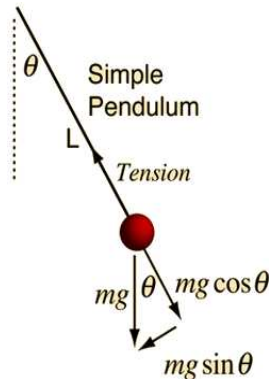


Section I.5. Wave Mechanics of a Single Particle

Moving in One Dimension

Note. We begin with a brief review of elementary physics. Consider a particle of mass m . If the particle has velocity v (as a scalar; we assume one dimensional motion) then its *kinetic energy* is $K = \frac{1}{2}mv^2$ and its momentum is $p = mv$. If the particle is in a gravitational field of strength g and the particle is at a height h then the *potential energy* is $U = mgh$. In SI units (International System of Units; “système international (d’unités)” in French, hence “SI”) we measure mass in kilograms (kg), time in seconds (s), distance in meters (m). The acceleration due to gravity is measured in m/s^2 . So kinetic energy is measured in $\text{kg m}^2/\text{s}^2$, momentum is in $\text{kg (m/s)} = \text{kg m/s}$. Energy is measured in joules (J) where $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$. Also, force is measured in newtons (N) where $1 \text{ N} = 1 \text{ kg m/s}^2$.

Note. Consider a mass m suspended by a string (or a massless rigid rod) of length L . Let θ be the angle by which the string is displaced from vertical. Then the forces on the mass satisfy:



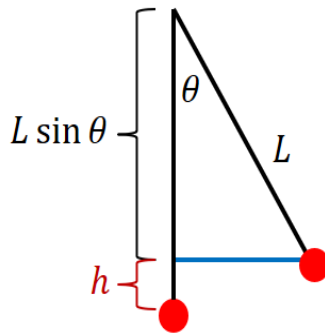
With θ as a function of time, we find from Newton's Laws of Motion that $\frac{d^2\theta}{dt^2} + \frac{g}{L}\sin\theta = 0$. But this is a nonlinear differential equation (because of the $\sin\theta$ term). A standard way to solve this differential equation is to assume that θ is small so that $\sin\theta \approx \theta$ (θ is measured in radians) and then the differential equation is approximated by the linear differential equation $\frac{d^2\theta}{dt^2} + \frac{g}{L}\theta = 0$. With initial conditions $\theta(0) = \theta_0$ and $\frac{d\theta}{dt}(0) = 0$, then the solution is $\theta(t) = \theta_0 \cos(\sqrt{g/L}t)$. Since arclength s is related to central angle θ by the equation $s = \theta L$ then the rate of change of arclength with time is $L d\theta/dt$; that is, the velocity is $L d\theta/dt$ (notice that to get the two components of velocity we use θ ; here we rather treat velocity as one dimensional), so

$$L \frac{d\theta}{dt} = -L\theta_0 \sqrt{\frac{g}{L}} \sin\left(\sqrt{\frac{g}{L}}t\right) = -\theta_0 \sqrt{gL} \sin\left(\sqrt{\frac{g}{L}}t\right).$$

Hence the kinetic energy as a function of time is

$$K = \frac{1}{2}mv^2 = \frac{1}{2}m \left(-\theta_0 \sqrt{gL} \sin\left(\sqrt{\frac{g}{L}}t\right) \right)^2 = \frac{m\theta_0^2 gL}{2} \sin^2\left(\sqrt{\frac{g}{L}}t\right).$$

The height of the mass above its lowest position is $h = L(1 - \sin\theta)$:



So the potential energy is

$$U = mgh = mgL(1 - \sin\theta) = mgL(1 - \sin\left(\theta_0 \cos\left(\sqrt{\frac{g}{L}}t\right)\right)).$$

In the absence of friction, the total energy $K + U$ is a constant (but we have approximated, so we don't have a precise constant energy in our solution).

Note. We now consider a particle of mass m which moves in one dimension, denoted x , with time denoted t . We assume a “potential energy well” (such as gravitational potential, elastic potential due to a spring, or electrical potential energy due to an electric charge in an electric field) described by $V(x)$. In the momentum of the particle is $p = mv$ then the kinetic energy is $\frac{1}{2}mv^2 = p^2/(2m)$. So the total energy is $E = \frac{p^2}{2m} + V(x)$. *Classically*, we describe the position of the particle by the function $x(t)$ (the “trajectory” of the particle).

