Modern Algebra

Chapter I. Basic Ideas of Hilbert Space Theory

I.5. Wave Mechanics of a Single Particle Moving in One Dimension—Proofs of Theorems



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Theorem I.5.A (continued 1)

Proof (continued).

by the conjugate of Schroedinger's equation for $\frac{\partial \psi^*(x,t)}{\partial t}$

and Schroedinger's equation for $\frac{\partial \psi(x,t)}{\partial t}$

$$= \frac{\hbar}{2mi} \int_{-\infty}^{\infty} \left(\frac{\partial^2 \psi^*(x,t)}{\partial x^2} \psi(x,t) = \psi^*(x,t) \frac{\partial^2 \psi(x,t)}{\partial x^2} \right) dx$$

$$= \frac{\hbar}{2mi} \int_{-\infty}^{\infty} \left(\frac{\partial^2 \psi^*}{\partial x^2} \psi + \frac{\partial \psi^*}{\partial x} \frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x} \partial \psi \partial x - \psi^* \frac{\partial^2 \psi}{\partial x^2} \right) dx$$

$$= \frac{\hbar}{2\pi i} \int_{-\infty}^{\infty} \frac{\partial}{\partial x} \left[\frac{\partial \psi^*}{\partial x} \psi - \psi^* \frac{\partial \psi}{\partial x} \right] dx$$

$$= \frac{\hbar}{2mi} \left(\frac{\partial \psi^*}{\partial x} \psi - \psi^* \frac{\partial \psi}{\partial x} \right) \bigg|^{\infty}$$

$$= 0 \text{ since } \lim_{x \to \pm \infty} \psi(x, t) = \lim_{x \to \pm \infty} \frac{\partial \psi(x, t)}{\partial x} = 0.$$

Theorem I.5.A

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.

$$\lim_{x\to\pm\infty}\psi(x,t)=0$$
 and $\lim_{x\to\pm\infty}\left(\frac{\partial\psi(x,t)}{\partial x}\right)=0$.

Proof. We justify the claim by showing $\frac{d}{dt}[\|\psi(x,t)\|^2] = 0$. We have

$$\begin{split} \frac{d}{dt}[\|\psi(x,t)\|^2] &= \frac{d}{dt} \left[\int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx \right] = \frac{d}{dt} \left[\int_{-\infty}^{\infty} \psi^*(x,t) \psi(x,t) \, dx \right] \\ &= \int_{-\infty}^{\infty} \frac{\partial}{\partial t} [\psi^*(x,t) \psi(x,t)] \, dx \text{ by Leibniz's Rule} \\ &= \int_{-\infty}^{\infty} \left(\frac{\partial \psi^*(x,t)}{\partial t} \psi(x,t) + \psi^*(x,t) \frac{\partial \psi(x,t)}{\partial t} \right) \, dx \\ &= \int_{-\infty}^{\infty} \left\{ \left(\frac{\hbar}{2mi} \frac{\partial \psi^*(x,t)}{\partial x^2} - \frac{1}{i\hbar} V(x) \psi^*(x,t) \right) \psi(x,t) \right. \\ &\left. + \psi^*(x,t) \left(-\frac{\hbar}{2mi} \frac{\partial^2 \psi(x,t)}{\partial x^2} + \frac{1}{i\hbar} V(x) \psi(x,t) \right) \right\} \, dx \dots \end{split}$$

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Theorem I.5.A (continued 2)

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, $\lim_{x\to\pm\infty}\psi(x,t)=0$ and $\lim_{x\to\pm\infty}\left(\frac{\partial\psi(x,t)}{\partial x}\right)=0$.

Proof (continued). So $\frac{d}{dt}[\|\psi(x,t)\|^2]=0$ and $\|\psi(x,t)\|^2$ is a constant real valued continuous function of t. That is, $\|\psi(x,t)\|$ is constant with respect to t, as claimed.

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Theorem I.5.1

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 $C^1_{(2)}(\mathbb{R})$, then

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

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

In each solution $\psi(x)$ of the time-independent Schroedinger equation (5.7) has the property that $\psi(x)$, $d\psi(x)/dx$, $V(x)\psi(x) \in \mathcal{C}^1_{(2)}(\mathbb{R})$, 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.

