The Kronig-Penney Model

Andrew D. Baczewski

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Motivation

Previously, we have addressed some of the deficiencies of the free electron model of the electronic structure of solids. Among them are the following:

- Overestimation of the linear contribution to the low temperature specific heat of metalloids (e.g., Gallium, Beryllium).

- Underestimation of the linear contribution to the low temperature specific heat of transition metals (i.e., effective mass enhancement of d electron systems).

- Manifestly a poor choice of models for insulators and semiconductors.

The simplest 'corrections' to the free electron model are based upon either a perturbation of the free electron picture (i.e., nearly free electron), or the adoption of a framework that is more similar to the molecular orbital picture used in explaining simple chemical bonds (i.e., the tight-binding model). The nearly free electron model, in particular, will be a very natural extension of the free electron model that we already know and love, in so far as it is essentially degenerate perturbation theory applied to the free electron model. Before moving on to this more general model, it is constructive to consider an exactly solvable model with some of the same salient features, wherein we can examine the influence of a periodic potential on the motion of a free electron.

Statement of the Problem

We are concerned with solving the following stationary, single particle Schrodinger Equation:

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_{KP}(x) \right)\psi(x) = E\psi(x) \tag{1}$$

Here, we will call V_{KP} the 'Kronig-Penney' potential, which takes the following functional form:

$$V_{KP}(x) = \sum_{n=-\infty}^{\infty} V_{well}(x - n(a+b)) \tag{2a}$$

$$V_{well}(x) = \left(\begin{array}{ll} 0 & \text{for } 0 \leq x \leq a \\ V_0 & \text{for } a < x < a+b \end{array} \right. \tag{2b}$$

In terms of physically intuitive constructs, $V_{KP}(x)$ describes a potential with infinite spatial support, and spatial periodicity $(a + b)$. Here, each unit cell consists of a repulsive barrier of strength V_0 and width b; the spacing between barriers is then a. The problem that we now seek to solve is a complete description of the eigenfunctions and eigenvalues of this Schrodinger Equation utilizing Bloch's Theorem.

Construction of Eigenfunctions

Previously, we have discussed Bloch's Theorem, wherein the eigenfunctions of a Schrodinger Equation subject to a periodic potential, $V_{per}(\vec{r})$ are constrained as follows:

$$\psi_{n,\vec{k}}(\vec{r} + \vec{t}) = e^{i\vec{k}\cdot\vec{t}}\psi_{n,\vec{k}}(\vec{r}) \tag{3}$$

Here, $\vec{t}$ is a real lattice vector associated with the periodicity of $V_{per}(\vec{r})$, and $(n, \vec{k})$ are a set of 4 quantum numbers (2 in 1D, 3 in 2D) that uniquely characterize the eigenstate. Here, n is typically deemed the 'band index' and $\vec{k}$ the 'quasi-momentum', 'crystal momentum', or 'Bloch wavenumber'. The physical relevance of these quantities will become clear as we move forward. For the problem we are interested in, the Bloch Theorem indicates that our eigenfunctions will be constrained as follows:

$$\psi_{n,k}(x + n(a+b)) = e^{ikn(a+b)}\psi_{n,k}(x) \tag{4}$$

We can begin to flesh out the form of $\psi_{nk}(x)$ starting from a knowledge of the eigenfunctions associated with scattering from a single well, $V_{well}(x)$. In this case, we expect solutions of the following form:

$$\psi(x) = \left\{ \begin{array}{ll} e^{iKx} + re^{-iKx} & \text{for } -\infty < x \le a \text{ (left of barrier)} \\ ce^{-Qx} + de^{Qx} & \text{for } a \le x \le b \text{ (inside of barrier)} \\ te^{iKx} & \text{for } a+b \le x < \infty \text{ (right of barrier)} \end{array} \right. \tag{5}$$

As you should recall from introductory quantum mechanics, each portion of this solution clearly satisfies the Schrodinger Equation for a piecewise homogeneous potential, and the precise values of r, c, d, and t are found by enforcing the continuity of $\psi(x)$ and its derivative at discontinuities in the potential. Some other points worth remembering follow:

