**Physical Electronics**
**Quantum Mechanics Handout**
**April 10, 2003**

# 1 Schrödinger's Equation

## One-Dimensional, Time-Dependent version

Schrödinger's equation originates from conservation of energy.

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{1}$$

The first term has to do with *Kinetic* energy, the second is closely related to *Potential* energy, and the sum of the two is something like *total* energy. $\Psi$ is called the *wavefunction.* In the one-dimensional case, $\Psi = \Psi(x,t)$ and $V = V(x)$.

We can solve equation (1) by the method of *separation of variables.* Assume $\Psi(x,t)$ is a product of functions of $x$ and $t$ alone:

$$\Psi(x,t) = \psi(x)\phi(t) \tag{2}$$

Plug this into equation (1) to obtain

$$\frac{-\hbar^2}{2m}\phi(t)\frac{d^2\psi}{dx^2} + V(x)\psi(x)\phi(t) = i\hbar\psi(x)\frac{d\phi}{dt}\ . \tag{3}$$

Divide both sides of (3) by $\psi(x)\phi(t)$:

$$\frac{-\hbar^2}{2m}\left(\frac{1}{\psi}\frac{d^2\psi}{dx^2}\right) + V(x) = i\hbar\frac{1}{\phi}\frac{d\phi}{dt} \tag{4}$$

The two sides of equation (4) are equal, but they depend on entirely different variables. The only way for this to be true is for both sides to equal some constant, $G$.

Solving the time-dependent portion of the separated equation (4) we obtain

$$i\hbar\frac{1}{\phi}\frac{d\phi}{dt} = G \Longrightarrow \phi(t) = e^{-\frac{i}{\hbar}Gt}\ . \tag{5}$$

This is similar to the form of an electromagnetic wave, $e^{-i\omega t}$. By analogy,

$$\omega = \frac{E}{\hbar} \Longrightarrow G = E$$

therefore the solution to the time-dependent Schrödinger equation is

$$\Psi(x,t) = \psi(x)e^{-\frac{i}{\hbar}Et} \tag{6}$$

**Time-Independent version**

The time-independent § equation is similar:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + (V(x) - E)\,\phi = 0\;. \tag{7}$$

This may be extended to three dimensions as

$$\frac{-\hbar^2}{2m}\nabla^2\psi + (V(x,y,z) - E)\,\phi(x,y,z) = 0\;. \tag{8}$$

# 2 Born Interpretation of the Wavefunction

The intensity of an electromagnetic wave is proportional to the square of the **E** or **B** field. If we use the photon model of light instead of the wave model, then that intensity at any location should be proportional to the probability of finding a photon there. Reasoning by analogy from this, Max Born suggested that the probability density for a particle is given by

$$P(x) = |\Psi|^2 = \Psi^*(x)\Psi(x)\;, \tag{9}$$

where $\Psi^*$ is the complex conjugate of $\Psi$.

If the particle exists, then the probability of finding it *somewhere* is exactly one. This 'startling' observation leads to the *normalization* of the wavefunction

$$\int_{-\infty}^{\infty} \Psi^*\Psi\,dx = 1\;. \tag{10}$$

Probability theory tells us that the expected value, or *expectation value*, of a measurement of some parameter $Q$ is

$$\langle Q\rangle = \frac{\int_{-\infty}^{\infty} QP(x)\,dx}{\int_{-\infty}^{\infty} P(x)\,dx} \tag{11}$$

Thus for a particle, with normalized wavefunction, the expectation value of position $x$ becomes

$$\langle x\rangle = \int_{-\infty}^{\infty} \Psi^* x \Psi\,dx\;. \tag{12}$$

For electromagnetic waves of the form $e^{i(kx-\omega t)}$,

$$-i\hbar\frac{\partial}{\partial x}\left[e^{i(kx-\omega t)}\right] = \hbar k e^{i(kx-\omega t)} = p_x\left[e^{i(kx-\omega t)}\right]\;. \tag{13}$$

Therefore we associate the operator $-i\hbar\frac{\partial}{\partial x}$ with momentum $p_x$. With a normalized wavefunction,

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \Psi^* \left( -i\hbar \frac{\partial}{\partial x} \right) \Psi \, dx \; . \tag{14}$$

Notice the importance of operator position!

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**Example 2.1 (Momentum of a Free Particle)**
For a particle unconstrained by any potential ($V(x) = 0$), the time-independent Schrödinger equation (7) becomes

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - E\psi = 0 \tag{15}$$

The general solution is

$$\psi(x) = Ae^{\frac{i}{\hbar}\sqrt{2mE}x} + Be^{-\frac{i}{\hbar}\sqrt{2mE}x} \; . \tag{16}$$

From (6), the time-dependent wave function is

$$\begin{aligned} \Psi(x,t) &= \psi(x)e^{-\frac{i}{\hbar}Et} \\ &= Ae^{\frac{i}{\hbar}(\sqrt{2mE}x - Et)} + Be^{-\frac{i}{\hbar}(\sqrt{2mE}x + Et)} \; . \end{aligned} \tag{17}$$

This represents two waves, one ($A$) moving in the $+x$ direction and one ($B$) moving in the $-x$ direction. If we know that the particle is moving in the $+x$ direction we can set $B = 0$.

