Time evolution of the wave function leading to the Fowler-Nordheim electron emission

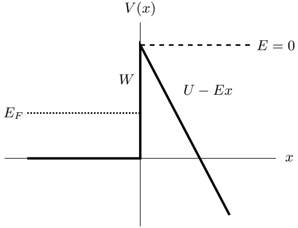
Joel L. Lebowitz

Rutgers University

joint work with **Ovidiu Costin, Rodica D. Costin** and **Ian Jauslin**

The microscopic theory of the emission of electrons from a flat cold metal surface by a constant field was developed by Fowler and Nordheim (FN) in the early days of quantum mechanics. They considered an idealized situation in which the electrons in the conduction band are treated, a la Sommerfeld, as free independent particles, with energies given by a Fermi distribution with maximum energy $E_F = \hbar^2 k_F^2/2m$; the deviation from this zero-temperature distribution is negligible at ordinary temperatures.

Considering metals of macroscopic size like those used in experiments at that time, FN modeled the system to be infinite: occupying all of the half-space $x < 0$. In the absence of an external field the electrons are confined by a step function potential (caused by the positive ions) of magnitude $U = E_F + W$, where W is the work function. Applying an external field E for $x \geqslant 0$, leads to a one-dimensional tunneling problem in a triangular potential, $V(x)$.



The one-dimensional Schrödinger equation describing such a “free” electron is then given by

$$i\frac{\partial\psi(x,t)}{\partial t} = -\frac{\partial^2\psi}{\partial x^2} + V(x)\psi \tag{1}$$

where

$$V(x) = \begin{cases} 0, & x < 0 \\ U - Ex, & x > 0 \end{cases} \tag{2}$$

in units $\hbar = 2m = |e| = 1$. These are essentially atomic units with an extra factor of $\sqrt{2}$ in the length.

When $E = 0$, the Schrödinger equation has generalized 'stationary' solutions, for an electron with energy k_0^2, $\psi(x,t) = e^{-ik_0^2 t}\psi_0(x)$, with $k_0 > 0$,

$$\psi_0(x) = \begin{cases} e^{ik_0 x} + R_0 e^{-ik_0 x} & x < 0 \\ T_0 e^{-\sqrt{U-k_0^2}x} & x > 0 \end{cases} \tag{3}$$

in which R_0 and T_0 are the *reflection* and *transmission* coefficients (we use a normalization in which the amplitude of the incoming wave $k_0 > 0$ is 1):

$$R_0 = \frac{ik_0 + \sqrt{U - k_0^2}}{ik_0 - \sqrt{U - k_0^2}}, \quad T_0 = \frac{2ik_0}{ik_0 - \sqrt{U - k_0^2}}. \tag{4}$$

These constants ensure that $\psi_0(x)$ and $\partial\psi_0(x)$ are continuous at $x = 0$.

For $k_0^2 < U$, $\psi_0(x)$ decays exponentially for $x > 0$, with

$$1 + R_0 = T_0, \quad |R_0| = 1. \tag{5}$$

The current in this state vanishes:

$$j_0(x) = i(\psi \partial_x \psi^* - \psi^* \partial_x \psi) = 2k_0(1 - |R_0|^2) = 0. \tag{6}$$

When $E > 0$, there is the possibility for an electron moving in the $+x$ direction, with kinetic energy $k_0^2 < U$, to tunnel through the potential barrier and be emitted. To obtain the probability of tunneling, FN computed the generalized stationary solutions of the Schrödinger equation for an electron with energy k_0^2: $\psi(x,t) = e^{-ik_0^2 t}\psi_E(x)$ with

$$\psi_E(x) = \begin{cases} e^{ik_0 x} + R_E e^{-ik_0 x} & x < 0 \\ T_E \Phi(x) & x > 0 \end{cases}, \quad k_0 > 0. \tag{7}$$

where $\Phi(x)$ is proportional to the Airy function $\mathrm{Ai}(e^{-\frac{i\pi}{3}}(E^{\frac{1}{3}}x - E^{-\frac{2}{3}}(V - k_0^2)))$, which decays as $x \to \infty$. FN write the solution in terms of equivalent Hankel (or Bessel) functions. The term $e^{-\frac{i\pi}{3}}$ is a cube root of -1.

This solution yielded the tunneling probability $D(k_0) = 1 - |R_E|^2$ of the electron as a function of k_0, U and E. Integrating $2k_0 D(k_0)$ over the "supply function" corresponding to the density of electrons in the Fermi sea moving in the $+x$ direction with energy k_0^2, leads to an expression for the steady state current j_E in a static field E, which is given roughly by

$$j_E \sim c_1 E^2 e^{-\frac{c_2}{E}}. \tag{8}$$

The FN formula for j_E, with various corrections for the idealizations made, e.g. flat surface, independent electrons, Schottky effect, etc, serves as the backbone of cold electron emission theory and experiment. There is a vast literature on the subject (the original FN paper has more than 6000 citations).

