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Use of the Laplace Transform Method to Solve the One-Dimensional Periodic-Potential Problem

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The one-dimensional periodic-potential problem is solved using the Laplace transform method. This method allows an easy generalization of the Kronig-Penney model so that it is applied to solve far more complex one-dimensional periodic structure.

THE LAPLACE TRANSFORM METHOD

All the information regarding the dynamic states of an electron moving in a one-dimensional crystal are contained in the wave function $\psi(x, t)$, which is the solution of the Schrödinger equation

$$H\psi(x, t) = i\hbar[\partial\psi(x, t)/\partial t], \quad (1)$$

where H is the Hamiltonian operator given by

$$H = -(\hbar^2/2m)(d^2/dx^2) - eV(x) \quad (2)$$

and $V(x)$ is the potential energy which acts upon the electron. This potential energy is always periodic with period a , that is, $V(x+na) = V(x)$ for any integer n .

The stationary states, which are the ones with

perfectly defined energy, are of the form

$$\psi(x, t) = \psi(x) \exp(-iEt/\hbar) \quad (3)$$

and they satisfy the eigenvalue equation

$$[d^2/dx^2 + 2U(x)/a^2]\psi(x) = -K^2\psi(x), \quad (4)$$

where

$$U(x) \equiv (ma^2e/\hbar^2)V(x), \quad (5)$$

$$K^2 \equiv (2m/\hbar^2)E. \quad (6)$$

Ordinary differential equations with periodic coefficients like Eq. (4) were already studied by the mathematicians and Floquet; later, Bloch showed that the solutions of these equations are of the form

$$\psi(x) = e^{ikx}u(x), \quad (7)$$

where $u(x)$ is a periodic function with the same period as the potential, that is, $u(x+na) = u(x)$ for n an integer. Then the solutions of Eq. (4) are plane waves modulated by the periodic function $u(x)$ and this function has the value one when the effects of the lattice upon the electron are neglected. From Eq. (7) it is possible to relate the value of the wave function equally at all points x located on different cells of the lattice, among themselves, because, if Eq. (7) is true and n is an integer, then

$$\begin{aligned} \psi(x+na) &= \exp[ik(x+na)]u(x+na) \\ &= \exp(ikna)\psi(x). \end{aligned} \quad (8)$$

The same thing can be done for the derivative of $\psi(x)$:

$$\psi'(x+na) = \exp(ikna)\psi'(x). \quad (9)$$

The number k (a vector in the three-dimensional case) naturally depends on the eigenvalue E of Eq. (4). This number must be real in order to have the wave function in Eq. (7) finite for all

values of x . There are, however, some values of E for which k is not real, and that means that not all solutions E of Eq. (4) are allowed, It is through the relation between E and k that we can determine the allowed values of E , which constitute the allowed energy band, and the forbidden values of E , which form the forbidden energy band (or gap).

The dispersion relation E vs k will be determined in what follows for several unidimensional cases with the help of the Laplace transform method.

Let us multiply each side of Eq. (4) by $\exp(-sx)$ and integrate from zero to infinity. Next, let us define $y(s)$ or $L\{\psi(x)\}$, the Laplace transform, by

$$L\{\psi(x)\} = y(s) = \int_0^\infty e^{-sx}\psi(x)dx, \quad (10)$$

$$L^{-1}\{y(s)\} = \psi(x), \quad (11)$$

then Eq. (4) becomes

$$\int e^{-sx} (d^2\psi/dx^2)dx + 2a^{-2} \int e^{-sx} U(x)\psi(x)dx = -K^2 y(s). \quad (12)$$

Using expression (A10) of the Appendix for the Laplace transform of the derivative and rearranging the terms we get

$$\begin{aligned} L\{\psi(x)\} &= y(s) \\ &= \frac{s}{s^2 + K^2} \psi(0) + (s^2 + K^2)^{-1} \psi'(0) \\ &\quad - 2a^{-2} \frac{L\{U(x)\psi(x)\}}{s^2 + K^2}. \end{aligned} \quad (13)$$

