Problem Set 3 Solutions
Chemistry 675, Fall 2024

1

Consider the potential:

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

with energy $0 < E < V_0$.

(a) Draw the potential energy surface making sure to remember axes labels

(b) Calculate the wavefunction in all regions of space.

$$\Psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{-\kappa x} & x \geq 0 \end{cases}$$

where $k = \sqrt{\frac{2mE}{\hbar^2}}$ and $\kappa = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}$.

The boundary conditions at $x = 0$ (continuity of $\Psi(x)$ and $\frac{d\Psi(x)}{dx}$) give the relations between A, B, and C.

Continuity of $\Psi(x)$ gives $A + B = C$ and continuity of $\frac{d\Psi(x)}{dx}$ gives $ik(A - B) = -\kappa C$.

(c) Determine the reflection and transmission coefficients

The reflection coefficient R and the transmission coefficient T are given by:

$$R = \left|\frac{B}{A}\right|^2$$

$$T = \left|\frac{C}{A}\right|^2$$

The coefficients depend on the ratio between E and V_0. For $E < V_0$, the particle will be partially reflected and partially transmitted into the region $x \geq 0$.

2.

The wavepacket is given by:

$$\Psi(x, t = 0) = \left(\frac{A^2}{\pi}\right)^{1/4} e^{-\frac{a^2(x-L/2)^2}{2} + ik_0 x}$$

with $L = 10\,\text{au}$, $a = 2\,\text{au}$, and $k_0 = 10\,\text{au}$.

(a) Given that the position x must be a length and the argument of an exponent must be unitless, convert L, a, and k0 to SI units. We can convert the units from atomic units (au) to SI units using the following:

$$1\,\text{au of length} = 5.29177 \times 10^{-11}\,\text{m}$$
$$1\,\text{au of momentum} = 1.99285 \times 10^{-24}\,\text{kg m/s}$$

Thus,

$$L = 10\,\text{au} = 5.29177 \times 10^{-10}\,\text{m}, \quad a = 2\,\text{au} = 1.05835 \times 10^{-10}\,\text{m}, \quad k_0 = 10\,\text{au} = 1.99285 \times 10^{-23}\,\text{kg m/s}.$$

(b) Compute the average momentum of the electron. The average momentum of the electron is given by:

$$\langle p \rangle = \hbar k_0 = (1.05457 \times 10^{-34}\,\text{Js}) \times (10\,\text{au}) = 1.05457 \times 10^{-33}\,\text{kg m/s}.$$

(c) Expand the wavefunction in terms of particle-in-a-box basis states. The wavefunction can be expanded in terms of particle-in-a-box eigenstates $\psi_n(x)$:

$$\Psi(x, t = 0) = \sum_n c_n \psi_n(x),$$

where $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$, and c_n are the expansion coefficients, determined by:

$$c_n = \int_0^L \psi_n^*(x) \Psi(x, 0)\, dx.$$

(d) Plot $|\Psi(x,t)|^2$ at several times between 0 and 2 au, and describe the motion of the particle. The plot of $|\Psi(x,t)|^2$ at several times can be computed numerically by solving the time-dependent Schrödinger equation.

(e) Compute the amount of time for a classical electron of momentum k_0 to pass from the center of the box to the wall. The time for a classical electron to travel from the center of the box to the wall is given by:

$$t = \frac{L/2}{v} = \frac{L/2}{\frac{\hbar k_0}{m}},$$

where v is the velocity of the electron, $v = \frac{\hbar k_0}{m}$.

(f) How do the results change for different a? Changing a affects the initial localization of the wavepacket. A larger a will result in a more spread-out wavepacket, while a smaller a will give a more localized wavepacket.

(g) How do the results change for different L? Changing L affects the energy levels of the particle in the box. A larger L will reduce the energy spacing of the energy eigenstates of particle-in-a-box, while a smaller L will increase the energy level spacing. If the energy (momentum) spacing of the basis are small, dispersion of the wave packet would be slower, and vice versa.

3. Consider a right-moving particle subject to the potential
Consider the potential:

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

(a) The wavefunction for $E < V_0$ can be determined as:

$$\Psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ C\cosh(\kappa x) + D\sinh(\kappa x) & 0 \le x \le L \\ Fe^{ikx} & x > L \end{cases}$$

where $\kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$.

(b) The reflection and transmission coefficients are:

$$R = \left|\frac{B}{A}\right|^2, \quad T = \left|\frac{F}{A}\right|^2.$$

Quantum tunneling occurs for $E < V_0$, allowing the particle to have a nonzero transmission probability despite the classical forbidden region.

(c) For $E > V_0$, the wavefunction takes the form:

$$\Psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{iqx} + De^{-iqx} & 0 \le x \le L \\ Fe^{ikx} & x > L \end{cases}$$

where $q = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$.

(d) For $E > V_0$, quantum reflection occurs. The reflection and transmission coefficients are calculated as:

$$R = \left|\frac{B}{A}\right|^2, \quad T = \left|\frac{F}{A}\right|^2.$$