Nearly-Free-Electron Model

Reading:

Brennan Chapter 8.3

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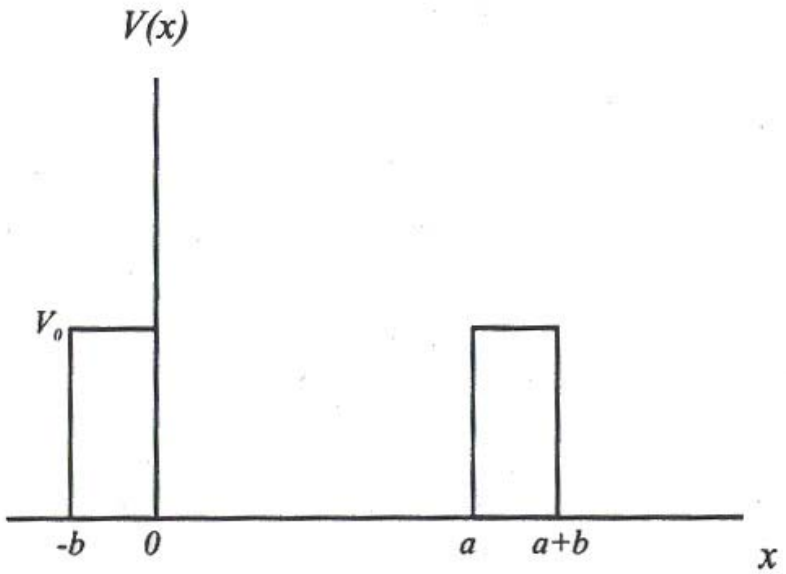
The Kronig-Penney Model (review)

The solution to the Schroedinger equation for a periodic rectangular barrier predicts that only discrete bands of energy are allowed.



Brennan, Figure 8.2.1. One dimensional periodic potential with period *a+b*.

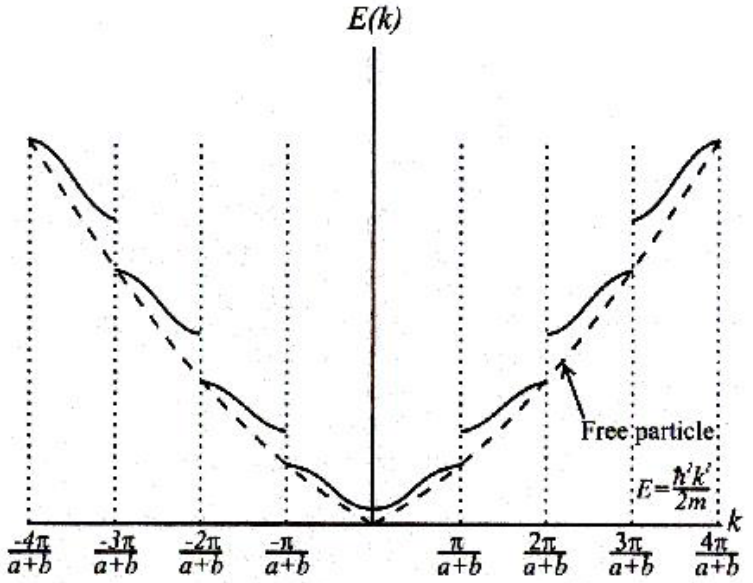


Figure 8.2.3. Sketch of $E(k)$ versus k for both a free particle (dashed curve) and a particle in a periodic potential. Note the presence of gaps at multiples of $\pi/(a+b)$ that correspond to the imaginary values of k in Fig. 8.2.2.

According to this model, discontinuities in allowed energies appear at $k=n\pi/(a+b)$, where a and b relate to the periodicity of the rectangular potential.

What about any arbitrary periodic potential? Will discrete bands of energy show up in the solution as expected?