The wave function $\psi(x)$ in terms of its value and its derivative at the origin [i.e., $\psi(0)$ and $\psi'(0)$] can be determined at once from Eq. (13) by taking the inverse Laplace transform. Proceeding in this way we verify by Eq. (11) that the left-hand side of Eq. (13) is $\psi(x)$, and that inverse Laplace transform of the first and second terms of the right-hand side are given by (A6) and (A5), respectively. Thus,

$$\begin{aligned} \psi(x) &= \psi(0) \cos(Kx) + \psi'(0) \sin(Kx)/K \\ &\quad - 2a^{-2} L^{-1}[L\{U(x)\psi(x)\}/(s^2 + K^2)]. \end{aligned} \quad (14)$$

Since the wave function $\psi(x)$ must satisfy Bloch's theorem, which means that $\psi(x)$ has to represent travelling waves, then the boundary con-

ditions expressed by Eqs. (8) and (9) have to be satisfied. For $0 \leq x \leq a$ (that is, for x inside the unit cell nearest to the origin), the boundary conditions of Eqs. (8) and (9) relate the value of the wave function and its derivative at $x=a$ with those values of the wave function at the origin, that is,

$$\psi(a) = e^{ika}\psi(0), \quad (15)$$

$$\psi'(a) = e^{ika}\psi'(0). \quad (16)$$

Equation (14) with the conditions expressed by Eqs. (15) and (16) will give us a system of two linear equations on $\psi(0)$ and $\psi'(0)$; this system will have solutions only for definite relations between the energy E and the momentum k , that is, the dispersion relation.

PARTICULAR CASES

The Free Electron

Let us consider the easiest case which corresponds to a free electron. In this case there is no lattice so $U(x) = 0$ for all values of x . Then the last term of Eq. (14) is zero and we get

$$\psi_0(x) = \psi(0) \cos(Kx) + \psi'(0) \sin(Kx)/K. \quad (17)$$

Taking the value of Eq. (17) and its derivative at the point $x=a$ and taking into account the boundary conditions of Eqs. (15) and (16), we get a set of two linear equations in $\psi(0)$ and $\psi'(0)$. This set of equations will possess a non-trivial solution if and only if the determinant of the coefficients of $\psi(0)$ and $\psi'(0)$ is equal to zero:

$$\Delta_0 = \begin{vmatrix} \cos(Ka) - e^{ika} & \sin(Ka)/K \\ -e^{-ika}K \sin(Ka) & e^{-ika} \cos(Ka) - 1 \end{vmatrix} = 0. \quad (18)$$

To facilitate further calculations we have multiplied the derivative of Eq. (17) at $x=a$ by $\exp(-ika)$ on both sides. From Eq. (18) we get

$$\Delta_0 = 2(\cos ka - \cos Ka) = 0. \quad (19)$$

Then

$$Ka = ka \pm 2\pi l \quad (l = 0, 1, 2, \dots). \quad (20)$$

Having in mind the definition of K in terms of E ,

we get the dispersion relation for free electrons,

$$E_n = (\hbar^2/2m)[k \pm (2\pi l/a)]^2. \quad (21)$$

Equation (20), which is the condition for the determinant (18) to be zero, allows us to determine the constant $\psi'(0)$ in terms of $\psi(0)$, which is in this case $\psi'(0) = i(k \pm 2\pi l/a)\psi(0)$. When this value is substituted into Eq. (17), we get

$$\psi_0(x) = \psi(0) \exp[i(k \pm 2\pi l/a)x]. \quad (22)$$

The Monatomic Case

Let us consider now the monatomic case or, as it is known, the Kronig-Penney model. In this model the monatomic crystal is made up of equal atoms located at $x=0, a, 2a, 3a, \dots$. The electrostatic potential of each atom is represented by a Dirac delta function of strength P located at the positions of the atoms and can be represented by

$$U(x) = a \sum_{n=-\infty}^{\infty} P\delta(x-na). \quad (23)$$

The wave function of the problem can be obtained from Eq. (14) where the last term now is not equal to zero. It is easy to see that using Eq. (23) we get

$$\begin{aligned} L\{U(x)\psi(x)\} &= \int_0^{\infty} e^{-sz} [a \sum_{n=-\infty}^{\infty} P\delta(x-na)\psi(x)] dx \\ &= aP \sum_{n=0}^{\infty} e^{-sna}\psi(na). \end{aligned} \quad (24)$$