Now we can find the expectation value of the momentum.

$$\begin{aligned} \langle p_x \rangle &= \frac{\int_{-\infty}^{\infty} \Psi^* \left(-i\hbar\frac{\partial}{\partial x}\right) \Psi \, dx}{\int_{-\infty}^{\infty} \Psi^* \Psi \, dx} \\ &= \frac{\sqrt{2mE} \int_{-\infty}^{\infty} \Psi^* \Psi \, dx}{\int_{-\infty}^{\infty} \Psi^* \Psi \, dx} = \sqrt{2mE} \end{aligned} \tag{18}$$

This is exactly what we would expect from classical (Newtonian) physics.

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## 3 Boundary Conditions on Wave Functions

Since the expectation value of $x$ must be finite, $\psi$ must be finite. The expectation value of $p_x$ must also be finite, so $\frac{d\psi}{dx}$ must be finite. Since $\frac{d\psi}{dx}$ is finite, $\psi$ must be continuous. Next, since from equation (7)

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}(V - E)\psi \tag{19}$$

and the energy must be finite, $\frac{d^2\psi}{dx^2}$ is finite which implies that $\frac{d\psi}{dx}$ is continuous. Finally, both $\psi$ and $\frac{d\psi}{dx}$ must be single-valued or we must abandon any hope of correspondence to reality.

In summary, both $\psi$ and $\frac{d\psi}{dx}$ must be finite, continuous, and single-valued at all points. We can use these constraints as boundary conditions to help us solve the Schrödinger equation.

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**Example 3.1 (Potential Barrier $V_o < E$)**
Solve the time-independent Schrödinger equation (7) in regions 1 and 2 separately, then use the boundary conditions on $\psi$ at $x = 0$ to match the solutions.

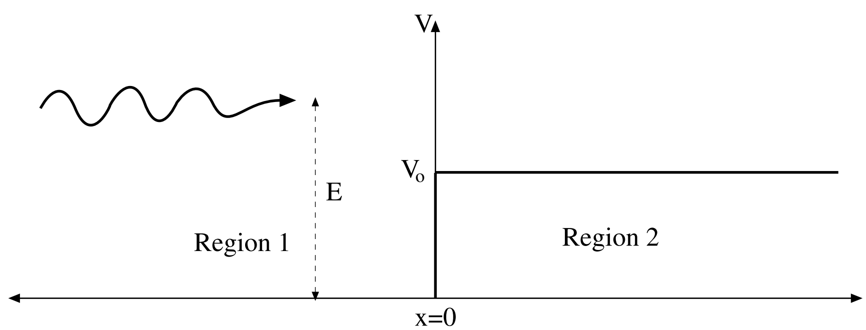


Figure 1: Particle of energy $E$ incident on a region with $V_o < E$

In region 1 ($x < 0$),

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} = E\psi_1 \Longrightarrow \psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x} \tag{20}$$

where

$$k_1 \equiv \frac{\sqrt{2mE}}{\hbar} \ . \tag{21}$$

In region 2 ($x > 0$)

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + V\psi_2 = E\psi_2 \Longrightarrow \psi_2(x) = Ce^{ik_2x} + De^{-ik_2x} \tag{22}$$

where

$$k_2 \equiv \frac{\sqrt{2m(E-V)}}{\hbar} \; . \tag{23}$$

Now apply boundary conditions. The first, and simplest, is to note that in region 2 the solution should represent a wave moving to the right *only*; so $D = 0$. Next, apply the condition of continuity of $\psi$ and $\frac{d\psi}{dx}$ at $x = 0$:

$$\psi_1|_{x=0} = \psi_2|_{x=0} \Longrightarrow A + B = C \tag{24}$$

$$\left.\frac{d\psi_1}{dx}\right|_{x=0} = \left.\frac{d\psi_2}{dx}\right|_{x=0} \Longrightarrow ik_1(A-B) = ik_2C \; . \tag{25}$$

Find $B$ and $C$ in terms of $A$:

$$A + B = C \Longrightarrow 2A = \left(1 + \frac{k_2}{k_1}\right)C$$

$$\Longrightarrow C = \frac{2k_1}{k_1+k_2}A \tag{26}$$

$$A - B = \frac{k_2}{k_1}C \Longrightarrow \left(1 - \frac{k_1}{k_2}\right)A + \left(1 + \frac{k_1}{k_2}\right)B = 0$$

$$\Longrightarrow B = \frac{k_1-k_2}{k_1+k_2}A \tag{27}$$

In principle, $A$ should be determined by applying the normalization condition (10) to $\psi$, but for unbounded traveling wave solutions this is a bit tricky. Instead, find the probability of the particle being transmitted and being reflected. In order to do this, we need to know the flux of the particles incident on the barrier. Current density is the flux of the charge density ($\mathbf{J} = \rho\mathbf{v}$), so we need to multiply the probability density $|\psi|^2$ by the velocity of the particle $\frac{p}{m} = \frac{\hbar k}{m}$.