Note. In wave mechanics, the “state” of one particle is postulated to be described by a *wave function* $\psi(x, t)$. We require that $\int_{-\infty}^{\infty} |\psi(x, t)|^2 dx = 1$ for all t . For fixed x , we require $\psi(x, t)$ to be continuously differential with respect to t . For fixed t we require that $\psi(x, t)$ have a piecewise continuous second derivative with respect to x (for now; this will insure that the Riemann integral of the second partial of ψ with respect to x exists...later we shift to Lebesgue integration and can drop this condition). So for fixed t , $\psi(x, t)$ is an element of $\mathcal{C}_{(2)}^1(\mathbb{R})$ (the superscript of “1” indicates a continuous first derivative [which we have since the second derivative exists] and the subscript of “(2)” indicates that the functions are square integrable). In addition, we require $\lim_{x \rightarrow \pm\infty} f'(x) = 0$ for each t , where $f(x) = \psi(x, t)$ with t fixed.

Note. The inner product $\mathcal{C}_{(2)}^1(\mathbb{R})$ is $\langle f, g \rangle = \int_{-\infty}^{\infty} f^*(x)g(x) dx$, so the condition $\int_{-\infty}^{\infty} |\psi(x, t)|^2 dx = 1$ for all t is a normalization condition of $\|\psi(x, t)\| = 1$ for all t . We also let $\Psi(t) \in \mathcal{C}_{(2)}^1(\mathbb{R})$ denote the “vector function” $f_t(x) = \psi(x, t)$ (instead of a vector as an n -tuple indexed by $1, 2, \dots, n$, think of the vector as an $|\mathbb{R}|$ -tuple with x as the index).

Note. Classically, a particle of mass m with positive functions $x(t)$ satisfies (by Newton's Second Law, $F = ma$) $F = m\ddot{x} = m\frac{d^2x}{dt^2}$. The force is related to the potential function as $F(x) = -\frac{d}{dx}[V(x)]$, so that $-\frac{dV}{dx} = m\frac{d^2x}{dt^2}$. So Newton's Second Law yields a relation between the potential function (a function of position only, to a constant with respect to time) and the position function $x(t)$.

Note. In wave mechanics, it is postulated that the wave function $\psi(x, t)$ (describing the state of one particle) satisfies *Schroedinger's equation*:

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

where $\hbar = h/(2\pi)$ for Plank's constant h (numerically, $\hbar = 1.054 \times 10^{-34}$ J/s).

Note. Prugovečki calls the following a “heuristic recipe.” If we take the classical formula relating energy, momentum, and potential, $E = p^2/(2m) + V(x)$, replace energy E with the operator $i\hbar\frac{\partial}{\partial t}$, and replace momentum p with $-i\hbar\frac{\partial}{\partial x}$, then we get the operator relation

$$i\hbar\frac{\partial}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x).$$

Applying this to wave function $\psi(x, t)$ produces Schroedinger's equation.

Note. For the next result, we need Leiniz's Rule which states that if $f(x, t)$ and $\frac{\partial}{\partial x}[f(x, t)]$ are continuous in x and t then

$$\frac{d}{dt} \left[\int_a^b f(x, t) dx \right] = \int_a^b \frac{\partial}{\partial t} [f(x, t)] dx.$$

Theorem I.5.A. Schroedinger's equation implies that $\|\psi(x, t)\|$ is a constant with respect to time t where for each fixed t , $\lim_{x \rightarrow \pm\infty} \psi(x, t) = 0$ and $\lim_{x \rightarrow \pm\infty} \left(\frac{\partial \psi(x, t)}{\partial x} \right) = 0$.

Note. In 1926, Niels Bohr (1885–1962) introduced the interpretation of the wave function as a probability distribution. The probability of finding the particle in interval $I \subset \mathbb{R}$ at time t is $P_t(I) = \int_I |\psi(x, t)|^2 dx$.

Note. Classically, we describe the dynamics of a single particle of mass m with position $x(t)$ in a potential field $V(x)$ as:

$$\begin{aligned} \text{Differential Equation: } & F = -\frac{dV(x)}{dx} = m\ddot{x} = m\frac{d^2x(t)}{dt^2} \\ \text{Initial Conditions: } & \begin{cases} x(0) = x_0 \\ \dot{x}(0) = v_0. \end{cases} \end{aligned}$$

So solving this second order (ordinary) initial value problem yields a unique position $x(t)$ of the particle at time t .