Theorem I.5.1 (continued 2)

Proof (continued). ...

$$= -\frac{\hbar^2}{2m} \psi^* \frac{d\psi_2}{dx} \bigg|_{-a}^a - \int_{-a}^a -\frac{\hbar^2}{2m} \frac{d\psi_1^*}{dx} \frac{d\psi_2}{dx} dx + \int_{-a}^a V \psi_1^* \psi_2 dx$$

$$| \text{let } u = \frac{d\psi_1^*}{dx} \text{ and } dv = \frac{d\psi_2}{dx} dx$$

$$| \text{so } du = \frac{d^2\psi_1^*}{dx^2} dx \text{ and } v = \psi_2$$

$$| = \left(-\frac{\hbar^2}{2m} \psi_1^* \frac{d\psi_2}{dx} + \frac{\hbar^2}{2m} \frac{d\psi_1^*}{dx} \psi_2 \right) \bigg|_{-a}^a$$

$$-\frac{\hbar^2}{2m} \int_{-a}^a \psi_2 \frac{d^2\psi_1^*}{dx^2} dx + \int_{-1}^a V \psi_1^* \psi_2 dx$$

$$| = -\frac{\hbar^2}{2m} \left(\psi_1^* \frac{d\psi_2}{dx} - \frac{d\psi_1^*}{dx} \psi_2 \right) \bigg|_{-a}^a + \int_{-a}^a \left(-\frac{\hbar^2}{2m} \frac{d^2\psi_1^*}{dx^2} + V \psi_1^* \right) \psi_2 dx .$$

Theorem I.5.1 (continued 1)

Proof. We have (not writing the variable x):

$$\int_{-a}^{a} \psi_1^* \left(-\frac{\hbar^2}{2m} \frac{d^2 \psi_2}{dx^2} + V \psi_2 \right) dx$$

$$= \int_{-a}^{a} -\frac{\hbar^{2}}{2m} \psi_{1}^{*} \frac{d^{2} \psi_{2}}{dx^{2}} dx + \int_{-a}^{a} V \psi_{1}^{*} \psi_{2} dx$$

$$let u = -\frac{\hbar^{2}}{2m} \psi_{1}^{*} \text{ and } dv = \frac{d^{2} \psi_{2}}{dx^{2}} dx$$

$$so du = -\frac{\hbar^{2}}{2m} \frac{d \psi_{1}^{*}}{dx} dx \text{ and } v = \frac{d \psi_{2}}{dx}$$

$$= -\frac{\hbar^{2}}{2m} \psi^{*} \frac{d \psi_{2}}{dx} \Big|_{-a}^{a} - \int_{-a}^{a} -\frac{\hbar^{2}}{2m} \frac{d \psi_{1}^{*}}{dx} \frac{d \psi_{2}}{dx} dx + \int_{-a}^{a} V \psi_{1}^{*} \psi_{2} dx \dots$$

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Theorem 1.5

Theorem I.5.1 (continued 3)

Proof (continued). Since $\psi_1, \psi_2 \in \mathcal{C}^1_{(2)}(\mathbb{R})$ then $\lim_{x \to \pm \infty} \psi_1(x) = \lim_{x \to \pm \infty} \psi_2(x) = \lim_{x \to \pm \infty} \frac{d\psi_1(x)}{dx} = \lim_{x \to \pm \infty} \frac{d\psi_2(x)}{dx} = 0$ and so $\lim_{x \to \infty} -\frac{\hbar^2}{2m} \left(\psi_1^* \frac{\psi_2}{dx} - \frac{d\psi_1^*}{dx} \psi_2 \right) \bigg|_{x=0}^x = 0.$

If we know $d^2\psi_1/dx^2$, $d^2\psi_2/dx^2\in\mathcal{C}^1_{(2)}(\mathbb{R})$ then we know the inner product is defined and so the limit as $a\to\infty$ of the two integrals above exist, so that

$$\lim_{a \to \infty} \left(\int_{-a}^{a} \psi_1^* \left(-\frac{\hbar^2}{2m} \frac{d^2 \psi_2}{dx^2} + V \psi_2 \right) dx \right)$$

$$= \lim_{a \to \infty} \left(\int_{-a}^{a} \left(-\frac{\hbar}{2m} d^2 \psi_1^* dx^2 + V \psi_1^* \right) dx \right)$$

so the inner product claim of the theorem holds. (BUT it does seem that we need the added assumption $d^2\psi_1/dx^2$, $d^2\psi_2/dx^2 \in \mathcal{C}^1_{(2)}(\mathbb{R})$ in order to insure convergence of the above integrals.

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Theorem I.5.1 (continued 4)

Proof (continued). If we know that ψ_1 and ψ_2 satisfy the time-independent Schroedinger equation then we know $-\frac{\hbar^2}{2m}\frac{d^2\psi_i}{dx^2}=E_i\psi_i-V\psi_i\in\mathcal{C}^1_{(2)}(\mathbb{R}) \text{ for } i=1,2.)$

