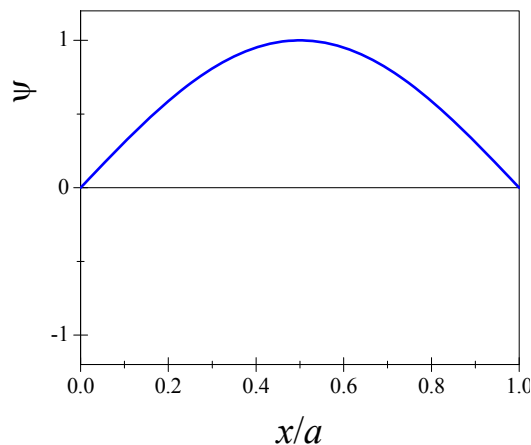
Importantly, note that the eigenfunctions for the particle in a box are orthogonal to one another.

Indeed they are said to be *orthonormal* in that each function is also normalised.

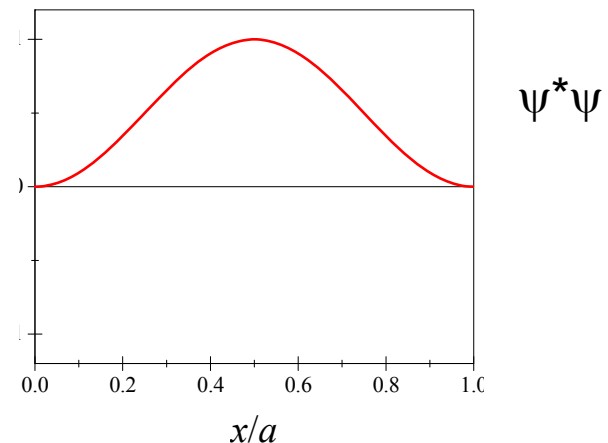
- Examples:** (i) Show pictorially that the hydrogen atom 2s and 2p_z orbitals are orthogonal;
(ii) Show that the two lowest energy wavefunctions for a particle in a box are orthogonal.

Where is the particle most likely to be?

We can calculate the most probable position of the particle from knowledge of $\psi^*\psi$.
For example, for $n = 1$



$$n = 1$$



i.e. particle is most likely to be found at the centre of the box.

This results is clearly at odds with classical expectations where each position in the box is equally likely.

However as n increases the wavefunction begins to have so many nodes that in the limit as $n \rightarrow \infty$ each position is equally probable \Rightarrow *Correspondence Principle*.

Further comparisons between classical and quantum results

Classically we expect that the probability density is **uniform i.e.** *all positions in box are equally likely*. Thus for a box of length L , the *probability density* $P(x) = \psi^* \psi = 1/L$ and so the *average values of x and x^2 are*:

$$\langle x \rangle = \int_0^L x P(x) dx = \frac{1}{L} \int_0^L x dx = \frac{L}{2}$$

$$\langle x^2 \rangle = \int_0^L x^2 P(x) dx = \frac{L^2}{3}$$

Compare with the **quantum** case where $n = 1$ i.e. $\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$

$$\langle x \rangle = \frac{2}{L} \int_0^L x \sin^2\left(\frac{\pi x}{L}\right) dx = \frac{L}{2}$$

then

$$\langle x^2 \rangle = \frac{2}{L} \int_0^L x^2 \sin^2\left(\frac{\pi x}{L}\right) dx = \frac{L^2}{3} - \frac{L^2}{2\pi^2}$$

As $n \rightarrow \infty$, find that $\langle x^2 \rangle \rightarrow$ **classical result**.

Momentum of the particle

Given the wavefunction $\psi = D \sin(kx)$, what is the particle's momentum?