Note. In the wave mechanics of one particle, we seek $\psi(x, t)$ satisfying Schroedinger's equation and such that $\psi(x, t_0) = \psi_0(x)$ for some time t_0 and some $\psi_0(x) \in \mathcal{C}_1^1(\mathbb{R})$ for some time t_0 and some $\psi_0(x) \in \mathcal{C}_{(2)}^1(\mathbb{R})$. That is, we want $\psi(x, t)$ where

$$\begin{aligned} \text{Partial Differential Equation: } & i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x)\psi(x, t) \\ \text{Initial Conditions: } & \psi(x, t_0) = \psi_0(x). \end{aligned}$$

Progovcečki claims that this initial condition problem has a unique solution for $\psi_0(x) \in \mathcal{C}_{(2)}^1(\mathbb{R})$ since Schroedinger's equation is of the first order in t . We could use some more justification from the theory of PDEs and IVPs here.

Note. We now perform some manipulation that are a little uninspired. We seek a solution $\psi(x, t)$ of a certain form. The approach is inspired by the technique of separation of variables. We search for a solution of the form

$$\psi(x, t) = \psi(x) \exp(-(i/\hbar)Et) \quad (5.6)$$

where E is some constant. We assume a solution of this form and use Schroedinger's equation to produce an "eigenvalue problem" (in Prugovečki's terminology). We've claimed above that a solution to the IVP is unique, so if this approach works to produce a solution then we have succeeded in finding the unique solution.

Note. Applying Schroedinger's equation to (5.6) gives

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = i\hbar \psi(x) \left(\frac{-iE}{\hbar} \right) \exp(-(i/\hbar)Et)$$

and

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x) \psi(x, t) = -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} \exp(-(i/\hbar)Et) + V(x) \psi(x) \exp(-(i/\hbar)Et)$$

or

$$E\psi(x) = -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x). \quad (5.7)$$

This is called the *time-independent Schroedinger equation*. Notice that it is a second order linear ODE. Prugovečki claims that (5.7) has a family \mathcal{E}_p of functions $\pi(x) \in \mathcal{C}_{(2)}^1(\mathbb{R})$ as solutions for a set S_p of values of E . The numbers for a set S_p are the *eigenvalues* of (5.7).

Note. Recall that if \vec{v}_i and \vec{v}_j are eigenvectors associated with distinct eigenvalues λ_i and λ_j , respectively, of a Hermitian matrix A (that is, A equals its conjugate transpose; if A is real this simply implies that A is symmetric) then \vec{v}_i and \vec{v}_j are orthogonal. See Theorem 9.6, “Orthogonality of Eigenspaces of a Hermitian Matrix,” of my online notes <http://faculty.etsu.edu/gardnerr/2010/c9s3.pdf> for Eigenvalues and Diagonalization (of complex matrices). Also recall that the eigenvalues of a Hermitian matrix (and hence of a real symmetric matrix) are real (see Theorem 9.5, “The Spectral Theorem for Hermitian Matrices” from the same website). In a similar way, the next result shows that solutions to the time-independent Schroedinger equation which correspond to distinct eigenvalues are orthogonal.

Theorem I.5.1. If $\psi_1(x)$ and $\psi_2(x)$, their first derivatives $d\psi_1(x)/dx$ and $d\psi_2(x)/dx$, as well as $V(x)\psi_1(x)$ and $V(x)\psi_2(x)$ are from $\mathcal{C}_{(2)}^1(\mathbb{R})$, then

$$\left\langle \psi_1(x) \left| -\frac{\hbar^2}{2m} \frac{d^2\psi_2(x)}{dx^2} + V(x)\psi_2(x) \right. \right\rangle = \left\langle -\frac{\hbar^2}{2m} \frac{d^2\psi_1(x)}{dx^2} + V(x)\psi_1(x) \left| \psi_2(x) \right. \right\rangle.$$

In each solution $\psi(x)$ of the time-independent Schroedinger equation (5.7) has the property that $\psi(x), d\psi(x)/dx, V(x)\psi(x) \in \mathcal{C}_{(2)}^1(\mathbb{R})$, then each eigenvalue E of the time-independent Schroedinger equation is a real number, and if $\psi_1(x)$ and $\psi_2(x)$ are two eigenfunctions of the time-independent Schroedinger equation corresponding to two distinct eigenvalues $E_1 \neq E_2$, then $\psi_1(x)$ and $\psi_2(x)$ are orthogonal.