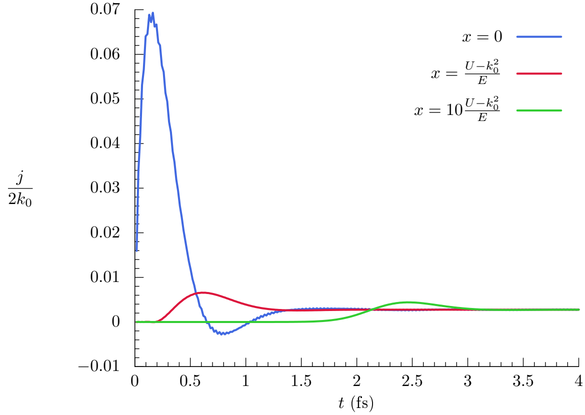
In our work we go beyond FN by considering a situation in which the initial wave function of the system is the generalized stationary solution at $E = 0$, $\psi_0(x)$ in (3). At $t = 0$, we turn the field on, and study the time evolution of $\psi(x, t)$. In particular, we ask how long it will take, if ever, for the initial state $\psi(x, 0) = \psi_0(x)$ to approach the stationary state $\psi_E(x)$. (Of course, turning on E instantaneously is an idealization, which we shall accept here, but consider in future work.)

We have been able to prove that, for $\psi(x,0)=\psi_0(x)$, $\psi(x,t)$ approaches, for long times, the FN solution

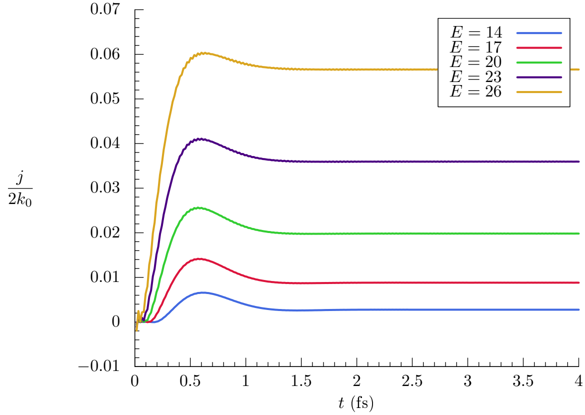
$$\psi(x,t) \sim e^{-ik_0^2 t}\psi_E(x) \tag{9}$$

In fact, this is still true if one takes $\psi(x,0)=\psi_0(x)+f(x)$ where $f(x)$ is square integrable. This follows from general results about systems with absolutely continuous spectrum. To get the form of the decay, one needs to do the computation. In our case, the deviation $\psi(x,t)-\psi_E(x)$ goes asymptotically as $t^{-\frac{3}{2}}$.

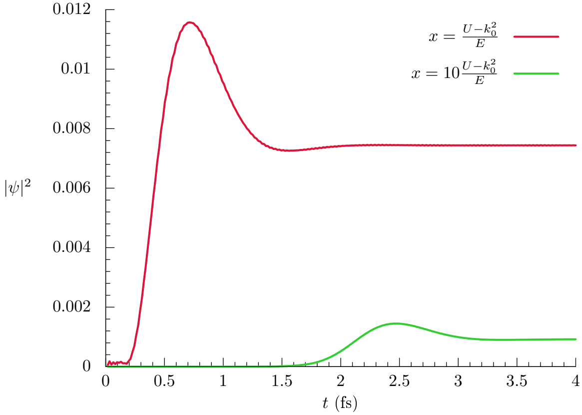
After a detailed analysis described below, we find that for $U \approx 9$ eV, $\hbar^2 k_0^2/2m = E_F \approx 4.5$ eV and $E \approx 14\text{-}22\ \mathrm{V} \cdot \mathrm{nm}^{-1}$, the time it takes the current $j(x,t)$ to approximately reach its final FN value is, looking at the position $x_0 = \frac{U - k_0^2}{E}$ at which the particle crosses the barrier, of the order of femtoseconds. This is similar to the "tunneling time" as defined by Landauer et al, i.e. the time it takes a particle with speed $2\sqrt{U - k_0^2 - Ex}$ to cross the barrier. (There are other definitions of tunneling times which we are exploring with Kevin Jensen, Dan Shiffler, and others).



