Consider a square wave potential with lattice constant a. In the first unit cell, this means:

- $U=U_{max}$ for $-a/4 < x < a/4$,
- $U=0$ for $-a/2 < x < -a/4$ and $a/4 < x < a/2$,

This is repeated throughout the crystal.

1. Find the two lowest energy eigenvalues at the center and edge of the first Brillouin zone, as well as one point halfway between.
2. Find the wave function corresponding to each of these two bands at the three specified k-values.
3. Graph the electron density as a function of position corresponding to each of these six wave functions.

Note: I changed the subscript on the constant in the amplitude, since I will use U_o for another purpose later.

We are going to use the central equation from the nearly free electron model to tackle this problem. The Central Equation states:

$$0 = \left(\frac{\hbar^2 k^2}{2m} - E_k \right) \psi_k + \sum_G U_G \psi_{k-G}.$$

This defines not just one but a set of equations connecting each ψ_k with every ψ_{k+G}, for all *G*. Physically, this means connecting the coefficients of all the different bands corresponding to the same reduced-zone *k*. That is in principle an infinite number of G-values, bands, and coefficients.

It is a *set* of equations, not just 1, because I can substitute any value for my original *k* to get a different set of equations. In particular, if I choose a *k* differing by a reciprocal lattice vector *G*, I will get a different equation involving the very same set of wavefunction coefficients ψ_k. I can generate as many of these equations as I want just by choosing different values of $G = \frac{2\pi n}{a}$.

However, how many ψ_k's we need to use depends on how many bands we are looking for and to a lesser extent how many components of U_G are significant. Low energy eigenvectors typically have very little contribution from higher G basis functions. Thus not all the ψ_k's are connected appreciably. This is especially true if the U_G 's fall off quickly.

This problem is not the best to illustrate this, since square waves have pretty intense high frequency components. Let's give up some accuracy and just use five basis functions to

find five bands. Then the lowest energy two that we are solving for should be pretty accurate.

So we will consider only bands with G-values of {-2, -1, 0, 1, or 2} times the primitive reciprocal lattice vector $\frac{2\pi}{a}$. That gives five bands. We will assume coefficients of all higher G-value basis functions are zero.

The central equation is

$$0=\left(\frac{\hbar^2k^2}{2m}-E\right)\psi_k+\sum_G U_G\psi_{k-G}$$

where $G=ng,$ for any integer n and $g=\frac{2\pi}{a},$ or

$$0=\left(\frac{\hbar^2k^2}{2m}-E\right)\psi_k+\sum_n U_{ng}\psi_{k-ng}$$

We want to consider only five of our wavefunction
frequency coeficients: $\psi_{k-2g},\psi_{k-g},\psi_k,\psi_{k+g},\psi_{k+2g}.$
We will assume all others are zero. So we need five equations.
Our equations result from replacing k with $k+jg,$ $j=$ integer,
and keeping only terms in the sum with ψ coefficients of
$\psi_{k-2g},\psi_{k-g},\psi_k,\psi_{k+g},\psi_{k+2g}.$

$$0=\left(\frac{\hbar^2(k+jg)^2}{2m}-E\right)\psi_{k+mg}+\sum_n U_{ng}\psi_{k+jg-ng}$$

$$=\left(U_0+\frac{\hbar^2(k+jg)^2}{2m}-E\right)\psi_{k+mg}+\sum_{n\neq 0} U_{ng}\psi_{k+jg-ng}$$

$$=\left(\lambda_{k+jg}-E\right)\psi_{k+jg}+\sum_{n\neq 0} U_{ng}\psi_{k+jg-ng},$$

with $\lambda_{k+jg}\equiv U_0+\frac{\hbar^2(k+jg)^2}{2m}.$

Once again, we keep only terms including $\psi_{k-2g},\psi_{k-g},\psi_k,\psi_{k+g},\psi_{k+2g}.$
Then our equations are,

for $j=-2$:

$$0=\left(\lambda_{k-2g}-E\right)\psi_{k-2g}+U_{-g}\psi_{k-g}+U_{-2g}\psi_k+U_{-3g}\psi_{k+g}+U_{-4g}\psi_{k+2g}$$

for $j=-1$:

$$0=U_g\psi_{k-2g}+\left(\lambda_{k-g}-E\right)\psi_{k-g}+U_{-g}\psi_k+U_{-2g}\psi_{k+g}+U_{-3g}\psi_{k+2g}$$

for $j=0$:

$$0=U_{2g}\psi_{k-2g}+U_g\psi_{k-g}+\left(\lambda_k-E\right)\psi_k+U_{-g}\psi_{k+g}+U_{-2g}\psi_{k+2g}$$

for $j=1$:

$$0=U_{3g}\psi_{k-2g}+U_{2g}\psi_{k-g}+U_{-g}\psi_k+\left(\lambda_{k+g}-E\right)\psi_{k+g}+U_{-g}\psi_{k+2g}$$

for $j=2$:

$$0=U_{4g}\psi_{k-2g}+U_{3g}\psi_{k-g}+U_{2g}\psi_k+U_g\psi_{k+g}+\left(\lambda_{k+2g}-E\right)\psi_{k+2g}.$$

We can cast this in matrix-vector form:

$$\begin{pmatrix} (\lambda_{k-2g}-E) & U_{-g} & U_{-2g} & U_{-3g} & U_{-4g} \\ U_{g} & (\lambda_{k-g}-E) & U_{-g} & U_{-2g} & U_{-3g} \\ U_{2g} & U_{g} & (\lambda_{k}-E) & U_{-g} & U_{-2g} \\ U_{3g} & U_{2g} & U_{-g} & (\lambda_{k+g}-E) & U_{-g} \\ U_{4g} & U_{3g} & U_{2g} & U_{g} & (\lambda_{k+2g}-E) \end{pmatrix} \begin{pmatrix} \psi_{k-2g} \\ \psi_{k-g} \\ \psi_{k} \\ \psi_{k+g} \\ \psi_{k+2g} \end{pmatrix} = 0.$$

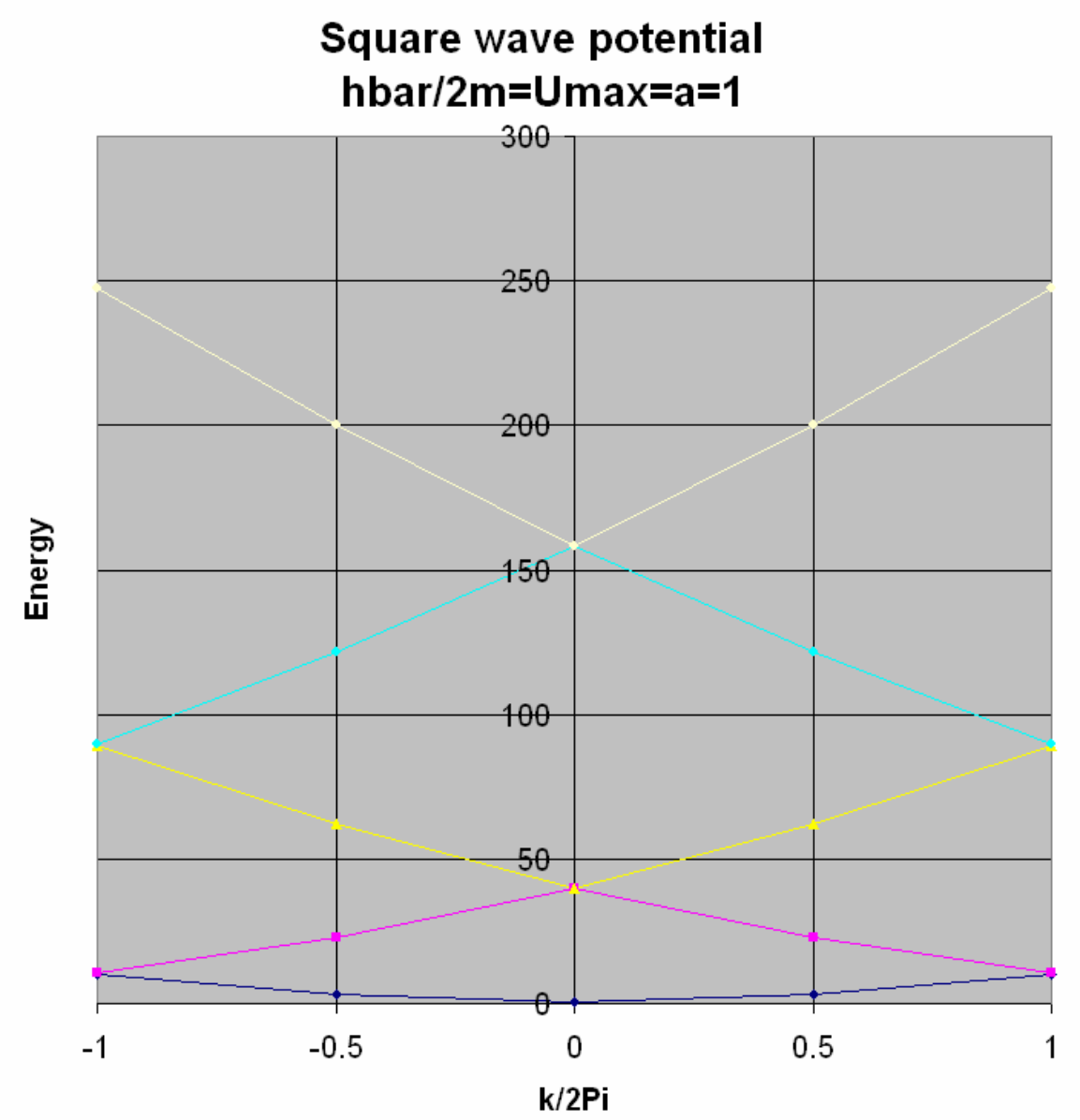
We can solve this set of equations a couple of ways. Taking the E terms to the other side of the equation makes this an eigenvector/eigenvalue problem. Ultimately, this is what we want to do, because we want both the wavefunctions and the energy eigenvalues.