Note. So we see that the time-independent Schroedinger equation behaves much like a Hermitian matrix. This will be elaborated on in Chapter IV, “The Axiomatic Structure of Quantum Mechanics.” We will then use Lebesgue integration and this will allow us to weaken the hypotheses of Theorem I.5.1 (and so address the concerns raised in its proof).

Definition. The family \mathcal{E}_b of solutions to the time-independent Schroedinger equation in $\mathcal{C}_{(2)}^1(\mathbb{R})$ consists of the *bounded states*. The set S_p of eigenvalues are the only possible energy values that a system in a bound state can assume and are called the *energy eigenvalues of the bound states* and S_p is the *point energy spectrum*.

Note. In Exercise I.5.3, for a given energy eigenvalue $E \in S_p$ the corresponding set of eigenfunctions is a linear space, denoted M_E , of $\mathcal{C}_{(2)}^1(\mathbb{R})$. If M_E is one dimensional then every eigenvalue E is *nondegenerate*; otherwise E is *degenerate*.

Note. In Exercise I.4.2 it is to be shown that $\mathcal{C}_{(2)}^1(\mathbb{R})$ is not complete. By Theorem I.4.1 there is a completion of $\mathcal{C}_{(2)}^1(\mathbb{R})$ which we denote $\mathcal{H}^{(1)}$ (a Hilbert space). In Chapter II we show that $\mathcal{H}^{(1)}$ is separable. It is *assumed* that each element of $\mathcal{H}^{(1)}$ can represent a physical state at a certain time.

Theorem I.5.B. Let $\mathcal{H}_b^{(1)}$ be the (topologically) closed subspace of $\mathcal{H}^{(1)}$ which is spanned by \mathcal{E}_b (where \mathcal{E}_b is the set of “bound states”; that is, the set of $\mathcal{C}_{(2)}^1(\mathbb{R})$ which are solutions of the time-independent Schroedinger equations). Then an orthonormal basis of $\mathcal{H}_b^{(1)}$ is given by $T = \cup_{E \in S_p} T_E$ where T_E is an orthonormal basis for M_E . NOTE: You may assume that $\mathcal{H}^{(1)}$ is separable (as will be shown in Chapter II).

Note. “In practice” (Prugovečki says on page 50) the elements of the T_E of Theorem I.5.B can be chosen to belong to $\mathcal{C}_{(2)}^1(\mathbb{R})$. Since T is countable (by Exercise I.5.5), denote it as $T = \{\Psi_1, \Psi_2, \dots\}$. Then by Theorem I.4.6, every $\Psi \in \mathcal{H}_b^{(1)}$ satisfies $\Psi = \sum_{k=1}^{\infty} \langle \Psi_k | \Psi \rangle \Psi_k$.

Note. We will show below that the solution to the initial-value problem for the Schroedinger equation for bound states, where the initial state is $\Psi_0 \in \mathcal{H}_b^{(1)}$ at time $t = t_0$ is

$$\Psi(t) = \sum_{k=1}^{\infty} \exp\left(-\frac{i}{\hbar} E_k(t - t_0)\right) \langle \Psi_k, \Psi_0 \rangle \Psi_k \quad (5.11)$$

where E_k is the eigenvalue corresponding to eigenfunction $\psi(x) \in \mathcal{C}_{(2)}^1(\mathbb{R})$ which represents Ψ_k as described in Theorem 4.1 (where incomplete space \mathcal{E} is embedded in complete space $\tilde{\mathcal{E}}$; \mathcal{E} is not a subspace of $\tilde{\mathcal{E}}$ “represent” elements of $\tilde{\mathcal{E}}$, just as $\varphi(x) \in \mathcal{C}_{(2)}^1(\mathbb{R})$ represents $\Psi_k \in \mathcal{H}_b^{(1)}$). First we establish that the series in (5.11) actually converges for every $t \in \mathbb{R}$ to a $\Psi(t) \in \mathcal{H}_b^{(1)}$.