The inverse Laplace transform which appears

in Eq. (14) is

$$\begin{aligned} L^{-1} \left\{ \frac{L\{U(x)\psi(x)\}}{s^2+K^2} \right\} \\ &= aPJ^{-1} \left\{ \sum_{n=0}^{\infty} \frac{e^{-sna}\psi(na)}{s^2+K^2} \right\} \\ &= aP \sum_{n=0}^{\infty} \psi(na) L^{-1} \left\{ \frac{e^{-sna}}{s^2+K^2} \right\} \\ &= aP \sum_{n=0}^{\infty} \psi(na) \frac{\sin K(x-na)}{K} u(x-na), \end{aligned} \quad (25)$$

where we used expression (A3) of the Appendix to get the final term of Eq. (25). The step function $u(x)$ is also defined in the Appendix. Consequently, the wave function for the monatomic case is

$$\begin{aligned} \psi_1(x) &= \psi(0) \cos Kx + \psi'(0) \sin(Kx)/K \\ &\quad - \frac{2P}{aK} \sum_{n=0}^{\infty} \psi_1(na) \sin[K(x-na)]u(x-na). \end{aligned} \quad (26)$$

The last term in the wave function above is only different from zero when $0 \leq x \leq a$ for $n=0$, due to the property of the step function. To apply the boundary conditions expressed by Eqs. (15) and (16), we proceed in the same way as we did for the free electrons, but here we have to notice that when we use Eq. (16) the last term of Eq. (26) contains the product of the sine, the derivative of the step function, which is the Dirac delta function, and that this product is always zero. In this way we get the determinant of the coefficients of $\psi(0)$ and $\psi'(0)$ which is

$$\Delta_1 = \begin{vmatrix} \cos Ka - e^{ika} - (2P/aK) \sin Ka & \sin(Ka)/K \\ e^{-ika} (-K \sin Ka - (2P/a) \cos Ka) & e^{-ika} \cos(Ka) - 1 \end{vmatrix} = 0. \quad (27)$$

Solving this determinant we get the dispersion relation

$$\cos ka = \cos Ka - (P/aK) \sin Ka. \quad (28)$$

Combining the equation which corresponds to the first line of the determinant with Eq. (28), we obtain a relation between $\psi(0)$ and $\psi'(0)$

and this relation when introduced in Eq. (26) gives the complete wave function of the problem.

It is instructive to observe that the strength P of the Dirac delta function is related to the binding strength of the electron. To see this we consider two extreme cases: P equal to zero, in which case Eq. (28) transforms into Eq. (19) for the free electron, and P going to infinity, in which case the solutions of Eq. (28) are finite if and only if $\sin Ka = 0$, which means $Ka = n\pi$, ($n = 0, 1, 2, 3, \dots$). This last case corresponds to the energy levels of a particle bound to an infinite barrier potential.

Diatomic Case

In the diatomic case there are two distinct types of atom per unit cell. Each atom is represented by a Dirac delta function of strength P_1 and P_2 located at $0, \pm a, \pm 2a, \dots$ and at $\beta_2 a, a + \beta_2 a, 2a + \beta_2 a, \dots$ respectively, where $0 < \beta_2 < 1$ and β_1 is taken to be zero. The potential energy of the whole lattice is then

$$\begin{aligned}
 U(x) &= a \sum_{n=-\infty}^{\infty} P_1 \delta(x-na) \\
 &\quad + a \sum_{n=-\infty}^{\infty} P_2 \delta[x - (n+\beta_2)a] \\
 &= a \sum_{n=-\infty}^{\infty} \sum_{i=1}^2 P_i \delta[x - (n+\beta_i)a]. \tag{29}
 \end{aligned}$$

In the particular case of $\beta_2 = \frac{1}{4}$, the model expressed by Eq. (29) is useful to represent the zincblend structure in the [111] direction, or else to represent NaCl in the [100] direction when $\beta_2 = \frac{1}{2}$. It is easy to see that substituting Eq. (29) in Eq. (25) and taking this result into

Eq. (14), we get for the wave function

$$\begin{aligned}
 \psi_2(x) &= \psi(0) \cos Kx + \psi'(0) [\sin(Kx)/K] \\
 &\quad - \frac{2}{aK} \sum_{n=0}^{\infty} P_1 \psi_2(na) \sin[K(x-na)] u(x-na) \\
 &\quad - \frac{2}{aK} \sum_{n=0}^{\infty} P_2 \psi_2(na + \beta_2 a) \\
 &\quad \times \sin[K(x-na-\beta_2 a)] u(x-na-\beta_2 a). \tag{30}
 \end{aligned}$$