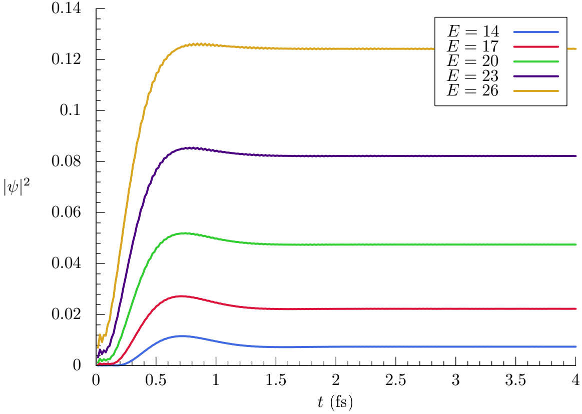
$$E = 14\text{V} \cdot \text{nm}^{-1},\ x_0 = \frac{U-k_0^2}{E} \approx 0.321\ \text{nm},\ v_F = 2k_0 \approx 0.629\ \text{nm} \cdot \text{fs}^{-1}.$$



$$x = x_0 = \frac{U - k_0^2}{E} \approx 0.321 \text{ nm}, \; v_F = 2k_0 \approx 0.629 \text{ nm} \cdot \text{fs}^{-1}.$$



$$E = 14\text{V} \cdot \text{nm}^{-1},\ x_0 = \frac{U-k_0^2}{E} \approx 0.321 \text{ nm},\ v_F = 2k_0 \approx 0.629 \text{ nm} \cdot \text{fs}^{-1}.$$



$$x = x_0 = \frac{U - k_0^2}{E} \approx 0.321 \text{ nm}, \ v_F = 2k_0 \approx 0.629 \text{ nm} \cdot \text{fs}^{-1}.$$

This will clearly affect results for short pulses of a few femtoseconds or less. These are now common for laser fields. The initial value problem for oscillating fields is much more complex and will be considered in the coming period.

Now, for the computations. To obtain $\psi(x,t)$ we first solve for $\hat{\psi}_p(x)$, the Laplace transform of $\psi(x,t)$, which we obtain in a closed form. We then compute the long time asymptotics analytically, and the short time behavior numerically by inverting the Laplace transform. We found this method better than direct computations of the time dependent solution of the Schrödinger equation for the non-square integrable functions we are dealing with.

The Laplace transform of ψ is

$$\hat{\psi}_p(x) := \int_0^\infty dt\; e^{-pt}\psi(x,t) \tag{10}$$

It satisfies the equation

$$(-\partial_x^2 + \Theta(x)(U - Ex) - ip)\hat{\psi}_p(x) = -i\psi(x,0). \tag{11}$$

where $\psi(x,0) \equiv \psi_0(x)$ consists of three terms: an incoming, a reflected, and a transmitted wave.

$$\psi(x,0) = \psi^{(\mathrm{I})}(x,0) + \psi^{(\mathrm{R})}(x,0) + \psi^{(\mathrm{T})}(x,0) \tag{12}$$

with

$$\psi^{(\mathrm{I})}(x,0) = \Theta(-x)e^{ik_0x}, \quad \psi^{(\mathrm{R})}(x,0) = R_0\Theta(-x)e^{-ik_0x} \tag{13}$$

$$\psi^{(\mathrm{T})}(x,0) = T_0\Theta(x)e^{-\sqrt{U-k_0^2}x} \tag{14}$$

where $k_0 > 0$ and

$$\Theta(x) = \begin{cases} 0, \ x < 0 \\ 1, \ x > 0. \end{cases} \tag{15}$$

We solve this equation under the condition that $\hat{\psi}_p(x)$ is bounded as $|x| \to \infty$, remembering that $\sqrt{-ip}$ has a positive real part:

$$\hat{\psi}_p(x) = \begin{cases} C_1(p)e^{\sqrt{-ip}x} - \dfrac{i\psi_0(x)}{-ip + k_0^2}, \text{ if } x < 0 \\ \\ C_2(p)\varphi_p(x) + T_0 F_p^{(\mathrm{T})}(x), \text{ if } x > 0 \end{cases} \tag{16}$$

where

$$F_p^{(\mathrm{T})}(x) := 2\pi \left(\varphi_p(x) \int_0^x dy\ \eta_p(y) e^{-\sqrt{U - k_0^2}y} + \eta_p(x) \int_x^\infty dy\ \varphi_p(y) e^{-\sqrt{U - k_0^2}y} \right). \tag{17}$$

The functions

$$\varphi_p(x) = \mathrm{Ai}\left(e^{-\frac{i\pi}{3}}\left(E^{\frac{1}{3}}x - E^{-\frac{2}{3}}(U - ip)\right)\right) \tag{18}$$

$$\eta_p(x) = e^{-\frac{i\pi}{3}}\mathrm{Ai}\left(-\left(E^{\frac{1}{3}}x - E^{-\frac{2}{3}}(U - ip)\right)\right) \tag{19}$$

are two solutions of $(-\partial_x^2 + U - Ex - ip)f = 0$. They both decay as $x^{-\frac{1}{4}}$ as $x \to \infty$, and have good behavior for large p. The constants $C_1(p)$ and $C_2(p)$ are set so that $\hat{\psi}_p$ and $\partial\hat{\psi}_p$ are continuous at $x = 0$.