Theorem I.5.2. For any fixed $t \in \mathbb{R}$, the sequence $\{\Phi_1(t), \Phi_2(t), \dots\}$,

$$\Phi_n(t) = \sum_{k=1}^n c_k(t) \Psi_k$$

where $c_k(t) = \exp\left(-\frac{i}{\hbar} E_k(t - t_0)\right) \langle \Psi_k | \Psi_0 \rangle$,

is convergent in the norm of $\mathcal{H}_b^{(1)}$ to some $\Psi(t) \in \mathcal{H}_b^{(1)}$. For $t = t_0$, $\lim_{n \rightarrow \infty} \Phi_n(t_0) = \Psi(t_0)$ satisfies the initial condition $\Psi(t_0) = \Psi_0$.

Note. We now use the orthonormal basis $\{\Psi_n\}$ and the $\varphi(x)$ in \mathcal{E}_b to find a solution to the Schroedinger equation. We currently include lots of hypotheses, but will give a proof in Chapter IV including less hypotheses.

Theorem I.5.C. Suppose the series

$$\sum_{k=1}^{\infty} \exp\left(-\frac{i}{\hbar} E_k(t - t_0)\right) \langle \Psi_k | \Psi_0 \rangle \varphi_k(x)$$

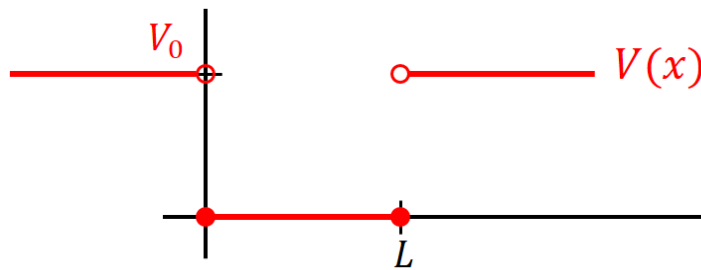
converges in the $\mathcal{H}_b^{(1)}$ norm for each fixed value of t and converges pointwise for each value of x and t to a limit function $\varphi(x, t)$, and that $\partial^2 \varphi(x, t) / \partial x^2$ and $\partial \varphi(x, t) / \partial t$ can be obtained by differentiating the series term by term twice in x and once in t . Here, $\varphi_k(x)$ satisfies the time-independent Schroedinger equation for $E = E_k$. Then $\varphi(x, t)$ is a solution to Schroedinger's equation

$$i\hbar \frac{\partial \varphi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \varphi(x, t)}{\partial x^2} + V(x) \varphi(x, t).$$

Note. We devote the remainder of this section to the study of a solution to Schroedinger's equation for a specific potential function $V(x)$. The level of rigor will slip some in what follows. Consider

$$V(x) = \begin{cases} 0 & \text{for } 0 \leq x \leq L \\ V_0 > 0 & \text{for } x < 0 \text{ and } x > L. \end{cases}$$

This is called the *square-well potential*:



The force (recall that the force is dV/dx) is 0 except at the walls $x = 0$ and $x = L$ of the potential well. Prugovečki says the energy is infinite at $x = 0$ and $x = L$. For this potential function, the time independent Schroedinger equation is

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}E\psi(x) = 0 \text{ for } 0 \leq x \leq L$$

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi(x) = 0 \text{ for } x < 0, x > L$$

(like Prugovečki, we include $x = 0$ and $x = L$ in Schroedinger's equation, though this is arguable. Notice that we have second order ordinary ODEs with constant coefficients and so there are two linearly independent solutions for each. We might expect to see sine and cosine functions, but since $\psi(x)$ is a complex valued function of a real variable, we instead express solutions in terms of exponential functions, recalling Euler's formula: $e^{ix} = \cos x + i \sin x$.

Theorem I.5.D. The general solution of

$$\begin{aligned} \frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}E\psi(x) &= 0 \text{ for } 0 \leq x \leq L \\ \frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi(x) &= 0 \text{ for } x < 0, x > L \end{aligned}$$

is

$$\psi(x) = \begin{cases} ce^{ikx} + de^{-ikx} & \text{where } k = \sqrt{2mE}/\hbar \text{ for } 0 \leq x \leq L \\ a_1e^{-ik'x} + b_1e^{ik'x} & \text{where } k' = \sqrt{2m(E - V_0)}/\hbar \text{ for } x < 0 \\ a_2e^{ik''x} + b_2e^{-ik''x} & \text{where } k'' = \sqrt{2m(E - V_0)}/\hbar \text{ for } x > L. \end{cases}$$

