Problem Set # 5, Due: Wednesday Feb 22 by 11:00am

PHY 362K - Quantum Mechanics II, UT Austin, Spring 2017
(Dated: February 22, 2017)

Some problems on: periodic potentials and band-structure

I. TIGHT-BINDING MODELS

In class, we discussed the "nearly free electron" model, in which the periodic potential due to the ions forming the crystal was viewed as small perturbation to the freely moving electron. In this problem, we will consider an alternative description valid in the opposite limit where the electrons are tightly bound to the ions of the crystal – called a "tight-binding model". Such models are quite useful for modeling the properties of materials, and are often simpler to work with than the corresponding

For example, consider a regularly spaced 1D chain of ions (e.g. H^+ ions), where the j^{th} ion sits at position $x_j = ja$, and a is the spacing between ions. Suppose we can focus on only a single orbital of each ion (e.g. the 1s orbital of H^+), and ignore all higher energy orbitals.

Consider a single electron moving in the potential of these nuclei. We can denote the state where the electron is in the j^{th} hydrogen 1s orbital by $|j\rangle$. An electron initially in the state $|j\rangle$ (i.e. in the $1s$ orbital of the atom at position $x = ja$) can tunnel to 1s orbital of the neighboring atoms atom on either side at positions $x = (j \pm 1)a$ (i.e into the state $|(j \pm 1)\rangle$). Denote the tunneling amplitude for this process by t. Due to the exponential decay of the 1s wave-function away from the Hydrogen nucleus, we expect $t \approx e^{-a/a_0}$ where a_0 is the Bohr radius for a single ion), so for $a \gg a_0$ we can safely ignore longer-range tunneling events.

We can approximate this nearest-neighbor tunneling by the "tight-binding" Hamiltonian:

$$\hat{H}_{\text{TB}} = \sum_{j=1}^{N} -t\left(|j+1\rangle\langle j| + |j\rangle\langle j+1|\right) \tag{1}$$

defined for a $1d$ chain of N-atoms, with periodic boundary conditions: $|j+N\rangle \equiv |j\rangle$. Note that the $-$ sign for $\hat{H}$ reflects the fact that tunneling tends to lower the kinetic energy of an electron by allowing it to spread out.

1. Show that $|\psi_k\rangle = \sum_{j=0}^{N} \frac{e^{ikja}}{\sqrt{N}}|j\rangle$ is an eigenstate of $\hat{H}_{\text{TB}}$, and find its energy eigenvalue, $\varepsilon_{\text{TB}}(k)$. (where the subscript TB denotes that this is the energy in the tight-binding approach).

   Solution: If we apply $\hat{H}_{\text{TB}}$ to $|\psi_k\rangle$, we obtain:

$$\begin{aligned}
\hat{H}_{\text{TB}}|\psi_k\rangle &= \left(\sum_{j=1}^{N} -t\left(|j+1\rangle\langle j| + |j\rangle\langle j+1|\right)\right)\left(\sum_{l=1}^{N}\frac{e^{ikla}}{\sqrt{N}}|l\rangle\right) \\
&= -\frac{t}{\sqrt{N}}\sum_{j=1}^{N}\sum_{l=1}^{N} e^{ikla}\left(\langle j|l\rangle|j+1\rangle + \langle j+1|l\rangle|j\rangle\right) \\
&= -\frac{t}{\sqrt{N}}\left(\sum_{j=1}^{N} e^{ikja}|j+1\rangle + \sum_{j=1}^{N} e^{ik(j+1)a}|j\rangle\right)
\end{aligned}$$

This first sum, $\sum_{j=1}^{N} e^{ikja}|j+1\rangle$, can be rewritten as $e^{-ika}\sum_{j=1}^{N} e^{ik(j+1)a}|j+1\rangle = e^{-ika}\sum_{j=2}^{N+1} e^{ikja}|j\rangle$. But the periodic boundary conditions require $e^{ik(N+1)a}|N+1\rangle = e^{ika}|1\rangle$, therefore this sum can be written as $e^{-ika}\sum_{j=1}^{N} e^{ikja}|j\rangle$. Applying this result, we find

$$\begin{aligned}\hat{H}_{\mathrm{TB}}|\psi_k\rangle &= -t\left(e^{-ika}\sum_{j=1}^{N}\frac{e^{ikja}}{\sqrt{N}}|j\rangle + e^{ika}\sum_{j=1}^{N}\frac{e^{ikja}}{\sqrt{N}}|j\rangle\right)\\ &= -t\left(e^{-ika}+e^{ika}\right)|\psi_k\rangle\\ &= -2t\cos(ka)|\psi_k\rangle\end{aligned}$$

