

$$A^2/2 \int_0^a (1 - \cos(2n\pi/a)x) dx = 1$$

$$A^2/2 [x - a/2n\pi \sin(2n\pi/a)x]_{(0 \leq x \leq a)} = 1$$

$$A^2/2 [a - 0 + a/2n\pi \sin(2n\pi/a) 0 - 0] = 1$$

$$A^2 = 2/a,$$

Hence $\Psi_{(x)} = (2/a)^{1/2} \sin(n\pi x/a) \dots \dots \dots (29)$

Equation (29) is now the desired solution. We can now calculate the probability of finding the particle at any point, x, once the values of n, x and a are known.

Note also that we can now calculate ΔE for n equals two different values e.g. 2 and 3 from equation (28)

The probability is $|\Psi_{(x,n)}|^2$ so if the value of n, x and a are known, then it can be evaluated.

Particle in a Three Dimensional Box

We have been dealing with particle in a box. Here we want to expand the box to three dimensions. The particle is confined to a regular shape with sides of a, b, and c by having an infinite potential outside the box.

The time-independent Schrodinger equation for a single particle of mass m, moving in three dimensions is

$$\nabla^2 \Psi_{(x,y,z)} = -E \Psi_{(x,y,z)} \dots \dots \dots (32)$$

Where the Hamittonian operator is $\hat{H} = -(\hbar^2/2m) \nabla^2 \Psi + V_{(x,y,z)} \dots \dots \dots (33)$

And $\nabla^2 = d^2/dx^2 + d^2/dy^2 + d^2/dz^2 \dots \dots \dots (34)$

Where ∇^2 = laplacian operator or Del square.

The wave function is normalized so that $\int_{(-\infty \leq x \leq +\infty)} \Psi^*_{(x,y,z)} \Psi_{(x,y,z)} dx dy dz = 1 \dots \dots \dots (35)$

If a particle can move in three dimensions, its probability density P(x,y,z) is given by

$$P_{(x,y,z)} = \Psi^*_{(x,y,z)} \Psi_{(x,y,z)} \dots \dots \dots (36)$$

The probability that x coordinate is between x and x + dx, the y coordinate is between y + dy and the z coordinate is between z + dz is $P_{(x,y,z)}dx dy dz = \Psi^*_{(x,y,z)}\Psi_{(x,y,z)}dx dy dz$ which can be shortened to $\Psi^*\Psi dT$ where dT represents the differential element of volume dx dy dz.

Since the potential within the box is zero, the following partial differential equation for the region inside the box is obtained as $-\hbar^2/2m(d^2/dx^2 + d^2/dy^2 + d^2/dz^2)\Psi = E\Psi$ (37)

If we assume that the wave function Ψ is the product of three functions each depending on just one coordinate we will have;

$$\Psi_{(x,y,z)} = X_{(x)} Y_{(y)} Z_{(z)}..... (38)$$

By substituting this for Ψ in equation (37) and then divide by $X_{(x)} Y_{(y)} Z_{(z)}$ we obtained

$$-\hbar^2/2m(1/X_{(x)}[d^2X_{(x)}/dx^2] + 1/Y_{(y)}[d^2Y_{(y)}/dy^2] + 1/Z_{(z)}[d^2Z_{(z)}/dz^2]) = E\Psi..... (39)$$

Since the terms on the left hand side of the equation are a function of different independent variable and this can be varied independently of one another, each must equal a constant in order that the sum of the three terms equals a constant for all values of x, y and z.

$$E_x + E_y + E_z = E..... (40)$$

This converts the partial differential equation (39) into three ordinary differential equations that can be easily solved

$$-\hbar^2/2m(1/X_{(x)}[d^2X_{(x)}/dx^2]) = E_x..... (41)$$

$$-\hbar^2/2m(1/Y_{(y)}[d^2Y_{(y)}/dy^2]) = E_y..... (42)$$

$$-\hbar^2/2m(1/Z_{(z)}[d^2Z_{(z)}/dz^2]) = E_z..... (43)$$

These equations are just like equation (27) and may be solved in the same way to obtain

$$X_{(x)} = A_{(x)} \text{Sin } n_x\pi x/a = A_{(x)} \text{Sin } (2mE_x/\hbar^2)^{1/2}x..... (44)$$

$$Y_{(y)} = A_{(y)} \text{Sin } n_y\pi y/b = A_{(y)} \text{Sin } (2mE_y/\hbar^2)^{1/2}y..... (45)$$

$$Z_{(z)} = A_{(z)} \text{Sin } n_z\pi z/c = A_{(z)} \text{Sin } (2mE_z/\hbar^2)^{1/2}z..... (46)$$

