# Quantum Chemistry

Lecture 1

Postulates of Quantum Mechanics
The Schrödinger Equation
The Particle in a Box
Uncertainty principle
Applications

**NC State** University

**Postulate 1. Any state of a system of N particles can be described by a wave function $\Psi$.**

$$\Psi = \Psi(1,2,3, \ldots N, t)$$

**Corollary 1.1: the probability density of the particles in the system is defined as $\Psi^*\Psi$.** The wave function, $\Psi$, must be continuous and differentiable. The function must single valued. Finally, the square of the wave function, defined as $\Psi^*\Psi$, must integrable. These mathematical requirements are needed to ensure that the wave function is smooth and lacks discontinuities that would be physical unreasonable descriptions of the particle/waves in the system. The idea that the probability density must integrable arises since the probability is calculated by

$$P_{ab} = \int_a^b \Psi^*\Psi d\tau$$

where the differential volume element, $d\tau$, is relevant to the space being considered.

**Corollary 1.2:** A meaningful probability in quantum mechanics can only be calculated if the wave function is properly normalized. The normalization condition states that the probability of binding the particle in all of the relevant space is equal 1.

$$\int_{-\infty}^{\infty} \Psi^* \Psi d\tau = 1$$

The limits of the integral need to be set according to the system so that the encompass all of the space that the particle/wave may occupy. We will show a practical method to normalize a wave function so that this condition can always be met.

**Postulate 2. Every observable property of a system has a corresponding linear Hermitian operator.** Since wave functions can be complex and physical properties are calculated by an operator equation, it is important that the operator always give a real eigenvalue. The value of the energy, momentum etc. cannot be complex. The Hermitian property of the operator guarantees that the observable will be real.

**Postulate 3.** If the operator $\hat{\alpha}$ corresponds to an observable for a set of identical systems in state and $\psi$ is an eigenfunction of $\hat{\alpha}$ with eigenvalue *a*, such that,

$$\hat{\alpha}\psi = a\psi$$

then, a series of measurements on different members of the set always leads to the value *a*.

**Postulate 4.** If the operator $\hat{\beta}$ corresponds to an observable for a set of identical systems in state and $\psi_i$ is an not eigenfunction of $\hat{\beta}$ then the average of a series of measurements on different members of the set is given by

$$\langle \beta \rangle = \frac{\langle \psi_i | \hat{\beta} | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle}$$

This quantity is the average value of $\beta$, and it is also known as the expectation value.

**Postulate 5.** The state function $\psi(t)$ evolves with time as

$$H\psi(t) = i\hbar \frac{\partial}{\partial t} \psi(t)$$

The time dependent wave function compatible with this definition is:

$$\psi(t) = \psi e^{-iEt/\hbar}$$

where the stationary wave function, $\psi$, is a solution of the equation

$$H\psi = E\psi$$

# Definition of Commutator

The quantum mechanical momentum operator can be derived from the energy operator. Since

$$\frac{p^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

We can conclude that

$$p = -i\hbar\frac{\partial}{\partial x}$$

**Postulate 6:** the eigenvalues of two operators will be simultaneously measurable to any accuracy if those operators commute. We define the commutator as:

$$[a, b] = ab - ba$$

# Definition of a test function

In order to determine whether two operators commute we usually need to operate on a test function, which is an eigenfunction of the operators. For example, the wave function,

$$\psi(x) = e^{ikx}$$

$$pe^{ikx} = -i\hbar\frac{\partial}{\partial x}e^{ikx} = \hbar k$$

is an eigenfunction of the momentum. We can see this since

There is also a test function for the time-dependent operator introduced in posulate 5,

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

such that

$$He^{i\omega t} = i\hbar\frac{\partial}{\partial t}e^{-i\omega t} = \hbar\omega$$

# H and p commute

We now ask whether the energy and momentum are simultaneously measurable. If the operators commute, then we can say that energy and momentum can be measured simultaneously to arbitrary accuracy (i.e. to the best possible accuracy under experimental conditions).

$$[H,p]\psi(x) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x) - \left(-i\hbar\frac{\partial}{\partial x}\right)\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\psi(x)$$

If we factor out the constants we find that

$$\frac{i\hbar^3}{2m}\frac{\partial^3}{\partial x^3}\psi(x) - \left(\frac{i\hbar^3}{2m}\frac{\partial^3}{\partial x^3}\right)\psi(x) = 0$$

From this reasoning we see that the momentum and energy are simultaneously measurable in a quantum mechanical system.

# p and x do not commute

Now we consider momentum, p, and position, x. The commutator is,

$$[p,x]e^{-ikx} = \left(-i\hbar\frac{\partial}{\partial x}\right)xe^{ikx} - x\left(-i\hbar\frac{\partial}{\partial x}\right)e^{ikx}$$

In this case we see that we must apply the product rule to the first term,

$$\left(-i\hbar\frac{\partial}{\partial x}\right)xe^{ikx} = -i\hbar e^{ikx} - \hbar kxe^{ikx}$$

The second term is

$$-x\left(-i\hbar\frac{\partial}{\partial x}\right)e^{ikx} = \hbar kxe^{ikx}$$

Two of the terms cancel and we have

$$[p,x] = -i\hbar$$

# E and t do not commute

A similar relationship holds for energy and time. To see this we define the time-dependent energy Hamiltonian as using the equation

$$-i\hbar\frac{\partial}{\partial t}\Psi(t) = E\Psi(t)$$

One solution to this equation is

$$\Psi(t) = e^{iEt/\hbar}$$

The mathematical solution of the time-energy commutator is entirely analogous to the position-momentum commutator.

$$[E,t]e^{\frac{iEt}{\hbar}} = \left(-i\hbar\frac{\partial}{\partial t}\right)te^{iEt/\hbar} - t\left(-i\hbar\frac{\partial}{\partial t}\right)e^{iEt/\hbar}$$

Once again two of the terms cancel and we have

$$[E,t] = -i\hbar$$

# Significance of commutator for [p,x] and [E,t]

The momentum and position do not commute. This is also a statement of the Uncertainty Principle. The position and momentum of particle are not simultaneously measurable with arbitrary accuracy. Instead, there is a limitation on how accurately we can measure both the position and momentum simultaneously.

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

A similar comment holds for energy and time. We can see the Precise (mathematical) analogy in the form of the commutators for these two quantities. They both have the same form.

$$\Delta t \Delta E \geq \frac{\hbar}{2}$$

# Planck-Einstein definition of a photon

A photon is a particle of electromagnetic radiation. It is also called a “wave packet”. The energy of a photon is:

$$\mathbf{E = h\nu}$$

We can also express this as:

$$\mathbf{E = hc/\lambda}$$

# Wave equation implies particle

Energy:

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

Momentum:

$$p = \hbar k = h/\lambda$$

The only exception is a photon since it has no rest mass.

# Photon energy-momentum relation

Energy:

$$E = pc = hc/\lambda = h\nu$$

Momentum:

$$p = h/\lambda$$

The DeBroglie relation works for all particles including the photon (with zero mass).

# The Schrödinger equation for a free particle

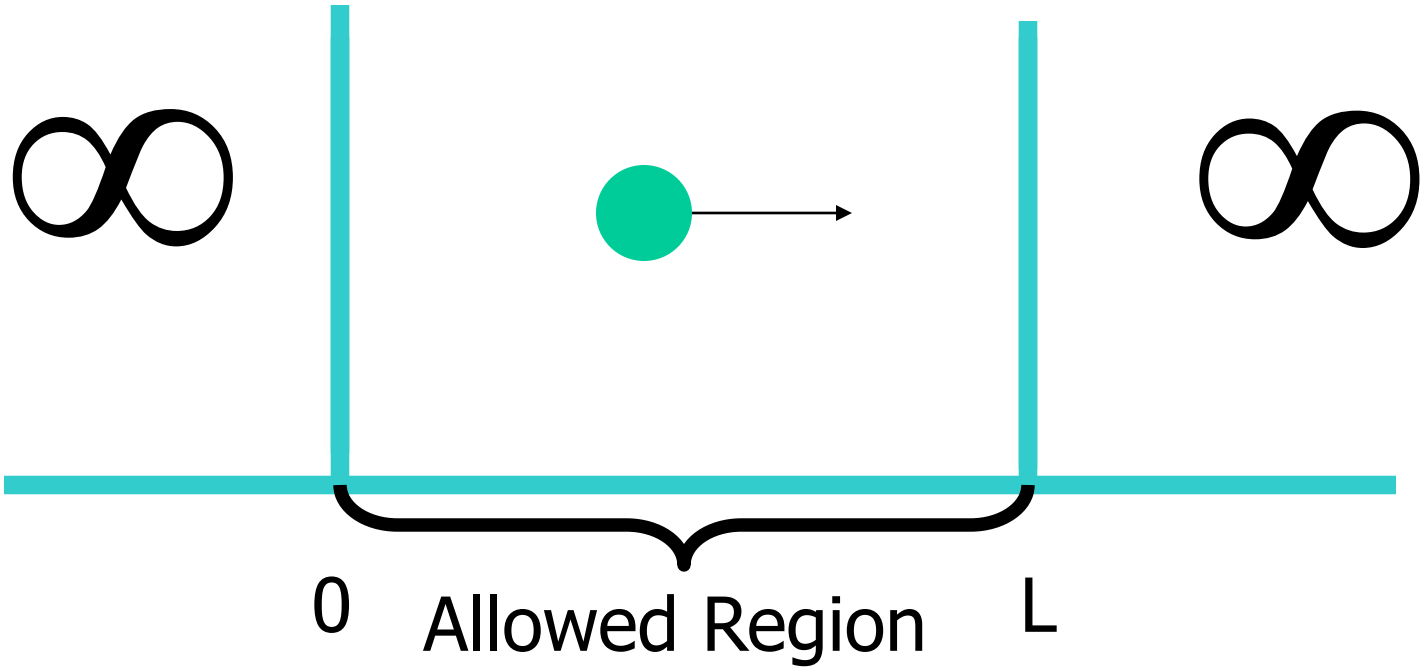
$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi = E\Psi$$

The solutions are:

$$\Psi = Ce^{ikx} + De^{-ikx}$$

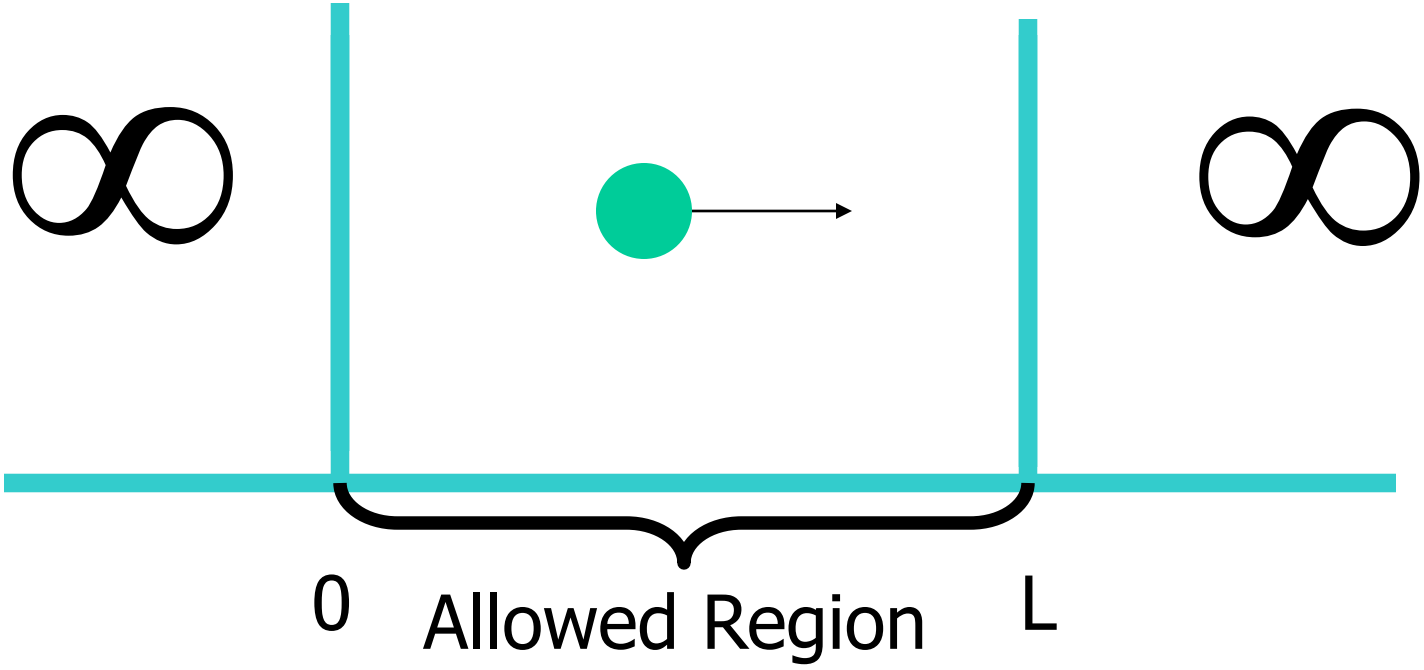
# The particle in a box problem

Imagine that a particle is confined to a region of space. The only motion possible is translation. The particle has only kinetic energy. While this problem seems artificial at first glance it works very well to describe translational motion in quantum mechanics.



