

Lecture 20 – Quantum Tunneling of Electrons

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Introduction

Until now, we have been discussing reaction rates on a somewhat phenomenological basis. In this lecture, we will become much more fundamental, and merge our analysis of reaction rates with quantum mechanics. First, we'll discuss the concept of *tunneling*, a phenomenon by which particles can pass through a potential well *even when classically they don't have the energy to do so*. Tunneling is a quantum mechanical phenomenon, and thus is important for small mass particles in which classical laws break down (e.g. important for electrons, but not so much for ions or atoms).

So far, our classical theory of reaction rates has produced:

$$R \propto e^{-E_A / kT}$$

with some proportionality constant that depends on vibrational frequencies or some hopping attempt.

A 'quantum' particle can go over energy barriers even at T=0K. Thus, the classical rate equation does not strictly apply, especially as we go to low temperatures. As mentioned earlier, this is especially important in electrons where tunneling is very important. Electron tunneling is in fact responsible for many important research areas, such as imaging (see scanning tunneling microscopy) or the breakdown of Moore's law in electronics, and so this is not just a purely academic topic. However, in the appropriate limits (e.g. mass of the particle grows large), we do recover classical laws even when analyzing from a quantum perspective, as we would expect.

We'll next analyze the classic problem of tunneling through a 1D potential barrier to introduce the concept of tunneling.

1. Tunneling in a 1D Potential Barrier

Consider a potential barrier (as opposed to a potential well), as represented in Figure 1. The potential is constant V_0 between $x=-a$ and $x=a$, and zero outside of this region. A particle starts on one side of the barrier, and we want to know the possibility of it crossing to the other side of the barrier. Our particle has energy $E < V_0$, so that classically it has no chance of crossing the barrier (e.g. at 0K, or neglecting any additional energy which may come from an Arrhenius-type temperature effect).

We'll define the quantity τ as the *transmission probability* of the particle going through the well even under these conditions.

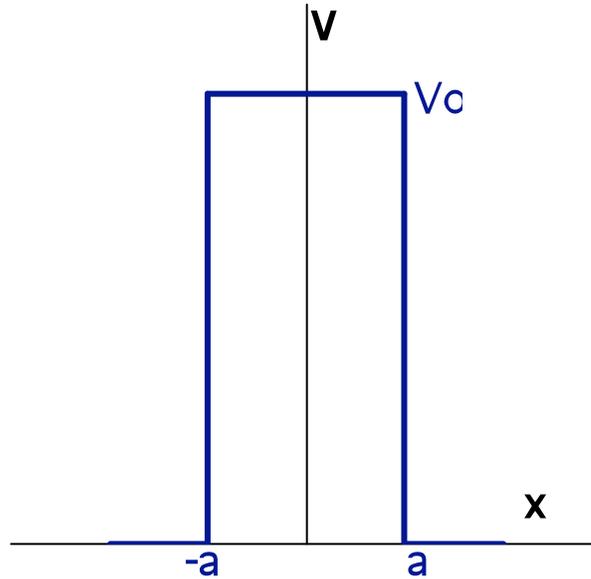


Figure 1. A simple potential barrier for tunneling analysis.

Because of the simple nature of this potential, we can in fact solve the Schrödinger equation analytically for this setup:

$$H_{op}\psi = E\psi$$

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

Since our $V(x)$ is a piecewise function, we can solve this equation separately in each region of x where V is constant. We already solved this equation for $V=0$ in a previous lecture (free electron gas), and so we know the solution to $\psi(x)$ were $V=0$:

$$\psi(x) = \begin{cases} e^{ikx} - R e^{-ikx} & \text{for } x < -a \\ T e^{ikx} & \text{for } x > a \end{cases}$$

where $E = \hbar^2 k^2 / 2m$

This form of the solution assumes a “transmission problem”:

- We absorbed the two coefficients for the region $x < -a$ into one coefficient, R (while applying normalization conditions)
- For $x > a$, we set the coefficient for the e^{-ikx} term to be zero, leaving only one term. This is because the e^{-ikx} term represents a left-traveling wave (when combined with the time-dependent part of the solution), and we are dealing with rightward-traveling waves only in this region (due to our problem definition).

The reflection coefficient R and transmission coefficient T determine the probability of the particle going through the barrier (Figure 2).