Use the momentum operator.... $\hat{p}_x \psi = \frac{\hbar}{i} \frac{d}{dx} (D \sin kx) = k \frac{\hbar}{i} D \cos kx \neq \text{const.} \psi$

ψ is **not** an eigenfunction p_x (see later) but we can evaluate the *expectation value* (see last lecture).

$$\langle \hat{p}_x \rangle = \frac{\int \psi^* \hat{p}_x \psi \, dx}{\int \psi^* \psi \, dx} = \frac{\frac{\hbar}{i} D^2 \int_0^L (\sin kx) \frac{d}{dx} (\sin kx) \, dx}{D^2 \int_0^L (\sin^2 kx) \, dx} = \frac{\frac{k\hbar}{i} D^2 \int_0^L (\sin kx)(\cos kx) \, dx}{D^2 \int_0^L (\sin^2 kx) \, dx} = 0$$

$\langle p_x \rangle = 0$ – this **does not** mean that the kinetic energy is 0!

$$E = \frac{\langle \hat{p}_x^2 \rangle}{2m} \neq \frac{\langle \hat{p}_x \rangle^2}{2m}$$

Eigenfunctions of the momentum operator

Consider the following eigenvalue equation: $\hat{p}_x \psi = p \psi$

(where p is a constant)

$$\frac{\hbar}{i} \frac{d\psi}{dx} = p \psi$$

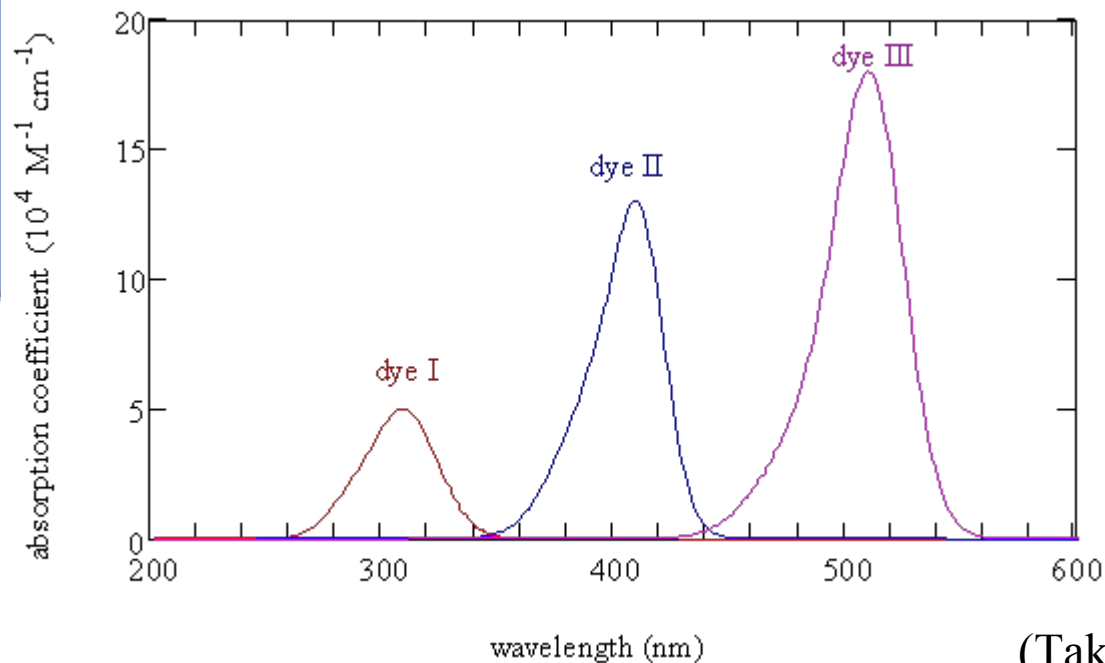
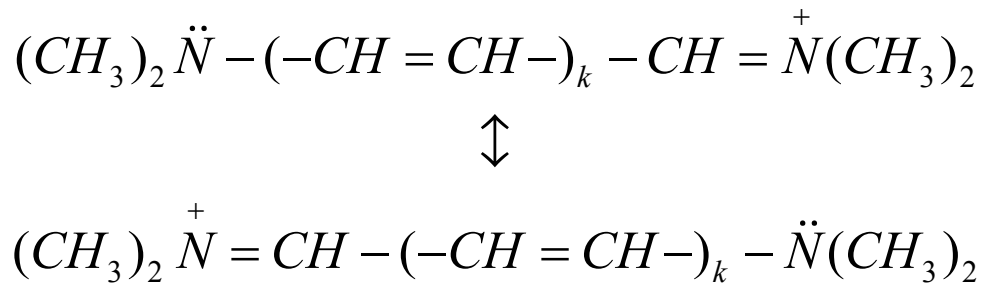
General solution: $\psi = A e^{\left(\frac{ip}{\hbar}\right)x} = A e^{ikx}$ NB. k can be positive or negative.