If we restrict the values of x to $0 \leq x \leq a$, we verify that the only contribution to the sums of the right-hand side of Eq. (30) comes from the term $n=0$ due to the properties of the step function. Comparing the wave functions for the diatomic and monatomic [Eq. (26)] cases we see that they differ by

$$\begin{aligned}
 \psi_2(x) &= \psi_1(x) - (2/aK) P_2 \psi_2(\beta_2 a) \\
 &\quad \times \sin[K(x-\beta_2 a)] u(x-\beta_2 a). \tag{31}
 \end{aligned}$$

It is interesting to notice that this difference only happens for points x such that $x \geq \beta_2 a$, that is, for points x located at the right side of the second atom in the unit cell. At the left of this atom the two wave functions coincide. This is a consequence of the fact that the range of the potential in the Dirac delta function model is practically zero.

In applying boundary conditions expressed by Eqs. (15) and (16), we observe that to form the determinant of the coefficients of $\psi(0)$ and $\psi'(0)$ we need the value of the wave function $\psi_2(x)$ at $x = \beta_2 a$. But from Eq. (31) it is easy to see that

$$\psi_2(\beta_2 a) = \psi_1(\beta_2 a), \tag{32}$$

where $\psi_1(\beta_2 a)$ can be obtained from Eq. (26) with $x = \beta_2 a$. For this value of x the last sum in Eq. (26) is only different from zero for n equal to zero, due to the fact that the argument of the step function $u(\beta_2 a - na)$ is always negative for n not equal to zero. With this in mind, $\psi_2(\beta_2 a)$ is obtained in terms of $\psi(0)$ and $\psi'(0)$, and we can write the determinant of the coefficients as

$$\Delta_2 = \begin{vmatrix} \cos Ka - e^{ika} + \phi_1 & [\sin(Ka)/K] + \phi_2 \\ e^{-ika} [-K \sin(Ka) + \phi_3] & e^{-ika} \cos(Ka) - 1 + e^{-ika} \phi_4 \end{vmatrix} = 0, \tag{33}$$

where

$$\phi_1 = (2P_1/aK) \sin Ka - (2P_2/aK) \cos(K\beta_2 a) \sin K(a - \beta_2 a) + (4P_1P_2/a^2K^2) \sin(K\beta_2 a) \sin K(a - \beta_2 a), \quad (34)$$

$$\phi_2 = - (2P_2/aK) (\sin K\beta_2 a/K) \sin K(a - \beta_2 a), \quad (35)$$

$$\phi_3 = - (2P_1/a) \cos Ka - (2P_2/aK) \cos(K\beta_2 a) \cos K(a - \beta_2 a) + (4P_1P_2/a^2K) \sin(K\beta_2 a) \cos K(a - \beta_2 a), \quad (36)$$

$$\phi_4 = - (2P_2/aK) \sin(K\beta_2 a) \cos K(a - \beta_2 a). \quad (37)$$

This determinant and others much more complicated that may appear are written in this way to facilitate their solution. We can see at once that the terms $\phi_1, \phi_2, \phi_3, \phi_4$ involve the strength of the potential, and that they arise due to the introduction of one or more atoms inside the unit cell when compared to the free electron case. In a general sense we can say that whatever is the number of atoms per cell in the one-dimensional model, the terms of the main diagonal of the determinant will give the contribution

$$D_1 = e^{ika} - 2 \cos Ka + e^{-ika} \cos^2 Ka - (\phi_1 + \phi_4) + e^{-ika} [(\phi_1 + \phi_4) \cos Ka + \phi_1 \phi_4], \quad (38)$$

and the terms off diagonal will give

$$D_2 = e^{-ika} \sin^2 Ka - e^{-ika} [\phi_3 \sin(Ka)/K - \phi_2 K \sin Ka + \phi_2 \phi_3]. \quad (39)$$

Then

$$\Delta_2 = D_1 + D_2 = 2 \cos ka - 2 \cos Ka - (\phi_1 + \phi_4) + e^{-ika} \times [(\phi_1 + \phi_4) \cos Ka + \phi_1 \phi_4 - \phi_3 \sin(Ka)/K - \phi_2 K \sin Ka + \phi_2 \phi_3] = 0. \quad (40)$$