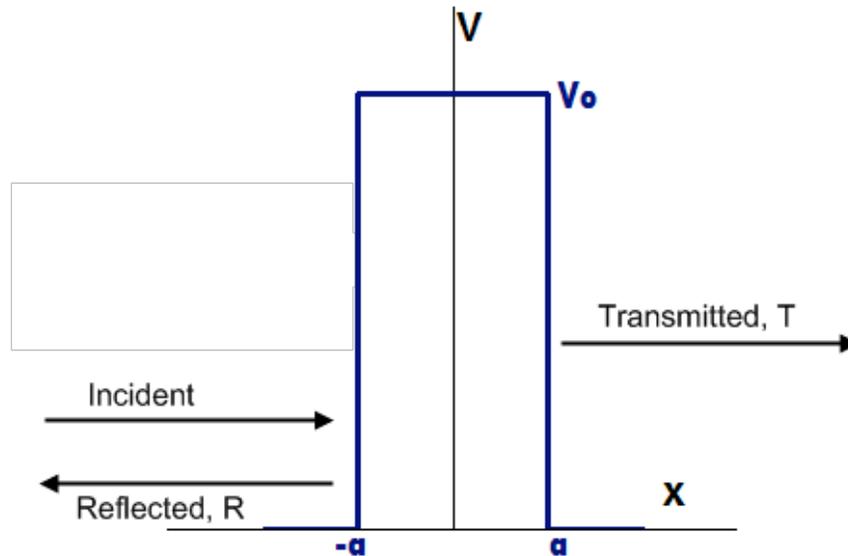


Figure 2. Reflection and Transmission coefficients R & T determine the probability of reflection and transmission through the well.

Next, we solve for the solution to $\psi(x)$ inside the potential well. For x inside the well, we get:

$$H_{op}\psi = E\psi$$

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V_0\psi = E\psi$$

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + (V_0 - E)\psi = 0$$

$$\text{since } E < V_0, \quad \kappa^2 \equiv \frac{2m(V_0 - E)}{\hbar^2} > 0$$

$$\frac{d^2\psi}{dx^2} - \kappa^2\psi = 0$$

The quantity κ can be expressed as an inverse length $2/\lambda_t$, where λ_t represents the *tunneling length*. It will become clearer later why this is so.

The above differential equation is easy to solve, and we end up with an exponential solution:

$$\psi(x) = Ae^{\kappa x} - Be^{-\kappa x} \text{ for } -a < x < a$$

We now have four boundary conditions which let us determine the unknown coefficients A, B, R, and T. These boundary conditions require the continuity of the wavefunction and its derivative at the two interfaces, $x=+a$ and $x=-a$. This straightforward calculation yields an exponentially decaying solution within the barrier (Figure 3) and yields the transmission coefficient T :

$$\|T\|^2 = \frac{(2k\kappa)^2}{(k^2 + \kappa^2)^2 \sinh^2(2\kappa a) + (2k\kappa)^2}$$

(For example, see S. Gasiorowicz, *Quantum Physics*.)

A low tunneling probability $T \ll 1$ corresponds to a wide, tall barrier, $\kappa a \gg 1$, and in this limit, the transmission coefficient simplifies to

$$\|T\| \sim \left(\frac{4k\kappa}{k^2 + \kappa^2} \right) e^{-2\kappa a}$$

The key point is that the transmission probability decays exponentially with barrier width (beyond the tunneling length) and also exponentially with the square root of the energy to the barrier since:

$$e^{-2\kappa a} = e^{-a/\lambda_t} = e^{-2a\sqrt{\frac{2m}{\hbar^2}(V_0 - E)}}$$