Therefore $|\psi_k\rangle$ is an eigenstate of $\hat{H}_{\mathrm{TB}}$ with eigenvalue $E_{\mathrm{TB}}(k) = -2t\cos(ka)$.

2. Sketch $\varepsilon_{\mathrm{TB}}(k)$ for $k \in (-\frac{\pi}{a}, \frac{\pi}{a}]$. (Note that, the states $|\psi_k\rangle$ are invariant under shifting $k \to k + \frac{2\pi}{a}$, so we should restrict k to this range).

Solution:

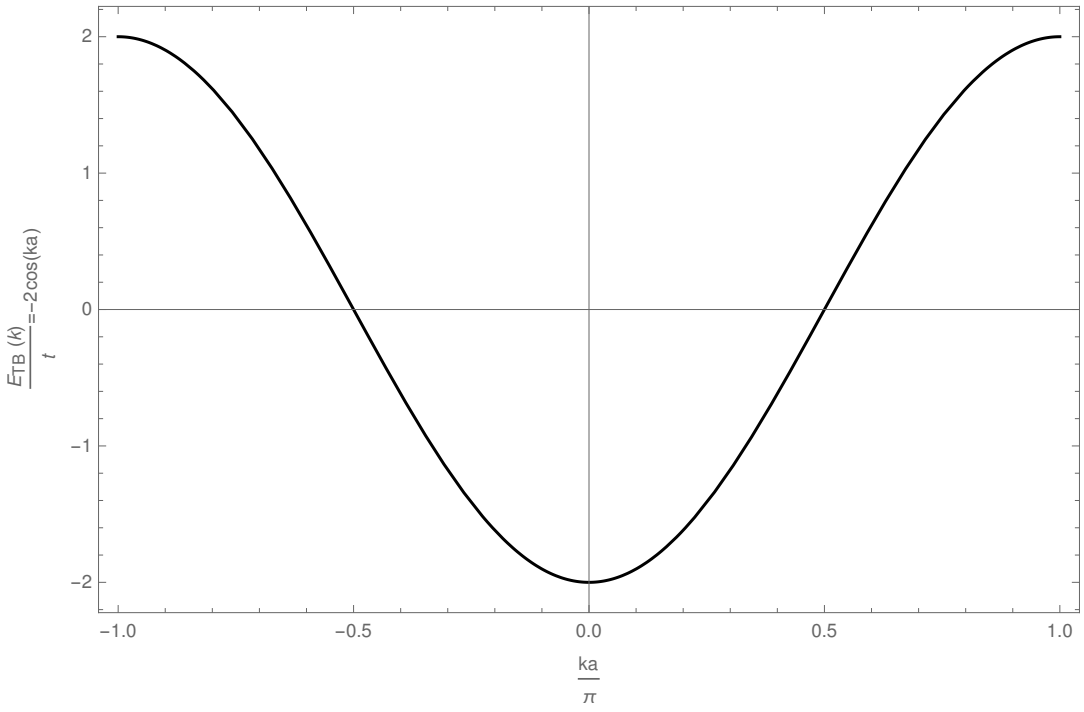

FIG. 1: A graph of the ratio $\frac{E_{\mathrm{TB}}(k)}{t}$ versus $\frac{ka}{\pi}$, where $\frac{ka}{\pi} \in (-1, 1]$.

II. KRONIG-PENNEY MODEL

Consider a particle in a 1D periodic potential that is piecewise constant:

$$\hat{H} = \frac{\hat{p}^2}{2m} + U(\hat{x}) \quad \text{with: } U(x) = \begin{cases} 0, & na < x < (n+1/2)a \\ V, & (n+1/2)a < x < (n+1)a \end{cases} \tag{2}$$

where V is a constant. $U(x)$ is a "square-wave" potential that alternates between constant values 0 and V over intervals of length $a/2$, and has period a.

