CHEM 3541

Physical Chemistry

Week 8 & 9

One particle in a 3D box

Hamiltonian:

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

$$V(x,y,z) = \begin{cases} 0, \ 0 < x < L_1 \ and \ 0 < y < L_2 \ and \ 0 < z < L_3 \\ +\infty, \ otherwise \end{cases}$$

Schrödinger Equation

$$\hat{H}\psi(x,y,z) = E\psi(x,y,z)$$

Within $0 < x < L_1, 0 < y < L_2$, and $0 < z < L_3$

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right] = E\psi$$

Boundary conditions

$$\psi(0,y,z) = \psi(L_1,y,z) = 0$$
$$\psi(x,0,z) = \psi(x,L_2,z) = 0$$
$$\psi(x,y,0) = \psi(x,y,L_3) = 0$$

Separation of variables

Let $\psi(x, y, z) = X(x)Y(y)Z(z)$ and plug this equation into S.E., we get

$$-\frac{\hbar^2}{2m}\left(\frac{\mathrm{d}^2 X}{\mathrm{d}x^2}YZ + \frac{\mathrm{d}^2 Y}{\mathrm{d}y^2}XZ + \frac{\mathrm{d}^2 Z}{\mathrm{d}Z^2}XY\right) = EXYZ$$

Dividing above equation by XYZ

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\mathrm{d}^2 X}{\mathrm{d}x^2} + \frac{1}{Y}\frac{\mathrm{d}^2 Y}{\mathrm{d}y^2} + \frac{1}{Z}\frac{\mathrm{d}^2 Z}{\mathrm{d}z^2}\right) = E$$

Each term in the LHS should be some constant, viz.

Continued

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} = E_1, -\frac{\hbar^2}{2m}\frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} = E_2, -\frac{\hbar^2}{2m}\frac{1}{Z}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2} = E_3$$

i.e.

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} = E_1X, -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} = E_2Y, -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2} = E_3Z$$