# The solution to the Schrödinger equation with boundary conditions

Suppose a particle is confined to a space of length L. On either side there is a potential that is infinitely large. The particle has zero probability of being found at the boundary or outside the boundary.



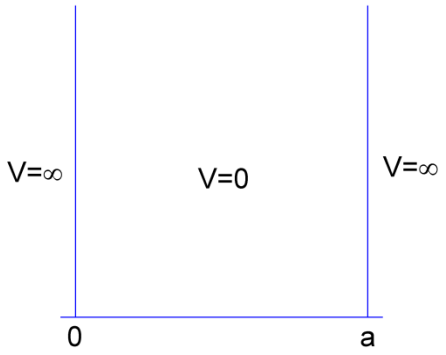
# The boundary conditions determine the values for the constants A and B

$$C = -D = \frac{1}{2i} \qquad \Psi = sin(kx)$$

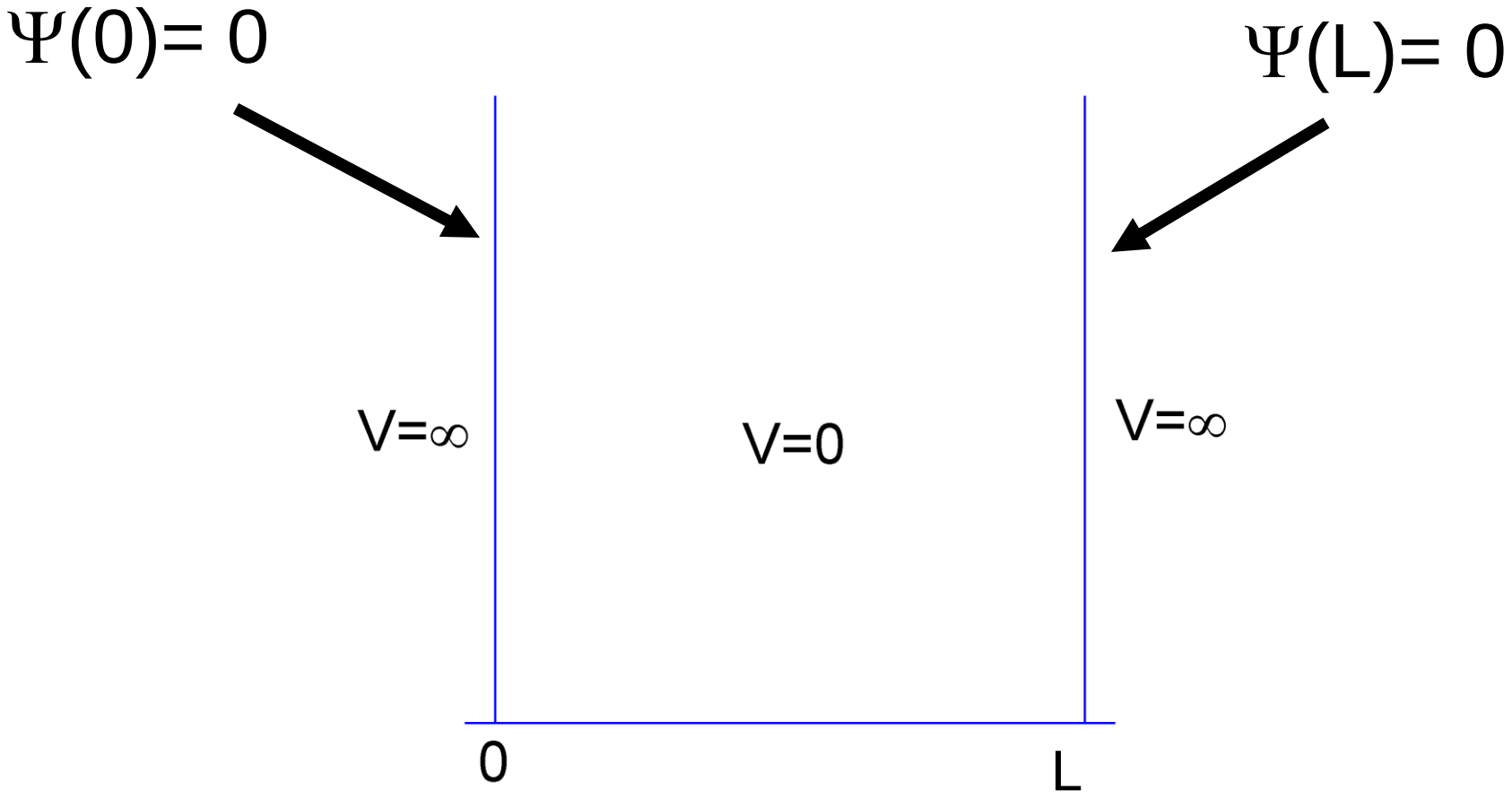
sin will vanish at 0 since x = 0 and sin 0 = 0.
sin will vanish at a if kL = nπ.
Therefore, k = nπ/L.

$$\Psi = \sin\left(\frac{n\pi x}{L}\right)$$

Not Normalized !



# The particle in a box has boundary conditions



# The solution to the Schrödinger equation with boundary conditions

The boundary condition is that the wave function will be zero at x = 0 and at x = L.

$$\Psi(0) = A\sin(k0) + B\cos(k0) = 0$$

From this condition we see that B must be zero.
This condition does not specify A or k.
The second condition is:

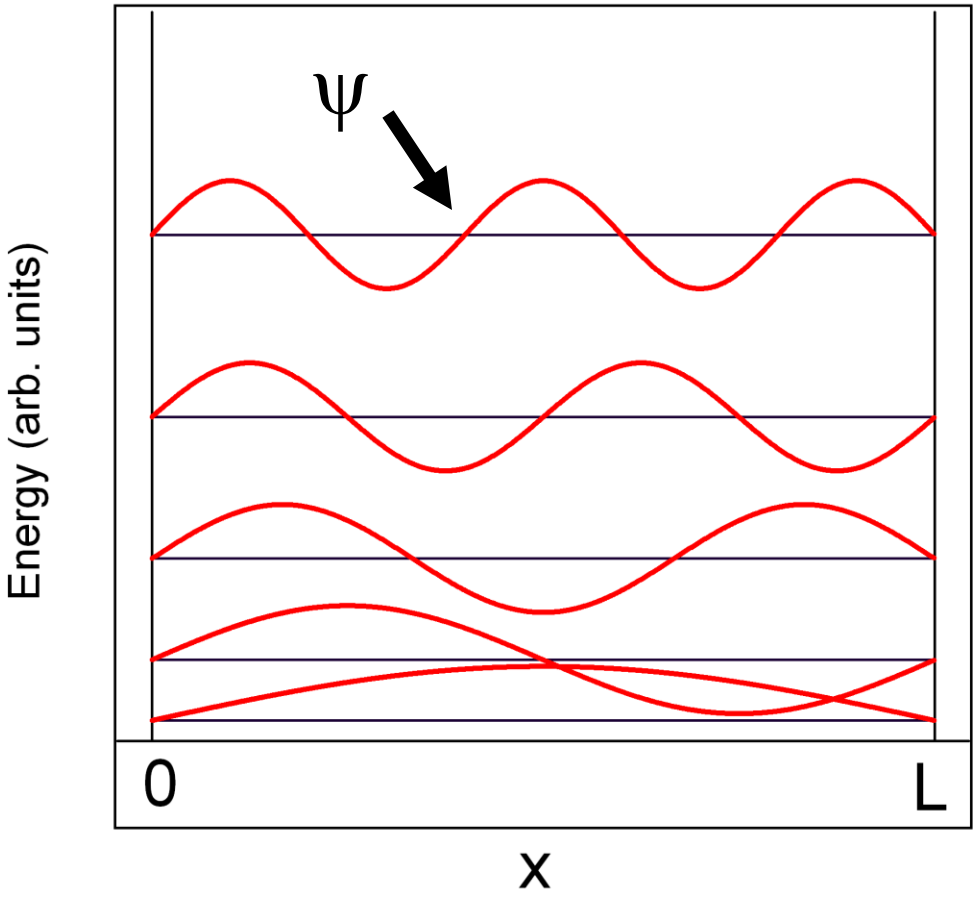
$$\Psi(L) = A\sin(kL) = 0 \quad \text{or} \quad kL = \arcsin(0)$$

From this condition we see that $kL = n\pi$. The conditions so far do not say anything about A. Thus, the solution for the bound state is:

$$\Psi_n(x) = A\sin(n\pi x/L)$$

Note that n is a quantum number!

# The solutions to the particle in a box

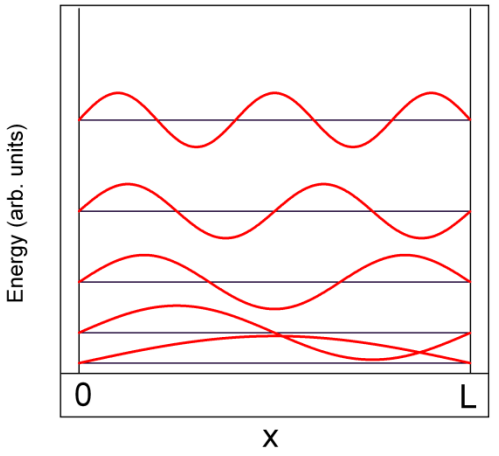



$$E = \frac{\hbar^2 k^2}{2m}$$

$$= \frac{\hbar^2 \left(\frac{n\pi}{L}\right)^2}{2m}$$

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

# The appearance of the wave functions




Note that the wave functions have nodes (i.e. the locations where they cross zero). The number of nodes is n-1 where n is the quantum number for the wave function. The appearance of nodes is a general feature of solutions of the wave equation in bound states. By bound states we mean states that are in a potential such as the particle trapped in a box with infinite potential walls. We will see nodes in the vibrational and rotational wave functions and in the solutions to the hydrogen atom (and all atoms). Note that the wave functions are orthogonal to one another. This means that the integrated product of any two of these functions is zero.

# The probability interpretation

The wave function is related to the probability for finding a particle in a given region of space. The relationship is given by:

$$P = \int \Psi^2 dV$$

If we integrate the square of the wave function over a given volume we find the probability that the particle is in that volume. In order for this to be true the integral over all space must be one.

$$1 = \int_{all\ space} \Psi^2 dV$$

If this equation holds then we say that the wave function is normalized.

# The normalized bound state wave function

For the wave function we have been considering, all space is from 0 to L. So the normalization constant A can be determined from the integral:

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

The solution to the integral is available on the downloadable MAPLE worksheet. The solution is just L/2. Thus, we have:

$$1 = A^2 \frac{L}{2}\ ,\ A^2 = \frac{2}{L}\ ,\ A = \sqrt{\frac{2}{L}}$$

As you can see the so-called normalization constant has been determined.

# The probability of finding the particle in a given region of space

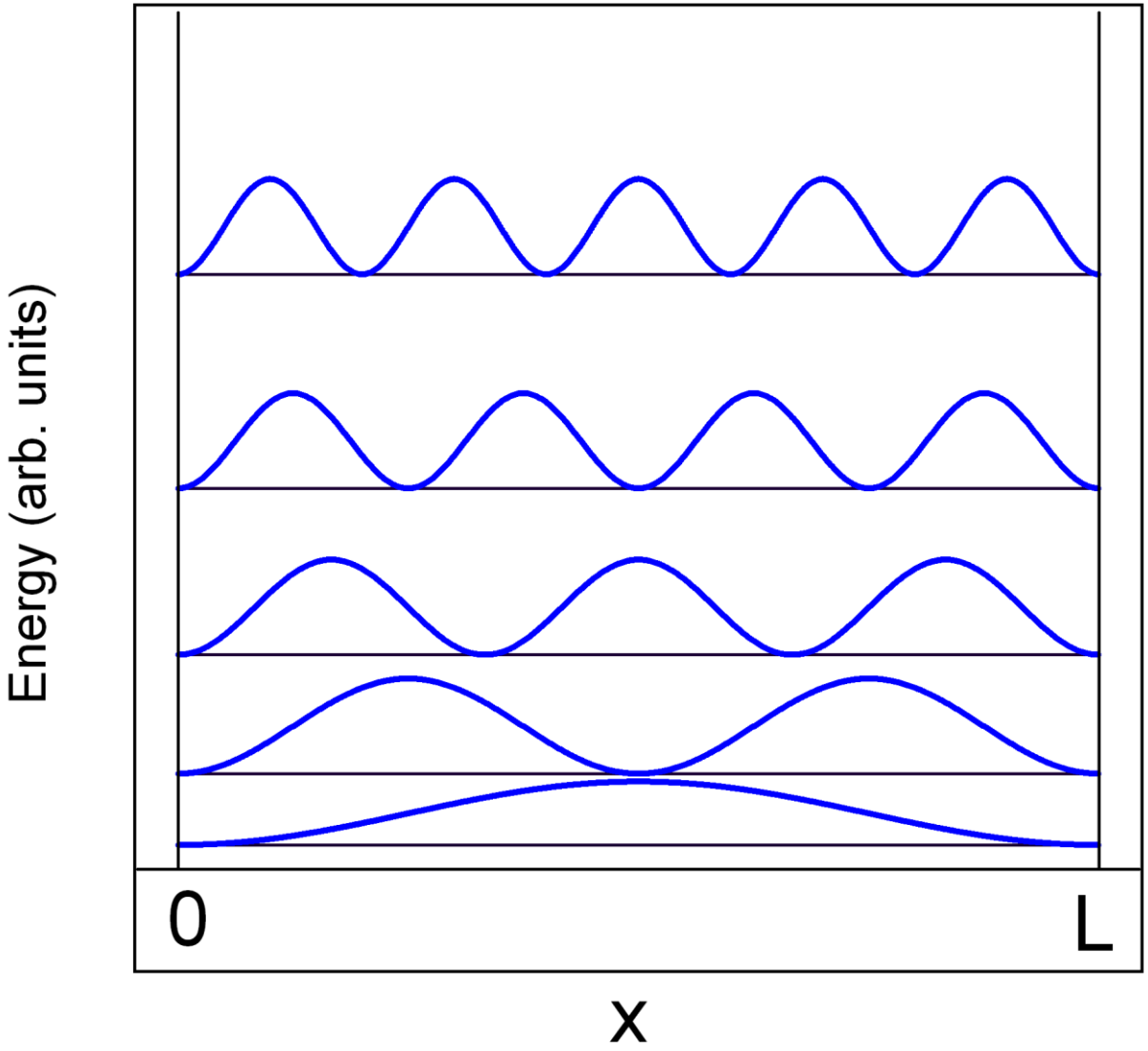
Using the normalized wave function

$$\Psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

one can calculate the probability of finding the particle in any region of space. Since the wave function is normalized, the probability P is a number between 0 and 1. For example: What is the probability that the particle is between 0.2L and 0.4L. This is found by integrating over this region using the normalized wave function (see MAPLE worksheet).