The Schroedinger Equation

Defining a periodic potential

Let's start with the Schroedinger equation, and go from there:

$$H\Psi = E\Psi$$

$$\frac{d^2}{dx^2}\Psi + \frac{2m}{\hbar^2}\left[E - V(x)\right]\Psi = 0$$

$$\frac{d^2}{dx^2}\Psi + \left[\frac{2mE}{\hbar^2} - \frac{2m}{\hbar^2}V(x)\right]\Psi = 0$$

To simplify this, we will make two helpful substitutions

$$\frac{2mE}{\hbar^2} = k_0^2$$

$$-\frac{2m}{\hbar^2}V(x) = \gamma f(x)$$

Finally, the Schroedinger equation becomes:

$$\boxed{\frac{d^2\Psi}{dx^2} + \left[k_0^2 + \gamma f(x)\right]\Psi = 0}$$

The Schroedinger Equation

Defining a periodic potential

$$\frac{d^2\Psi}{dx^2} + \left[k_0^2 + \gamma f(x)\right]\Psi = 0$$

But how do we define this new *f(x)*? Well, we know two things about our arbitrary periodic potential V(x):

- V(x) has a set lattice constant, or period, *a*.
- V(x) can be described as a Fourier series.

So, let's expand *f(x)*, a periodic function with the same periodicity as V(x), in terms of a complex Fourier series.

$$f(x) = \sum_{n=-\infty}^{+\infty} C_n e^{\frac{-i\,2\pi nx}{a}}$$

$$where \quad C_n = \frac{1}{a}\int_0^a f(x) e^{\frac{i\,2\pi nx}{a}} dx$$

and γ is a scaling factor

The Schroedinger Equation

Bloch functions and periodicity

As seen before, any periodic potential will result in a periodic wave function of the form

$$\text{n-dimensional}: \Psi_{nk}(r) = e^{ikr} u_{nk}(r)$$

$$\text{one dimensional}: \Psi_k(x) = e^{ikx} u_k(x)$$

where $u_k(x)$ is periodic, with the same periodicity of the potential. Therefore, we can expand it in terms of another complex Fourier series.

$$u_k(x) = \sum_{n=-\infty}^{+\infty} b_n e^{\frac{-i2\pi nx}{a}}$$

$$\Psi(x) = e^{ikx} \sum_n b_n e^{\frac{-i2\pi nx}{a}}$$

The wave function will retain the same magnitude each period a. Only its phase will change from one lattice point to the next. The properties of the Bloch function are retained.

But, this is not very useful unless we can relate this to $f(x)$. So we will make a few more observations about the nature of the wave function relating to the periodic potential, and then solve the Schroedinger equation. Hopefully, we can shine some light on this new wave function.

The Schroedinger Equation

Relating $f(x)$ to $u_k(x)$

From before…

$$\frac{d^2\Psi}{dx^2} + \left[k_0^2 + \gamma f(x)\right]\Psi = 0$$

If $\gamma = 0$, then V(x) is zero and the electron is free, which is represented as a simple plane wave.

$$\frac{d^2\Psi}{dx^2} + k_0^2\Psi = 0$$

$$\Psi(x) = b_0 e^{ik_0 x}$$

If $\gamma \neq 0$, we assume the electron to be traveling in a weak potential, and can thus expand the wave function into two parts. One corresponding to a plane wave, or a free electron, and another corresponding to a periodic correction factor. Hence the name, "nearly-free-electron model."

$$\Psi(x) = \underbrace{b_0 e^{ikx}}_{\text{“free electron” plane wave}} + \underbrace{\gamma e^{ikx} \sum_{n\neq 0} b_n e^{\frac{-i2\pi nx}{a}}}_{\text{periodic correction factor (small)}}$$

Solving the Schroedinger Equation

First Order Solution

$$\Psi(x) = b_0 e^{ikx} + \gamma e^{ikx} \sum_{n \neq 0} b_n e^{\frac{-i2\pi nx}{a}}$$

Now we have a general solution for our arbitrary, periodic potential. Remember, we are trying to determine if any periodic potential will result in discrete energy bandgaps. To do this, we will want to solve for the energy versus *k* relationship, which means we first must solve the Schroedinger equation to find the coefficients b_n. Plugging Ψ(x) into our simplified Schroedinger equation:

$$\frac{d^2\Psi}{dx^2} + \left[k_0^2 + \gamma f(x)\right]\Psi = 0$$

The full derivation is not shown here (Brennan p.419). After substituting, expanding the second-derivative term, and combining like terms, the result is:

$$b_0\left(k_0^2 - k^2\right)e^{ikx} + \gamma \sum_{n \neq 0}\left(k_0^2 - k^2\right)b_n e^{i\left(k - \frac{2\pi n}{a}\right)x}$$

$$+ b_0\gamma \sum_{n \neq 0} C_n e^{i\left(k - \frac{2\pi n}{a}\right)x} + \gamma^2 \sum_{n \neq 0}\sum_{n' \neq 0} C_n b_{n'} e^{i\left(k - \frac{2\pi n}{a} - \frac{2\pi n'}{a}\right)x}$$

$$+ \gamma \sum_{n \neq 0} b_n \left(\frac{4\pi n}{a}k - \frac{4\pi^2 n^2}{a^2}\right)e^{i\left(k - \frac{2\pi n}{a}\right)x} = 0$$

TOO COMPLEX!!

Solving the Schroedinger Equation

First Order Solution

The problem already seems to have blown up. However, we made the assumption that V(x) is weak, therefore γ must be small, and the γ^2 term (fourth term) can be neglected. Also, we can further simplify the equation. Consider only the terms in γ.

$$\gamma \sum_{n \neq 0} \left(k_0^2 - k^2\right) b_n e^{i\left(k - \frac{2\pi n}{a}\right)x} + \gamma \sum_{n \neq 0} b_n \left(\frac{4\pi n}{a} k - \frac{4\pi^2 n^2}{a^2}\right) e^{i\left(k - \frac{2\pi n}{a}\right)x}$$

$$+ b_0 \gamma \sum_{n \neq 0} C_n e^{i\left(k - \frac{2\pi n}{a}\right)x}$$

We want to combine these into one simple term, and we can by defining the following relation:

$$k = k_n + \frac{2\pi n}{a}$$

Combining the first two terms and substituting in the above relation:

$$\gamma \sum_{n \neq 0} \left(k_0^2 - k^2 + \frac{4\pi n}{a} k - \frac{4\pi^2 n^2}{a^2}\right) b_n e^{i\left(k - \frac{2\pi n}{a}\right)x} + b_0 \gamma \sum_{n \neq 0} C_n e^{i\left(k - \frac{2\pi n}{a}\right)x}$$

$$\gamma \sum_{n \neq 0} \left(k_0^2 - k_n^2 - \frac{4\pi n}{a} k_n - \frac{4\pi^2 n^2}{a^2} + \frac{4\pi n}{a} k - \frac{4\pi^2 n^2}{a^2}\right) b_n e^{i\left(k - \frac{2\pi n}{a}\right)x} + \gamma \sum_{n \neq 0} b_0 C_n e^{i\left(k - \frac{2\pi n}{a}\right)x}$$

$$\gamma \sum_{n \neq 0} \left(k_0^2 - k_n^2 - \frac{4\pi n}{a} k + \frac{8\pi^2 n^2}{a^2} + \frac{4\pi n}{a} k - \frac{8\pi^2 n^2}{a^2}\right) b_n e^{i\left(k - \frac{2\pi n}{a}\right)x} + \gamma \sum_{n \neq 0} b_0 C_n e^{i\left(k - \frac{2\pi n}{a}\right)x}$$

Solving the Schroedinger Equation

First Order Solution

Continued…

$$\gamma \sum_{n \neq 0} \left(k_0^2 - k_n^2 - \frac{4\pi n}{a} k + \frac{8\pi^2 n^2}{a^2} + \frac{4\pi n}{a} k - \frac{8\pi^2 n^2}{a^2} \right) b_n e^{i\left(k - \frac{2\pi n}{a}\right)x} + \gamma \sum_{n \neq 0} b_0 C_n e^{i\left(k - \frac{2\pi n}{a}\right)x}$$

$$\gamma \sum_{n \neq 0} \left(k_0^2 - k_n^2 \right) b_n e^{i\left(k - \frac{2\pi n}{a}\right)x} + \gamma \sum_{n \neq 0} b_0 C_n e^{i\left(k - \frac{2\pi n}{a}\right)x}$$

$$\boxed{\gamma \sum_{n \neq 0} \left[\left(k_0^2 - k_n^2 \right) b_n + b_0 C_n \right] e^{i\left(k - \frac{2\pi n}{a}\right)x}}$$