If $\psi_1(x)$ and $\psi_2(x)$ satisfy the conditions of the theorem and if in addition they are solutions of the time-independent Schroedinger equation with eigenvalues E_1 and E_2 (so that the issue raised about $d^2\psi_1/dx^2$ and $d^2\psi_2/dx^2$ are not a concern) then by the first part of the theorem concerning inner products and from the time-independent Schroedinger equation we conclude $\langle \psi_1(x) \mid E_2\psi_2(x) \rangle = \langle E_1\psi_1(x) \mid \psi_2(x) \rangle$. If we take $\psi_1(x) = \psi_2(x) = \psi(x)$ and $E_1 = E_2 = E$ in this equation, then we get $E\langle \psi \mid \psi \rangle = \langle \psi \mid E\psi \rangle = \langle E\psi \mid \psi \rangle = E^*\langle \psi \mid \psi \rangle$. So if ψ is a nontrivial solution of the time-independent Schroedinger equation (i.e., $\psi(x) \not\equiv 0$) then $\|\psi\|^2 = \langle \psi \mid \psi \rangle > 0$ and so $E = E^*$ in this case. That is, the eigenvalues of the time-independent Schroedinger equation are real.

Theorem I.5.B

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 $T = \bigcup_{E \in S_p} T_E$ 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).

Proof. First, since we assume $\mathcal{H}^{(1)}$ is separable, then by Theorem I.4.2 $\mathcal{H}_{b}^{(1)}$ is also separable. For each $E \in S_b$, M_E is a subspace of $\mathcal{H}_{b}^{(1)}$ and so M_E is also separable. By Theorem I.4.5, each M_E has an at most countably infinite orthonormal system T_E spanning M_E . Consider $T = \cup_{E \in S_p} T_E$. Now every element of \mathcal{E}_b is some (countable) sum of elements of T. Since the closure of the span of \mathcal{E}_b is $\mathcal{H}_b^{(1)}$, then the closed subspace spanned by T is $\mathcal{H}_b^{(1)}$.

Theorem I.5.1 (continued 5)

Proof (continued). Finally, let ψ_1 and ψ_2 be solutions to the time-independent Schroedinger equation with associated eigenvalues E_1 and E_2 , respectively, where $E_1 \neq E_2$. Then $\langle \psi_1 \mid E_2 \psi_2 \rangle = \langle E_1 \psi_1 \mid \psi_2 \rangle$, or (since E_1 and E_2 are real) $E_2 \langle \psi_1 \mid \psi_2 \rangle = E_1 \langle \psi_1 \mid \psi_2 \rangle$, or $(E_2 - E_1) \langle \psi_1 \mid \psi_2 \rangle = 0$. Since $E_1 \neq E_2$ then we must have $\psi_1 \perp \psi_2$, as claimed.

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Theorem 1.5.E

Theorem I.5.B (continued)

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 $T = \bigcup_{E \in S_p} T_E$ 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).

Proof (continued). Since each T_E is orthonormal and by Theorem I.5.1 every element of T_{E_1} is orthonormal to every subset of T_{E_2} for $E_1 \neq E_2$, then set T is orthonormal. So T is linearly independent (see Exercise I.4.12) and by Exercise I.5.3, T is countable. So T is an orthonormal basis of $\mathcal{H}_b^{(1)}$, as claimed.

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Theorem 1.5.2

Theorem 1.5.2. For any fixed $t \in \mathbb{R}$, the sequence $\{\Phi_1(t), \Phi_2(t), \ldots\}$,

$$\begin{split} &\Phi_n(t) = \sum_{k=1}^n c_k(t) \Psi_k \\ &\text{where } c_k(t) = \exp\left(-\frac{i}{\hbar} E_k(t-t_0)\right) \langle \Psi_k \mid \Psi_0 \rangle, \end{split}$$

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

Proof. Since $\{\Psi_1, \Psi_2, \ldots\}$ is an orthonormal basis in $\mathcal{H}_h^{(1)}$, by Theorem 1.4.6(d)

$$\sum_{k=1}^{\infty} |c_k(t)|^2 = \sum_{k=1}^{\infty} \left| \exp\left(-\frac{i}{\hbar} E_k(t-t_0)\right) \langle \Psi_k \mid \Psi_0 \rangle \right|^2$$

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Theorem 1.5.2 (continued 2)

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

$$\Phi_n(t) = \sum_{k=1}^n c_k(t) \Psi_k$$
 where $c_k(t) = \exp\left(-rac{i}{\hbar} E_k(t-t_0)\right) \langle \Psi_k \mid \Psi_0 \rangle$,

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

Proof (continued). With $t = t_0$, $c_k = \langle \Psi_k \mid \Psi_0 \rangle$ for $k \in \mathbb{N}$ and so

$$\Psi(t_0) = \lim_{n \to \infty} \Phi_n(t_0) = \lim_{n \to \infty} \sum_{k=1}^n c_k(t_0) \Psi_k = \sum_{k=1}^\infty c_k(t_0) \Psi_k = \sum_{k=1}^\infty \langle \Psi_k \mid \Psi_0 \rangle \Psi_k$$

by Theorem I.4.6, as claimed.