Where a, b and c are the lengths of the sides in the x, y and z directions respectively, n_x , n_y and n_z are non-zero integers called quantum numbers and $E_x = \hbar^2 n_x^2/8ma^2$ and so on.

Thus there is a quantum number for each coordinate. When the wave function is normalized, we obtained $\Psi_{(x,y,z)} = (8/abc)^{1/2} \text{Sin } n_x\pi x/a \text{ Sin } n_y\pi y/b \text{ Sin } n_z\pi z/c$ (47)

When the Eigen function is substituted in eqn (37) we obtained:

$$E = \frac{h^2}{8m}(n_x^2/a^2 + n_y^2/b^2 + n_z^2/c^2) \dots\dots\dots (48)$$

The three quantum numbers are independent and for a given set of three quantum numbers there is in general, a unique value for the $a \neq b \neq c$.

If the sides of the box are equal; if $a = b = c$, the energy levels are given by

$$E = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \dots\dots\dots (49)$$

If $a \neq b \neq c$, there may be several combinations (n_x, n_y, n_z) that yield the same energy for example (2,1,1), (1,2,1) and (1,1,2) have the same energy. These three states of the system (with different wave function) make up a level that we can refer to as the 211 level. Such an energy level is said to be degenerate and the degeneracy is equal to the number of independent wave functions associated with a given energy level as shown below. Note that 111 level is non-degenerate.

n_x, n_y, n_z	111	211	221	311	222	321	322	411	331
Degeneracy	1	3	3	3	1	6	3	3	3

The degeneracy of a translational energy level increases rapidly with energy. If $n^2 = n_x^2 + n_y^2 + n_z^2$, the $E = \frac{h^2}{8ma^2} \cdot n^2$

If we think of allowed values of n_x , as point along x-axis, n_y along the y-axis and n_z along the z-axis, then n can be thought of as the length of a vector in this three dimensional space. All such vectors with the same length have the same energy they represent degenerate states.

The Degeneracy of quantum levels at thermal energy

The most probable translational energy for an atom in a gas at temperature T . is equal to $3/2KT$. Where $K = R/N_A =$ Boltzman constant.

Reduced Mass and Moment of Inertial of Molecules

Let define μ as the reduced mass = $m_1m_2/m_1+m_2 \dots\dots\dots(50)$

Where m are the molar mass in kg. E.g. The reduced mass for CO is given by $\mu = m_1m_2/m_1+m_2 = (12 \times 10^{-3})(16 \times 10^{-3})/(12+16) \times 10^{-3} \times 6.022 \times 10^{23} = 1.139 \times 10^{-26}$ kg

The moment of Inertia (I) is defined by the equation $I = \mu R_e^2$ for the rotation of a classical particle about the axis. Where R_e is the equilibrium internuclear distance between the nuclei of a molecules.

Rotational energy levels of Molecules

A rotating molecule has quantized angular momentum. In considering the rotational energy levels of molecules, the rotational quantum number is denoted by J so that

$$E = \frac{h^2}{2I} J(J+1) \dots \dots \dots (51)$$

The square of the total angular momentum is given by $L^2 = J(J+1) \hbar$ where J = 0, 1, 2.

The angular momentum vector L with respect to a particular direction is defined as $L_z = -\hbar, 0, \hbar$

Where the choice of the z axis is entirely arbitrary.

Calculate the reduced mass and the moment of inertia of CO the equilibrium internuclear distance is 123.5×10^{-12} . What are the values of L_z given that J = 1, C = 12, O = 16.

Summary Particle in a Three-Dimensional Box

Consider a particle constrained to move in a rectangular box of dimensions a, b, and c in length. Within the box (i.e. between $x = 0$ and a; $y = 0$ and b and $z = 0$ and c), the potential energy is zero at the walls and everywhere outside the box, the potential is ∞ .