Putting this back into our previous equation, we get a much simpler form to deal with:

$$b_0 \left(k_0^2 - k^2 \right) e^{ikx} + \gamma \sum_{n \neq 0} \left[\left(k_0^2 - k_n^2 \right) b_n + b_0 C_n \right] e^{i\left(k - \frac{2\pi n}{a}\right)x} = 0$$

This will make our job much easier. Now for another trick…

Solving the Schroedinger Equation

First Order Solution

$$b_0\left(k_0^2 - k^2\right)e^{ikx} + \gamma\sum_{n\neq 0}\left[\left(k_0^2 - k_n^2\right)b_n + b_0 C_n\right]e^{i\left(k-\frac{2\pi n}{a}\right)x} = 0$$

Let's multiply the above equation by:

$$e^{-ik_m x}$$

$$where \quad k_m = k - \frac{2\pi m}{a}$$

Then we'll integrate over a full period ($0 \rightarrow a$):

$$b_0\left(k_0^2 - k^2\right)\int_0^a e^{\frac{i2\pi mx}{a}}dx + \gamma\sum_{n\neq 0}\left[\left(k_0^2 - k_n^2\right)b_n + b_0 C_n\right]\int_0^a e^{\frac{i2\pi(m-n)x}{a}}dx = 0$$

Note that the two integrals are of similar form, which has the following useful property:

$$\int_0^a e^{\frac{i2\pi\lambda x}{a}}dx = \begin{cases} 0 & \text{if } \lambda \neq 0 \\ a & \text{if } \lambda = 0 \end{cases}$$

Solving the Schroedinger Equation

First Order Solution

$$b_0\left(k_0^2 - k^2\right)\int_0^a e^{\frac{i2\pi mx}{a}}dx + \gamma\sum_{n\neq 0}\left[\left(k_0^2 - k_n^2\right)b_n + b_0 C_n\right]\int_0^a e^{\frac{i2\pi(m-n)x}{a}}dx = 0$$

$$\int_0^a e^{\frac{i2\pi\lambda x}{a}}dx = \begin{cases} 0 & \text{if } \lambda \neq 0 \\ a & \text{if } \lambda = 0 \end{cases}$$

Case 1: $\mathrm{m} = 0$

$$b_0\left(k_0^2 - k^2\right)\int_0^a dx + \gamma\sum_{n\neq 0}\left[\left(k_0^2 - k_n^2\right)b_n + b_0 C_n\right]\int_0^a e^{\frac{-i2\pi nx}{a}}dx = 0$$

$$b_0\left(k_0^2 - k^2\right)a + \gamma\sum_{n\neq 0}\left[\left(k_0^2 - k_n^2\right)b_n + b_0 C_n\right](0) = 0$$

$$b_0\left(k_0^2 - k^2\right)a = 0$$

$$\boxed{k = k_0}$$

Within the summation, $n \neq 0$. Therefore the integral is always zero when $m=0$.

Solving the Schroedinger Equation

First Order Solution

$$b_0\left(k_0^2-k^2\right)\int_0^a e^{\frac{i2\pi mx}{a}}dx+\gamma\sum_{n\neq 0}\left[\left(k_0^2-k_n^2\right)b_n+b_0C_n\right]\int_0^a e^{\frac{i2\pi(m-n)x}{a}}dx=0$$

$$\int_0^a e^{\frac{i2\pi\lambda x}{a}}dx=\begin{cases}0 & \text{if } \lambda\neq 0\\ a & \text{if } \lambda=0\end{cases}$$

Case 2: $m \neq 0$

$$b_0\left(k_0^2-k^2\right)\int_0^a e^{\frac{i2\pi mx}{a}}dx+\gamma\sum_{n\neq 0}\left[\left(k_0^2-k_n^2\right)b_n+b_0C_n\right]\int_0^a e^{\frac{i2\pi(m-n)x}{a}}dx=0$$

$$b_0\left(k_0^2-k^2\right)(0)+\gamma\sum_{n\neq 0}\left[\left(k_0^2-k_n^2\right)b_n+b_0C_n\right]\int_0^a e^{\frac{i2\pi(m-n)x}{a}}dx=0$$