1. Find the general form of solutions to the Schrodinger equation with this Hamiltonian for eigenstates with energy ε in the region $0 < x < a$, by solving $\hat{H}\psi(x) = \varepsilon\psi(x)$ in the regions $0 < x < a/2$ and $a/2 < x < a$, and matching the wave-function and its derivative at $x = a/2$.
   Note: if you are having trouble with this part, please look back at the related but simpler problem of a finite square well, in Griffiths

   Solution: The time independent Schrodinger equation, $\hat{H}\psi(x) = E\psi(x)$ becomes $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi$ for $0 < x < \frac{a}{2}$ and $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi = E\psi$ for $\frac{a}{2} < x < a$. If we define $k = \frac{\sqrt{2mE}}{\hbar}$ and $k' = \frac{\sqrt{2m(E-V)}}{\hbar}$, then we can rewrite these equations as

$$\frac{\partial^2\psi}{\partial x^2} = -k^2\psi, \qquad 0 < x < \frac{a}{2}$$
$$\frac{\partial^2\psi}{\partial x^2} = -k'^2\psi, \qquad \frac{a}{2} < x < a$$

   These differential equations have well known solutions in terms of exponential functions. Therefore we can write

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & 0 < x < \frac{a}{2} \\ Ce^{ik'x} + De^{-ik'x} & \frac{a}{2} < x < a \end{cases} \tag{3}$$

   If we now enforce continuity of ψ and its derivative at $x = \frac{a}{2}$, we obtain the following two equations

$$\begin{cases} Ae^{ik\frac{a}{2}} + Be^{-ik\frac{a}{2}} & = Ce^{ik'\frac{a}{2}} + De^{-ik'\frac{a}{2}} \\ kAe^{ik\frac{a}{2}} - kBe^{ik\frac{a}{2}} & = k'Ce^{ik'\frac{a}{2}} - k'De^{ik'\frac{a}{2}} \end{cases} \tag{4}$$

2. Use Bloch's theorem: $\psi(x+a) = e^{iQa}\psi(x)$, and the derivative of this equation: $\frac{d\psi(x+a)}{dx} = e^{iQa}\frac{d\psi(x)}{dx}$, to fix the remaining free parameters from your previous solution. Find a condition on ε and k for an "allowed" solution to exist (i.e. a solution for which Q is real, which is required both for finite systems of length L periodic boundary conditions, $\psi(x+L) = \psi(x)$, as well as for infinite systems in order to avoid exponentially growing solutions).

   Solution: If we apply Bloch's theorem with $x = 0$, we obtain the following two equations

$$\begin{cases} A + B & = e^{-iQa}\left(Ce^{ik'a} + De^{-ik'a}\right) \\ A - B & = e^{-iQa}\left(k'Ce^{ik'a} - k'De^{-ik'a}\right) \end{cases} \tag{5}$$

We can write the equations listed in equations 3 and 4 in matrix form as follows

$$\begin{pmatrix} e^{ik\frac{a}{2}} & e^{-ik\frac{a}{2}} & -e^{ik'\frac{a}{2}} & -e^{-ik'\frac{a}{2}} \\ ke^{ik\frac{a}{2}} & -ke^{ik\frac{a}{2}} & -k'e^{ik'\frac{a}{2}} & k'e^{-ik'\frac{a}{2}} \\ 1 & 1 & -e^{i(-Q+k')a} & -e^{-i(Q+k')a} \\ 1 & -1 & -k'e^{i(-Q+k')a} & k'e^{-i(Q+k')a} \end{pmatrix} \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{6}$$

This homogeneous linear system only has a nontrivial solution when the determinant of the 4×4 coefficient matrix on the left hand side is equal to zero.