$$P = \int_{0.2L}^{0.4L} \Psi(x)^2 dx = \frac{2}{L} \int_{0.2L}^{0.4L} \sin\left(\frac{n\pi x}{L}\right)^2 dx \approx 0.25$$

# The appearance of the probability $\Psi^2$



# The uncertainty principle

When we measure the properties of very small particles, we cannot help but affect them. The very act of measuring causes a change in the particle's properties. Therefore, the description of the the measurement is a probability rather than a fixed value. We have seen the Born interpretation of the square of the wavefunction as a probability density. The consequence of this is that certain variables are linked By the uncertainty that is inherent in the measurement. Position and momentum are two such conjugate variables. Note that the units of position is the reciprocal of the momentum (if we factor out Planck's constant).

x has units of meter, k has units of meter$^{-1}$

Momentum is $p = \hbar k$.

t has units of time, $\nu$ has units of time $^{-1}$

Energy is $E = \hbar\omega$.

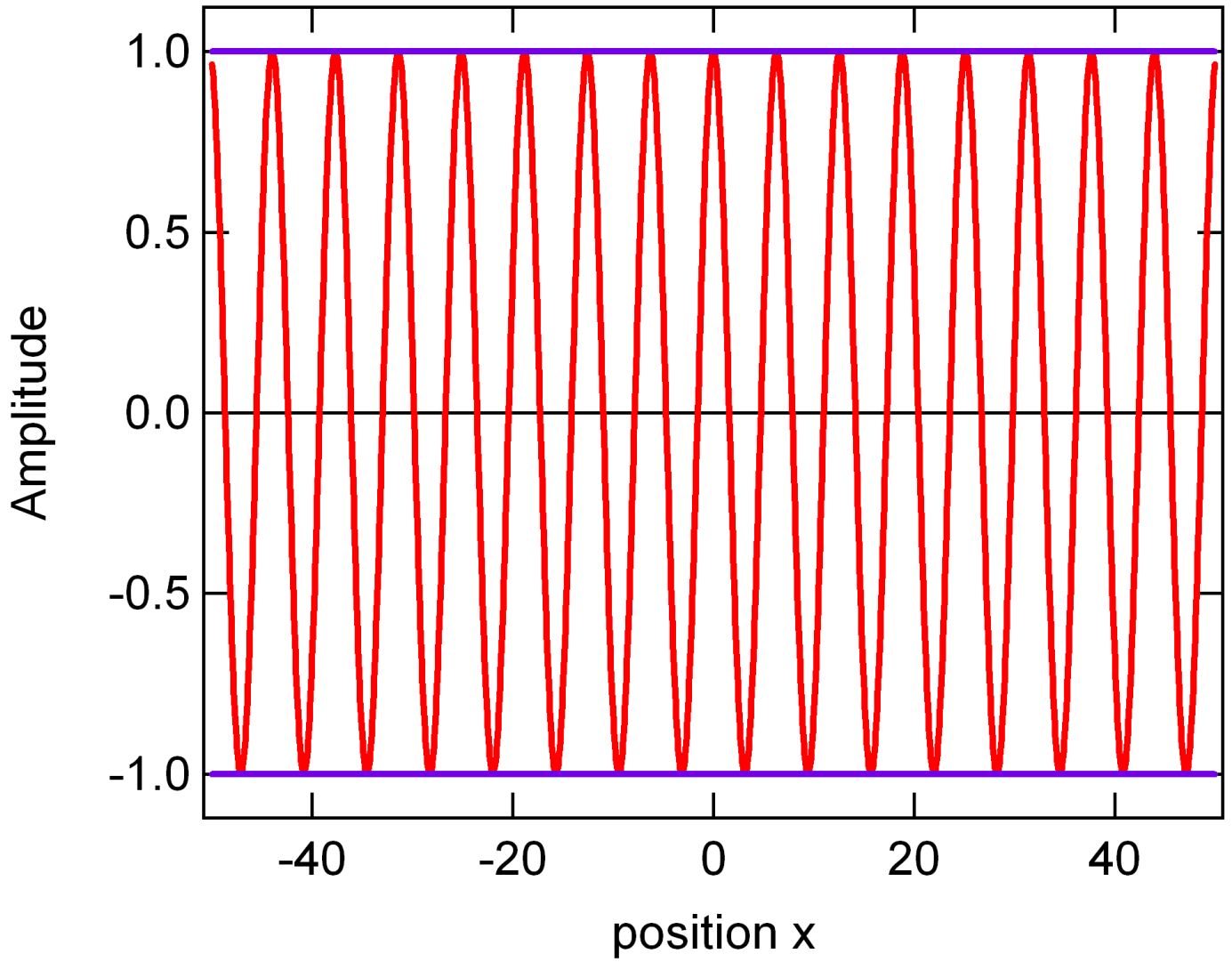
# Where is the particle in the box?

Since we are using a probability function we do not really know exactly where the particle is. We know that the highest probability occurs for the position L/2. We can guess that this is the average position in the box. However, the more precisely we specify the location of the particle the less information we have about how fast the particle is moving. This is a statement of the famous Uncertainty Principle.

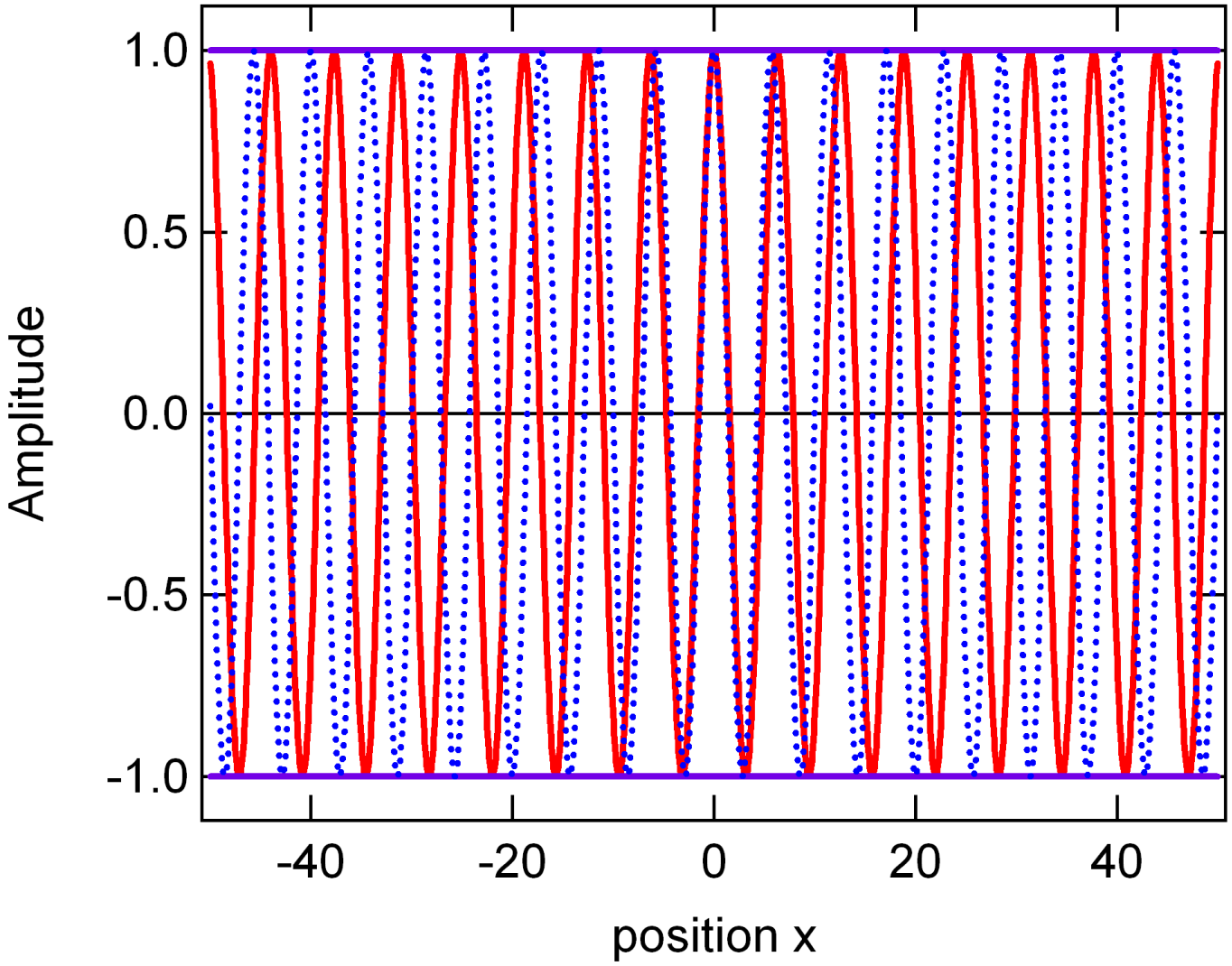
$$\Delta x \Delta p \geq \hbar/2$$

Let's look at the Uncertainty Principle using the particle-in-a-box example. If we know that the particle is in the lowest level then Uncertainty in its position is approximately equal to the width of the probability distribution.

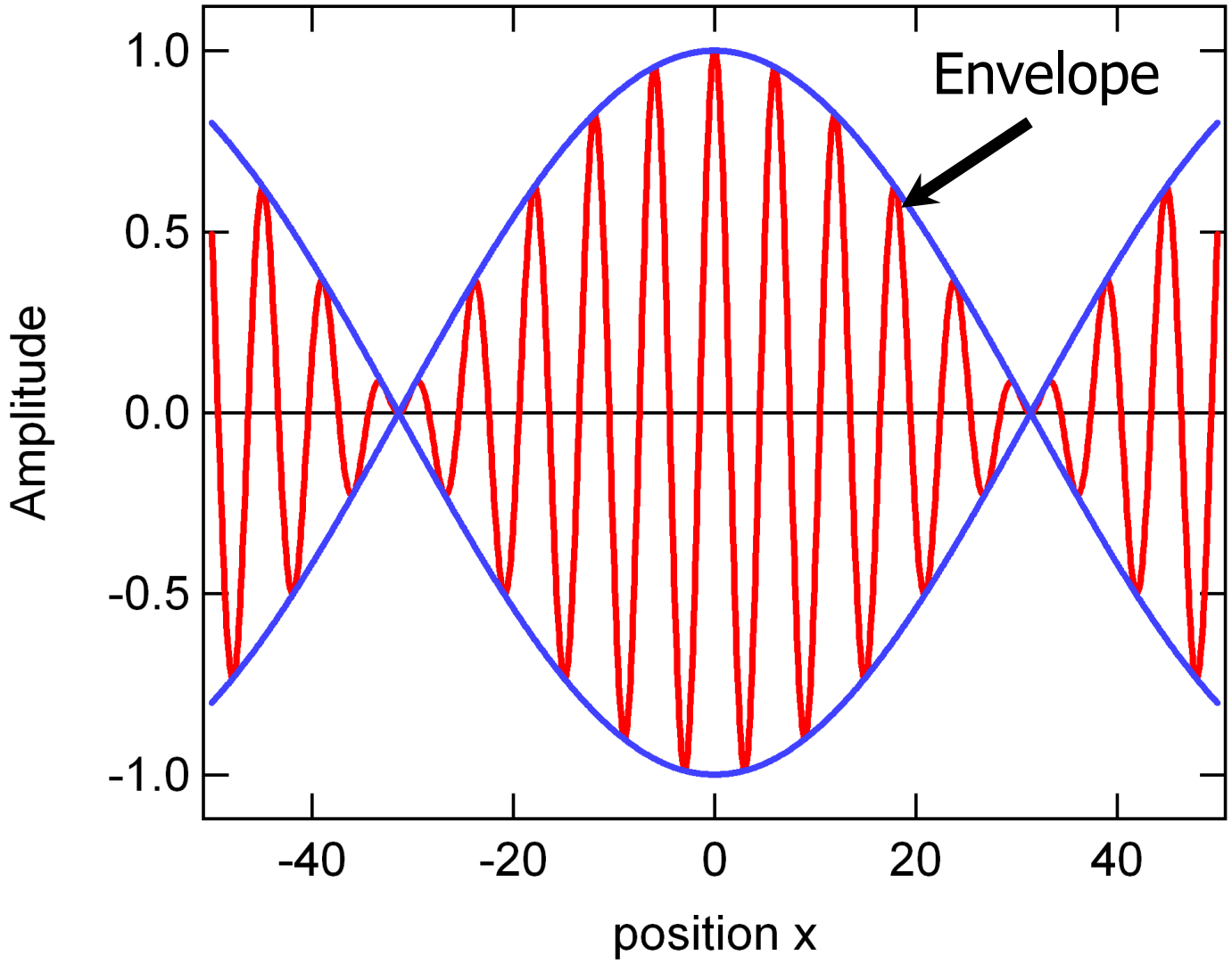
# The location of a particle in free space is not defined