The first term goes to zero for all $m\neq 0$, and the second term goes to zero for all $m\neq n$. That only leaves the case when $m=n$. Lastly, we substitute $k=k_0$ in the final step.

$$\gamma\sum_{n=m}\left[\left(k_0^2-k_n^2\right)b_n+b_0C_n\right]\int_0^a dx=0$$

$$\gamma\left[\left(k_0^2-k_m^2\right)b_m+b_0C_m\right]a=0$$

$$b_m=\frac{b_0C_m}{\left(k_m^2-k^2\right)}$$

Solving the Schroedinger Equation

First Order Solution

Substituting the value for the coefficients into the wave function, and we've at last found a first order solution for our electron in a periodic potential.

$$\Psi(x) = b_0 e^{ikx} + \gamma e^{ikx} \sum_{n \neq 0} b_n e^{\frac{-i2\pi nx}{a}}$$

$$\Psi(x) = b_0 e^{ikx} + \gamma e^{ikx} \sum_{n \neq 0} \frac{b_0 C_n}{\left(k_n^2 - k^2\right)} e^{\frac{-i2\pi nx}{a}}$$

$$\Psi(x) = b_0 e^{ikx} \left[1 - \gamma \sum_{n \neq 0} \frac{C_n}{\left(k^2 - k_n^2\right)} e^{\frac{-i2\pi nx}{a}} \right]$$

The implications of this wave function are immediately apparent. For *n=0,* the term inside the brackets becomes 1 and the electron is represented as a plane wave. For all other *n*, a small correction factor given by the summation and scaled by γ will slightly alter the plane wave periodically, with period *a*, as formerly predicted. This is a free electron with a small, periodic correction.

However, the solution diverges when k=k$_n$ (the denominator goes to zero). A singularity occurs in this case. Let's move on and find this wave's energy.

What is the Energy of the Electron?

First Order Energy Correction

$$\Psi(x) = b_0 e^{ikx}\left[1 - \gamma \sum_{n\neq 0} \frac{C_n}{\left(k^2 - k_n^2\right)} e^{\frac{-i2\pi nx}{a}}\right]$$

As before, we'll start with a first-order solution (neglecting γ^2). We found previously that $k=k_0$ in the first-order case. Plugging this in for the energy solution:

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 k_0^2}{2m}$$

This tells us that for a first-order approximation, the energy of the electron in a periodic potential is the same as the energy of a free electron. This must mean that the energy correction factor has gone to zero for first-order. While the first-order solution helped approximate the wave function, we will have to go back to the second-order (γ^2) to determine the energy of the electron.

$$b_0\left(k_0^2 - k^2\right)e^{ikx} + \gamma \sum_{n\neq 0}\left[\left(k_0^2 - k_n^2\right)b_n + b_0 C_n\right]e^{i\left(k-\frac{2\pi n}{a}\right)x}$$
$$+ \gamma^2 \sum_{n\neq 0}\sum_{n'\neq 0} C_n b_{n'} e^{i\left(k-\frac{2\pi n}{a}-\frac{2\pi n'}{a}\right)x} = 0$$

Reminder

$$k_n = k - \frac{2\pi n}{a}$$

What is the Energy of the Electron?

Second Order Energy Correction

As before, multiply by e^{-ikx} and integrate over a full period ($0 \rightarrow a$):

$$b_0\left(k_0^2 - k^2\right)\int_0^a dx + \gamma \sum_{n\neq 0}\left[\left(k_0^2 - k_n^2\right)b_n + b_0 C_n\right]\int_0^a e^{\frac{-i\,2\pi nx}{a}}dx$$

$$+ \gamma^2 \sum_{n\neq 0}\sum_{n'\neq 0} C_n b_{n'}\int_0^a e^{\frac{-i\,2\pi\left(n+n'\right)x}{a}}dx = 0$$

$$\boxed{b_0\left(k_0^2 - k^2\right)a + \gamma^2 \sum_{n'\neq 0} C_{-n'} b_{n'} a = 0}$$

The second integral goes to zero, since $n \neq 0$ for all n. The third integral goes to zero in all cases except where $n' = -n$. Now, $-n'$ has been substituted in for all n, and the double summation becomes a single summation. Also…

$$f(x) = \sum_{n=-\infty}^{+\infty} C_n e^{\frac{-i\,2\pi nx}{a}} \Rightarrow \begin{cases} n = -n \quad \Rightarrow \quad f(x) = \displaystyle\sum_{n=-\infty}^{+\infty} C_{-n} e^{\frac{i\,2\pi nx}{a}} \\ f(x) = f^*(x) \quad \Rightarrow \quad f^*(x) = \displaystyle\sum_{n=-\infty}^{+\infty} C_n^* e^{\frac{i\,2\pi nx}{a}} \end{cases}$$

$$\therefore\ C_{-n} = C_n^*$$

What is the Energy of the Electron?