We then invert the Laplace transform:

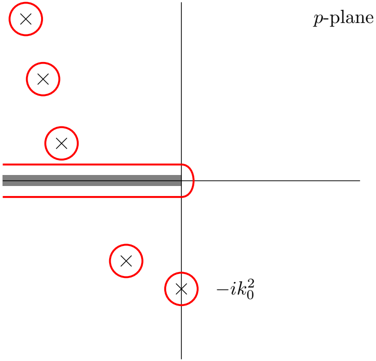
$$\psi(x,t) = \frac{1}{2i\pi} \int_{\gamma-i\infty}^{\gamma+i\infty} dp\ e^{pt} \hat{\psi}_p(x) \tag{20}$$

in which $\gamma > 0$ is an arbitrary small parameter taken close to 0.
As is well known the integral on the right hand side of (20) can be computed by studying the singularities, poles and branch points of $\hat{\psi}_p(x)$, lying in the half plane $\mathcal{R}e(p) \leq 0$. In particular, the only terms which do not decay as $t \to \infty$ come from poles on the imaginary p-axis.

Analyzing $\hat{\psi}_p(x)$, we find that the singularities of $\hat{\psi}_p(x)$ are

- a pole on the imaginary axis, located at $-ik_0^2$, which comes from $\psi^{(\mathrm{I})}(x,0)$ with $k_0 > 0$,
- poles with strictly negative real parts, coming from the zeros which occur in the denominator of $C_1(p)$ and $C_2(p)$.
- a branch cut along the negative real axis, coming from the $\sqrt{-ip}$ terms.

We deform the integration contour as in the figure below.



Note that the pole at $-ik_0^2$ comes entirely from $\psi^{(\mathrm{I})}(x)$.

The residues of the poles with a negative real part decay exponentially in time (because of the factor e^{pt} in (20)). The integral along the branch cut yields a term which decays as $t^{-\frac{3}{2}}$. Finally, the residue at $-ik_0^2$ yields the only term which does not decay in time. This yields

$$\psi(x,t) = e^{-ik_0^2 t}\psi_E(x) + \left(\frac{t}{\tau_E(x)}\right)^{-\frac{3}{2}} + O(t^{-\frac{5}{2}}) \tag{21}$$

Thus, we see that the wave function tends to the Fowler-Nordheim solution, with a rate $t^{-\frac{3}{2}}$. We have not written out here the exponentially decaying terms which are important for short times.

Note that all the contributions as $t \to \infty$ come from the incident wave $\psi^{(I)}(x,0)$. In fact, as already noted, the asymptotic value of $\psi(x,t)$ would be unchanged if we added any square-integrable function to the initial condition, or if we added a wave moving away from the origin (e.g. a term e^{-ikx} with $k > 0, x < 0$ or e^{ikx} with $k > 0, x > 0$).

Looking at the $t^{-\frac{3}{2}}$ corrections to the limiting form, we have, for the values $U = 9$ eV, $k_0^2 = 4.5$ eV, $E = 14$ V $\cdot$ nm^{-1}, and at $x = x_0$,

$$|\tau_E(x)| \approx 3.94 \text{ as.} \tag{22}$$

The current behaves as

$$j(x,t) = j_E \left(1 + (t/\sigma_E(x,t))^{-\frac{3}{2}} + O(t^{-\frac{5}{2}})\right) \tag{23}$$

and σ_E oscillates around 0 with an amplitude, at E=14 V $\cdot$ nm^{-1} and $x = x_0$, of roughly 7 as.

Delta function potential

An illustrative example for the use of the Laplace transform to solve initial value problems is to consider the Schrödinger equation

$$i\partial_t\psi = (-\partial_x^2\psi + \gamma\delta\psi) \tag{24}$$

with the initial condition

$$\psi(x,0) = e^{ik_0x}\Theta(-x) \tag{25}$$

with $k_0 > 0$ (i.e. there is an incident beam, with particle energy k_0^2 coming from the left).