Recall S.E for 3-dimensional box

$$\frac{d^2\Psi}{dx^2} + \frac{d^2\Psi}{dy^2} + \frac{d^2\Psi}{dz^2} + 8\pi^2m/h^2 (E - V) \Psi = 0$$

Where Ψ and V are $f(x, y, z)$. Since $V = 0$ inside the box, then the last equation becomes

$$\frac{d^2\Psi}{dx^2} + \frac{d^2\Psi}{dy^2} + \frac{d^2\Psi}{dz^2} + 8\pi^2m/h^2 E\Psi = 0 \dots \dots \dots (52)$$

Equation (52) may be solved by writing the wave function as the product of three functions each depending on one coordinate

$$\Psi_{(x,y,z)} = X_{(x)} Y_{(y)} Z_{(z)} \dots \dots \dots (53)$$

Differentiating equation (7)

$$\frac{d\Psi}{dx} = Y_{(y)} Z_{(z)} \frac{dX}{dx}$$

$$\frac{d^2\Psi}{dx^2} = Y_{(y)} Z_{(z)} \frac{d^2X}{dx^2} \dots \dots \dots (54a)$$

and by a similar reasoning

$$\frac{d^2\Psi}{dy^2} = X_{(x)} Z_{(z)} \frac{d^2Y}{dy^2} \dots \dots \dots (54b)$$

$$d^2\Psi/dz^2 = X_{(x)} Y_{(y)} d^2Z/dz^2 \dots\dots\dots (54c)$$

Substituting equations 54a, 54b and 54c into equation (52)

$$Y_{(y)} Z_{(z)} d^2X/dx^2 + X_{(x)} Z_{(z)} d^2Y/dy^2 + X_{(x)} Y_{(y)} d^2Z/dz^2 + 8\pi^2m/h^2 E X_{(x)} Y_{(y)} Z_{(z)} = 0 \dots\dots (56)$$

$$-h^2/8\pi^2m (1/X_{(x)}[d^2X_{(x)}/dx^2] + 1/Y_{(y)}[d^2Y_{(y)}/dy^2] + 1/Z_{(z)}[d^2Z_{(z)}/dz^2]) = E \dots\dots\dots (57)$$

We can write the energy level as the sum of three contributions associated with the coordinates

$$E = E_x + E_y + E_z \dots\dots\dots (58)$$

Using eqn (57) in (58) we can separate the expression obtained into three equations

$$-h^2/8\pi^2m (1/X_{(x)}[d^2X_{(x)}/dx^2]) = E_x \dots\dots\dots (59)$$

$$-h^2/8\pi^2m (1/Y_{(y)}[d^2Y_{(y)}/dy^2]) = E_y \dots\dots\dots (60)$$

$$-h^2/8\pi^2m (1/Z_{(z)}[d^2Z_{(z)}/dz^2]) = E_z \dots\dots\dots (61)$$

Each of eqns 59, 60, 61 is similar to the expression for the particle in a one dimensional box. Hence their solutions are

$$X_{(x)} = (2/a)^{1/2} \text{Sin } (n_x\pi x/a) \quad E_{n,x} = n_x^2 h^2/8ma^2$$

$$Y_{(y)} = (2/b)^{1/2} \text{Sin } (n_y\pi y/b) \quad E_{n,y} = n_y^2 h^2/8mb^2$$

$$Z_{(z)} = (2/c)^{1/2} \text{Sin } (n_z\pi z/c) \quad E_{n,z} = n_z^2 h^2/8mc^2$$

Where a,b,c are lengths in x,y,z direction respectively and n_x, n_y, n_z are quantum numbers.

