ME 697R: Computational Methods for Nanoscale Energy Transport

Chapter 5: First Principles Method
Section 5.2: Electronic Structure of Solids

Reading: Kittel, pp. 174-182

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The motion of an electron in a crystalline solid can be reduced to the problem of an electron in a periodic potential. The lattice determines the form of the potential:

$$V(r + a) = V(r) \quad \text{for any lattice vector } a$$

Now seek to solve:

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right)\psi(r) = E\psi(r)$$

Bloch’s Theorem:

$$\psi_{nk}(r) = \exp(ik \cdot r)u_{nk}(r)$$

where

$$u_{nk}(r + a) = u_{nk}(r)$$
F. Bloch proved important theorem that the solutions to the Schrödinger equation for a periodic potential must be of a form:

\[ \psi_k(r) = u_k(r)e^{ik \cdot r} \]

- cell periodic part with periodicity of the lattice
- plane-wave component

We now give a simplified proof of the Bloch theorem, which assumes 1D lattice with atoms at positions \( x = 0, a, 2a, \ldots, Na \), that are arranged on a ring. Guided by the symmetry of the ring, we now make the periodic assumption, that leads to:

\[
\psi(x + a) = C \psi(x) \quad \Rightarrow \quad \psi(x + Na) = C^N \psi(x) = \psi(x)
\]

\( \Rightarrow \quad C^N = 1 \quad \Rightarrow \quad C = e^{i2\pi n/N} \)

Let \( \psi(x) = u_k(x)e^{ik_n x} \) where \( k_n = 2\pi n / Na \), and \( u_k(x) = u_k(x + a) \)

Then \( \psi(x + a) = u_k(x + a)e^{ik_n(x+a)} = u_k(x)e^{i2\pi n(x+a)/Na} = u_k(x)e^{i2\pi n x + i2\pi n/N} = C\psi(x) \)
The Kronig-Penney Model

- Coulomb potential

- We simplify the potential, in order to be able to solve the problem analytically.
The Kronig-Penney Model

- We will eventually let $V \to \infty$ and $d \to 0$ in the problem.
The Kronig-Penney Model

- We now solve the time-independent Schrödinger equation.

\[ 0 < x < a \]

\[- \frac{h^2}{2m} \frac{d^2 \psi_1}{dx^2} = E \psi_1 \]

\[ \frac{d^2 \psi_1}{dx^2} + \alpha^2 \psi_1 = 0 \]

\[ \alpha^2 = \frac{2mE}{h^2} \]

- So, we seek a general solution of the Bloch form:

\[ \psi_i(x) = e^{ikx} u_i(x), \quad u_i(x + a + d) = u_i(x) \]
The Kronig-Penney Model

\[ \frac{d^2 u_1}{dx^2} + 2ik \frac{du_1}{dx} + (\alpha^2 - k^2)u_1 = 0 \]

\[ \frac{d^2 u_2}{dx^2} + 2ik \frac{du_2}{dx} - (\gamma^2 + k^2)u_2 = 0 \]

\[ u_i = e^{\delta x} \]

\[ \delta_1^2 + 2ik\delta_1 + (\alpha^2 - k^2) = 0 \]

\[ \delta_1 = -ik \pm i\alpha \]

\[ \delta_2^2 + 2ik\delta_2 - (\gamma^2 - k^2) = 0 \]

\[ \delta_2 = -ik \pm \gamma \]

\[ u_1 = Ae^{-ikx + i\alpha x} + Be^{-ikx - i\alpha x} \]

\[ u_2 = Ce^{-ikx + \gamma x} + De^{-ikx - \gamma x} \]
The Kronig-Penney Model

- Continuity boundary condition

\[
\begin{align*}
    u_1(0) &= u_2(0) & \Rightarrow & & A + B = C + D \\
    \frac{du_1}{dx} \bigg|_{x=0} &= \frac{du_2}{dx} \bigg|_{x=0} & \Rightarrow & & -(k - \alpha)A - i(k + \alpha)A \\
    &= - (ik - \gamma)C - (ik + \gamma)D
\end{align*}
\]

- Periodic boundary condition

\[
\begin{align*}
    u_1(a) &= u_2(a) = u_2(-d) & \Rightarrow & & Ae^{-i(k-\alpha)a} + Be^{-i(k+\alpha)a} \\
    &= Ce^{(ik-\gamma)d} + De^{(ik+\gamma)d}
\end{align*}
\]

\[
\begin{align*}
    \frac{du_1}{dx} \bigg|_{x=a} &= \frac{du_2}{dx} \bigg|_{x=-d} & \Rightarrow & & -(k - \alpha)Ae^{-i(k-\alpha)a} - i(k + \alpha)Be^{-i(k+\alpha)a} \\
    &= -(ik - \gamma)Ce^{(ik-\gamma)d} - (ik + \gamma)De^{(ik+\gamma)d}
\end{align*}
\]
The Kronig-Penney Model

- In the matrix form:

\[
\begin{bmatrix}
0 & 1 & -1 & -1 \\
-i(k - \alpha) & -i(k + \alpha) & (ik - \gamma) & (ik + \gamma) \\
e^{-i(k-\alpha)a} & e^{-i(k+\alpha)a} & -e^{(ik-\gamma)d} & -e^{(ik+\gamma)d} \\
-i(k - \alpha)e^{-i(k-\alpha)a} & -i(k + \alpha)e^{-i(k+\alpha)a} & -(ik - \gamma)e^{(ik-\gamma)d} & -(ik + \gamma)e^{(ik+\gamma)d}
\end{bmatrix}
\begin{bmatrix}
A \\
B \\
C \\
D
\end{bmatrix} = 0
\]

- This requires the determinant of the large square matrix to vanish:

\[
\det[\text{coeff.}] = 0
\]
To simplify this, we take the limit \( V \to \infty \) and \( d \to 0 \) in such a manner that \( Vd = Q \).

\[
\frac{\gamma^2 - \alpha^2}{2\alpha \gamma} \sinh(\gamma d) \sin(\alpha a) + \cosh(\gamma d) \cos(\alpha a) = \cos[k(a + d)]
\]

- The wavevector \( k \) is real only for certain allowed ranges of \( E \).
The Kronig-Penney Model

- **Graphical solution**

\[ P \frac{\sin(\alpha a)}{\alpha a} + \cos(\alpha a) \]

Regions where the equation is satisfied, hence where the solution exists.

- In general, as the energy increases (\(\alpha a\) increases), each successive band gets wider, and each successive gap gets narrower.
**Note:**

\[ \alpha^2 = \frac{2mE}{\hbar^2} \Rightarrow E = \frac{\alpha^2 \hbar^2}{2m} = f(ka) \]
As energy increases, the bands get WIDER and the gaps get NARROWER.

**Extended zone scheme**

**Reduced zone scheme**
Band Structure of Silicon

- In 3D, \( k \) can be along many different directions.