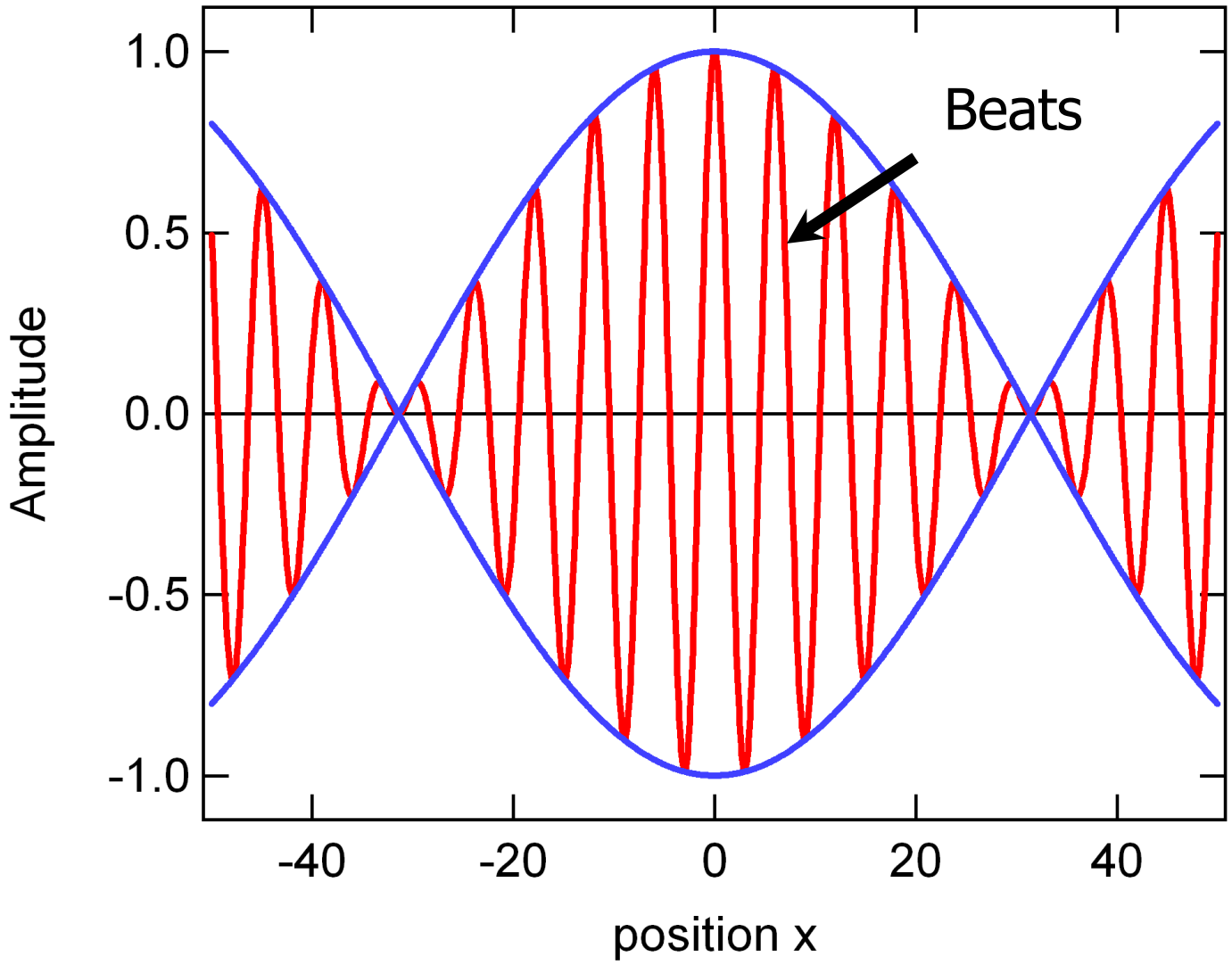
# Consider a superposition of a wave with moment hk and h(1.1k)



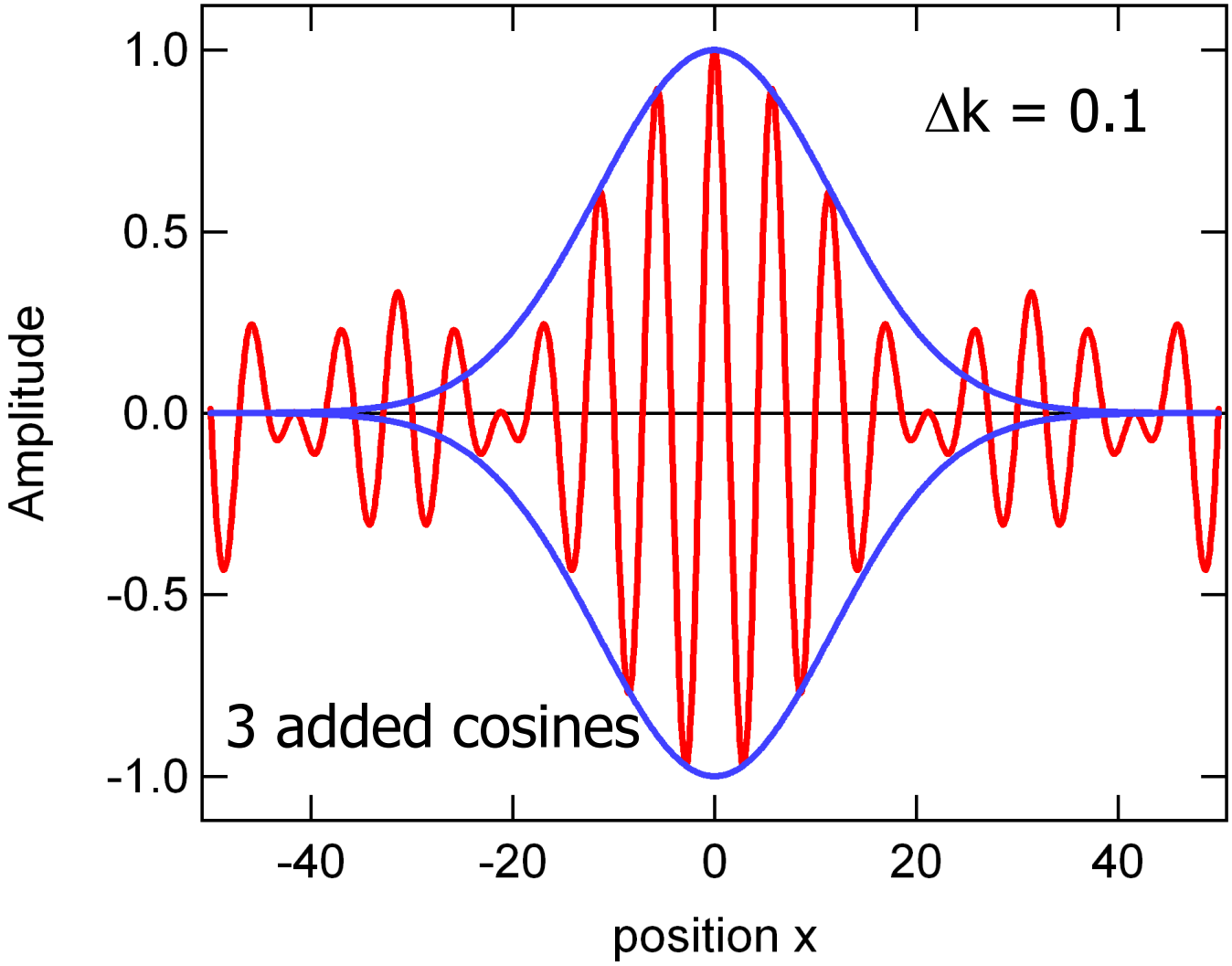
# The sum has a characteristic envelope frequency at $(\omega_2 - \omega_1)/2$



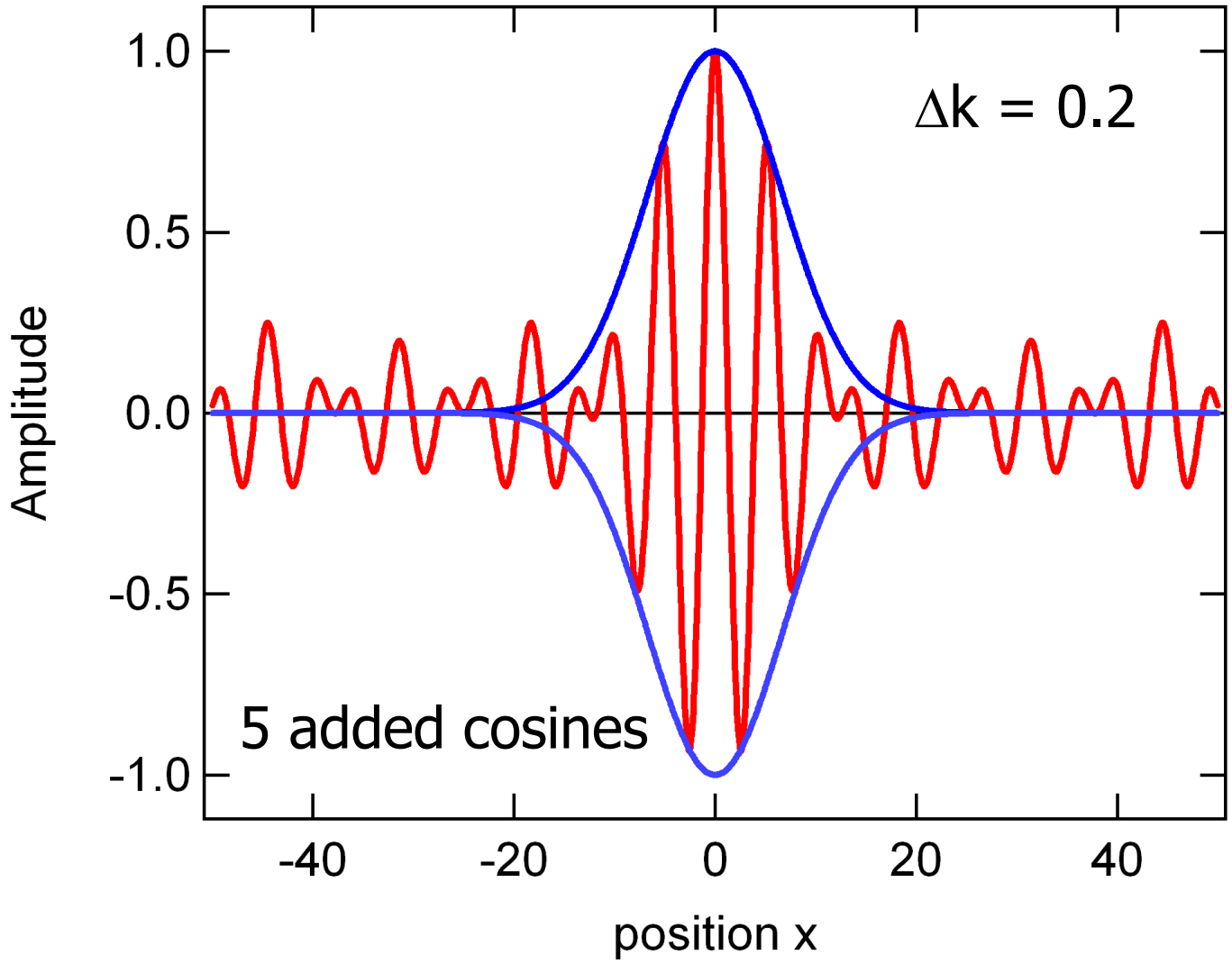
# The sum has a characteristic beat frequency at $(\omega_2 + \omega_1)/2$