Second Order Energy Correction

Continued…

$$C_{-n} = C_n^*$$

$$b_0\left(k_0^2 - k^2\right)a + \gamma^2 \sum_{n\neq 0} C_n^* b_n a = 0$$

Plugging in the coefficients b_n found in the first-order solution:

$$b_n = \frac{b_0 C_n}{\left(k_n^2 - k^2\right)}$$

$$b_0 a\left(k_0^2 - k^2\right) + b_0 a \gamma^2 \sum_{n\neq 0} \frac{C_n^* C_n}{\left(k_n^2 - k^2\right)} = 0$$

Dividing out $b_0 a$ and solving for $(k_0)^2$, we get:

$$\left(k_0^2 - k^2\right) + \gamma^2 \sum_{n\neq 0} \frac{C_n^* C_n}{\left(k_n^2 - k^2\right)} = 0$$

$$k_0^2 = k^2 + \gamma^2 \sum_{n\neq 0} \underbrace{\frac{C_n^* C_n}{\left(k^2 - k_n^2\right)}}$$

Note: the singularity has shown up again. (at $k=k_n$)

What is the Energy of the Electron?

Second Order Energy Correction

Continued…

$$k_0^2 = k^2 + \gamma^2 \sum_{n \neq 0} \frac{C_n^* C_n}{\left(k^2 - k_n^2\right)}$$

Multiply both sides by $\hbar^2/2m$ to get:

$$\frac{\hbar^2}{2m} k_0^2 = \frac{\hbar^2}{2m} k^2 + \frac{\hbar^2}{2m} \gamma^2 \sum_{n \neq 0} \frac{C_n^* C_n}{\left(k^2 - k_n^2\right)}$$

Recall → $E = \dfrac{\hbar^2 k_0^2}{2m}$ and $k_n = k - \frac{2\pi n}{a}$

$$E = \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2 \gamma^2}{2m} \sum_{n \neq 0} \frac{C_n^* C_n}{\left[k^2 - \left(k - \frac{2\pi n}{a}\right)^2\right]}$$

$$E(k) = \frac{\hbar^2 k^2}{2m} + \sum_{n \neq 0} \frac{|V_n|^2}{\left[\frac{\hbar^2}{2m} k^2 - \frac{\hbar^2}{2m}\left(k - \frac{2\pi n}{a}\right)^2\right]} \quad \text{where} \quad V_n = -\sqrt{\frac{\hbar^2 \gamma^2}{2m}} C_n$$

Does this predict the expected Bandgaps?

Bandgap Location

$$E(k) = \frac{\hbar^2 k^2}{2m} + \sum_{n \neq 0} \frac{|V_n|^2}{\left[\frac{\hbar^2}{2m} k^2 - \frac{\hbar^2}{2m}\left(k - \frac{2\pi n}{a}\right)^2\right]} \quad where \quad V_n = -\sqrt{\frac{\hbar^2 \gamma^2}{2m}} C_n$$

We've finally derived a solution for the energy of the electron in relation to k. What we really want to know is if this properly predicts Bandgaps. In other words, in any arbitrary, periodic potential, are there certain discrete bands of energy that electrons are not allowed to populate? Recall…

$$E = \frac{\hbar^2 k^2}{2m} + \sum_{n \neq 0} \frac{|V_n|^2}{\left[k^2 - k_n^2\right]} \quad where \quad k_n = k - \frac{2\pi n}{a}$$

We can see that a singularity appears in the energy at $k^2=(k_n)^2$, or at $k=\pm k_n$. At these points, the correction term blows up to infinity, which is clearly not possible. We can identify the location of these points in terms of k:

$$k = +k_n \qquad k = -k_n$$

$$k = k - \frac{2\pi n}{a} \qquad -k = k - \frac{2\pi n}{a}$$

$$\frac{2\pi n}{a} = 0 \qquad 2k = \frac{2\pi n}{a}$$

$$n = 0 \qquad k = n\frac{\pi}{a}$$

Does this predict the expected Bandgaps?