Since $\Psi_{(x,y,z)} = X_{(x)} Y_{(y)} Z_{(z)}$ and $E = E_x + E_y + E_z$, then

$$\Psi_{(x,y,z)} = (8/V)^{1/2} \text{Sin } n_x\pi x/a \text{ Sin } n_y\pi y/b \text{ Sin } n_z\pi z/c \dots\dots\dots (62)$$

Where V is the volume of the box.

$$E_{x,y,z} = h^2/8m(n_x^2/a^2 + n_y^2/b^2 + n_z^2/c^2) \dots\dots\dots (63)$$

Whenever the 3-dimensional box has geometrical symmetry, more interesting results are often obtained, in a cubic box, $a = b = c$ thus eqn (63) becomes

$$E = h^2/8m(n_x^2 + n_y^2 + n_z^2) \dots\dots\dots (64)$$

Suppose $n_x = 3, n_y = n_z = 2$ then

$$\Psi_{(x,y,z)} = (8/V)^{1/2} \text{Sin } 3\pi x/a \text{ Sin } 2\pi y/b \text{ Sin } 2\pi z/c \dots\dots\dots (65)$$

$$E = h^2/8m(3^2 + 2^2 + 2^2) = 17h^2/8ma^2 \dots\dots\dots (66)$$

Assuming we have another set of values $n_x = 2, n_y = 3, n_z = 2$ then

$$\Psi_{(x,y,z)} = (8/V)^{1/2} \sin 2\pi x/a \sin 3\pi y/b \sin 2\pi z/c \dots \dots \dots (67)$$

$$E = h^2/8m(2^2 + 3^2 + 2^2) = 17h^2/8ma^2 \dots \dots \dots (68)$$

Suppose $n_z = 3, n_y = n_x = 2$ then

$$\Psi_{(x,y,z)} = (8/V)^{1/2} \sin 2\pi x/a \sin 2\pi y/b \sin 3\pi z/c \dots \dots \dots (69)$$

$$E = h^2/8m(2^2 + 2^2 + 3^2) = 17h^2/8ma^2 \dots \dots \dots (70)$$

Even though these states are different, their energies (eqn 59, 60, 61) are the same. The three states are said to be degenerate because they have equal energy.

For a situation where $n_x = n_y = n_z = 1$ it corresponds to only one state of the system. The same is true of $n_x = n_y = n_z = 2$ but for the situation such as $n_i = 2, 2, 1$ or $3, 1, 1$, three degenerate states are obtained (figure 5 not shown): Quantized energy levels of a particle in a cubic box

Suppose we wish to calculate the transition energy between the level $E_{2,2,2}$ and $E_{3,2,1}$ the,

$$\Delta E = 14h^2/8ma^2 + 12h^2/8ma^2 = hv$$

$$hv = 2h^2/8ma^2 = h^2/4ma^2$$

Given appropriate data, it should be possible for us to evaluate v . If the value of a , is known, the transition energy can be evaluated.

Zero Point Energy

According to the old quantum theory the energy level of a harmonic oscillator is $E = nhv$

The lowest energy level with $n = 0$ would have zero energy. Based on the wave treatment of the system, the energy level corresponds to the state with quantum numbers $n_x = n_y = n_z = 1$.

The difference between these two values is called the zero point energy.

Free Electron Model

The simple calculation done for the particle in a one-dimensional box can be applied to estimate the absorption frequency of some organic molecules, presumably conjugated dienes. The method often employed is the free electron model. For the π electrons of these molecules. The energy for the lowest electronic transition is that required to raise an electron from the highest filled level (HOMO) to the lowest unfilled level (LUMO). For molecules with conjugated dienes, it has been found that the electronic absorption bands shift to longer wavelengths (Bathochromic or red shift) as the number of conjugated dienes is increased each carbon atom contributes one electrons are free to move the entire length of the series of π -orbitals and are not localized on a

given carbon atom. In the free electron model, it is assumed that π -system is a region of uniform potential and that P.E rises sharply to infinity at the end of the system.

Hence the energy level, E , available to the following electron would be expected to be analogous to that of particle restricted to move in one direction. The π -electrons are assigned to orbitals so that there are two in each level (with opposite spin) starting with the lowest, for completely conjugated hydrocarbon, the no of π -electrons is even and the quantum number of the HOMO is $n = N/2$ where N is the number of π -electrons involved and parallels the number of carbon atoms in the system. In absorption, an electron from the HOMO is excited to the LUMO with quantum no $n^1 = (N/2 + 1)$. The difference in energy between these levels is $\Delta E = h^2/8ma^2(n^{12} - n^2) = h^2/8ma^2[(N/2 + 1)^2 - (N/2)^2]$