Theorem I.5.2 (continued 1)

Proof (continued).

$$\begin{split} \sum_{k=1}^{\infty} |c_k(t)|^2 &=& \sum_{k=1}^{\infty} |\langle \Psi_k \mid \Psi_0 \rangle|^2 \text{ since } \left| \exp \left(-\frac{i}{\hbar} E_k(t-t_0) \right) \right| = 1 \\ & \text{ because } E_k \text{ is real by Theorem I.5.1} \\ &=& \|\Psi_0\|^2 < \infty. \end{split}$$

So for given $\varepsilon > 0$, there is $N \in \mathbb{N}$ such that $\sum_{k=N}^{\infty} |c_k(t)|^2 < \varepsilon^2$. So if m, n > N (with $m \ge n$, say) then

$$|\Phi_m(t) - \Phi_n(t)|^2 = \left|\sum_{k=n}^m c_k(t)\Psi_k\right|^2 = \sum_{k=n}^m |c_k(t)|^2 \le \sum_{k=N}^\infty |c_k(t)|^2 < \varepsilon^2,$$

and so $\{\Phi_n(t)\}\$ is a Cauchy sequence in $\mathcal{H}_b^{(1)}$ and hence, since $\mathcal{H}_b^{(1)}$ is complete, converges to some $\Psi(t) \in \mathcal{H}_{b}^{(1)}$

Theorem I.5.C

Theorem I.5.C. Suppose the series

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

converges in the $\mathcal{H}_{h}^{(1)}$ 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 $\partial \psi(x,t)/\partial t$ 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

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

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Theorem I.5.C (continued)

Proof. By the hypotheses on differentiability, we have

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

$$\frac{\partial^2 \varphi(x,t)}{\partial x^2} = \sum_{k=1}^{\infty} \exp\left(-\frac{i}{\hbar} E_k(t-t_0)\right) \langle \Psi_k \mid \Psi_0 \rangle \frac{d^2 \varphi_k(x)}{dx^2}$$

(notice the inner product is an integral over x so $\langle \Psi_k | \Psi_0 \rangle$ is a constant).

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

$$= -\frac{\hbar}{2m}\sum_{k=1}^{\infty} \exp\left(-\frac{i}{\hbar}E_k(t-t_0)\right) \langle \Psi_k \mid \Psi_0 \rangle \frac{d^2 \varphi_k(x)}{dx^2}$$

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

Theorem I.5.D

Theorem I.5.D. The general solution of

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

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

is

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

Proof. Since the ODE is second order linear and in each of the three regions $\psi(x)$ is a linear combination of two linearly independent functions, we just need to confirm that $\psi(x)$ satisfies the ODE in each region.

Theorem I.5.C (continued)

Proof (continued).

$$= \sum_{k=1}^{\infty} \exp\left(-\frac{i}{\hbar} E_k(t-t_0)\right) \langle \Psi_k \mid \Psi_0 \rangle \left(-\frac{\hbar^2}{2m} \frac{d^2 \varphi_k(x)}{dx^2} + V(x) \varphi_k(x)\right)$$

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

since $\varphi_k(x)$ is a solution to the time-independent Schroedinger

equation for
$$E = E_k : -\frac{\hbar^2}{2m} \frac{d^2 \varphi_k(x)}{dx^2} + V(x) \varphi_k(x) = E_k \varphi_k(x)$$

= $\frac{\hbar}{-i} \frac{\partial \varphi(x,t)}{\partial t} = i\hbar \frac{\partial \varphi(x,t)}{\partial t}$.

So

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

is a solution to the Schroedinger equation, as claimed.

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Theorem I.5.D (continued)

Proof (continued). For $0 \le x \le L$ we have

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}E\psi(x) = -k^2ce^{ikx} - k^2de^{-kx} + \frac{2m}{\hbar^2}E(ce^{ikx} + de^{-ikx})$$

$$= -\frac{2mE}{\hbar^2}ce^{ikx} - \frac{2mE}{\hbar^2}de^{-ikx} + \frac{2m}{\hbar^2}Ece^{ikx} + \frac{2m}{\hbar^2}de^{-ikx} = 0.$$

For x < 0 (and similarly for x > L)

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}E\psi(x) = -(k')^2 a_1 e^{-ik'x} - (k')^2 b_1 e^{-k'x}
+ \frac{2m}{\hbar^2}(E - V_0)(a_1 e^{-ik'x} + b_1 e^{ik'x})
= -\frac{2m(E - V_0)}{\hbar^2} a_1 e^{-ik'x} - \frac{2m(E - V_0)}{\hbar^2} b_1 e^{-k'x}
+ \frac{2m(E - V_0)}{\hbar^2} a_1 e^{-ik'x} + \frac{2m(E - V_0)}{\hbar^2} b_1 e^{ik'x} = 0.$$