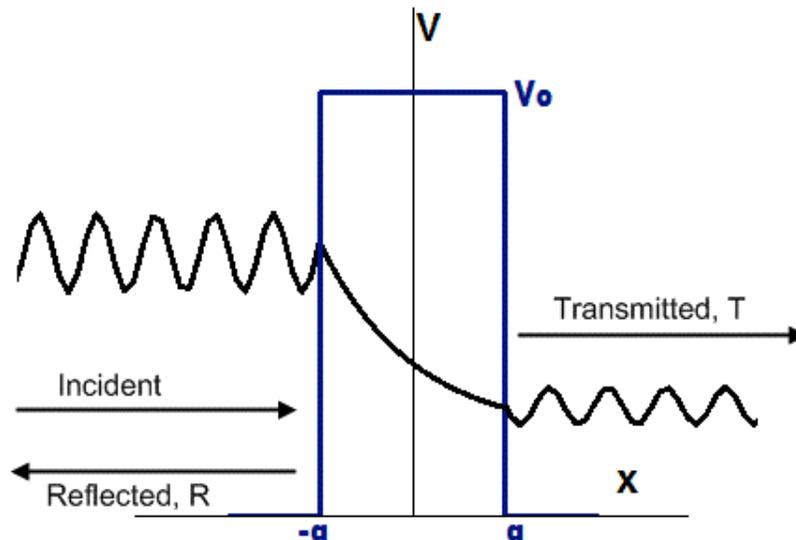


Figure 3. Visual schematic of ψ for the tunneling problem. We get a nonzero value of the wavefunction ψ at the other side of the barrier, and thus an electron may exist past the barrier!

Our solution is visualized in Figure 3.

2. Relation to General Barriers

For a general 1D barrier (not necessarily a step), we can model the barrier as a collection of smaller step-like barriers, each of width Δx_i and with height $V(x_i)$ (Figure 4). This is not always rigorous, but it applies here.

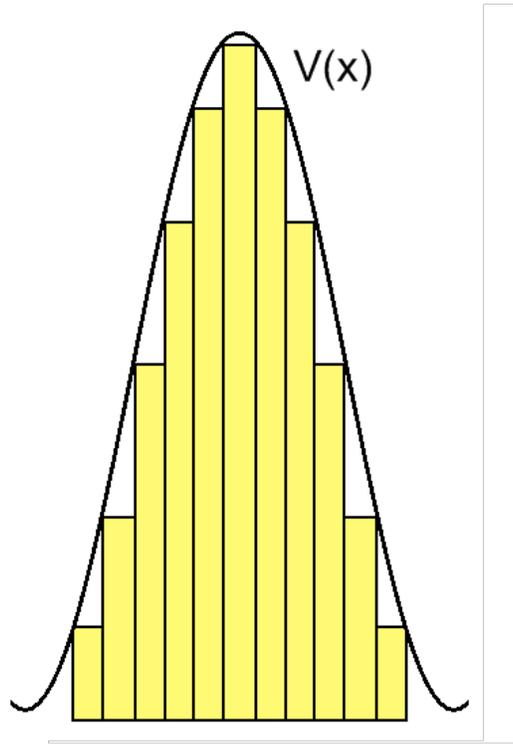


Figure 4. A general barrier approximated as several smaller barriers.

Assuming independence of transmission events, the total transmission probability for crossing the overall barrier is:

$$T = \prod \|T_i\|$$

where the T_i are the transmission probabilities of the individual step barriers. Assuming a large number of very thin barriers, we can approximate as follows

$$\begin{aligned} \log T &= \prod_i \log \|T_i\| \approx \sum_i -2\kappa_i \Delta x \\ \log T &\approx -2 \sum_i \sqrt{\frac{2m}{\hbar^2} (V(x_i) - E)} \Delta x \\ \log T &\approx -2 \int dx \sqrt{\frac{2m}{\hbar^2} (V(x) - E)} \\ T &\approx e^{-2 \int dx \sqrt{\frac{2m}{\hbar^2} (V(x) - E)}} \end{aligned}$$

where the integral is over the barrier region with $V > E$. (This approximation is accurate enough for our purposes, but neglects subtle behavior near the “turning points” where $V = E$, which can be treated in the semiclassical limit by the “WKB approximation.”)

To get a general sense of the scaling of $T(E)$ in the regime of significant tunneling probability, it is natural to consider only energies E large enough to sample the energy landscape near the barrier, where we can approximate $V(x)$ as an inverted parabola, $(V(x) - E) \sim (E_b - E)(1 - (x/l_b)^2)$. Substituting into the approximation above yields a simple expression for the tunneling probability out of a well over a smooth barrier starting from energy E :

$$P_t(E) \approx e^{-\pi l_b \sqrt{\frac{2m}{\hbar^2}(E_b - E)}}$$

which is quite similar to the exact solution for tunneling through a single step barrier (we have exponential dependence on barrier “width” l_b and square root of exponential dependence on barrier height).