Bandgap Location

$$k = n\frac{\pi}{a} \quad \text{for all integer } n$$

So now we know that a discontinuity exists at all points where k is an integer multiple of π/a. We're not through yet. Lastly, we must ensure that at these points there is a jump in allowed energy, or a gap of disallowed energy values.

First, let's compare this to the Kronig-Penney model (periodic rectangular barrier). Recall, that model predicts bandgaps will occur at:

$$k = n\frac{\pi}{(a+b)}$$

Where a and b are the width of the barrier and the spacing between barriers. Adding the two together gives the period of the periodic potential. The general solution for an arbitrary, periodic potential accurately predicts the solution to the Kronig-Penney model. Why is this?

For any crystalline structure, as well as any periodic potential, Bragg reflection at the Brillouin zone edges allow electrons to have only a certain energy values. **These zone edges occur at $k=n\pi/a$, where a is the lattice constant (period) of the periodic potential.**

Does this predict the expected Bandgaps?

Energy Values at the Bandgaps

Now we need to show that a Bandgap occurs at $k=n\pi/a$. To do this, we must show that at these values of k, there are multiple values for energy.

Let's go back to the wave function:

$$\Psi(x) = b_0 e^{ikx} + \gamma e^{ikx} \sum_{n\neq 0} b_n e^{\frac{-i2\pi nx}{a}}$$

We'll focus only on the points of interest: where $k=k_n$. At these points, b_n blows up, so we will approximate the sum as only one term: b_n.

$$\Psi(x) = b_0 e^{ikx} + \gamma e^{ikx} b_n e^{\frac{-i2\pi nx}{a}}$$

$$\Psi(x) = b_0 e^{ikx} + \gamma b_n e^{i\left(k-\frac{2\pi n}{a}\right)x}$$

$$\Psi(x) = b_0 e^{ikx} + \gamma b_n e^{ik_n x}$$

$$\left(where \;\; k_n = k - \frac{2\pi n}{a}\right)$$

Does this predict the expected Bandgaps?

Energy Values at the Bandgaps

$$\Psi(x) = b_0 e^{ikx} + \gamma b_n e^{ik_n x}$$

Plugging this wave function into the Schroedinger equation, expanding the second-derivative, and collecting like terms results in:

$$b_0\left(k_0^2 - k^2\right)e^{ikx} + \gamma b_n\left(k_0^2 - k_n^2\right)e^{i\left(k-\frac{2\pi n}{a}\right)x}$$
$$+ \gamma b_0 \sum_{n\neq 0} C_n e^{i\left(k-\frac{2\pi n}{a}\right)x} + \gamma^2 b_n \sum_{n'\neq 0} C_{n'} e^{i\left(k-\frac{2\pi n}{a}-\frac{2\pi n'}{a}\right)x} = 0$$

Now, we'll perform two tricks on this equation to get two different equations.

Step 1: Multiply by e^{-ikx} and integrate over a full period ($0 \rightarrow a$):

$$b_0\left(k_0^2 - k^2\right) + \gamma b_n\left(k_0^2 - k_n^2\right)e^{\frac{-i2\pi nx}{a}} + \gamma b_0 \sum_{n\neq 0} C_n e^{\frac{-i2\pi nx}{a}} + \gamma^2 b_n \sum_{n'\neq 0} C_{n'} e^{\frac{-i2\pi\left(n+n'\right)x}{a}} = 0$$

$$b_0\left(k_0^2 - k^2\right)\int_0^a dx + (0) + (0) + \gamma^2 b_n \sum_{n'\neq 0} C_{n'}\int_0^a e^{\frac{-i2\pi\left(n+n'\right)x}{a}} dx = 0$$

$$b_0\left(k_0^2 - k^2\right)a + \gamma^2 b_n C_n^* a = 0 \quad (n' = -n)$$

Does this predict the expected Bandgaps?