Using Mathematica to find the determinant, we obtain the equation

$$2kk'\left(\cos(Qa) - \cos\left(\frac{ka}{2}\right)\cos\left(\frac{k'a}{2}\right)\right) + (k^2 + k'^2)\sin\left(\frac{ka}{2}\right)\sin\left(\frac{ka}{2}\right) = 0 \tag{7}$$

Using the definitions of k and k', we can recast this equation in terms of the dimensionless quantities $x = \frac{ma^2E}{\hbar^2}$ and $\nu = \frac{ma^2V}{\hbar^2}$ as

$$\cos(Qa) = \cos\left(\sqrt{\frac{x}{2}}\right)\cos\left(\sqrt{\frac{x-\nu}{2}}\right) - \left(\frac{2x-\nu}{2\sqrt{x^2-x\nu}}\right)\sin\left(\sqrt{\frac{x}{2}}\right)\sin\left(\sqrt{\frac{x-\nu}{2}}\right) \tag{8}$$

An allowed solution is one for which Q is real. When Q is real, $|\cos(Qa)| \leq 1$. Therefore the condition on E for an allowed solution to exist is for

$$\left|\cos\left(\sqrt{\frac{x}{2}}\right)\cos\left(\sqrt{\frac{x-\nu}{2}}\right) - \left(\frac{2x-\nu}{2\sqrt{x^2-x\nu}}\right)\sin\left(\sqrt{\frac{x}{2}}\right)\sin\left(\sqrt{\frac{x-\nu}{2}}\right)\right| \leq 1 \tag{9}$$

3. From this condition, plot the the different energy eigenvalues ε for each $\frac{-\pi}{a} \leq Q \leq \frac{\pi}{a}$ where allowed solutions occur, please include a range of ε that is wide enough to include between 3 and 4 "bands" (values of ε for a given k). Make a grid of plots for 5 different values of V: $V/\left(\frac{\hbar^2}{ma^2}\right) = \{0.05, 0.1, 1, 10, 20\}$.
Please follow the guidelines for plots listed below, after the problem statement.