With $U_{\pm ng} = \frac{U_{\max}}{n\pi}\sin\left(\frac{n\pi}{2}\right)$, and $U_0 = \frac{U_{\max}}{2}$, the equation, rearranged as an eigenvector problem, becomes

$$\begin{pmatrix} \lambda_{k-2g} & \frac{1}{\pi} & 0 & -\frac{1}{3\pi} & 0 \\ \frac{1}{\pi} & \lambda_{k-g} & \frac{1}{\pi} & 0 & -\frac{1}{3\pi} \\ 0 & \frac{1}{\pi} & \lambda_{k} & \frac{1}{\pi} & 0 \\ -\frac{1}{3\pi} & 0 & \frac{1}{\pi} & \lambda_{k+g} & \frac{1}{\pi} \\ 0 & -\frac{1}{3\pi} & 0 & \frac{1}{\pi} & \lambda_{k+2g} \end{pmatrix} \begin{pmatrix} \psi_{k-2g} \\ \psi_{k-g} \\ \psi_{k} \\ \psi_{k+g} \\ \psi_{k+2g} \end{pmatrix} = E \begin{pmatrix} \psi_{k-2g} \\ \psi_{k-g} \\ \psi_{k} \\ \psi_{k+g} \\ \psi_{k+2g} \end{pmatrix}$$

See the accompanying Maple spreadsheet for the solution to the remainder of the problem.

Here are the resulting energy bands from the Maple results:



Although it looks like the bands touch, close inspection of the energies show that in every case we have a small band gap.

One additional note:

If we only wanted the energies, we could just note that a non-trivial solution requires that the determinant of the above equation be zero.

$$0=\begin{vmatrix} \left(\lambda_{k-2g}-E\right) & U_{-g} & U_{-2g} & U_{-3g} & U_{-4g} \\ U_{g} & \left(\lambda_{k-g}-E\right) & U_{-g} & U_{-2g} & U_{-3g} \\ U_{2g} & U_{g} & \left(\lambda_{k}-E\right) & U_{-g} & U_{-2g} \\ U_{3g} & U_{2g} & U_{-g} & \left(\lambda_{k+g}-E\right) & U_{-g} \\ U_{4g} & U_{3g} & U_{2g} & U_{g} & \left(\lambda_{k+2g}-E\right) \end{vmatrix}$$

With $U_{\pm ng}=\frac{U_{\max}}{n\pi}\sin\left(\frac{n\pi}{2}\right)$, and $U_0=\frac{U_{\max}}{2}$,the determinant equation becomes

$$0=\begin{vmatrix} \left(\lambda_{k-2g}-E\right) & \frac{1}{\pi} & 0 & -\frac{1}{3\pi} & 0 \\ \frac{1}{\pi} & \left(\lambda_{k-g}-E\right) & \frac{1}{\pi} & 0 & -\frac{1}{3\pi} \\ 0 & \frac{1}{\pi} & \left(\lambda_{k}-E\right) & \frac{1}{\pi} & 0 \\ -\frac{1}{3\pi} & 0 & \frac{1}{\pi} & \left(\lambda_{k+g}-E\right) & \frac{1}{\pi} \\ 0 & -\frac{1}{3\pi} & 0 & \frac{1}{\pi} & \left(\lambda_{k+2g}-E\right) \end{vmatrix}.$$