Note. Since $\psi(x)$ must satisfy the normalization condition $\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$ then we must have $\psi(x) \rightarrow 0$ as $|x| \rightarrow \infty$. This implies for $x < 0$ that in the solution of Theorem I.5.D we must have $k' - i\kappa$ and $b_1 = 0$ for real κ (or, equivalently, $k' = -i\kappa$ and $a_1 = 0$) and for $x > L$ we must have $k' = k'' = (\sqrt{2m(E - V_0)}/\hbar^2)i\kappa$ then

$$\kappa = \frac{\sqrt{2m(E - V_0)}}{i\hbar^2} = \sqrt{2m(E - V_0)}\sqrt{-1}\hbar^2 = \frac{\sqrt{2m(V_0 - E)}}{\hbar^2} > 0.$$

Note. Since $\psi(x) = \mathcal{C}_{(2)}^1(\mathbb{R})$, $\psi(x)$ is continuous and has a continuous first derivative (that's what the "1" indicates), so imposing these conditions at $x = 0$ and $x = L$ yields the following:

$$\begin{aligned} \lim_{x \rightarrow 0^-} \psi(x) &= \lim_{x \rightarrow 0^-} a_1e^{ik'x} = a_1 = \lim_{x \rightarrow 0^+} \psi(x) = \lim_{x \rightarrow 0^+} (ce^{ikx} + de^{-ikx}) = c + d, \\ \lim_{x \rightarrow 0^-} \frac{d\psi(x)}{dx} &= \lim_{x \rightarrow 0^-} \kappa a_1e^{-\kappa x} = \kappa a_1 = \lim_{x \rightarrow 0^+} \frac{d\psi(x)}{dx} = \lim_{x \rightarrow 0^+} (ikce^{ikx} - ikde^{-ikx}) = ik(c - d), \end{aligned}$$

$$\begin{aligned}
\lim_{x \rightarrow L^-} \psi(x) &= \lim_{x \rightarrow L^-} (ce^{ikx} + de^{-ikx}) = ce^{ikL} + de^{-ikL} \\
&= \lim_{x \rightarrow L^+} \psi(x) = \lim_{x \rightarrow L^+} a_2 e^{ik''x} = a_2 e^{ik''L} = a_2^{\kappa L}, \\
\lim_{x \rightarrow L^-} \frac{d\psi(x)}{dx} &= \lim_{x \rightarrow L^-} (ikce^{ikx} - ikde^{-ikx}) = ik(ce^{ikL} - de^{-ikL}) \\
&= \lim_{x \rightarrow L^+} \frac{d\psi(x)}{dx} = \lim_{x \rightarrow L^+} (ik''a_2 e^{ik''x}) = ik''a_2 e^{ik''L} = -\kappa a_2 e^{-\kappa L}.
\end{aligned}$$

That is, we need

$$\begin{aligned}
a_1 &= c + d & \kappa a_1 &= ik(c - d) \\
ce^{ikL} + de^{-\kappa L} &= a_2 e^{-\kappa L} & ik(ce^{ikL} - de^{-ikL}) &= -\kappa a_2 e^{-\kappa L}.
\end{aligned}$$

Eliminating A_1 in the top two equations gives $\kappa(c + d) = ik(c - d)$ or $(\kappa - ik)c + (\kappa + ik)d = 0$. Eliminating a_2 in the bottom two equations gives $-\kappa(ce^{ikL} + de^{-ikL}) = ik(ce^{ikL} - de^{-ikL})$ or $(\kappa + ik)e^{ikL}c + (\kappa - ik)de^{-ikL} = 0$ or $(\kappa + ik)e^{2ikL}c + (\kappa - ik)d = 0$.

So we have two linear equations in two unknowns:

$$\begin{aligned}
(\kappa - ik)c &+ (\kappa + ik)d &= 0 \\
(\kappa + ik)e^{2ikL}c &+ (\kappa - ik)d &= 0.
\end{aligned} \tag{5.15}$$

Since the system is homogeneous, for a nontrivial solution (where $c \neq 0 \neq d$) we need the determinant of the coefficient matrix to be 0. So we want

$$\begin{vmatrix} \kappa - ik & \kappa + ik \\ (\kappa + ik)e^{2ikL} & \kappa - ik \end{vmatrix} = (\kappa - ik)^2 - (\kappa + ik)^2 e^{2ikL} = 0$$

or

$$e^{2ikL} = \left(\frac{\kappa - ik}{\kappa + ik} \right)^2. \tag{5.18}$$

Now $k = \sqrt{2mE}/\hbar$ and $\kappa = \sqrt{2m(V_0 - E)}/\hbar$ where \hbar , m , and V_0 are constants.