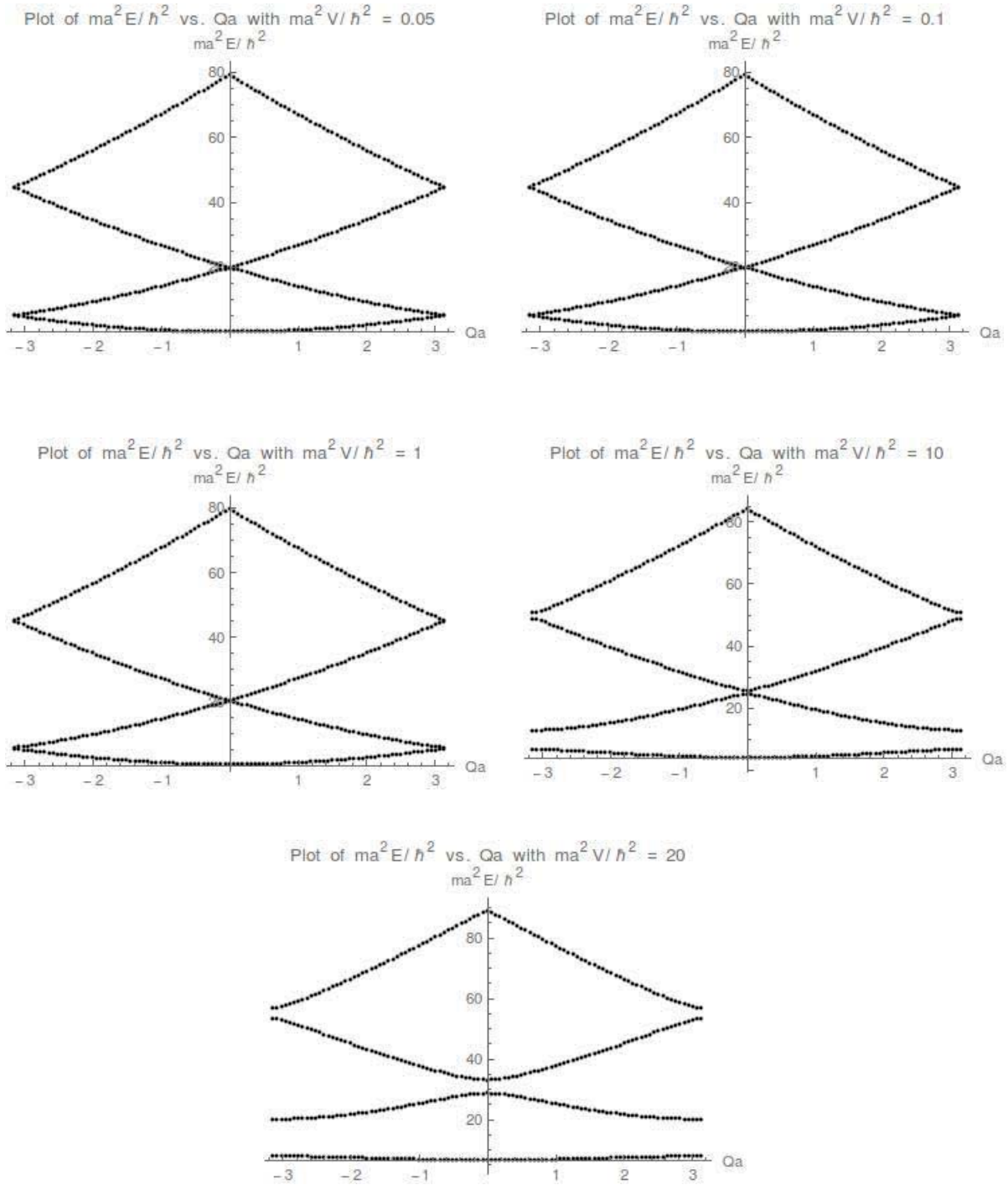

FIG. 2: Plots of the allowed values of the dimensionless energy, $\frac{ma^2E}{\hbar^2}$, for values of Qa ranging from $-\pi$ to π, as given by the solution of the Kronig Penny model.

4. When can we treat the potential $U(x)$ perturbatively? Compute the energy gap between the lowest and next lowest band at $k = \frac{\pi}{a}$, to first order using (degenerate) perturbation theory. Make a table comparing this perturbative estimate of the band-gap to the values obtained from the exact solutions, for the same values of V that you plotted in the previous problem.

Solution: We can treat the potential $U(x)$ perturbatively when it is small relative to the natural energy scale of the problem, $\frac{\hbar^2}{ma^2}$, which is to say when $V/\left(\frac{\hbar^2}{ma^2}\right) \ll 1$. If we treat $U(x)$ perturbatively, the unperturbed Hamiltonian is that of a free particle, $\hat{H}_0 = \frac{\hat{p}^2}{2m}$. For now we will assume that the lattice that this potential represents has a finite length $L = Na$ where N is an integer. Under this assumption, the eigenstates are $\psi_k(x) = \frac{1}{\sqrt{Na}}e^{ikx}$ with energies $E_k = \frac{\hbar^2 k^2}{2m}$. Note that this energy spectrum has degeneracies because k and $-k$ have the same energies but correspond to different states. For the states in question, with $k = \pm\frac{\pi}{a}$, we have the two degenerate eigenstates $|-\frac{\pi}{a}\rangle = \frac{1}{\sqrt{Na}}e^{-i\frac{\pi}{a}x}$ and $|\frac{\pi}{a}\rangle = \frac{1}{\sqrt{Na}}e^{i\frac{\pi}{a}x}$ with energy $E^0 = \frac{\hbar^2\pi^2}{2ma^2}$.

We will now construct the matrix that represents the perturbation $U(x)$ in the subspace spanned by these two degenerate states. This matrix is given by:

$$\begin{pmatrix} \langle\frac{\pi}{a}|U|\frac{\pi}{a}\rangle & \langle\frac{\pi}{a}|U|-\frac{\pi}{a}\rangle \\ \langle-\frac{\pi}{a}|U|\frac{\pi}{a}\rangle & \langle-\frac{\pi}{a}|U|-\frac{\pi}{a}\rangle \end{pmatrix}$$

Now consider the general matrix element $\langle k|U|k'\rangle$, this is given by

$$\begin{aligned}\langle k|U|k'\rangle &= \int_0^{Na}\left(\frac{1}{\sqrt{Na}}e^{-ikx}\right)U(x)\left(\frac{1}{\sqrt{Na}}e^{ik'x}\right)dx \\ &= \frac{1}{Na}\int_0^{Na}U(x)e^{i(k'-k)x}dx\end{aligned}$$