- The solution in each piecewise homogeneous region (excepting $a + b \le x < \infty$) is a linear combination of degenerate eigenfunctions (i.e., left- and right-moving solutions) with values of K and Q that satisfy the following dispersion relations:

$$E(K) = \frac{\hbar^2 K^2}{2m} \tag{6}$$

$$E(Q) = V_0 - \frac{\hbar^2 Q^2}{2m} \tag{7}$$

- We have implicitly enforced the boundary conditions at $\pm\infty$: the e^{iKx} term for $-\infty < x \le a$ represents incident probability flux that one can imagine as originating at $-\infty$, whereas the absence of a term proportional to e^{-iKx} for the $b \le x < \infty$ region indicates that there is no probability flux that is reflected at $+\infty$.

- It isn't very difficult to derive expressions for $t(K,Q)$, $r(K,Q)$, $c(K,Q)$, and $d(K,Q)$. One can either pose the boundary conditions and solve by substitution, or equivalently, write down the associated linear system as a matrix equation and solve by inversion.

$$\begin{pmatrix} e^{-iKa} & -e^{-Qa} & -e^{Qa} & 0 \\ -iKe^{-iKa} & Qe^{-Qa} & -Qe^{Qa} & 0 \\ 0 & e^{-Q(a+b)} & e^{Q(a+b)} & -e^{iK(a+b)} \\ 0 & -Qe^{-Q(a+b)} & Qe^{Q(a+b)} & -iKe^{iK(a+b)} \end{pmatrix} \begin{pmatrix} r \\ c \\ d \\ t \end{pmatrix} = \begin{pmatrix} -e^{iKa} \\ -iKe^{iKa} \\ 0 \\ 0 \end{pmatrix} \tag{8}$$

- This approach will work for an inhomogeneous problem, i.e., one in which we impress an incident flux on the system. In the case of the Kronig-Penney model, we are interested in solving the pure eigenproblem, wherein there is no exciting flux.

In solving the Kronig-Penney model, we will use an ansatz that is very similar to the one we used in solving the single finite barrier.

$$\psi(x) = \left(\begin{array}{ll} ce^{-Qx} + de^{Qx} & \text{for } -b \le x \le 0 \text{ (inside barrier)} \\ fe^{iKx} + ge^{-iKx} & \text{for } 0 \le x \le a \text{ (outside barrier)} \\ e^{ikn(a+b)}\psi(x - n(a+b)) & \text{for } x \in \mathbb{R} \backslash [-b, a], \text{ such that } x - n(a+b) \in [-b, a] \end{array} \right. \tag{9}$$

Here, the first two lines of our ansatz are simply a linear combination of the two degenerate solutions to the free particle Schrodinger equation in two of the countably infinite number of piecewise homogeneous regions of $V_{KP}(x)$. These two regions are otherwise known as the 'fundamental domain' of the problem, but it is perhaps simpler/more physically relevant to refer to them as the unit cell of the Kronig-Penney potential. The third line of our ansatz recursively defines $\psi(x)$ on the entire domain, by mapping an argument outside of the fundamental domain back

onto it using Bloch's Theorem. In short, the solution will take the same form outside of the fundamental domain, up to a phase shift.

It should be evident that this ansatz will satisfy the Schrodinger equation on the fundamental domain, but what about elsewhere? At this point, we have a free parameter, that we have not related to the parameters of our model, in the k that pops up due to the application of Bloch's Theorem. We will show, that by constraining the continuity of $\psi(x)$ and its derivative inside and outside of the fundamental domain, that we can construct a condition for k that must be satisfied by eigenfunctions of the Kronig-Penney potential. We first constrain continuity inside of the fundamental domain (i.e., at $x = 0$):

$$c + d = f + g \tag{10}$$
$$-Q(c - d) = iK(f - g) \tag{11}$$

We then constrain continuity outside the fundamental domain (i.e., at $x = a$):

$$fe^{iKa} + ge^{-iKa} = (ce^{Qb} + de^{-Qb})e^{ik(a+b)} \tag{12}$$
$$iK(fe^{iKa} - ge^{-iKa}) = -Q(ce^{Qb} - de^{-Qb})e^{ik(a+b)} \tag{13}$$