Thus $A e^{ikx}$ are eigenfunctions of the momentum operator with eigenvalues $p = \pm k\hbar$.

The particle in a box wavefunction $\psi = D \sin kx$ can be expressed as a linear combination of momentum eigenfunctions, i.e. $\psi = D \sin kx = D' (e^{ikx} + e^{-ikx})$.

A single measurement of the particle's momentum must give a definite result of $\pm k\hbar$. However, since $\sin kx$ contains equal amounts of $e^{\pm ikx}$, the **average value** of the momentum $\langle p_x \rangle = 0$.

An application of the particle in a box problem - the UV absorption spectrum of cyanine dyes



Dye I: $k = 1$

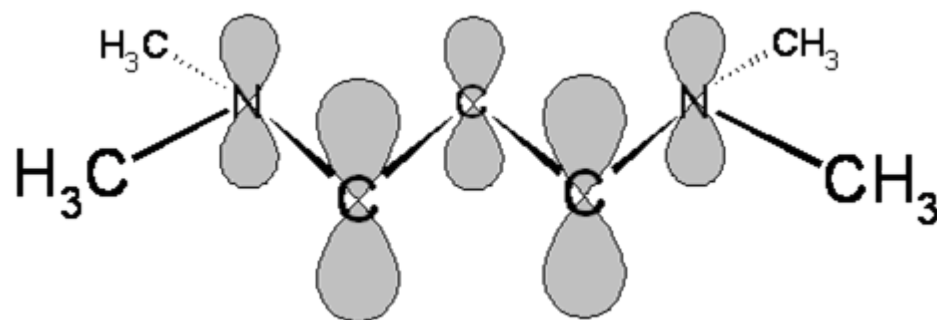
Dye II: $k = 2$

Dye III: $k = 3$

(Taken from www.jce.divched.org)

Electronic structure of cyanine dyes

Have both σ and π electrons \Rightarrow σ electrons have largest probabilities in the plane of the molecules while π electrons are most likely to be found above and below plane of molecule.