Now if $k = k' = \frac{\pi}{a}$, then we have

$$\begin{aligned}\langle\frac{\pi}{a}|U|\frac{\pi}{a}\rangle &= \frac{1}{Na}\int_0^{Na}U(x)dx \\ &= \frac{1}{Na}N\int_{a/2}^{a}Vdx = \frac{V}{2}\end{aligned}$$

Where the last line follows from the periodicity of $U(x)$. An identical argument shows that $\langle-\frac{\pi}{a}|U|-\frac{\pi}{a}\rangle = \frac{V}{2}$. If $k = -\frac{\pi}{a}$ and $k' = \frac{\pi}{a}$, then we have

$$\begin{aligned}\langle-\frac{\pi}{a}|U|\frac{\pi}{a}\rangle &= \frac{1}{Na}\int_0^{Na}U(x)e^{\frac{2\pi i}{a}x}dx \\ &= \frac{1}{Na}N\int_{a/2}^{a}Ve^{\frac{2\pi i}{a}x}dx = \frac{iV}{\pi}\end{aligned}$$

where the last line follows from the periodicity of $U(x$ and the exponential. A similar argument shows that $\langle\frac{\pi}{a}|U|-\frac{\pi}{a}\rangle = -\frac{iV}{2}$. Using these results, the matrix is

$$\begin{pmatrix} V/2 & -iV/\pi \\ iV/\pi & V/2 \end{pmatrix} \tag{10}$$

This matrix has eigenvectors $|1\rangle = |\frac{\pi}{a}\rangle + i|-\frac{\pi}{a}\rangle$ with eigenvalue $E_1^1 = \frac{V}{2} + \frac{V}{\pi}$ and $|2\rangle = |\frac{\pi}{a}\rangle - i|-\frac{\pi}{a}\rangle$ with eigenvalue $E_2^1 = \frac{V}{2} - \frac{V}{\pi}$. These eigenvalues represent the first order energy corrections, therefore the energy of the lower band is $E_l = E^0 + E_1^1 = \frac{\hbar^2\pi^2}{2ma^2} + \frac{V}{2} - \frac{V}{\pi}$ and the energy of the upper band is $E_u = E^0 + E_2^1 = \frac{\hbar^2\pi^2}{2ma^2} + \frac{V}{2} + \frac{V}{\pi}$. Therefore the band gap is given by perturbation theory to be

$$E_u - E_l = \frac{2V}{\pi} \tag{11}$$

We can compare this perturbative estimate with the results found in the previous problem using the following table

$V/\left(\frac{\hbar^2}{ma^2}\right)$	Exact gap	Perturbative estimate of gap
0.05	0.031831	0.031831
0.1	0.0636619	0.063662
1	0.636553	0.63662
10	6.30009	6.3662
20	12.2112	12.7324

5. In the previous problem, you explored the tight-binding approximation, which works in the opposite limit of perturbation theory. For what range of V do we expect the tight-binding model to be a good approximation? Compare the tight-binding model, $\varepsilon_{\mathrm{TB}}(k)$ to the lowest band for the Kronig-Penney model (previous problem), as follows: (i) choose the "hopping" parameter t such that the difference between the largest and smallest energy of the tight-binding band matches the difference between the largest and smallest energy of the lowest band from the Kronig Penney model, and add a constant energy ε_0 to $\varepsilon_{\mathrm{TB}}(k)$ so that the bottom and top of the tight-binding band matches the exact solution. Then, plot the Kronig Penney solution and tight-binding energies on top of each other for the values of V shown in the previous sections.

Solution: We would expect the tight binding model to be a good approximation when the potential is strong relative to the natural energy scale of the problem, which is to say when $V/\left(\frac{\hbar^2}{ma^2}\right) \gg 1$

Plots comparing the Kronig-Penny model and the tight binding model can be found below.