The reflected portion of the wave function is given by $Be^{-ik_1x}$ in region 1. The incident wave is given by $Ae^{ik_1x}$. The probability of reflection, the *reflection coefficient*, is then

$$R \equiv \frac{k_1|B|^2}{k_1|A|^2} = \frac{(k_1-k_2)^2}{(k_1+k_2)^2} \; . \tag{28}$$

Similarly, the *transmission coefficient* is

$$T \equiv \frac{k_2|C|^2}{k_1|A|^2} = \frac{k_2}{k_1}\frac{(2k_1)^2}{(k_1+k_2)^2} \ . \tag{29}$$

You may verify that $R + T = 1$.

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# 4 Kronig-Penney model

Imagine a one-dimensional potential lattice with spacing $L$, such as figure 2. This is a simple one-dimensional analogue to a crystal—the three-dimensional version is similar but much more complicated mathematically. To make things as simple as possible, we will assume that the potential $V_o$ is in the form of a step function, rather than a more realistic Coulomb potential. (In the final analysis of this model (equation 48), we will take a limit that renders the form of our potential irrelevant anyway.)

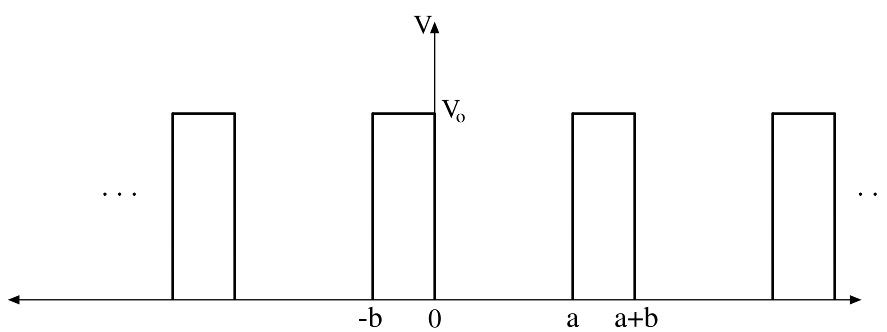


Figure 2: One-dimensional potential lattice

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} - E\psi_1 = 0 \qquad 0 < x < a \tag{30}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + (V_o - E)\psi_2 = 0 \qquad -b < x < 0 \tag{31}$$

The boundary conditions on $\psi$ are

$$\psi(x) = \psi(x+L) \tag{32}$$

$$\psi^*\psi|_x = \psi^*\psi|_{x+d} \tag{33}$$

One form of solution that meets these conditions is $\psi(x) = e^{ikx}u(x)$, where $u(x) = u(x+d)$. Applying condition (32) to this solution, we obtain

$$e^{ik(x+L)}u(x+L) = e^{ikx}u(x) \Longrightarrow e^{ikL} = 1 \Longrightarrow k = \frac{2n\pi}{L} \tag{34}$$

Now transform equations (30) and (31) into differential equations in terms of $u(x)$.

$$\frac{d\psi}{dx} = e^{ikx}u' + ike^{ikx}u \tag{35}$$

$$\frac{d^2\psi}{dx^2} = e^{ikx}u'' + 2ike^{ikx}u' - k^2eikxu \tag{36}$$

Define

$$\alpha^2 \equiv \frac{2mE}{\hbar^2} \tag{37}$$

$$\beta^2 \equiv \frac{2m(V_o - E)}{\hbar^2} \tag{38}$$

Now equations (30) and (31) become

$$u_1'' + 2iku_1' + (\alpha^2 - k^2)u_1 = 0 \qquad 0 < x < a \tag{39}$$

$$u_2'' + 2iku_2' - (\beta^2 + k^2)u_2 = 0 \qquad -b < x < 0 \tag{40}$$

And the solutions are

$$u_1(x) = Ae^{(-ikx+i\alpha x)} + Be^{(-ikx-i\alpha x)} \qquad 0 < x < a \tag{41}$$

$$u_2(x) = Ce^{(-ikx+\beta x)} + De^{(-ikx-\beta x)} \qquad -b < x < 0\ . \tag{42}$$