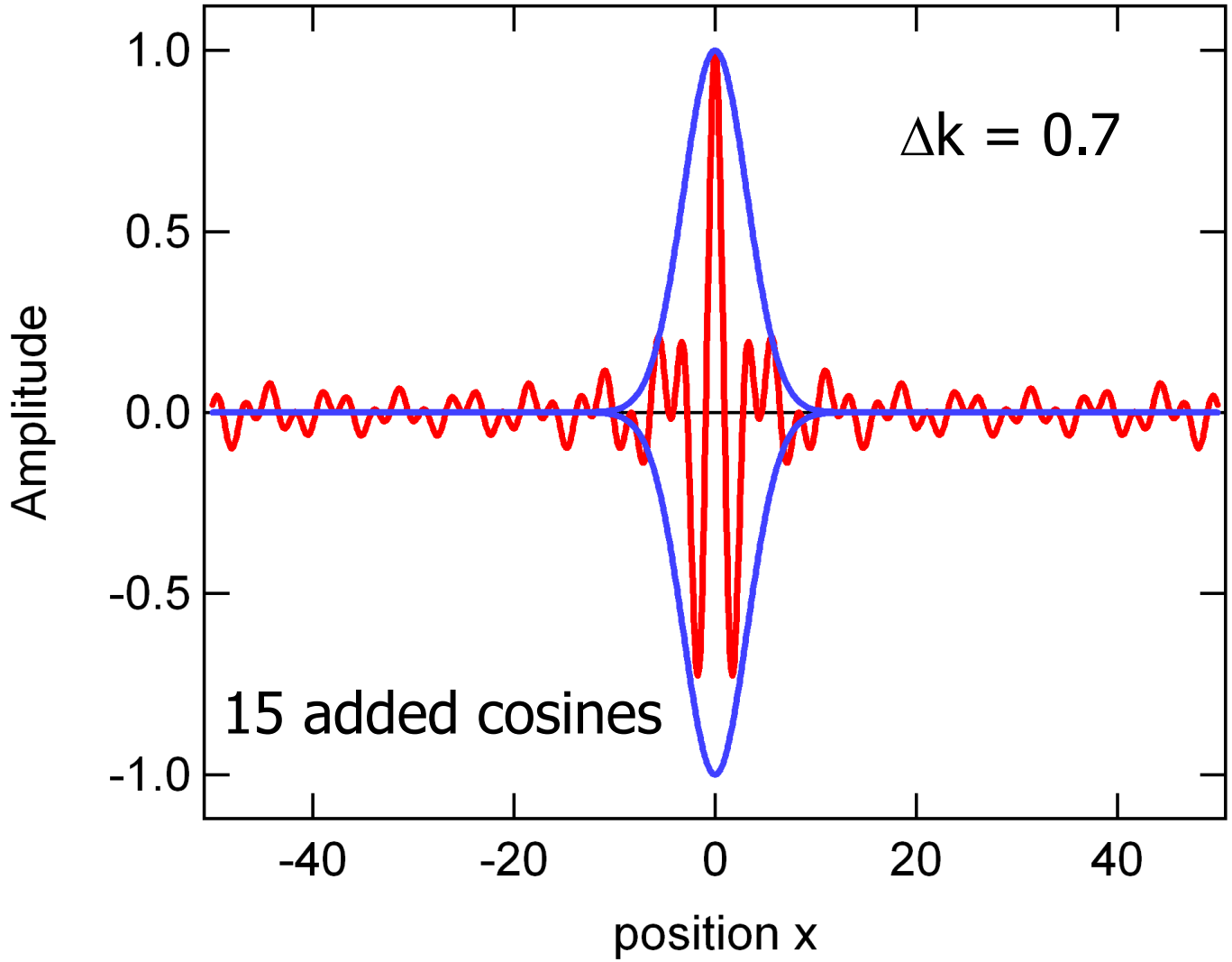
# As we add more frequencies we can speak of a bandwidth $\Delta k$



# As the bandwidth increases the position in x-space becomes more defined



# The superposition of waves in space leads to the description of a location



# Relevance of the example

Although the function used in the example is periodic it is relevant. Since in a given region of space (i.e. where a measurement can be made) the probability of observing the particle in a given region of space is dependent upon the number of contributing waves. If more waves contribute then the momentum of the particle is less certain. Thus, the we can know that moment precisely if we are totally uncertain of the position. As we begin to specify the position more precisely we find that the momentum is less well known. Since $p = \hbar k$, we can also express this condition as:

$$\Delta x \Delta k \geqslant 1/2$$

# Fourier transform related pairs

Position and momentum are related by a Fourier transform.

$$x \longleftrightarrow p$$

Time and energy are related by a Fourier transform.

$$t \longleftrightarrow E$$

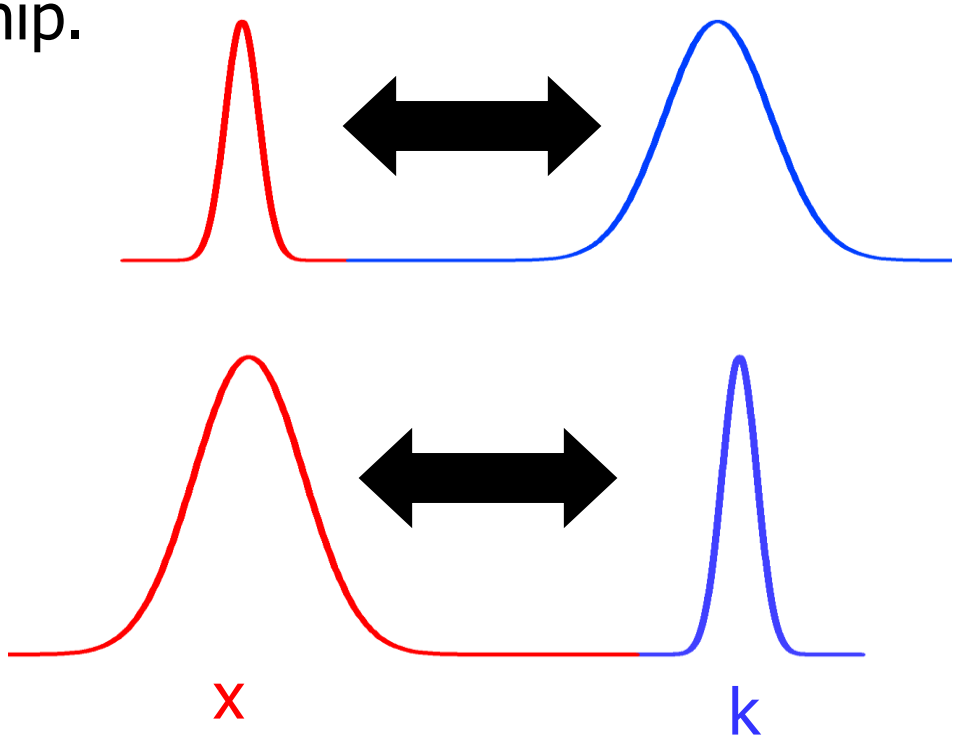
There is an uncertainty relationship for both of these related pairs. Thus, for time and energy we have

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

as well. These pairs can be related by a probability function that gives the width of the distribution in each space. Gaussian functions are particularly useful since the Fourier transform of a Gaussian is also a Gaussian.

# Gaussian Functions

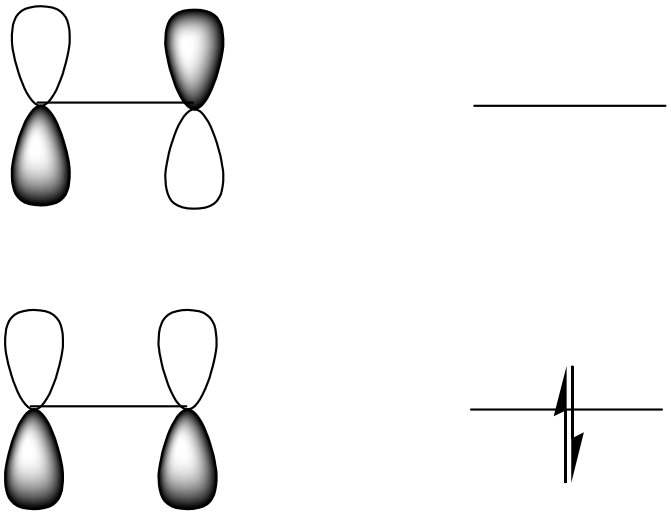
A Gaussian function has the form $\exp\{ -\alpha(x - x_0)^2 \}$. The Gaussian indicated is centered about the point $x_0$. The Fourier transform of a Gaussian in x-space is a Gaussian in k-space. Since $p = \hbar k$ we also call this momentum space. The figure shows the inverse relationship.



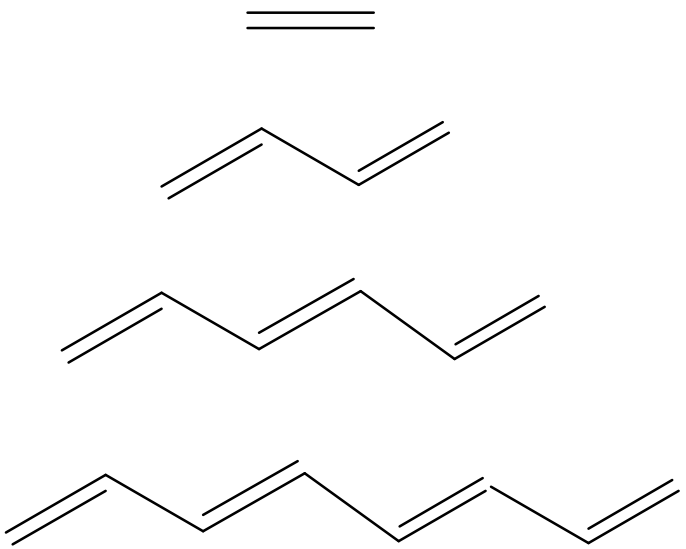
# Applications of particle in a box and “free electron” solutions

# Free electron model for electronic spectra

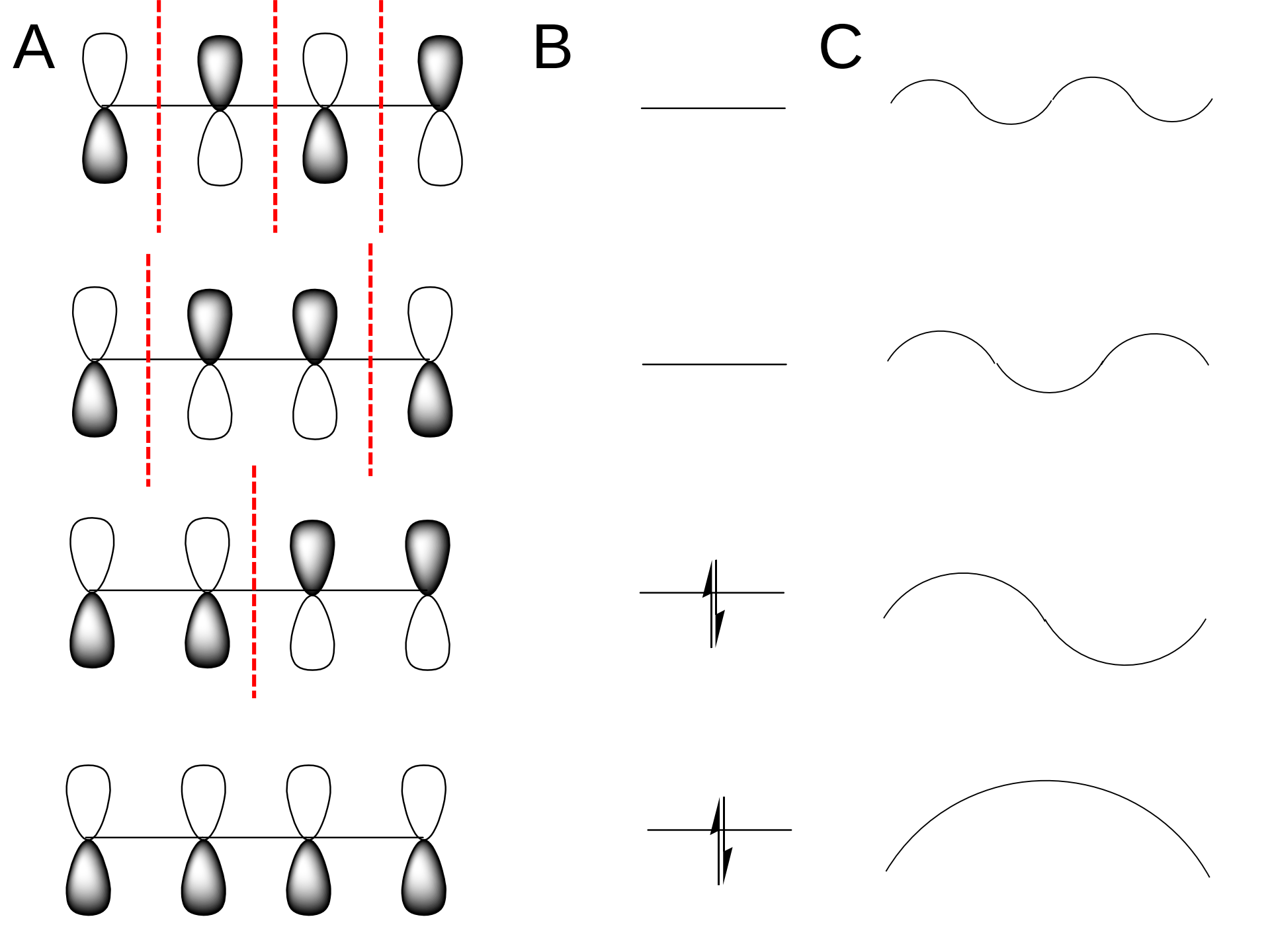
Before the advent of computers, models such as particle-in-a-box were used for linear polyenes. The idea of such a model is that the electrons from the p-orbitals in a molecule are particles and the molecule is the “box”. For example, we can think of ethylene as a short box with two electrons as shown in the figure. Although there are an infinite number of states, only two of them are really important in ethene since there are only two electrons. The HOMO and LUMO are shown on the left and the representation of the two lowest electronic states is shown.