So we need to find values of E for which (5.18) holds. Now $|e^{2ikL}| = 1$, so we

have $\left| \frac{\kappa - ik}{\kappa + ik} \right| = 1$ and hence $\frac{\kappa - ik}{\kappa + ik} = e^{i\varphi} = \cos \varphi + i \sin \varphi$. Now $\frac{\kappa - ik}{\kappa + ik} \frac{\kappa - ik}{\kappa - ik} = \frac{\kappa^2 - 2i\kappa k - k^2}{\kappa^2 + k^2}$ and so we need

$$\cos \varphi = \frac{\kappa^2 - k^2}{\kappa^2 + k^2} = \frac{2m(V_0 - E/\hbar^2 - 2me/\hbar^2)}{2m(V_0 - E)/\hbar^2 + 2me/\hbar^2} = \frac{V_0 - E - E}{(V_0 - E) + E} = \frac{V_0 - 2E}{V_0} = 1 - 2\frac{E}{V_0}$$

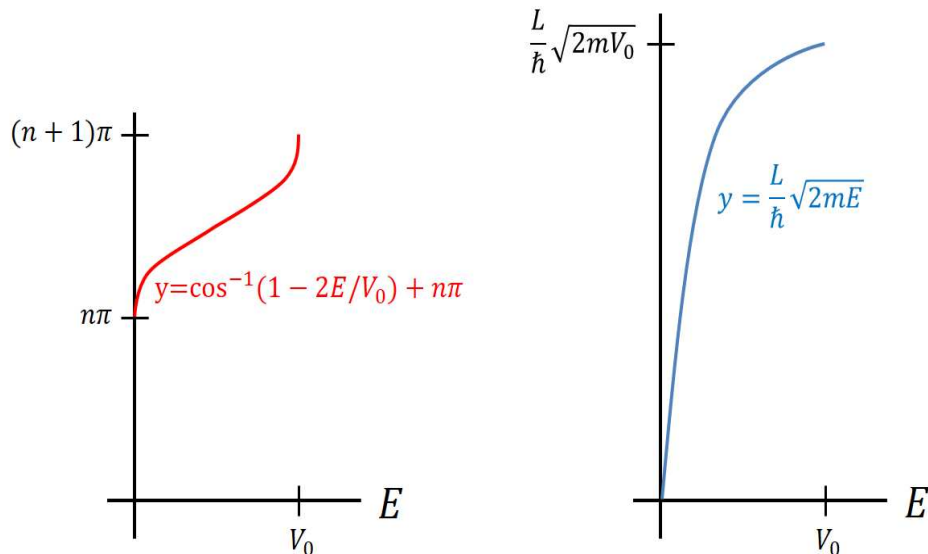
so that $0 \leq E \leq V_0$ is necessary, and

$$\begin{aligned} \sin \varphi &= \frac{2\kappa k}{\kappa^2 + k^2} = -2 \frac{(\sqrt{2m(V_0 - E)/\hbar})(\sqrt{2mE}/\hbar)}{2m(V_0 - E)/\hbar^2 + 2mE/\hbar^2} = -2 \frac{\sqrt{(V_0 - E)E}}{(V_0 - E) + E} \\ &= -2 \frac{\sqrt{(V_0 - E)E}}{V_0} = -2 \sqrt{\frac{(V_0 - E)E}{V_0^2}} = -2 \sqrt{\frac{E}{V_0} \left(1 - \frac{E}{V_0}\right)}. \end{aligned}$$

By (5.18) and our introduction of $E^{i\varphi}$, we have $e^{2i\varphi} = e^{2ikL}$ so that we have $2\varphi = 2kL + 2n\pi$ (since e^z has period $2\pi i$) or $\varphi = kL + n\pi$ where $n \in \mathbb{Z}$. Since $k = \sqrt{2mE}/\hbar$ then $\varphi = \frac{L}{\hbar}\sqrt{2mE} + n\pi$ for $n \in \mathbb{Z}$. We have $\cos \varphi = 1 - 2E/V_0$ from above, so one value of φ is $\cos^{-1}(1 - 2E/V_0)$. This leads to the relationship:

$$\frac{L}{\hbar}\sqrt{2mE} = \cos^{-1}(1 - 2E/V_0) + n\pi \quad \text{where } n \in \mathbb{Z} \quad (*)$$

(notice that **this differs from Proguvečki's equation** in two places; see page 54).