where $E_1 + E_2 + E_3 = E$

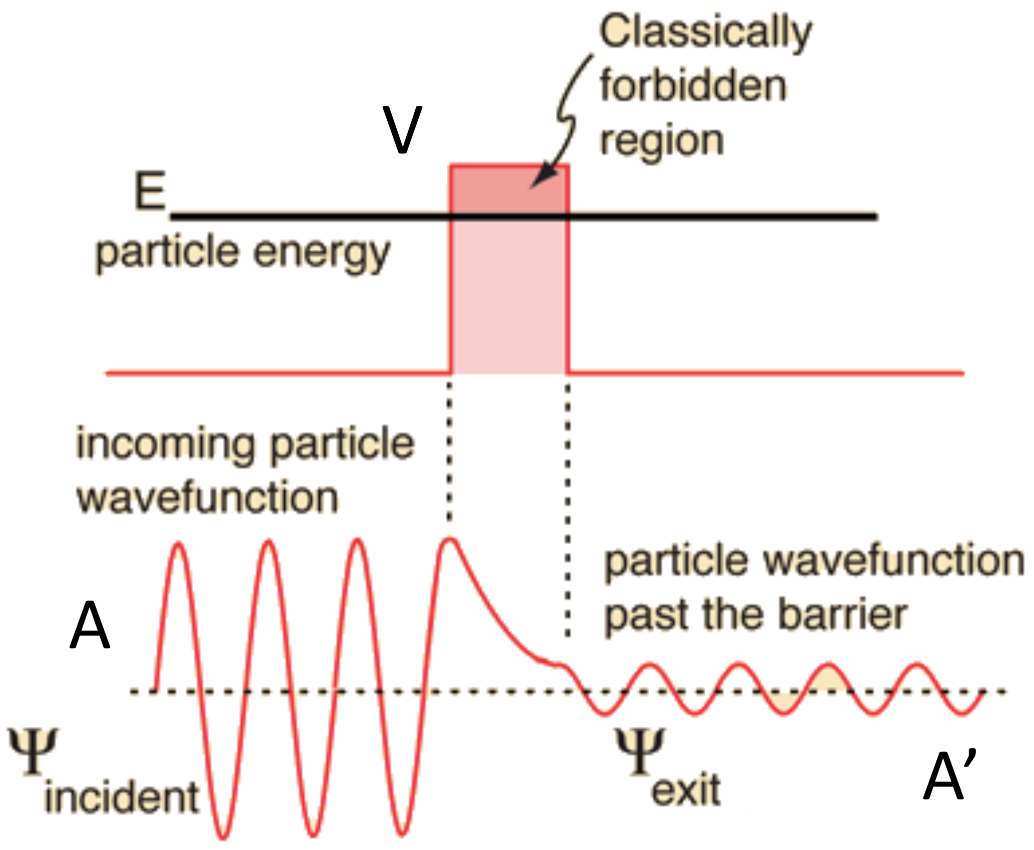
Continued

$$\psi_{n_1,n_2,n_3} = \begin{cases} \sqrt{\dfrac{8}{L_1 L_2 L_3}} \sin\dfrac{n_1 \pi x}{L_1} \sin\dfrac{n_2 \pi y}{L_2} \sin\dfrac{n_3 \pi z}{L_3}, within\ 3D\ box \\ 0, outside\ box \end{cases}$$

$$E_{n_1,n_2} = \frac{n_1^2 \pi^2 \hbar^2}{2mL_1^2} + \frac{n_2^2 \pi^2 \hbar^2}{2mL_2^2} + \frac{n_3^2 \pi^2 \hbar^2}{2mL_3^2}$$

Tunnelling

- Potential is zero in $x < 0$ or $x > L$ and constant V in $0 \leq x \leq L$
- The energy of incident wave function is E and $E < V$
- Denote the amplitude of incident and exit wave functions as A and A' respectively
- Transmission coefficient $T = \left|\frac{A'}{A}\right|$



http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/barr.html

Wavefunction in zero-potential region

$$-\frac{\hbar^2}{2m}\cdot\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}=E\psi, \psi=e^{\pm ikx}, k=\sqrt{2mE}/\hbar$$

- For $x<0$: $\psi_1(x)=Ae^{ikx}+Be^{-ikx}$, incident and reflection wavefunctions
- For $x>L$: $\psi_3(x)=A'e^{ikx}$, tunnelling wavefunction

Wavefunction in potential barrier

$$-\frac{\hbar^2}{2m}\cdot\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V\psi=E\psi, \psi=e^{\pm\kappa x}, \kappa=\sqrt{2m(V-E)}/\hbar$$

- For $0 \leq x \leq L$:

$$\psi_2(x)=Ce^{\kappa x}+De^{-\kappa x}$$

Boundary conditions

Wavefunction shall be smooth at boundaries, i.e.

$$\psi_1(0) = \psi_2(0), \psi_2(L) = \psi_3(L)$$

$$\psi_1'(0) = \psi_2'(0), \psi_2'(L) = \psi_3'(L)$$

thus we obtained four equations

$$A + B = C + D(1)$$

$$ikA - ikB = \kappa C - \kappa D(2)$$

$$Ce^{\kappa L} + De^{-\kappa L} = A'e^{ikL}(3)$$

$$\kappa Ce^{\kappa L} - \kappa De^{-\kappa L} = ikA'e^{ikL}(4)$$

Continued

- $\kappa(3) + (4)$: $C = \frac{\kappa + ik}{2\kappa} e^{(ik-\kappa)L} A'$
- $\kappa(3) - (4)$: $D = \frac{\kappa - ik}{2\kappa} e^{(ik+\kappa)L} A'$
- $ik(1) + (2)$:

$$A = \frac{(ik + \kappa)C + (ik - \kappa)D}{2ik}$$

$$= \frac{A'}{4i\kappa k} \left[(\kappa + ik)^2 e^{(ik-\kappa)L} - (\kappa - ik)^2 e^{(ik+\kappa)L} \right]$$