The absorption frequency in wave number is $\Delta E = h\nu$, $c = \lambda\nu$, $\Delta E = hc/\lambda = hc\bar{\nu}$

$$\bar{\nu} = \Delta E/hc = h(N+1)/8ma^2c \dots \dots \dots (71)$$

let us consider butadiene with the structure $C=C-C=C$, if the 4π -electrons are removed, we have $C^+-C^+-C^+-C^+$ at the boundary, the potential is infinitely large. The first transitions for the system corresponds to electron from $E_2^{4/2}$ to $E_3^{4/2+1}$

$$\begin{aligned} \Delta E &= E_3 - E_2 \\ &= 9h^2/8ma^2 - 4h^2/8ma^2 \end{aligned}$$

To estimate a , two methods are used;

When end effects are not neglected, a equals the sum of bond lengths and $1/2$ bond length of the extensions at both extremes $\frac{1}{2}b.LC = C-C=C\frac{1}{2}b.L$

When end effects are not neglected (better because $V = \infty$ at the extremes)

$$a = 1.54 (N-1)\text{\AA}, \text{ where } N = \text{number of carbon atoms.}$$

Examples: Calculate the lowest absorption wave number for octatetraene neglecting end effects.

Solution: First draw the structure end effect- $C=C-C=C-C=C-C=C$ - end effect

$$a = 1.54 (8-1)\text{\AA} = 10.78\text{\AA}$$

Draw the energy-level diagram to determine the quantum levels involved in the transition

$$\begin{aligned} \Delta E &= 5^2h^2/8ma^2 - 4^2h^2/8ma^2 \\ &= 9h^2/8ma^2 \end{aligned}$$

But $\Delta E = h\nu = hc\bar{\nu}$

$$hc\sigma = 9h^2/8ma^2, \quad \sigma = 9h/8ma^2c$$

$$\begin{aligned} \sigma &= 9 \times 6.626 \times 10^{-34} / 8 \times 9.11 \times 10^{-31} \times (10.78 \times 10^{-10})^2 \times 3 \times 10^8 \\ &= 2.347 \times 10^6 \text{ m}^{-1} \\ &= 2.347 \times 10^4 \text{ cm}^{-1} \end{aligned}$$

If it is energy, $\Delta E = hv = 9h^2/8ma^2$

$$\begin{aligned} &= 9 (6.626 \times 10^{-34})^2 / 8 \times 9.11 \times 10^{-31} (10.78 \times 10^{-10})^2 \\ &= 4.67 \times 10^{-19} \text{ J or } 2.91 \text{ eV} \end{aligned}$$

The Hydrogen Molecule Ion

The hydrogen molecule ion, H_2^+ consist of 2 protons and 1 electron and is thus the simplest molecular system that can be encountered in nature. The hydrogen molecule ios often represented as shown below:

We have one proton each at A and B. The potential energy for a hydrogen atom is $u = -e^2/r_A$

Similarly, the P.E for the hydrogen molecule ion is $u = -e^2/r_A - e^2/r_B + e^2/r_{AB} \dots \dots \dots (72)$

The first two terms in eqns 72 represent the electrostatic attraction between the nuclei and electron while the last term represent the repulsion between the nuclei. The kinetic energy for molecule is $\text{K.E} = P^2/2m = 1/2m (P_x^2 + P_y^2 + P_z^2)$

Where P = momentum of the electron, m = mass of the electron, and the electron is assumed to be moving in three directions. Note that we have assumed r_{AB} fixed which implies that only K.E term need be considered: the K.E due to the electron motion.

Recall S.E for a 3-dimensional system which is

$$d^2\Psi/dx^2 + d^2 \Psi/dy^2 + d^2\Psi/dz^2 + 8\pi^2m/h^2 (E - V_{(x,y,z)}) \Psi = 0$$

which can be written as $\square\Psi = E\Psi \dots \dots \dots (73)$

where $\square = -h^2/8\pi^2m(d^2/dx^2 + d^2/dy^2 + d^2/dz^2) \Psi + V_{(x,y,z)}$ is known as the Hamittonian operator and $\nabla^2 = d^2/dx^2 + d^2/dy^2 + d^2/dz^2$ is a Laplacian operator. Equation 73 is known as the Hamittonian form of the Schrodinger equation.