Notice from the graphs above that $y = \cos^{-1}(1 - 2E/V_0) + n\pi$ and $y = \frac{L}{\hbar}\sqrt{2mE}$ will intersect, but we need for n such that $n \geq 0$ and $n\pi < \frac{L}{\hbar}\sqrt{2mV_0}$. So for each appropriate $n \in \mathbb{Z}$ we can solve (*) (numerically since it is a transcendental equation) for E and we denote this solution as E_n . Each eigenvalue E_n is nondegenerate (Prugovečki says on page 54) and the corresponding solution is $\psi_n(X)$ to be given next.

Note. We will express the coefficients in $\psi_n(x)$ in terms of c_n (the coefficients of $e^{ik_n x}$). From the first equation in system (5.15), we have $d = \frac{-(\kappa - ik)}{\kappa + ik}c$ or $d_n = \frac{-(\kappa_n - ik_n)}{\kappa_n + ik_n}c_n$. By continuity of $\psi(x)$ at $x = 0$ we have $a_1 = c + d = c - \frac{\kappa - ik}{\kappa + ik}c = \frac{eik}{\kappa + ik}c$ of $a_{1,n} = \frac{2ik_n}{\kappa_n + ik_n}c_n$. By the continuity of $\psi(x)$ at $x = L$ we have $ce^{-\kappa L} + de^{-ikL} = a_2e^{-\kappa L}$ or

$$a_2 = ce^{\kappa L + ikL} + de^{\kappa L - ikL} = ce^{(\kappa + ik)L} - \frac{\kappa - ik}{\kappa + ik}ce^{(\kappa - ik)L}$$

or

$$a_{2,n} = c_n \left(e^{(\kappa_n + ik_n)L} - \frac{\kappa_n - ik_n}{\kappa_n + ik_n} e^{(\kappa_n - ik_n)L} \right).$$

So we have (notice $\kappa_n = -ik_n$):

$$\psi_n(x) = \begin{cases} a_{1,n}e^{\kappa_n x} & \text{where } k_n = \sqrt{2m(E_n - V_0)}/\hbar \text{ for } x < 0 \\ c_n e^{ik_n x} + d_n e^{-ik_n x} & \text{where } k_n = \sqrt{2mE_n}/\hbar \text{ for } 0 \leq x \leq L \\ a_{2,n}e^{-\kappa_n x} & \text{where } k_n = \sqrt{2m(E_n - V_0)}/\hbar \text{ for } x > L \end{cases}$$

or

$$\psi_n(x) = \begin{cases} c_n \frac{2ik_n}{\kappa_n + ik_n} e^{\kappa_n x} & \text{where } k_n = \sqrt{2m(E_n - V_0)}/\hbar \text{ for } x < 0 \\ c_n \left(e^{ik_n x} - \frac{\kappa_n - ik_n}{\kappa_n + ik_n} e^{-ik_n x} \right) & \text{where } k_n = \sqrt{2mE_n}/\hbar \text{ for } 0 \leq x \leq L \\ c_n \left(e^{(\kappa_n + ik_n)L} - \frac{\kappa_n - ik_n}{\kappa_n + ik_n} e^{(\kappa_n - ik_n)L} \right) e^{-\kappa_n x} & \text{where } k_n = \sqrt{2m(E_n - V_0)}/\hbar \\ & \text{for } x > L. \end{cases}$$

Finally, we can find the modulus of c_n using the normalization condition that $\int_{-\infty}^{\infty} |\psi_n(x)|^2 dx = 1$. We then have ψ_n determined (up to a multiple of a complex number of modulus 1) and then can use the $\psi_n(x)$ functions to solve Schroedinger's equation for this $V(x)$ as described in Theorem I.5.C.

Note. Classically, a particle in a square potential well could not escape (that is, if the particle has initial position x with $0 < x < L$ then it remains in $0 < x < L$). However, since $|\psi_n(x)|^2$ is not 0 for $x < 0$ nor for $x > L$ then this means (with the probabilistic interpretation of Bohr) that there is a nonzero probability that a particle starting in the potential well (that is, in $0 < x < L$) can be located outside the well in the future. The particle can “tunnel out” of the well in the quantum mechanical setting.

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