Continued

$$\frac{A}{A'e^{ikL}} = \frac{1}{4i\kappa k}\left[(\kappa + ik)^2 e^{-\kappa L} - (\kappa - ik)^2 e^{\kappa L}\right]$$

$$= \frac{1}{4i\kappa k}\left[(\kappa^2 - k^2)(e^{-\kappa L} - e^{\kappa L}) + 2i\kappa k(e^{-\kappa L} + e^{\kappa L})\right]$$

$$= \frac{1}{2}(e^{-\kappa L} + e^{\kappa L}) + i\frac{V - 2E}{4\sqrt{E(V - E)}} \cdot (e^{-\kappa L} - e^{\kappa L})$$

denote $\epsilon = \frac{E}{V}$

Transmission coefficient

$$\left|\frac{A}{A'}\right|^2 = \frac{1}{4}(e^{-\kappa L} + e^{\kappa L})^2 + \frac{1}{16}\frac{1-4\epsilon(1-\epsilon)}{\epsilon(1-\epsilon)}(e^{-\kappa L} - e^{\kappa L})^2$$

$$= \frac{1}{4}(e^{-\kappa L} + e^{\kappa L})^2 - \frac{1}{4}(e^{-\kappa L} - e^{\kappa L})^2 + \frac{(e^{-\kappa L} - e^{\kappa L})^2}{16\epsilon(1-\epsilon)}$$

$$= 1 + \frac{(e^{-\kappa L} - e^{\kappa L})^2}{16\epsilon(1-\epsilon)}$$

$$\therefore T = \left|\frac{A'}{A}\right| = \left[1 + \frac{\left(e^{-\kappa L} - e^{\kappa L}\right)^2}{16\epsilon(1-\epsilon)}\right]^{-1/2}$$

Discussion

- If $\epsilon \ll 1$, i.e. $E \ll V$: $T \approx \frac{4\sqrt{\epsilon(1-\epsilon)}}{(e^{-\kappa L}-e^{\kappa L})} \approx 0$
- If $\kappa L \gg 1$, i.e. high, wide barrier: $T \approx 4\sqrt{\epsilon(1-\epsilon)}e^{-\kappa L}$
- the heavier the mass, the smaller the T

Example 8A.2 (pp. 321)

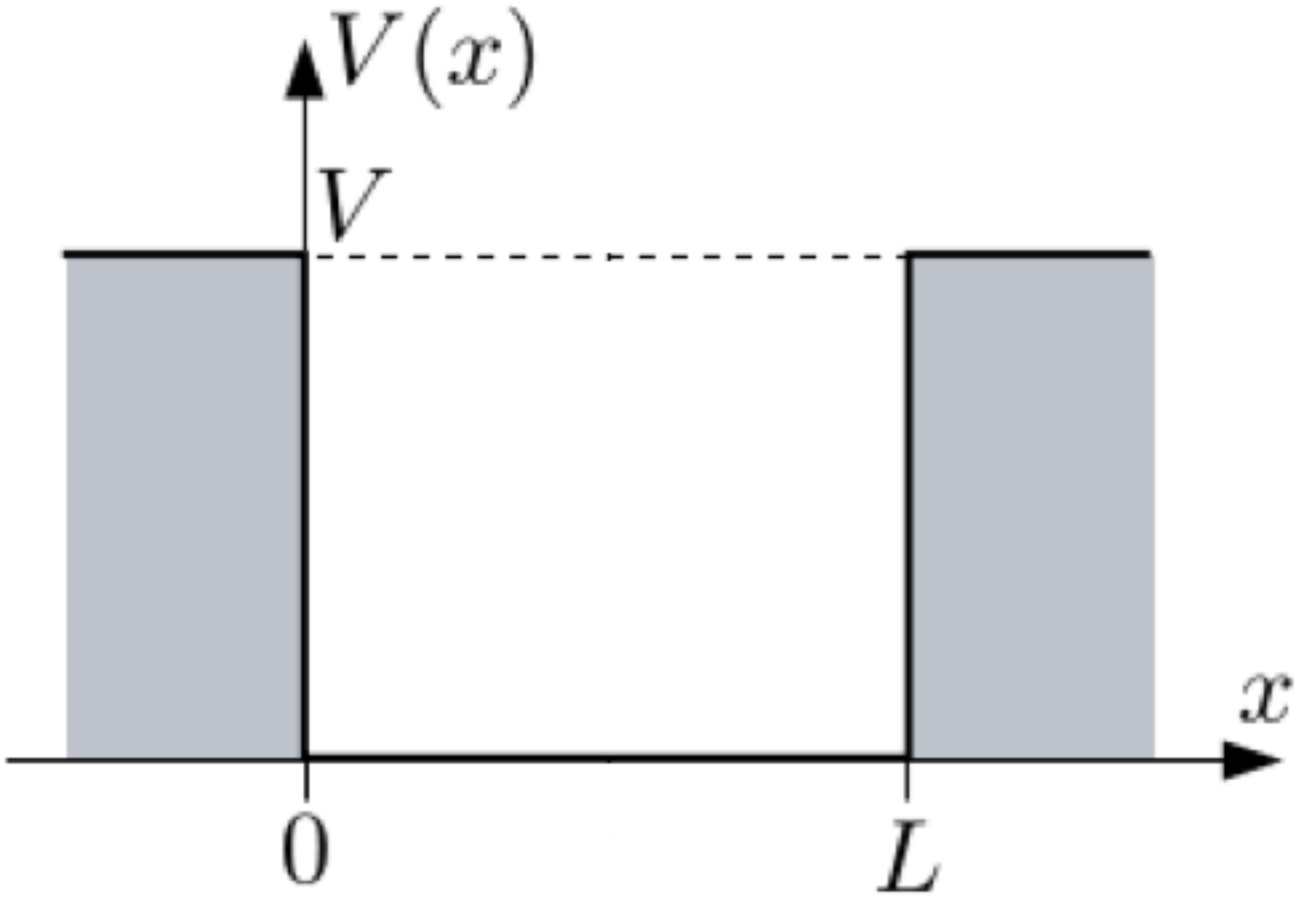
- Problem: β-Carotene is a linear polyene in which 10 single and 11 double bonds alternate along a chain of 22 carbon atoms. If we take each C-C bond length to be about 140 pm, then the length L of the molecular box in β-carotene is L = 2.94 nm. Estimate the wavelength of the light absorbed by this molecule from its ground state to the next higher excited state.
- Answer:

$$\Delta E = E_{12} - E_{11} = 1.60 \times 10^{-19}\ \mathrm{J}$$

$$\lambda = \frac{h}{\Delta E} = 1.24\ \mu\mathrm{m}$$

Particle in a finite square-well potential

- Potential is constant V in $x < 0$ or $x > L$ and zero in $0 \leq x \leq L$
- The energy of particle is E and $E < V$
- Denote $k = \sqrt{2mE}/\hbar$ and $\kappa = \sqrt{2m(V - E)}/\hbar$



Wavefunction in individual regions

- $0 < x < L$:
$$\psi_2(x) = Ae^{ikx} + Be^{-ikx}$$
- $x < 0$:
$$\psi_1(x) = Ce^{\kappa x} + C'e^{\kappa x}$$
- $x > L$:
$$\psi_3(x) = De^{-\kappa(x-L)} + D'e^{\kappa(x-L)}$$
- Boundary conditions at infinity:
$$\psi_1(-\infty) = \psi_3(+\infty) = 0, \therefore C' = D' = 0$$

Boundary conditions at interfaces

- $x = 0$
  - $\psi_1(0) = \psi_2(0)$, i.e. $C = A + B$
  - $\psi_1'(0) = \psi_2'(0)$, i.e. $\kappa C = ik(A - B)$
  - $A = \frac{ik+\kappa}{2ik} C, B = \frac{ik-\kappa}{2ik} C$
- $x = L$
  - $\psi_2(L) = \psi_3(L)$, i.e. $Ae^{ikL} + Be^{-ikL} = D$
  - $\psi_2'(L) = \psi_3'(L)$, i.e. $ik\left(Ae^{ikL} - Be^{-ikL}\right) = -\kappa D$
  - $A = \frac{ik-\kappa}{2ik} e^{-ikL} D, B = \frac{ik+\kappa}{2ik} e^{ikL} D$

Wavefunction

- From last slide, C can be expressed in terms of D as

$$C = \frac{ik-\kappa}{ik+\kappa} e^{-ikL} D \text{ or } C = \frac{ik+\kappa}{ik-\kappa} e^{ikL} D$$

- Use the first expression, we have

$$\psi(x) = D \cdot \begin{cases} \frac{ik-\kappa}{ik+\kappa} e^{-ikL} e^{\kappa x}, x \le 0 \\ \frac{ik-\kappa}{2ik} e^{-ikL} e^{ikx} + \frac{ik+\kappa}{2ik} e^{ikL} e^{-ikx}, 0 < x < L \\ e^{-\kappa(x-L)}, x \ge L \end{cases}$$