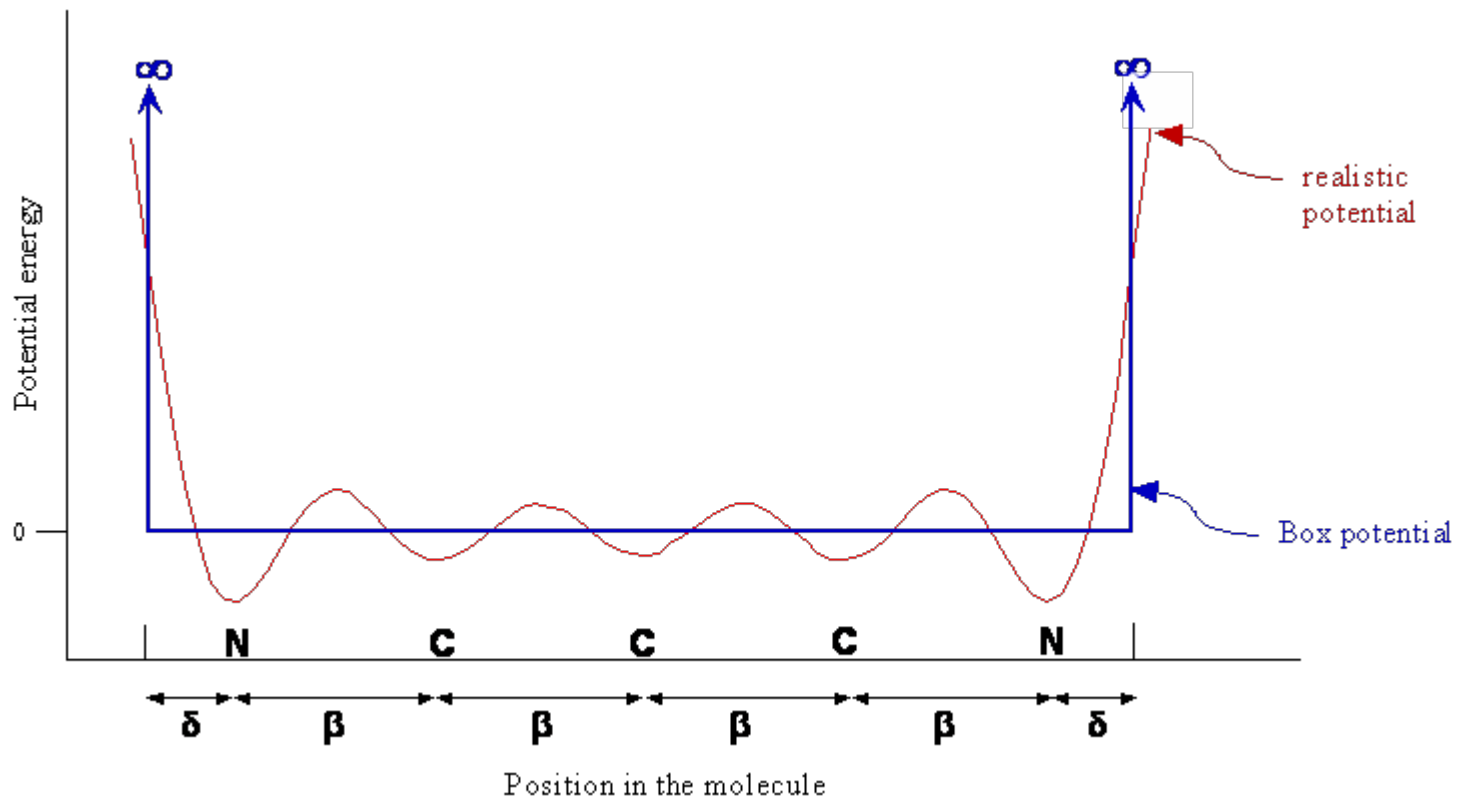


Decouple π electrons from σ framework \Rightarrow treat π electrons as being delocalised over the length of the molecule between the N atoms.

UV and visible light can then be absorbed and energy used to cause transition of π electrons from one energy level to another.

NB: Each carbon contributes one electron to the π system while the two N atoms contribute 3 electrons.

Is the particle in a box model justified for this problem?



Length of the box, $L = b\beta + 2\delta$, where b is the number of bonds.

Resonance condition

Absorption of a photon occurs when the energy of the photon ($= h\nu$) matches the *difference* in the energy between the two states involved in the transition (ΔE):

$$E_{\text{photon}} = h\nu = \Delta E = E_f - E_i = \frac{h^2}{8mL^2} (n_f^2 - n_i^2)$$

where n_i and n_f are quantum numbers for the initial and final states respectively.

Which values of n_i and n_f have to be used? Depends on the number of π electrons and the **Pauli Exclusion Principle** which allows a maximum of 2 electrons per orbital. Electron pairs must have *opposite* spins.

Thus, for Dye I, $k=1$ and we have a total of $(3+3) = 6$ π electrons that will pair in levels $n = 1, 2$ and 3 . Therefore the *highest occupied molecular orbital* (HOMO) has $n = 3$, while the *lowest unoccupied molecular orbital* (LUMO) has $n = 4$.

Hence lowest energy transition involves promotion of a π electron from $n = 3 \rightarrow n = 4$.

Example: If the length of the box L is 8.5\AA , what is the peak absorption wavelength for dye I?

Are all transitions possible? – Selection rules

Must always obey Pauli exclusion principle.

Transitions are *electric dipole transitions* – the oscillating electric field component of the radiation interacts with electrical charges, i.e. the positive nuclei and negative electrons that comprise an atom or molecule, and cause the transitions observed in uv-visible absorption and emission spectroscopies.

The interaction energy, U , between a system of charged particles and an electric field, E , is given by:

$$U = -\mu \cdot E$$

The dipole moment is defined for a collection of charges by: $\mu = \sum_i q_i r_i$

where r_i is the position vector of charged particle i . (See electrostatics lectures in Michaelmas term).

The transition dipole moment

In order to obtain the strength of interaction that causes a transition between two states, the *transition dipole moment* is used rather than the dipole moment.

For a transition between an initial state, ψ_i , to a final state ψ_f , the *transition dipole moment integral* is.

$$\mu_{fi} = \int \psi_f^* \hat{\mu} \psi_i d\tau$$

Just like the probability density is given by $\psi^* \psi$, so the probability for a transition (as measured by the absorption coefficient) is proportional to $\mu_{fi}^* \mu_{fi}$.