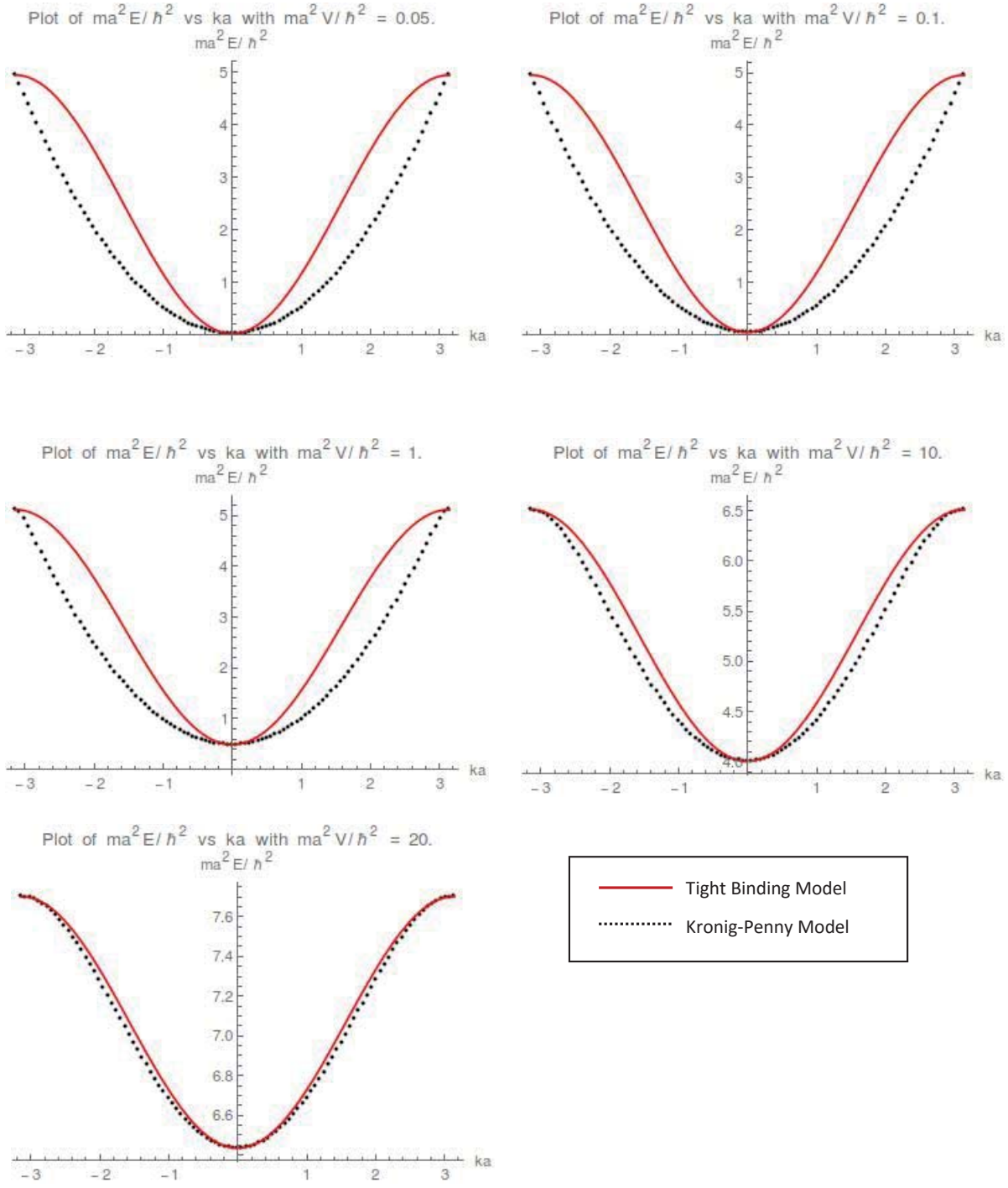

FIG. 3: Plots of the allowed values of the dimensionless energy, $\frac{ma^2E}{\hbar^2}$, for values of ka ranging from $-\pi$ to π for both the Kronig Penny model (dotted black curve) and the tight binding model (red curve). The shape of the tight binding model curve starts to agree more with the Kronig Penny model as V increases, which we would expect because larger V corresponds to tighter binding of electons to atoms.