The solutions that we are interested in are those which represent travelling waves [Eq. (8)] and this implies that the number k must be real. Of the two possible solutions of Eq. (40), the one which gives k real is the one which corresponds to the cancellation of the coefficient of $\exp(-ika)$. Imposing this condition on Eq. (40) we obtain, for the general case, the dispersion relation

$$\cos ka = \cos Ka + (\phi_1 + \phi_2)/2. \quad (41)$$

In the case under consideration (that is, diatomic case with two atoms per unit cell) Eq. (41), with the values of ϕ_1 and ϕ_4 given by Eqs. (34) and (35), respectively, will give

$$\cos ka = \cos Ka - [(P_1 + P_2)/aK] \sin Ka + (2P_1P_2/a^2K^2) \sin K\beta_2 a \sin K(a - \beta_2 a). \quad (42)$$

GENERAL CASE

As we mentioned before, the dispersion relation Eq. (41) for any one-dimensional periodic structure, based on Dirac delta functions, depends only on ϕ_1 and ϕ_4 . Consequently, we can get the energy versus momentum relation for an arbitrary number p of peaks per cell or p distinct atoms per unit cell. To this end, let $\beta_1 a, \beta_2 a, \dots, \beta_p a$ be the locations of the atoms inside the unit cell ($\beta_i < 1$ for all i), and let P_1, P_2, \dots, P_p be the strength of the Dirac delta function at those points, according to Fig. 1. The potential energy for the whole lattice can be written as

$$U(x) = a \sum_{n=-\infty}^{\infty} \sum_{i=1}^p P_i \delta[x - (n + \beta_i)a], \quad (43)$$

where $\beta_1 = 0$. Placing this value of the potential in

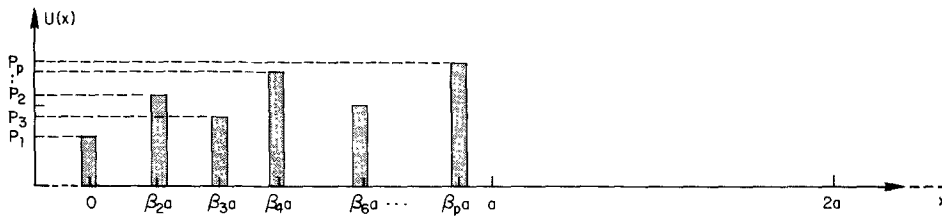


Fig. 1. The potential function $U(x)$ for the general case of p distinct atoms per unit cell.

Eq. (25) we get

$$L^{-1} \left\{ \frac{L\{U(x)\psi(x)\}}{s^2 + K^2} \right\} = a \sum_{n=0}^{\infty} \sum_{i=1}^p P_i \psi(na + \beta_i a) \times \frac{\sin K(x - na - \beta_i a)}{K} u(x - na - \beta_i a). \quad (44)$$

So the wave function expressed by Eq. (14) and corresponding to p atoms per cell and for x located in the unit cell nearest to the origin, that is $0 \leq x \leq a$, is given by

$$\psi_p(x) = \psi(0) \cos Kx + \psi'(0) \sin(Kx)/K - \frac{2}{aK} \sum_{i=1}^p P_i \psi_p(\beta_i a) \sin K(x - \beta_i a) u(x - \beta_i a). \quad (45)$$

This wave function must satisfy the boundary conditions as stated in Eqs. (15) and (16) to represent travelling waves. When we apply these conditions we verify that in order to have only two coefficients in Eq. (45), $\psi(0)$ and $\psi'(0)$, we have to relate the value of the wave function at the points $\beta_1 a, \beta_2 a, \dots, \beta_p a$ with the value of the wave function and its derivative at the origin. It is easy to see from Eq. (45) and from the structure of Eq. (13) that the wave function corresponding to p atoms per cell is related to the wave function for $p-1$ atoms per cell, and that this relation can be written symbolically as [see also Eq. (26)],

$$\psi_p(x) = \psi_{p-1}(x) - (2/aK) P_p \psi_p(\beta_p a) \times \sin[K(x - \beta_p a)] u(x - \beta_p a). \quad (46)$$