Energy Values at the Bandgaps

Step 2: Multiply by $e^{-ik_n x}$ and integrate over a full period ($0 \rightarrow a$):

$$b_0\left(k_0^2 - k^2\right)e^{\frac{-i2\pi nx}{a}} + \gamma b_n\left(k_0^2 - k_n^2\right) + \gamma b_0 \sum_{n\neq 0} C_n + \gamma^2 b_n \sum_{n'\neq 0} C_{n'} e^{\frac{-i2\pi n'x}{a}} = 0$$

$$(0) + \gamma b_n\left(k_0^2 - k_n^2\right)\int_0^a dx + \gamma b_0 C_n \int_0^a dx + (0) = 0$$

$$\underline{\gamma b_n\left(k_0^2 - k_n^2\right)a + \gamma b_0 C_n a = 0}$$

We end up with two equations and two unknowns. If we collect the coefficients of the b_0 and b_n terms into a matrix, then the determinant of these coefficients must go to zero.

$$b_0\left(k_0^2 - k^2\right) + \gamma^2 b_n C_n^* = 0$$

$$b_n\left(k_0^2 - k_n^2\right) + b_0 C_n = 0$$

$$\begin{vmatrix} \left(k_0^2 - k^2\right) & \gamma^2 C_n^* \\ C_n & \left(k_0^2 - k_n^2\right) \end{vmatrix} = 0$$

$$\left(k_0^2 - k^2\right)\left(k_0^2 - k_n^2\right) - \gamma^2 C_n^* C_n = 0$$

Does this predict the expected Bandgaps?

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$$\left(k_0^2 - k^2\right)\left(k_0^2 - k_n^2\right) - \gamma^2 C_n^* C_n = 0$$

Continued…

$$k_0^4 - k_0^2 k_n^2 - k_0^2 k^2 + k^2 k_n^2 - \gamma^2 C_n^* C_n = 0$$

$$k_0^4 - 2k_0^2 k^2 + k^2 k_n^2 - \gamma^2 C_n^* C_n = 0 \quad \left(k^2 = k_n^2\right)$$

If we treat the above as a second-order polynomial in $(k_0)^2$, we can solve for $(k_0)^2$ using the quadratic formula:

$$k_0^2 = \frac{2k^2 \pm \sqrt{4k^4 - 4k^2 k_n^2 + 4\gamma^2 C_n^* C_n}}{2}$$

$$k_0^2 = k^2 \pm \sqrt{4k^4 - 4k^4 + \gamma^2 C_n^* C_n} \quad (k = k_n)$$

$$k_0^2 = k^2 \pm \sqrt{\gamma^2 C_n^* C_n}$$

Multiply by $\hbar^2/2m$:

$$\frac{\hbar^2}{2m} k_0^2 = \frac{\hbar^2}{2m} k^2 \pm \frac{\hbar^2}{2m} \sqrt{\gamma^2 C_n^* C_n}$$

$$E = \frac{\hbar^2}{2m} k^2 \pm \sqrt{\frac{\hbar^4}{4m^2} \gamma^2 C_n^* C_n}$$

Does this predict the expected Bandgaps?

Energy Values at the Bandgaps

$$E = \frac{\hbar^2}{2m}k^2 \pm \sqrt{\frac{\hbar^4}{4m^2}\gamma^2 C_n^* C_n}$$

Since we are solving for energy at the zone boundaries, then $k=k_n=n\pi/a$. Also, we can use the term V_n inside the square root.

$$|V_n|^2 = \frac{\hbar^2}{2m}\gamma^2 C_n^* C_n$$

$$E = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2 \pm \sqrt{\frac{\hbar^2}{2m}|V_n|^2}$$

$$E = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2 \pm V_n\sqrt{\frac{\hbar^2}{2m}}$$

two distinct energy values at the zone edge

And so we have finally shown that not only do discontinuities occur at discrete values of k, but these discontinuities correspond to jumps in allowed electron energy, and this holds true for ***any periodic potential***. The gap widths can be calculated from the Fourier coefficients of the potential.

$$\Delta E = 2V_n\sqrt{\frac{\hbar^2}{2m}}$$