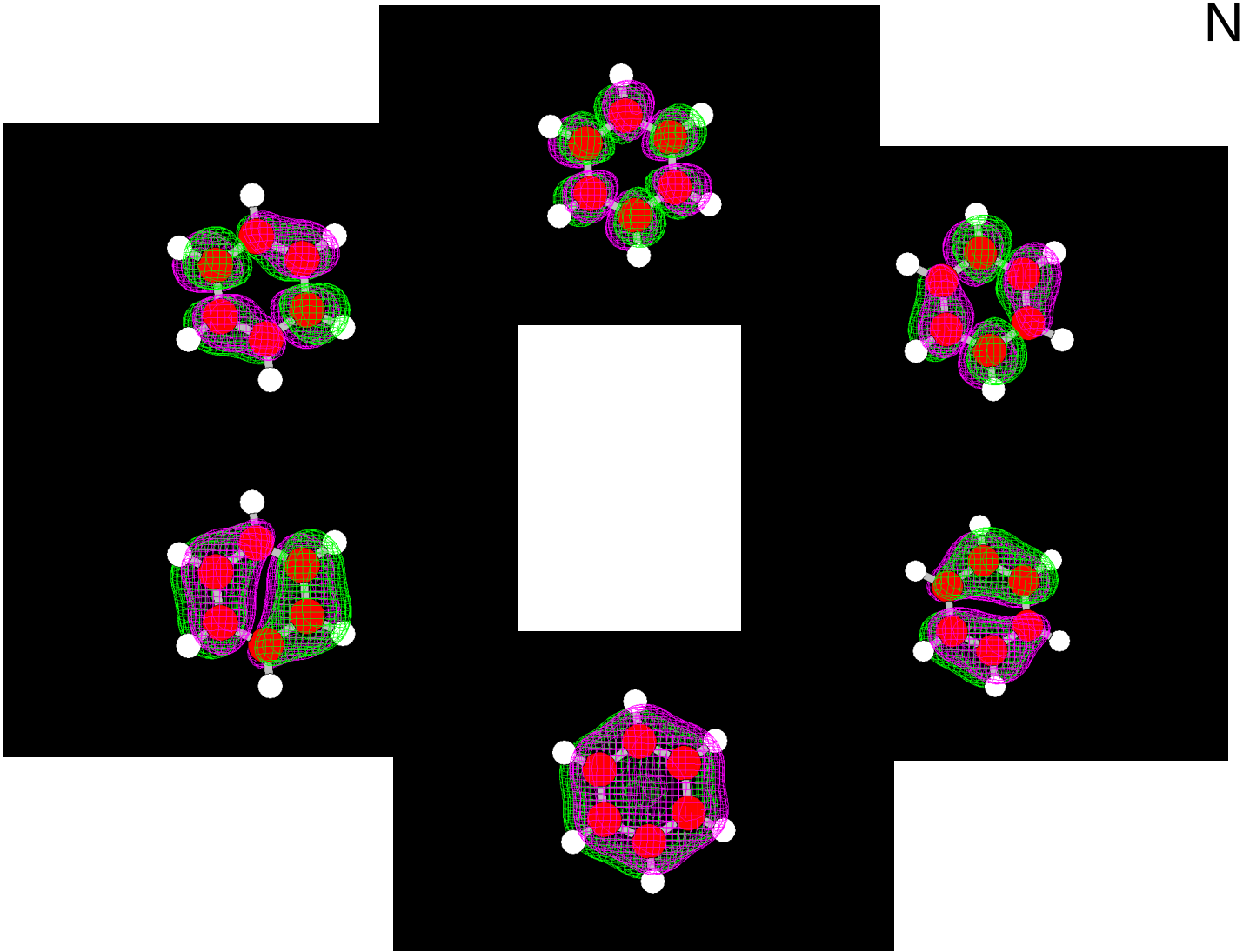
# Polyenes



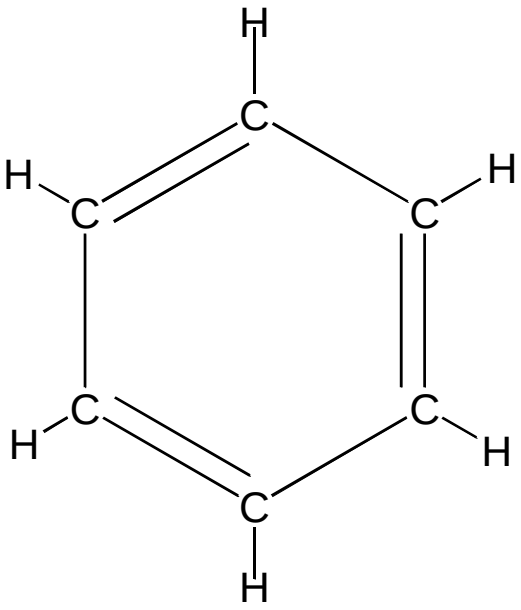
The first four members of the class of polyenes are shown. We can treat the p-system of these molecules using the model with 2, 4, 6 and 8 electrons, respectively. As a general rule the model can be applied to any number of p-orbitals, with the assumption each p-orbital will contribute one electron to the total. Then we populate the levels calculated using the particle-in-a-box and determine the transition between the HOMO and LUMO. This is illustrated for butadiene on the next slide.


A
B
C

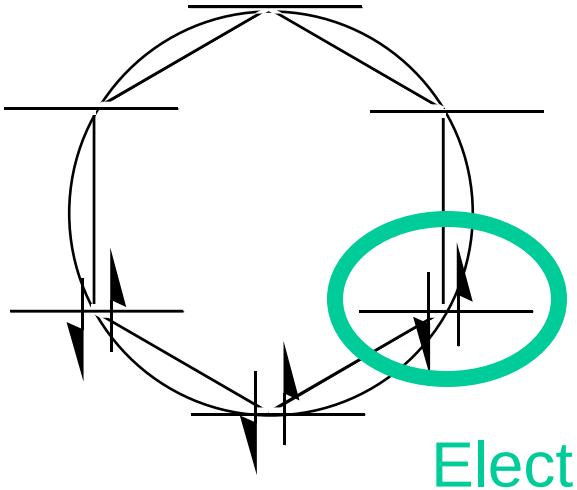
# Application to aromatic molecules: benzene



# We can construct molecular orbitals of benzene using the six electrons in $\pi$ orbitals




Benzene Structure

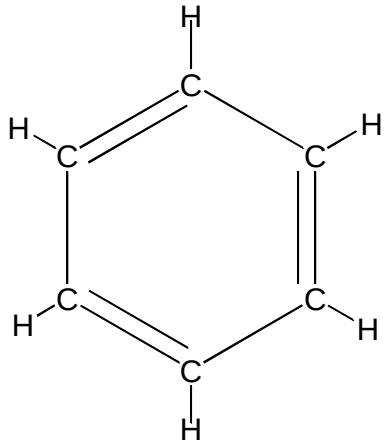


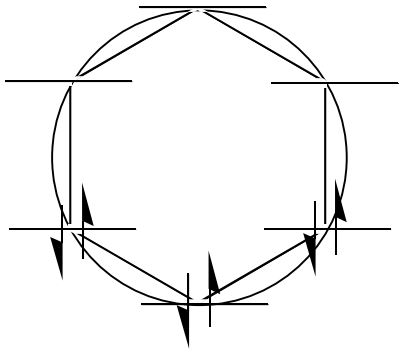
Electrons are spin-paired

Electronic Energy Levels

# The Free Electron Model Applied to Benzene

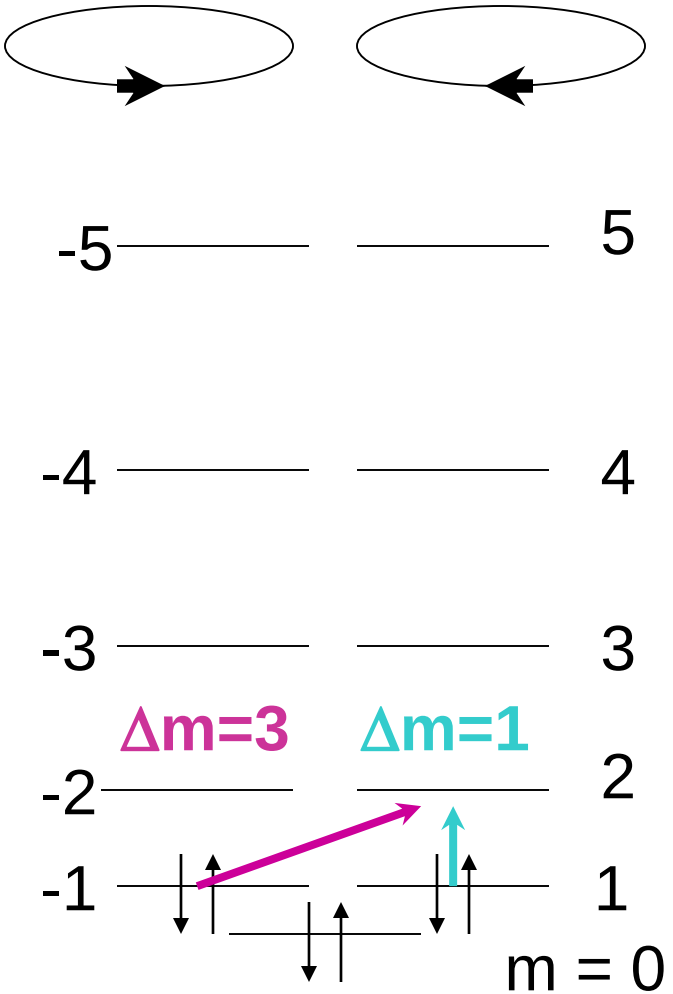
The $\pi$ system approximates circular electron path.



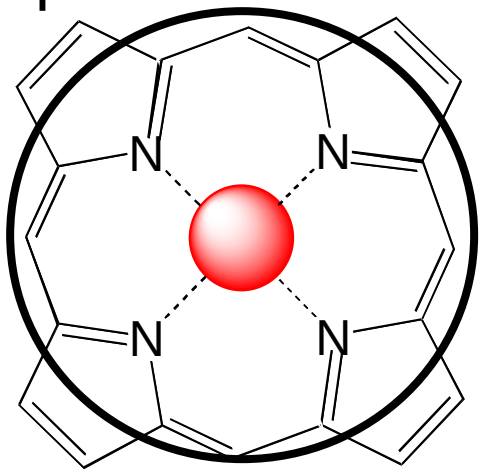
$$-\frac{\hbar^2}{2m_eR^2}\frac{\partial^2}{\partial\phi^2}\Phi = E\Phi$$

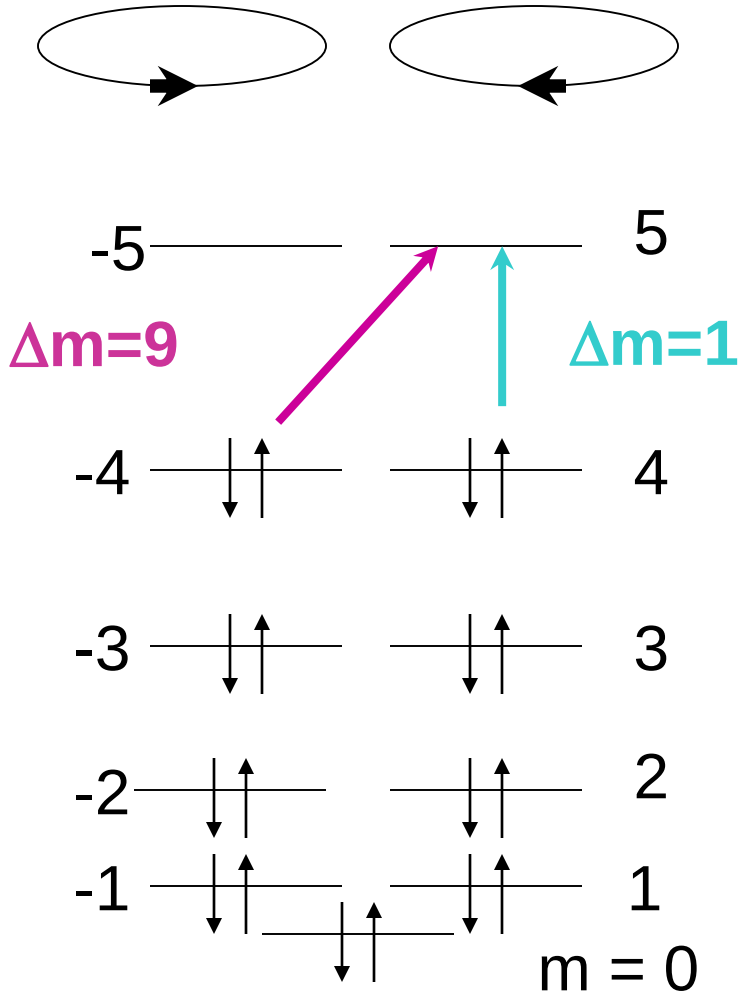
$$E = \frac{\hbar^2 m^2}{2m_eR^2} \quad , \quad \Phi = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$



# The Perimeter Model

The aromatic ring has 18 electrons.
The $\pi$ system approximates circular electron path.



