

Figure 9.11 Wavefunction for a particle of energy E incident from the left on a potential barrier of height V and width a .

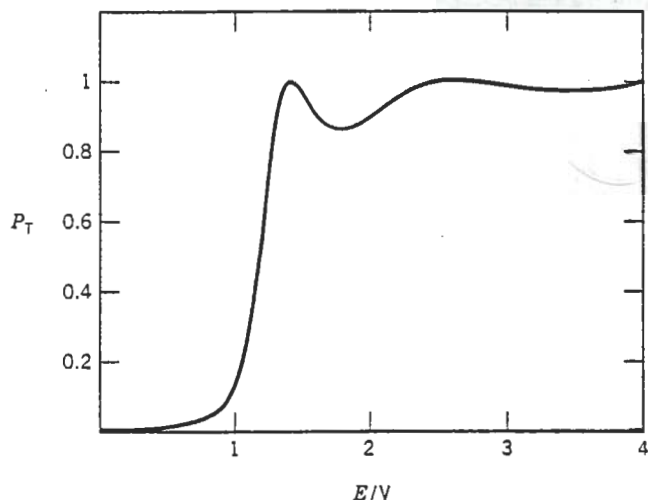


Figure 9.12 Probability of a proton tunneling through a 10-pm-wide potential barrier of height 1 eV.

Illustration 12.3

isotope effect

The ability of a proton to tunnel through a barrier contributes to the rapidity of proton transfer reactions in solution and therefore to the properties of acids and bases. To estimate the relative probabilities that a proton and a deuteron can tunnel through the same barrier of height 1.0 eV (1.6×10^{-19} J) and length 100 pm when their energy is 0.9 eV, we first evaluate

$$\kappa = \left\{ \frac{2(m/u) \times (1.67 \times 10^{-27} \text{ kg}) \times (1.6 \times 10^{-20} \text{ J})}{(1.055 \times 10^{-34} \text{ Js})^2} \right\}^{1/2} = \frac{(m/u)^{1/2}}{14 \text{ pm}}$$

The values of κ for a proton ($m = 1.0$ u) and a deuteron ($m = 2.0$ u) are $1/(14 \text{ pm})$ and $1/(9.9 \text{ pm})$, respectively, so $\kappa L \gg 1$ and eqn 28b can be used. The ratio of transmission probabilities is then

$$\frac{T_H}{T_D} = e^{-2(\kappa_H - \kappa_D)L} = 3.7 \times 10^2$$

(The ratio is very sensitive to rounding errors.) The result shows that the tunnelling probability of a proton (in the system specified) is nearly 80 million times greater than that of a deuteron. Therefore, we expect proton transfer reactions to be much faster than deuteron transfer reactions.

Self-test 12.4 Calculate the relative tunnelling probabilities when the barrier is twice as long, the other conditions being unchanged. [1.4×10^5]