If $\mu_{fi} = 0$ then the interaction energy is **zero** and no transition occurs – the transition is said to be *electric dipole forbidden*. Conversely, **if μ_{fi} is large**, then the transition probability and absorption coefficient are **large**.

The intensity of the transition is therefore proportional to.

$$\left| \int \psi_k^* \hat{\mu} \psi_j d\tau \right|^2$$

Transition dipole moment integral for particle in a box

Need to consider the transition dipole moment integral for one electron. The dipole moment operator for an electron in one dimension is $-ex$ and so

$$\mu_{fi} = -e \int_0^L \psi_f^*(x) x \psi_i(x) dx$$

Now evaluate μ_{fi} for various wavefunctions to see which are allowed ($\mu_{fi} \neq 0$) and which are forbidden ($\mu_{fi} = 0$).

Example: Is $n = 1 \rightarrow n = 2$ an allowed transition?

(If you have time!) consider the generalised transition $n_i \rightarrow n_f$:

$$\begin{aligned} \mu_{fi} &= -\frac{2e}{L} \int_0^L \sin\left(\frac{n_f \pi x}{L}\right) x \sin\left(\frac{n_i \pi x}{L}\right) dx \\ &= -\frac{e}{L} \int_0^L x \left(\cos\left(\frac{(n_f - n_i) \pi x}{L}\right) - \cos\left(\frac{(n_f + n_i) \pi x}{L}\right) \right) dx \end{aligned}$$

If we then define $\Delta n = n_f - n_i$ and $n_{tot} = n_f + n_i$ then the above integral becomes:

$$\mu_{fi} = -\frac{e}{L} \left(\frac{L}{\pi}\right)^2 \left\{ \frac{1}{\Delta n^2} (\cos(\Delta n \pi) - 1) - \frac{1}{n_{tot}^2} (\cos(n_{tot} \pi) - 1) + \frac{1}{\Delta n} \sin(\Delta n \pi) - \frac{1}{n_{tot}} \sin(n_{tot} \pi) \right\}$$

Looks bad!!!!!!

However, if Δn is even then n_{tot} is even and overall $\mu_{fi} = 0$ – **Forbidden!**

Δn is odd is allowed

If Δn is odd then n_{tot} is also odd and overall $\mu_{fi} \neq 0$ and is given by

$$\mu_{fi} = -\frac{2eL}{\pi^2} \left(\frac{1}{n_{tot}^2} - \frac{1}{\Delta n^2} \right) = \frac{8eL}{\pi^2} \left(\frac{n_i n_f}{(n_f^2 - n_i^2)^2} \right)$$

The general selection rule is Δn is *odd*.

However, we only really see a single peak in the absorption spectrum for each dye because other allowed transitions have very much smaller transition moments.

Example: For dye 1, compare the values of the transition dipole moment integrals for the two transitions $n = 3 \rightarrow n = 4$ and $n = 3 \rightarrow n = 6$.

*Also note that longer molecules have larger absorption coefficients because μ_{fi} increases with the length of the molecule (see uv spectra earlier in notes).

Using symmetry to evaluate integrals

An alternative to evaluating integrals is to use **symmetry**.....

Firstly, consider the **parity** of the particle in a box wavefunctions by shifting the positions of the potential barriers from 0 and L to $-L/2$ to $L/2$.

* For symmetric potentials $V(x) = V(-x)$ the ψ has a definite *parity*, i.e. $\psi_n(x) = \pm\psi_n(-x)$

$$V(x) = 0 \text{ for } -L/2 \leq x \leq L/2$$

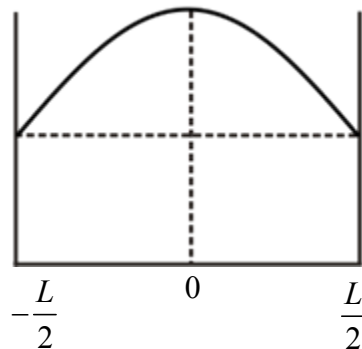
$$V(x) = \infty \text{ otherwise}$$

$$x \rightarrow x' = x - L/2$$

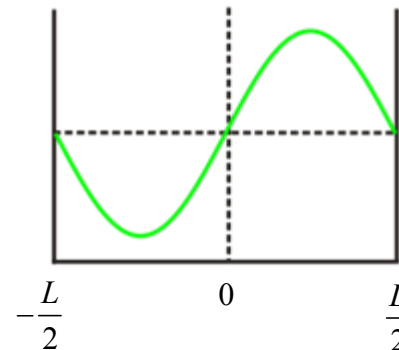
$$\psi_n(x) = \sqrt{\frac{2}{L}} \cos\left(\frac{n\pi x}{L}\right) = +\psi_n(-x) ; \text{ odd } n - \text{ even parity}$$