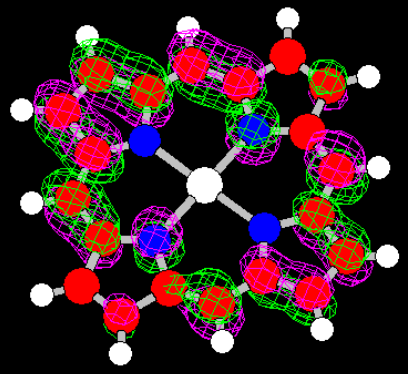




$$-\frac{\hbar^2}{2m_e R^2}\frac{\partial^2}{\partial\phi^2}\Phi = E\Phi$$

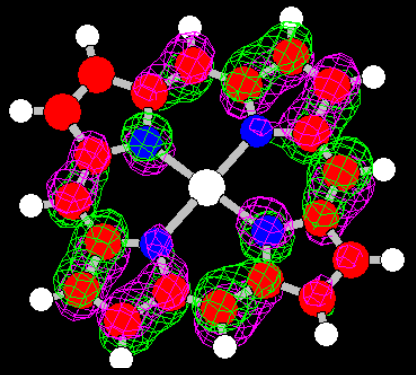
$$E = \frac{\hbar^2 m^2}{2m_e R^2} \quad , \quad \Phi = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

# Porphine orbitals

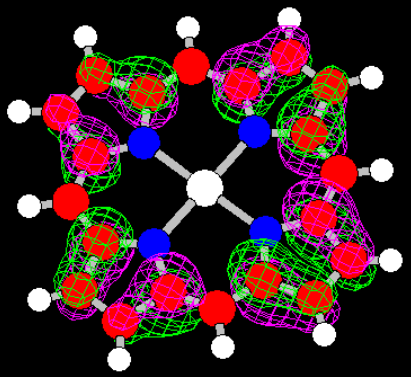
$e_g$



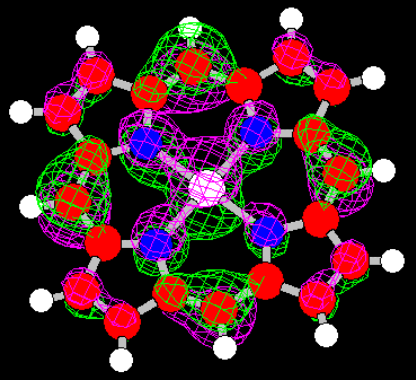
$e_g$



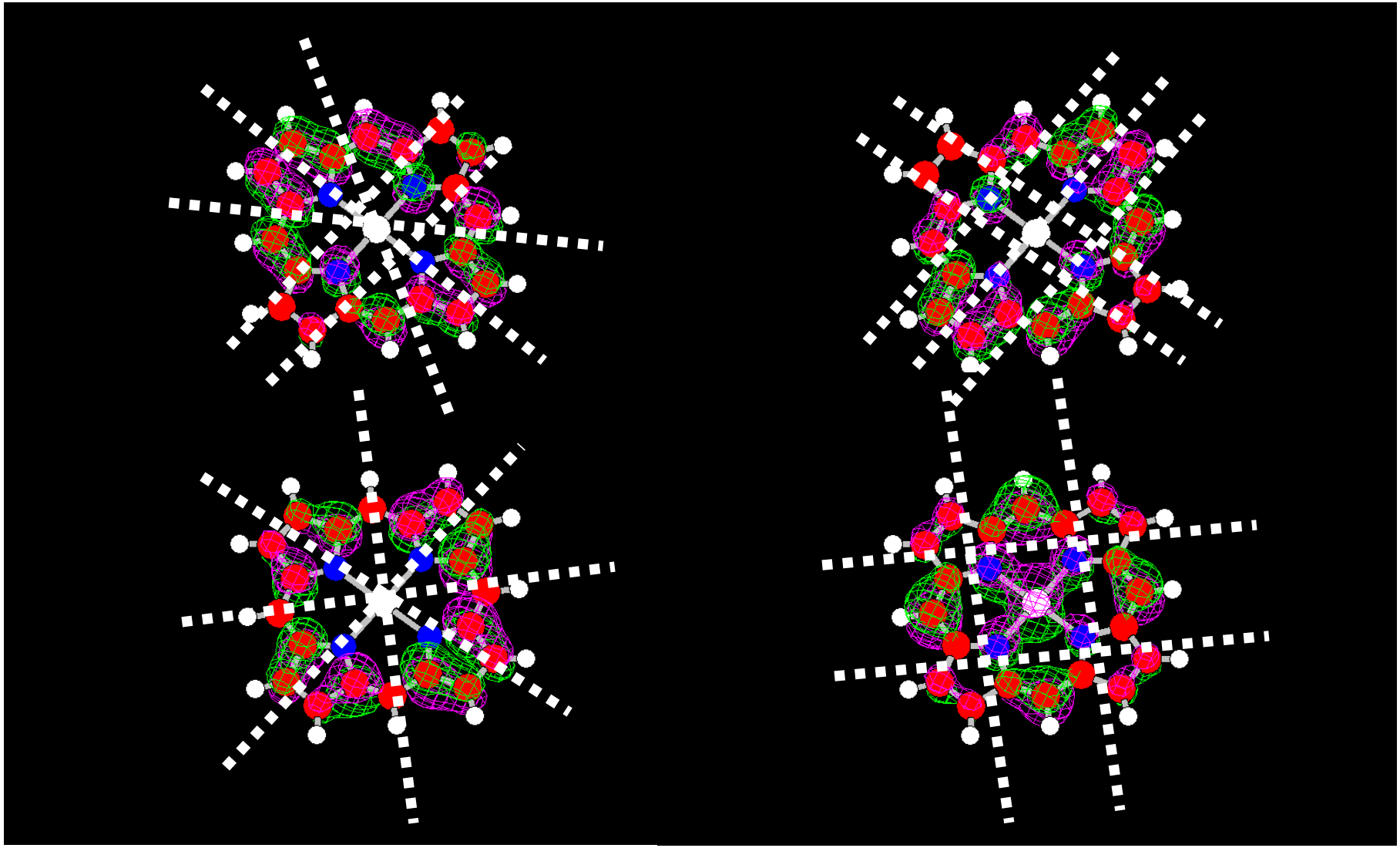
$a_{2u}$



$a_{1u}$



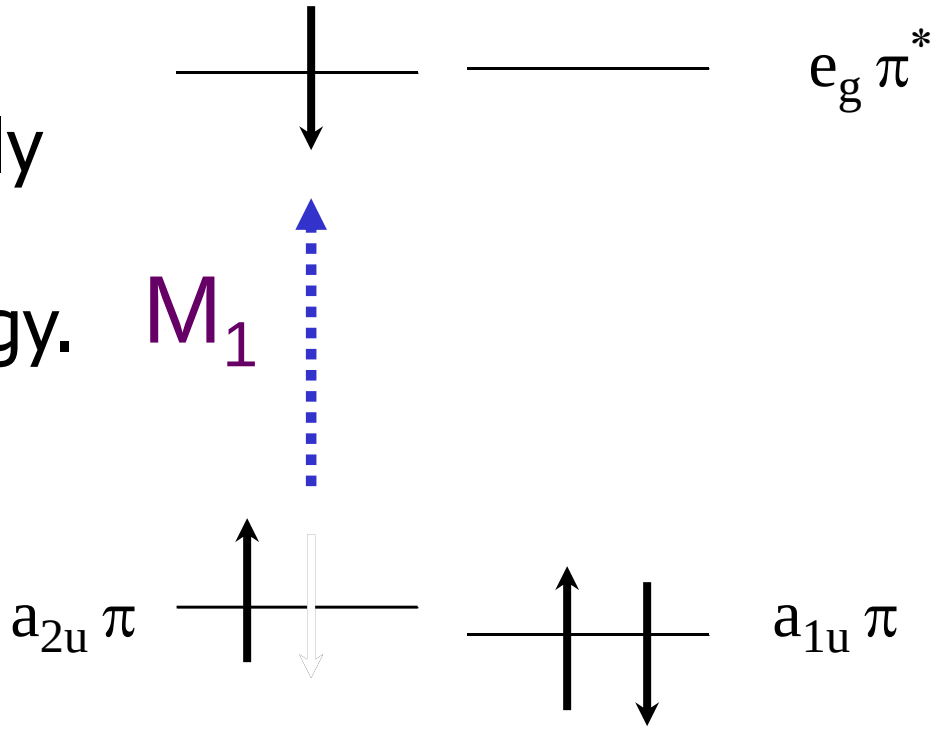
# Nodes in Porphine orbitals



# The four orbital model is used to represent the highest occupied and lowest unoccupied MOs of porphyrins

The two highest occupied orbitals ($a_{1u}$,$a_{2u}$) are nearly equal in energy. The $e_g$ orbitals are equal in energy. Transitions occur from:

$a_{1u} \rightarrow e_g$ and $a_{2u} \rightarrow e_g$.

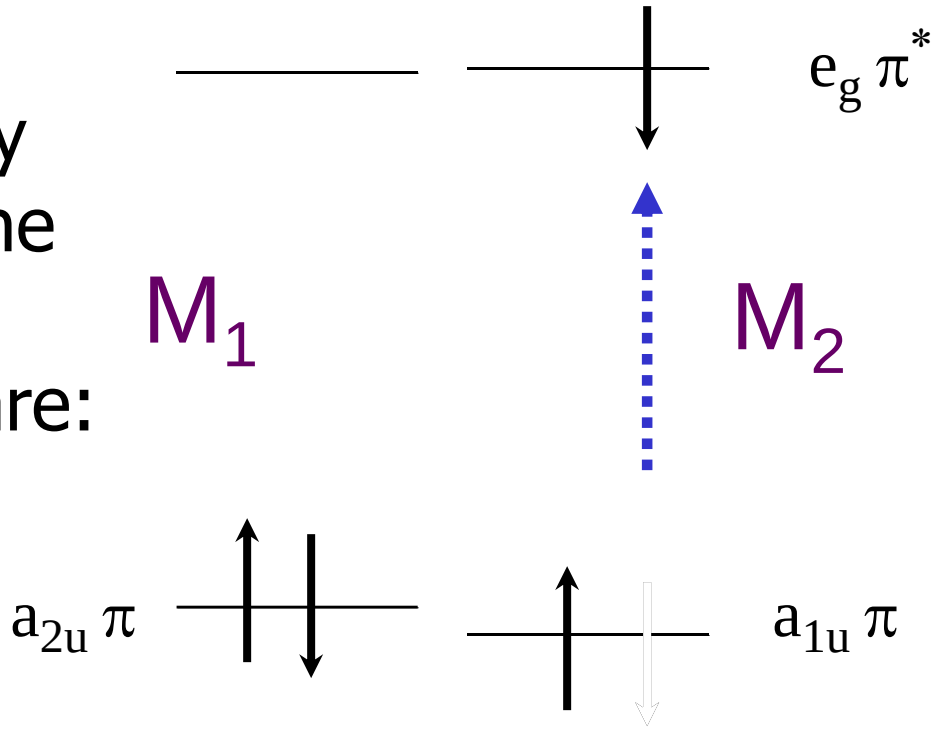


# The transitions from ground state $\pi$ orbitals $a_{1u}$ and $a_{2u}$ to excited state $\pi^*$ orbitals $e_g$ can mix by configuration interaction