Note that $\hbar = h/2\pi$ and $\square = -\hbar^2/2m\nabla^2 + u_{(x,y,z)} \dots \dots \dots (74)$

The Schrodinger eqn for the hydrogen molecule ion is $(-\hbar^2/2m\nabla^2 + e^2/r_{AB} - e^2/r_A - e^2/r_B)\Psi = E\Psi \dots \dots \dots (74)$

The wave eqn is simple and it is possible to get an exact solution. We now attempt to set up S.E for the hydrogen molecule which has two electrons and 2 nuclei as shown the figure below:

We are to write expression for the K.E, write expression for the P.E and put both expression in the S.E.

$$\begin{aligned} \text{The total K.E} &= (\text{K.E})_1 + (\text{K.E})_2 \\ &= P_1^2/2m + P_2^2/2m \end{aligned}$$

Where 1,2 stand for 1st and 2nd electrons

$$\text{The total K.E} = 1/2m (P_{x1}^2 + P_{y1}^2 + P_{z1}^2) + 1/2m (P_{x2}^2 + P_{y2}^2 + P_{z2}^2)$$

The P.E for the system is

$$U_{(x,y,z)} = -e^2/r_{1A} - e^2/r_{1B} - e^2/r_{2A} - e^2/r_{2B} + e^2/r_{AB} + *e^2/r_{12}..... (75)$$

* represents repulsion between the two electrons

The S.E for the hydrogen molecule is

$$[-\hbar^2/2m(\nabla^2 + \nabla^2) - e^2/r_{1A} - e^2/r_{1B} - e^2/r_{2A} - e^2/r_{2B} + e^2/r_{AB} + e^2/r_{12}]\Psi = E\Psi$$

Which transform to

$$(\nabla_1^2 + \nabla_2^2)\Psi + 8\pi^2m/h^2 [E + e^2/r_{1A} + e^2/r_{1B} + e^2/r_{2A} + e^2/r_{2B} - e^2/r_{AB} - e^2/r_{12}]\Psi = 0..... (78)$$

This is the required equation. Whereas it is possible to get an exact solution to eqn 2.8 by separating into any other coordinates (e.g. polar or spherical). We cannot solve eqn 3.0 exactly because of the presence of the repulsive term e^2/r_{12} . In this situation, we use an approximate method to get solution to the S.E. we always aim at the energy of the system in joint form compared with when the atoms are far apart. We have assumed that both nuclei A and B are fixed meaning that their K.E will be almost zero. Thus instead of the K.E being:

$$\text{K.E} = K_A + K_B + K.E_1 + K.E_2$$

We have neglected that due to the nucleus both eqns 2.8 and 3.0 giving us $\text{K.E} = K.E_1 + K.E_2$ for the hydrogen molecule. The justification for doing this is that the motions of nuclei in ordinary molecular vibrations are so slow compared to the motions of the electrons that it is possible to calculate the electronic states on the assumption that the nuclei are held in fixed position. Thus is the Borh-oppenheimer approximation. What this means is that in eqn 3.0 for instance, we consider r_{AB} constant. We can therefore calculate E for the fixed values of r_{AB} . If we change the value of r_{AB} , a corresponding value of $E(r_{AB})$ can be got. Thus it should be possible to make a plot of $E(r_{AB})$ against r_{AB} in the figure below (Figure (x; NOT SHOWN) potential energy curve showing the variation of the total energy of the system with the internuclear distance, r_{AB}).

Figure (x) is known as the potential energy curve. In this figure, the equilibrium inter nuclear distance is r_{eq} and it corresponds to the region where the total energy of the system is a minimum (i.e. the system is stable there). It is called the bond length. When r , is small the molecule is unstable and also when r , is large, it is unstable because the attractive force may not be large enough to offset the repulsive force. In between A and B, the molecule is stable but it is most stable at r_{eq} .

The attractive state leads to bonding molecular orbitals whereas the repulsive state leads to antibonding M.O.

We cannot obtain exact value of E for the hydrogen molecule because of the presence of the repulsive term which made it impossible for us to separate the molecule into hydrogen atoms for which two electrons are involved. Also the presence of ∇_1^2 and ∇_2^2 in the S.E for the hydrogen molecule suggests that we should look for another way of solving the equation. The approximate method known as the variation method is often employed.