For all points x , such that $x = \beta_j a$ with $j = 1, 2, \dots, p$, we can write

$$\psi_p(\beta_j a) = \psi_{p-1}(\beta_j a) \quad (47)$$

and this expression is always true because for $j < p$ the step function makes the last term of Eq. (46) zero, while for $j = p$, the sine is zero. In a similar way we get

$$\psi_{p-1}(x) = \psi_{p-2}(x) - (2/aK) P_{p-1} \psi_{p-1}(\beta_{p-1} a) \times \sin[K(x - \beta_{p-1} a)] u(x - \beta_{p-1} a), \quad (48)$$

which is the relation between the wave function for $p-1$ atoms per cell and the wave function for $p-2$ atoms per cell. In a similar way we verify that

$$\psi_{p-1}(\beta_j a) = \psi_{p-2}(\beta_j a) \quad j = 1, 2, \dots, p-1. \quad (49)$$

These recursion relations enable us to determine, for any number of distinct atoms per unit cell, the wave function at the positions of the atoms inside the unit cell in terms of the wave function and its derivative at the origin. This is what we need to calculate the coefficient of $\psi(0)$, which we called ϕ_1 , when we use boundary condition Eq. (15), and the coefficient of $\psi'(0)$, also called ϕ_2 , when we use boundary condition Eq. (16). With the values of ϕ_1 and ϕ_2 and with the help of Eq. (41), we get the dispersion relation for the case under study. Then the dispersion relation for a one-dimensional periodic

structure with p atoms per unit cell is

$$\begin{aligned} \cos ka = \cos Ka - \sum_{i=1}^p \frac{P_i}{aK} \sin Ka + 2 \sum_{i=1}^p \sum_{i>j}^p \frac{P_i P_j}{(aK)^2} \sin[K(\beta_j - \beta_i)a] \sin K[1 - (\beta_j - \beta_i)a] \\ - 4 \sum_{i=1}^p \sum_{i>j}^p \sum_{i>l}^p \frac{P_i P_j P_l}{(aK)^3} \sin[K(\beta_j - \beta_i)a] \sin[K(\beta_l - \beta_j)a] \sin K[1 - (\beta_l - \beta_i)a] + \dots \\ + (-1)^{p-1} \frac{P_1 P_2 \dots P_p}{(aK)^p} \sin[K(\beta_2 - \beta_1)a] \dots \sin[K(\beta_p - \beta_{p-1})a] \sin K[1 - (\beta_p - \beta_1)a]. \end{aligned} \quad (50)$$

APPENDIX

Table of Laplace Transform Used in the Text.¹

The Laplace transform of a function $f(x)$, for real x , is a function $y(s)$, also known as $L\{f(x)\}$, where

$$y(s) = L\{f(x)\} \equiv \int_0^\infty f(x)e^{-sx} dx. \quad (A1)$$

Given $y(s)$ we can get $f(x)$ by looking for a function which satisfies (A1). Then the inverse Laplace transform of a function $y(s)$ is a function $f(x)$ which satisfies

$$f(x) = L^{-1}\{y(s)\}. \quad (A2)$$

If $f(x) = L^{-1}\{y(s)\}$, then

$$L^{-1}\{e^{-as}y(s)\} = f(x-a)u(x-a), \quad (A3)$$

where the step function $u(x)$ satisfies:

$$\begin{aligned} u(x-a) = 1 & \text{ if } x > a, \\ u(x-a) = 0 & \text{ if } x < a. \end{aligned}$$

If a_1 and a_2 are constants, we can show that

$$L^{-1}\{a_1 y_1(s) + a_2 y_2(s)\} = a_1 f_1(x) + a_2 f_2(x). \quad (A4)$$

We note that if $y(s) = (s^2 + K^2)^{-1}$ then

$$f(x) = \sin(Kx)/K \quad (A5)$$

and if $y(s) = s/(s^2 + K^2)$ then

$$f(x) = \cos(Kx). \quad (A6)$$

Combining Eqs. (A5) and (A6) with Eq. (A3), we note that $y(s) = e^{-as}/(s^2 + K^2)$ implies

$$f(x) = [\sin K(x-a)/K]u(x-a) \quad (A7)$$

and $y(s) = se^{-as}/(s^2 + K^2)$ implies

$$f(x) = [\cos K(x-a)]u(x-a). \quad (A8)$$

We can also show that

$$L\{df(x)/dx\} = sy(s) - f(0), \quad (A9)$$

$$L\{d^2f(x)/dx^2\} = s^2y(s) - sf(0) - (df/dx)|_{x=0}. \quad (A10)$$

¹ F. B. Hildebrand, *Advanced Calculus for Applications* (Prentice Hall, Englewood Cliffs, NJ, 1962).