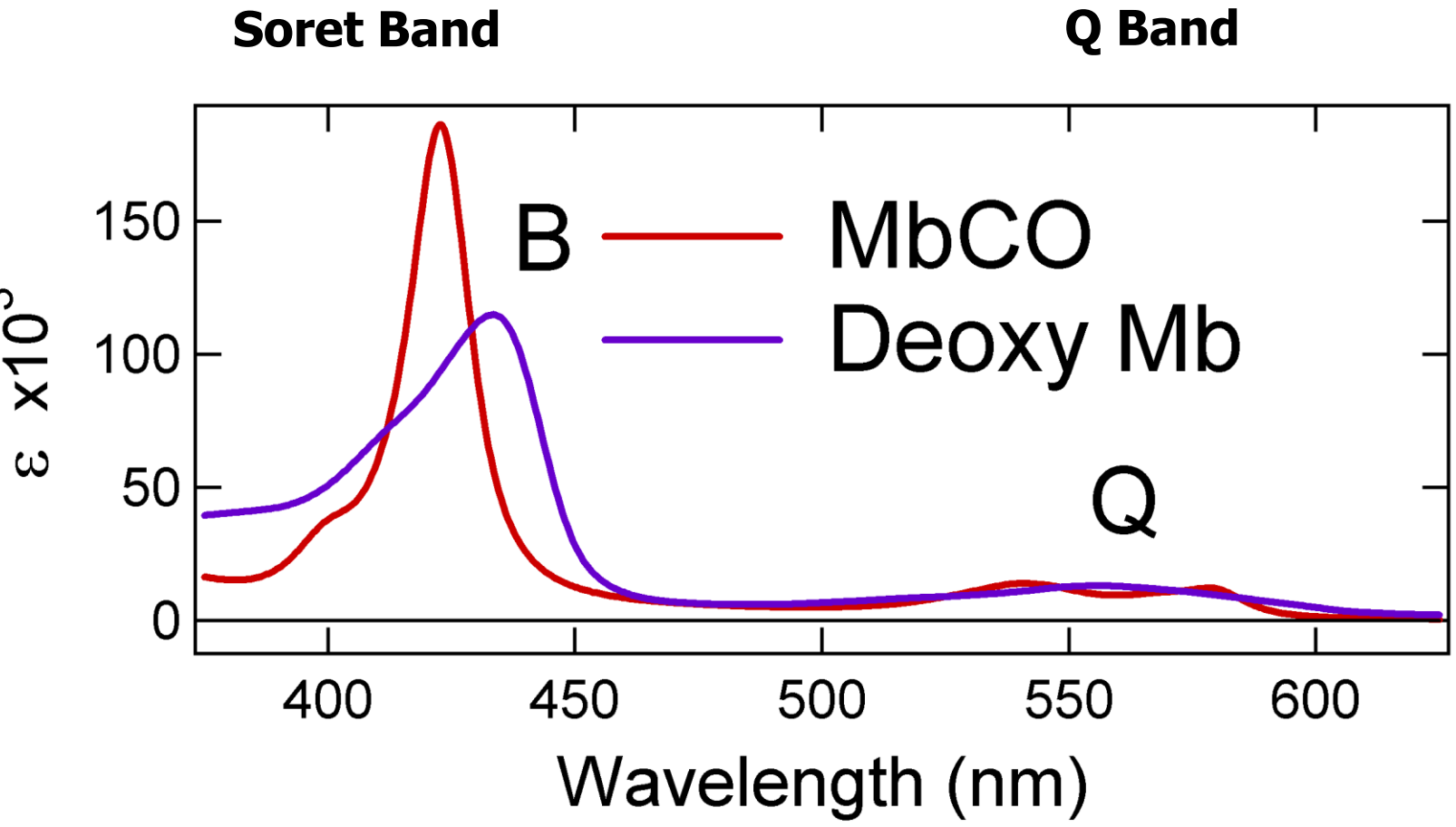
Two electronic transitions are observed. One is very strong (B or Soret) and the other is weak (Q).
The transition moments are:

$M_B = M_1 + M_2$

$M_Q = M_1 - M_2 \approx 0$

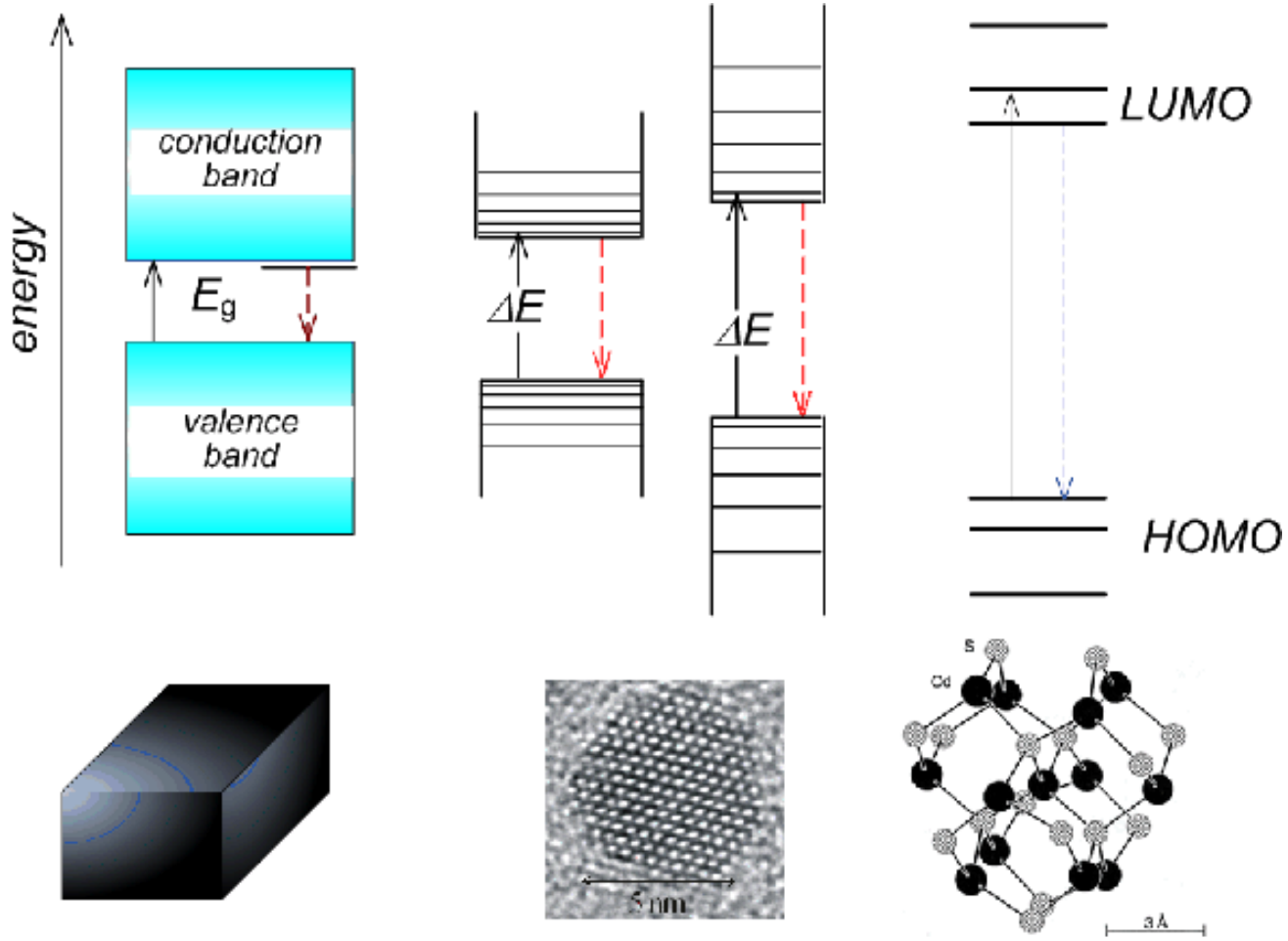


# Absorption spectra for MbCO and deoxy Mb



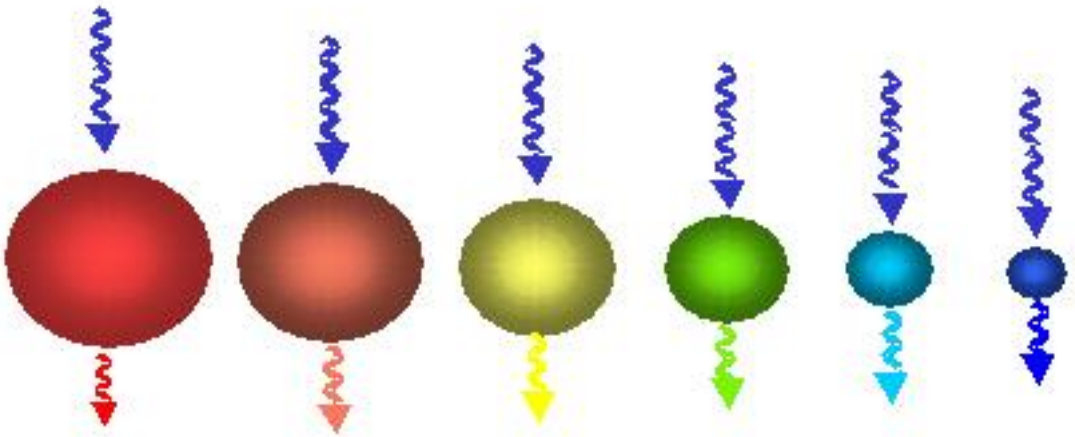

The spectrum of the heme has two bands. The B band or Soret Band is allowed and therefore intense. The Q band is forbidden. It is observed because of vibronic coupling with the Soret band.

# Quantum confinement in nanoparticles: An example of particle-in-a-box



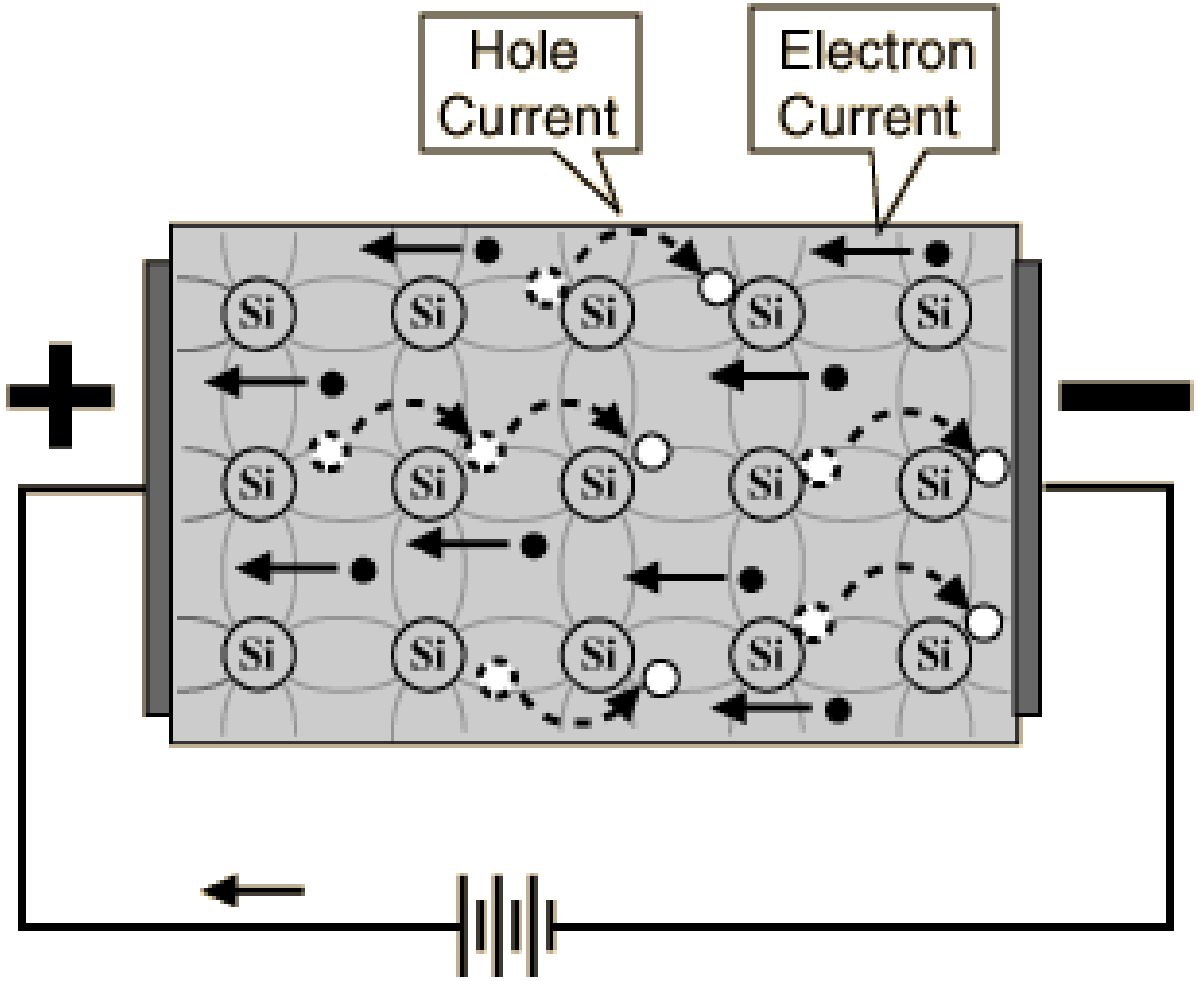

The semi-conductor band gap energy can depend on size.

# Quantum dots are semi-conductor nanoparticles whose color depends on size



Nanocrystals absorb light then re-emit the light in a different color – the size of the nanocrystal (at the Angstrom scale) determines the color

Felice Frankel

Six different quantum dot solutions are shown excited with a long wave UV lamp

# Free electron model of a conductor is widely used