3. Quantum Kramers Problem at $T=0$

We can now tackle the quantum problem of tunneling through wells at $T=0$, where no particles are excited over the well by thermal activation. The difference of this analysis from the last part is that we no longer have a single particle sitting at a small energy E . Rather, we have a distribution of particles sitting in their ground states, which are sitting at different energy levels based on the solution to the Schrödinger equation (note: we are talking about fermions, and specifically electrons, in the following analysis).

To get the allowed energy levels in the well, we would need to solve the Schrödinger equation for our particular $V(x)$. However, near the bottom of the well, we can approximate $V(x)$ as a parabola, and quote the energy levels we get from such a potential. In this case (quantum harmonic oscillator), we end up with evenly spaced energy levels spaced a distance $\hbar\omega$ apart (Figure 5).

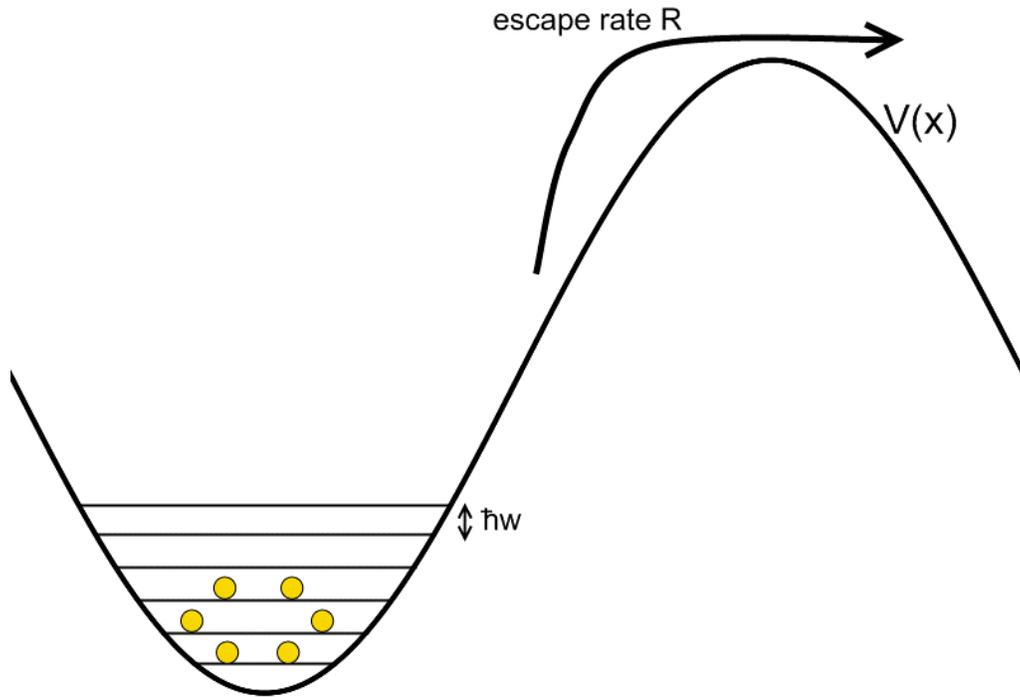


Figure 5. Our potential well, $V(x)$. We now have electrons sitting at discrete energy levels near the bottom of well, spaced as distance $\hbar w$ apart up to the Fermi energy E_F .

The exact form of these energy levels is:

$$E_n = (n + \frac{1}{2})w_{\min}$$

where:

$$w_{\min} = \sqrt{\frac{\hbar^2 k_{\min}}{m}}$$

using k_{\min} from our potential well near the minimum:

$$V_{\min}(x) \approx \frac{1}{2}k_{\min}x^2$$

At least in the lower region of the well, where it is well approximated by a parabola, the density of states $g(E)$ for this problem is constant (since the spacing between energy levels is constant), and equal to:

$$g(E) = \frac{1}{\hbar w_{\min}}$$

Note that if went to high energies E , our parabolic approximation to the potential (and thus our solution giving us equally-spaced energy levels) may no longer be valid. In this case, we expect the spacing between energy levels to be proportional to the curvature of the well. As the well approached smaller curvatures, we'd expect the spacing between states to grow smaller and the density of states to increase as we increased in energy.

However, we will stay close to the well minimum in our analysis and assume a constant density of states.

Now that we have our energy levels, we need to fill these energy levels with electrons. This is simple at 0K; the Fermi function $f(E)=1$ for $E < E_F$, and $f(E)=0$ for $E > E_F$.