$$= \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) = -\psi_n(-x) ; \text{ even } n - \text{ odd parity}$$

n = 1



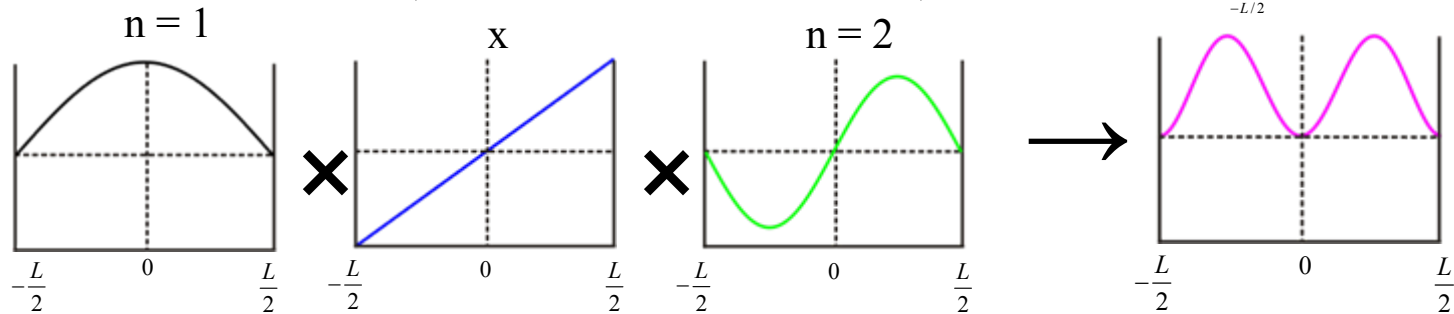
n = 2



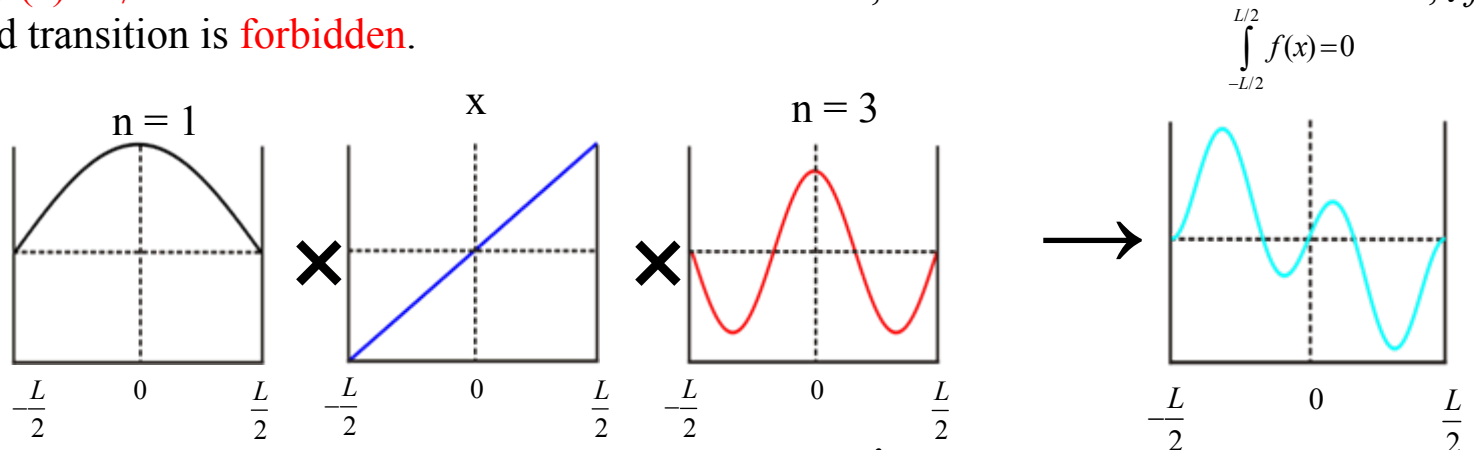
Symmetry II

For transition $n=1 \rightarrow n=2$ the transition dipole moment integral is:

$$\mu_{21} = -\frac{e}{L} \int_{-L/2}^{L/2} \sin\left(\frac{\pi x}{L}\right) x \cos\left(\frac{\pi x}{2L}\right) dx = -\frac{e}{L} \int_{-L/2}^{L/2} f(x) dx$$

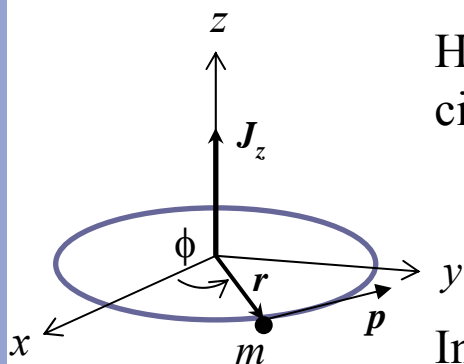


Clearly $\int f(x) dx \neq 0$ and the transition is allowed. In contrast, for the transition $n=1 \rightarrow n=3$, $\int f(x) dx = 0$ and transition is forbidden.



Conclusion: if integrand is odd / antisymmetric / *ungerade* then $\int f(x) dx = 0$ and transition is forbidden.

Particles in “round” boxes (or on a ring!)



Hamiltonian for a particle of mass m constrained to move in a circular path of radius r in the xy -plane ($V = 0$ everywhere) is:

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

In polar co-ordinates $x = r \cos \phi$, $y = r \sin \phi$ and the Hamiltonian becomes:

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right)$$

But radius of ring is fixed and so derivatives in r are 0 and Hamiltonian simplifies to:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} = -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2}$$

where $I = mr^2$ is the **moment of inertia** of the mass m on the ring of radius r .

SE is of the (familiar) form:

$$\frac{d^2 \psi}{dx^2} = -\frac{2IE}{\hbar^2} \psi = -m_l^2 \psi$$

N.B. m_l has nothing to do with mass m , it is the **angular momentum quantum number**.

$$\psi_{m_l}(\phi) = A e^{im_l \phi} \quad \text{with} \quad m_l = \pm \sqrt{\frac{2IE}{\hbar^2}}$$

Particle on a ring solutions

Cyclic boundary conditions:

$$\psi_{m_l}(\phi) = \psi_{m_l}(\phi + 2\pi)$$

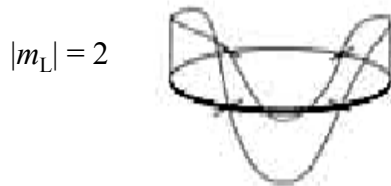
ψ has to be single-valued!

$$Ae^{im_l\phi} = Ae^{im_l(\phi+2\pi)} = Ae^{im_l\phi} e^{im_l 2\pi}$$

$$\text{i.e. } e^{im_l 2\pi} = (-1)^{2m_l} = 1$$

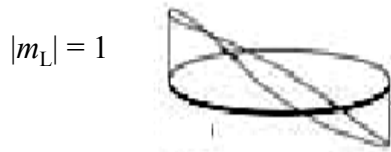
Therefore m_l can only take the values $0, \pm 1, \pm 2, \pm 3, \dots$

Again, boundary conditions lead to wavefunctions (eigenfunctions) with a restricted range of values for m_l (eigenfunctions) and results in quantised values for the energy E :



Eigenvalues:

$$E = \frac{m_l^2 \hbar^2}{2I} \quad m_l = 0, \pm 1, \pm 2, \pm 3, \dots$$



Normalisation of wavefunctions:

$$\int_0^{2\pi} \psi^* \psi \, d\phi = A^* A \int_0^{2\pi} e^{-im_l\phi} e^{im_l\phi} \, d\phi = A^* A \int_0^{2\pi} d\phi \Rightarrow A = \sqrt{\frac{1}{2\pi}}$$