The stationary solution for an incoming plane wave e^{ik_0x} with $k_0 > 0$ is given by $e^{-ik_0^2t}\psi_k(x)$ where

$$\psi_k(x) = \begin{cases} e^{ik_0x} + Re^{-ik_0x} & x < 0 \\ Te^{ik_0x} & x > 0 \end{cases} \tag{26}$$

with

$$R = \frac{\gamma}{2ik_0 - \gamma}, \quad T = \frac{2ik_0}{2ik_0 - \gamma} \tag{27}$$

The current, in the stationary state, is

$$2k_0 \left(\frac{4k_0^2}{4k_0^2 + \gamma^2} \right) \tag{28}$$

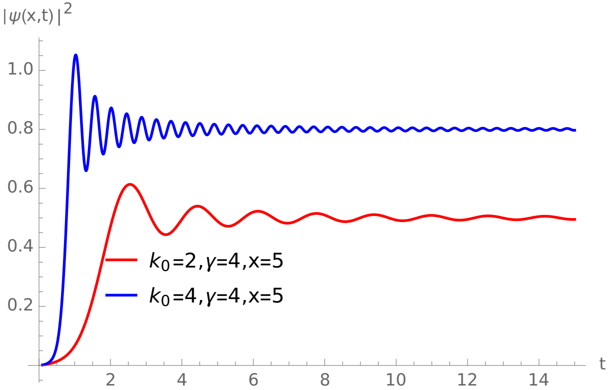
which goes to $2k_0$ for $\gamma = 0$ ant to 0 for $\gamma \to \infty$.

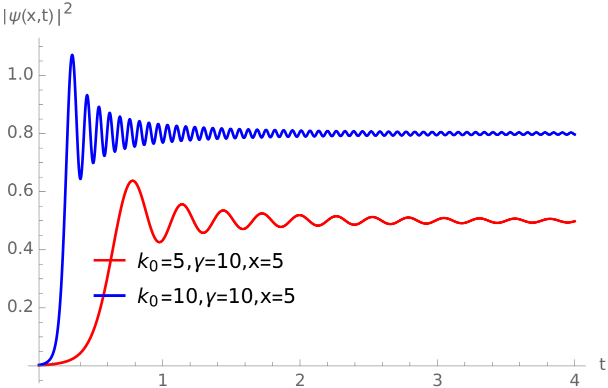
The solution $\psi(x,t)$ of the Schrödinger equation can be computed explicitly by inverting the Laplace transform: we have, for $x>0$,

$$\psi(x,t)=\frac{2k_0e^{-ik_0(k_0t-x)}\operatorname{erfc}\left(\frac{e^{\frac{3i\pi}{4}}(2k_0t-x)}{2\sqrt{t}}\right)+i\gamma e^{\frac{1}{4}\gamma(2x+i\gamma t)}\operatorname{erfc}\left(\frac{e^{\frac{i\pi}{4}}(\gamma t-ix)}{2\sqrt{t}}\right)}{2\left(2k_0+i\gamma\right)}. \tag{29}$$

Asymptotically in time, $\psi(x,t)$ goes to the stationary solution with, again, $t^{-\frac{3}{2}}$ corrections

$$\psi(x,t)\sim\frac{2k_0}{2k_0+i\gamma}e^{-ik_0(k_0t-x)}+\frac{\left(\frac{1}{2}+\frac{i}{2}\right)\left(\gamma+i\gamma k_0x+2ik_0\right)}{\sqrt{2\pi}\gamma^2k_0^2}t^{-\frac{3}{2}}+O(t^{-\frac{5}{2}}). \tag{30}$$


$|\psi(x,t)|^2$
1.0
0.8
0.6
0.4
0.2
2
4
6
8
10
12
14
t
k_0=2,γ=4,x=5
k_0=4,γ=4,x=5


$|\psi(x,t)|^2$
1.0
0.8
0.6
0.4
0.2
t
1
2
3
4
k_0=5,γ=10,x=5
k_0=10,γ=10,x=5

Tunneling time

A perennial question in ionization or transmission through a barrier is: how long does it take a particle to tunnel through the barrier? It is well known that there is no unique answer to this question. Time is not a well defined quantum operator and different definitions yield different answers. One relevant definition for our system would be the time it takes for the current to reach its asymptotic FN value, at a position x_0 where $U - k_0^2 = Ex_0$. Looking at the figures above, we see that this time depends only weakly on the field strength E which determines both the width of the barrier and the acceleration of the particle. There is a much stronger dependence on k_0, in the delta function potential, one consistent with a velocity $v_0 = 2k_0$ $(\equiv \frac{\hbar k_0}{m})$.