We can of course resolve these constraints into a linear system:

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ -Q & Q & -iK & iK \\ e^{ik(a+b)+Qb} & e^{ik(a+b)-Qb} & -e^{iKa} & -e^{-iKa} \\ -Qe^{ik(a+b)+Qb} & Qe^{ik(a+b)-Qb} & -iKe^{iKa} & iKe^{-iKa} \end{pmatrix} \begin{pmatrix} c \\ d \\ f \\ g \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{14}$$

This system of equations will only admit a non-trivial (i.e., non-zero) solution if the determinant of the matrix on the left hand side of this equation is zero. If you're persistent, you can do enough algebra that you can derive a constraint on k in terms of the model parameters from this determinant:

$$\frac{Q^2 - K^2}{2QK} \sinh(Qb)\sin(Ka) + \cosh(Qb)\cos(Ka) = \cos(k(a + b)) \tag{15}$$

Note that this may be different from the Equation that you took down during Friday's lecture. Namely, the $\sinh(Qb)$ and $\cosh(Qb)$ were different. This was in error.

In any case, for fixed values of the model parameters, a, b, and V_0, for a given value of k, we seek values of K that will yield a solution to this transcendental equation. These values of K will give rise to stationary states with energy:

$$E = \frac{\hbar^2 K^2}{2m} \tag{16}$$

We note, in anticipation of the solution, that there will be values of K for which there are no real values of k that satisfy this equation, in which case there will be a gap in the spectrum of energies.

Resolution of the Kronig-Penney Spectrum

Without taking any limits, Equation 15 is most readily solved using numerical methods, i.e., simple root-finding algorithms. In certain limits, it becomes constructive to consider the graphical solution of this equation, in which case one plots the left hand side of Equation 15 as a function of Ka, and finds where it crosses into the envelope of the cosine on the right hand side.

We will now, briefly consider one such limit, where the width of the potential barrier, $b \to 0$, and its height, $V_0 \to \infty$. This is essentially the limit that the potential becomes a periodic array of Dirac delta functions. In this limit, we can reduce Equation 15 to:

$$\frac{Q^2 - K^2}{2K} b\sin(Ka) + \cos(Ka) = \cos(ka) \tag{17}$$

Here, we have gone to leading order in the Taylor Expansions of the hyperbolic trigonometric functions on the left hand side, and simply let $b = 0$ on the right hand side. We then find it convenient to define the dimensionless quantity, $P = \frac{mV_0ba}{\hbar^2}$, which defines the effective strength of our potential:

$$P\frac{\sin(Ka)}{Ka} + \cos(Ka) = \cos(ka) \tag{18}$$

In this form, for a fixed value of P, it is rather simple to plot the left hand side as a function of Ka. When the value of the left hand side of this Equation is between -1 and 1 (the range of $\cos(ka)$ for real arguments), there will be a value of k for which a solution exists. When the value is outside of this interval, however, there will be no real k for which this Equation is satisfied, and there will be no energy eigenfunction that exists for that value of K. The resultant spectrum of solutions will then have gaps in the admissible energies. In other words, for certain energies, there will be no proper solutions to the Kronig-Penney model. Think of this like the Hydrogen atom in elementary quantum mechanics, wherein the energy was allowed to only take on certain values due to quantization. In this case, we no longer have a discrete set of energies, but instead bands of energies that form admissible eigenfunctions, with finite gaps between them wherein there are no such solutions.

It is very instructive to toy around with this model, so I recommend playing around with Equation 18 using your favorite plotting software. To this end, take note, that as $Ka \to \infty$, the energy gaps will tend to 0. One might expect this intuitively, on the basis that for very large values of K, the spectrum will approach that of a free electron, as the scale of the particle's kinetic energy will be much larger than that of the potential energy barriers.