Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 9
Sep 23^{rd}, 2013

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Objectives

- To introduce the concept of free particle as well as its quantum-mechanical description.

- To present the free particle potential incident on a step potential.

- To motivate quantum tunnelling by means of the step potential.

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A free particle in one dimension

- A particle is said to be free if it experiences no repulsive or attractive force, that is, if the potential energy field is zero

$$V(x)=0, \quad -\infty < x < \infty$$

- Therefore the Schrödinger equation is

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

- Similar to the case of a particle in a box, the former equation can be re-arranged as

$$\frac{d^2\psi}{dx^2}(x)+\left(\frac{2mE}{\hbar^2}\right)\psi(x)=0 \ ,$$

- As it has been discussed during the tutorial sessions, the form of the solution of this equation depends on the sign of *E*

A free particle in one dimension

- <u>Case I</u>. Negative energy (*E* < *0*)

$$\frac{d^2\psi}{dx^2}(x)-\left(\frac{2m|E|}{\hbar^2}\right)\psi(x)=0 \ , \ \beta^2=\frac{2m|E|}{\hbar^2}$$

- The solution to this equation is given by (*A* and *B* constants)

$$\psi(x)=Ae^{\beta x}+Be^{-\beta x}$$

- We notice that the **first exponential** diverges when *x* tends to minus infinity. Similarly the **second exponential** diverges when *x* tends to plus infinity. Therefore:

There is no physically acceptable wave-function when *E* < *0*

A free particle in one dimension

- Case II. Positive energy ($E > 0$)

$$\frac{d^2\psi}{dx^2}(x)+\left(\frac{2m|E|}{\hbar^2}\right)\psi(x)=0\ ,\ \alpha^2=\frac{2m|E|}{\hbar^2}$$

- The solution to this equation is given by (A and B constants)

$$\begin{aligned}\psi(x) &= Ae^{i\alpha x}+Be^{-i\alpha x}\\ &=\psi_+(x)+\psi_-(x)\end{aligned}$$

- The **first complex exponential** represents a particle traveling to the **right**. Similarly, the **second complex exponential** represents a particle traveling to the **left**.

The energy of a free particle is not quantized, i.e, it can take any positive value *E* > *0.* Allowed energies are continuous.

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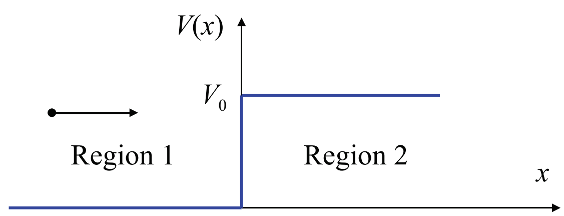
Free particle incident on a step potential

- Consider a particle with energy E, traveling to the right and incident on a step potential of height V_0.



- The potential can be expressed as (V_0 is a constant)

$$V(x)=\begin{cases}0, & x<0\\ V_0 & x>0\end{cases}$$

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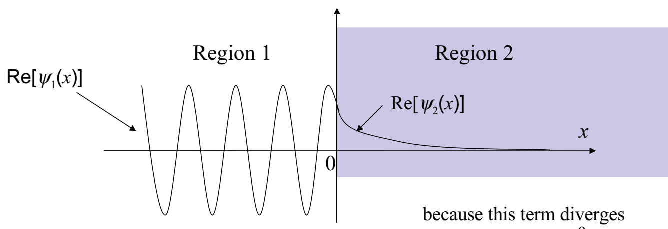
Wave-function for a particle with 0 < E < V_0

- Depending on the region, the wave-function looks like



because this term diverges

$$\psi_1(x) = Ae^{ikx} + Be^{-ikx} \qquad \psi_2(x) = Ce^{-\beta x} + \underbrace{\cancel{D}e^{\beta x}}_{=0} = Ce^{-\beta x}$$

$$k = \frac{\sqrt{2mE}}{\hbar} \qquad \beta = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

- The **transmission** and **reflection** coefficients are introduced

$$t = \left|\frac{C}{A}\right| \qquad r = \left|\frac{B}{A}\right|$$

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Transmission probability with 0 < E < V_0

- After imposing continuity conditions on the wave-function, the **transmission probabilities** is obtained

$$P_t = |t|^2 = \left|\frac{C}{A}\right|^2 = \frac{4k^2}{k^2 + \beta^2}$$

- Key result: **The particle can penetrate into the region where *E* < V_o**

- For a classical particle, a potential wall is rigid (hard). For a quantum particle, a finite potential wall is permeable (soft).

- Important note: The reader should try to obtain the above expression for P_t

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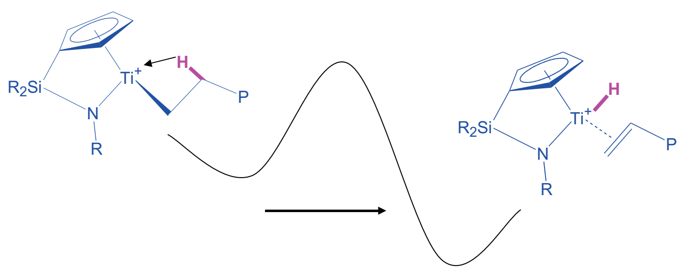
Application No.2a: Quantum tunneling

- Quantum tunneling plays an important role in physics and chemistry. Proton transfer reactions often involve **tunneling**.
- Consider a cut through the potential energy surface of the following chemical reaction (beta-hydride elimination)



- The rate of proton transfer is accelerated by tunneling.
- For heavier nuclei tunneling is less common. For macroscopic objects, tunneling is completely negligible.

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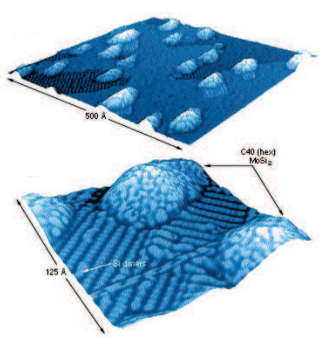
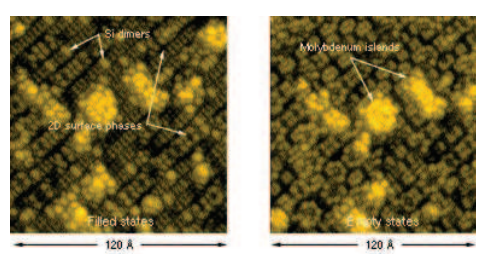
Application No.2b: Scanning tunneling microscopy (STM)

- In a STM, a very fine metal tip is placed close to a surface and a small voltage is applied. Electrons tunnel through the gap (vaccum) between the tip and the surface.



Images of a Si(100) surface doped with molybdenum



STM images of the same surface at a higher resolution. Brighter spots correspond to individual atoms.

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