Eigenfunctions

$$\psi_{m_l}(\phi) = \sqrt{\frac{1}{2\pi}} e^{im_l\phi} \quad m_l = 0, \pm 1, \pm 2, \pm 3, \dots$$

:

Properties of the solutions

1. Energy gaps decrease as moment of inertia increases. $\Delta E \rightarrow 0$ as $I \rightarrow \infty$ and so recover classical mechanics.
2. Zero point energy is 0 (when $m_l = 0$). **Does this contravene Heisenberg?**

Probability density: $\psi^* \psi = (1/2\pi)$ i.e. **independent of position on ring.**

Position on ring is completely uncertain and so Heisenberg allows us to know precisely the angular momentum \Rightarrow **zero point energy can be zero!**

- 3 Two wavefunctions with different quantum numbers can have the same energy. For example wavefunctions with $m_l = 1$ and -1 have the same energy, $\hbar^2/2I$. This is known as **degeneracy**.

Example: Let us treat the π -electrons in benzene as particles of mass m moving around the circumference of a flat disc of radius r . How well does this simple model reproduce the actual behaviour of the π -electrons in benzene?

Particle in a 3-d box

- In 3D the particle momentum is a vector with 3 components, p_x , p_y and p_z . The kinetic energy operator is therefore

$$\hat{T} = \frac{1}{2m} (\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

- Therefore the SE equation becomes

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

And is often abbreviated to

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + \hat{V}(x, y, z) \psi = E \psi$$

Kinetic energy	Potential energy	Total energy
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∇^2 is the Laplacian operator, also known as “del squared”.

Separation of variables

Once again let's assume that the potential energy inside the the box is 0.

Now we assume that the wavefunction is separable: $\psi(x, y, z) = X(x)Y(y)Z(z)$

and so SE becomes:

$$-\frac{\hbar^2}{2m} \left(YZ \frac{dX^2}{dx^2} + XZ \frac{dY^2}{dy^2} + XY \frac{dZ^2}{dz^2} \right) = EXYZ$$

Now divide by XYZ :

$$-\frac{\hbar^2}{2m} \left(\frac{1}{X} \frac{dX^2}{dx^2} + \frac{1}{Y} \frac{dY^2}{dy^2} + \frac{1}{Z} \frac{dZ^2}{dz^2} \right) = E$$

First term only depends on x , and must be constant because the RHS does not contain x . (Similarly for the other terms). Now we have three 1d equations to solve....

$$-\frac{\hbar^2}{2m} \frac{1}{X} \frac{dX^2}{dx^2} = E_x \quad \Rightarrow \quad -\frac{\hbar^2}{2m} \frac{dX^2}{dx^2} = E_x X \quad \text{where} \quad E_x + E_y + E_z = E$$

$$-\frac{\hbar^2}{2m} \frac{1}{Y} \frac{dY^2}{dy^2} = E_y \quad \Rightarrow \quad -\frac{\hbar^2}{2m} \frac{dY^2}{dy^2} = E_y Y$$

$$-\frac{\hbar^2}{2m} \frac{1}{Z} \frac{dZ^2}{dz^2} = E_z \quad \Rightarrow \quad -\frac{\hbar^2}{2m} \frac{dZ^2}{dz^2} = E_z Z$$

The interpretation of E_x is the component of kinetic energy from motion in x direction etc..

Eigenfunctions, -values and degeneracy in a 3-d box

Each of the 3 separated equations is a 1d equation for a particle in a box, whose solutions are known. Inserting appropriate boundary conditions (e.g. $\psi = 0$ when $x = 0$ and L_x) yields:

$$\psi(x, y, z) = N \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \quad n_x, n_y, n_z = 1, 2, \dots \quad \text{Eigenfunctions}$$

$$E(n_x, n_y, n_z) = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \quad n_x, n_y, n_z = 1, 2, 3, \dots \quad \text{Eigenvalues}$$

For the case of a cubic box, $L_x = L_y = L_z = L$ and so the eigenvalues are:

$$E(n_x, n_y, n_z) = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z = 1, 2, 3, \dots$$

n_x	n_y	n_z
1	1	1
2	1	1
1	2	1
1	1	2

← 1 level

} 3 levels

Degeneracy – *different* wavefunctions which the *same* energy.

Reflects symmetry of the box.