The boundary conditions—continuity—on $\psi$ and $\frac{d\psi}{dx}$ hold at all points. Of particular interest to us for this derivation are points $a$ and $-b$. Substituting $u_1$ and $u_2$ into the boundary conditions gives us

$$A + B = C + D \tag{43}$$

$$(-ik + i\alpha)A + (-ik - i\alpha)B = (-ik + \beta)C + (-ik - \beta)D \tag{44}$$

$$Ae^{(-ika+i\alpha a)} + Be^{(-ika-i\alpha a)} = Ce^{(ikb-\beta b)} + De^{(ikb+\beta b)} \tag{45}$$

$$(-ik + i\alpha)Ae^{(-ika+i\alpha a)} + (-ik - i\alpha)Be^{(-ika-i\alpha a)} = (-ik + \beta)Ce^{(ikb-\beta b)} + (-ik - \beta)De^{(ikb+\beta b)} \tag{46}$$

Put this into matrix form, and set the determinant of the coefficients equal to zero. (This ensures a non-trivial solution, according to Kramer's Rule.) Solve this determinant as best we can to obtain

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh(\beta b) \sin(\alpha a) + \cosh(\beta b) \cos(\alpha a) = \cos\left(k(b + a)\right) \tag{47}$$

Now for the tricky part. Let the width of the potential region $b \to 0$ while letting the potential $V_o \to \infty$ in such a way that $bV_o$ = constant but $\beta b \to 0$. (Remember the definition (38) of $\beta$.) This is equivalent to making our lattice out of very small hard pointlike objects. (Nuclei?) Take the limit of (47) as $\beta b \to 0$. In this limit, (47) becomes

$$\frac{\beta^2 b}{2\alpha} \sin(\alpha a) + \cos(\alpha a) = \cos(ka) \tag{48}$$

which can be re-written as

$$P \mathrm{sinc}(\alpha a) + \cos(\alpha a) = \cos(ka) \tag{49}$$

where

$$P \equiv \frac{a\beta^2 b}{2}\ . \tag{50}$$

This is most easily understood in graphical form. (Figure 3) The right-hand side of (49) only allows solutions in the region between -1 and 1. The shaded regions of figure 3 are the regions where solutions to the Schrödinger equation exist. Since $a$ is a constant, it is $\alpha$ that determines whether the region is an allowed region or not. It can be seen from the definition of $\alpha$ (37) that *energy* is the only variable, so the existence of solutions depends on the energy of the particle.

**Conclusion:** Energy *bands* exist in periodic structures.

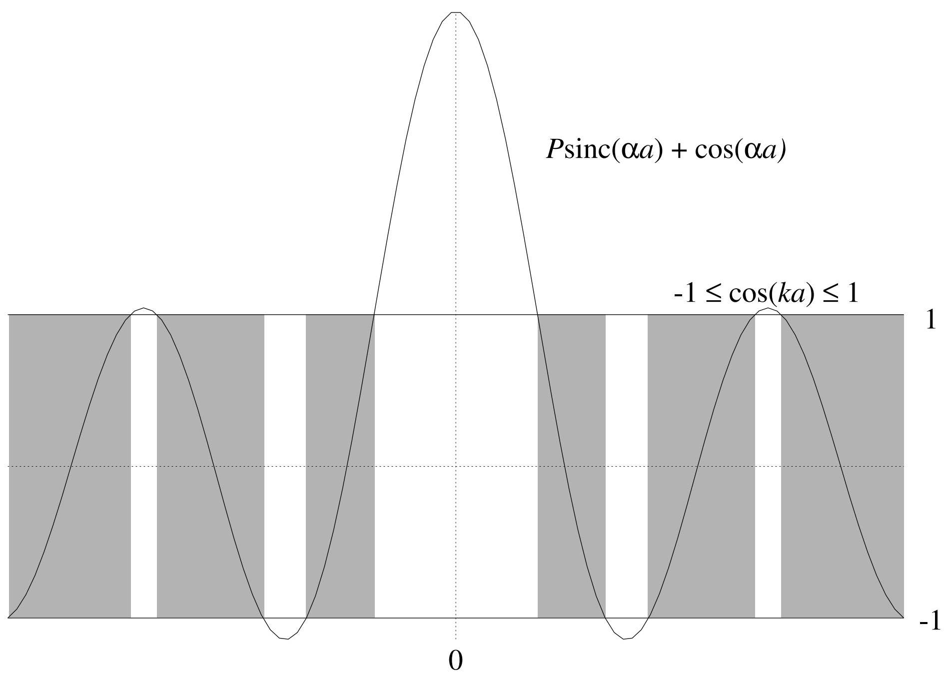


Figure 3: Kronig-Penney model in the point-potential limit