With this setup, we can solve for the probability of tunneling through the barrier. However, to get the rate, we need some sort of “attempt frequency” to escape. For the harmonic oscillator, we take this to be frequency of wave oscillations, E/h or $E/(2\pi\hbar)$. Thus, we can express the rate of escape as:

$$R = \int_0^{\infty} dE \left(\frac{E}{h} \right) n(E) P_t(E)$$

where $P_t(E)$ is the tunneling probability. Using the Fermi function, we can get $n(E)$ and rewrite this as:

$$R = \int_0^{E_F} dE \left(\frac{E}{h} \right) g(E) P_t(E)$$

Substituting the approximations above (ignoring changes in $P(E)$ for low energies where $V(x)$ resembles a parabola, rather than an inverted parabola), we have the approximation

$$R = \frac{1}{2\pi\hbar^2 n_{\min}} \int_0^{E_F} dE * E * e^{-\pi l_b \sqrt{\frac{2m}{\hbar^2}(E_b - E)}}$$

In the semiclassical limit (finely spaced energy levels compared to the barrier height), this integral is dominated by tunneling from the Fermi level through the barrier::

$$R \propto e^{-\pi l_b \sqrt{\frac{2m(E_b - E_f)}{\hbar^2}}}$$

In general, even at 0K, the transition rate rate is finite! Without getting into the details of our potential (other than E_b and l_b , along with well curvature), we have used our assumptions to derive a reaction rate for tunneling at 0K, decays exponentially with the product of the barrier width and the square root of the barrier energy.

4. Quantum Kramers Problem at $T > 0$

At $T > 0\text{K}$, the only formal complication is that the Fermi function is no longer a step function. Rather, we have:

$$f(E) = \frac{1}{1 + e^{\frac{E-\mu}{kT}}}$$

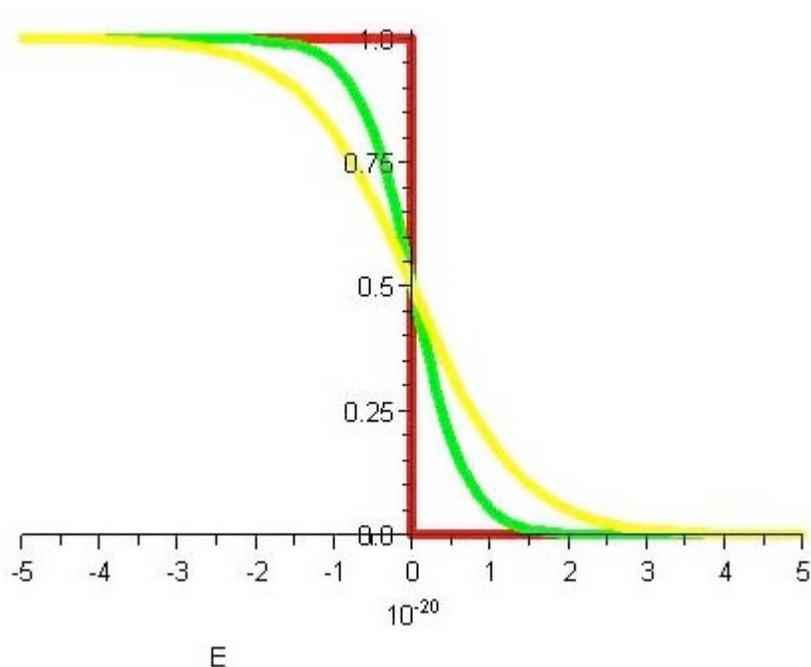


Figure 6. The Fermi-Dirac Distribution at $T=0\text{K}$ (Red), $T=250\text{K}$ (Green), and $T=500\text{K}$ (Yellow).

We still make the approximation that the Fermi level lies well below the barrier, $E_F \sim \mu \ll E_b$, now by more than the thermal energy kT , so that barrier crossings are still “rare”. In the semiclassical limit, we can recover the classical Kramers formula.

The main effect of quantum tunneling is to enhance the reaction kinetics, by allowing particles to sometimes tunnel through the barrier from a lower energy, rather than diffusing randomly over the top, as required by classical statistical mechanics. This effect has helped the theory of Faradaic reaction rates come closer into quantitative agreement with experimentally observed reaction rates, which are often larger than expected based on the classical theory.

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