NOTES 10: Bloch Model of Electrons in a Crystal

(changes from last notes shown in blue)

At the opposite extreme to the Fermi gas model is one in which the electrons interact only with the atoms of a crystal lattice. One of the many great discoveries of the early 20th century was that crystal lattices could display rich diffraction effects when illuminated by radiation having wavelength comparable to the interatomic spacing. This was first observed with X-rays, and later with neutrons. It was also suspected that electrons confined to the solid might also show such diffractive behavior owing to their inherent (de-Broglie) wave nature. To capture that behavior, it is necessary to start the analysis with quantum mechanics and its canonical (*Schrödinger*) wave equation,

$$\left\{ -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r}) \right\}\psi = U\psi \tag{1}$$

where the first term represents the kinetic energy operator, the second term represents the potential energy operator, and the right side is the (total) energy operator. In the Bloch model of the electron, the potential energy always satisfies the translational symmetry of the crystal,

$$V(\vec{r}) = V\left(\vec{r} + \vec{R}\right) \tag{2}$$

where $\vec{R}$ is a lattice vector.

Before addressing the exact solution to the Bloch model of (1) and (2), it is important to realize that the quantum mechanics is being applied here for a completely different reason than in the Fermi-model, which was the particle indistinguishability. It is also useful to address certain aspects of the problem for a very special case of (2) called the one-dimensional delta-function potential. As shown schematically in Fig. 1, this potential has the form

$$V(x) = \sum_n -V_0\delta\left(x + n\cdot d\right) \tag{3}$$

where n is any integer, positive or negative. The sum, called the *Dirac comb* in sampling and signal-processing theory, is especially useful for the Bloch model because it allows us to assume the electrons are truly free everywhere except at the atomic sites. That is, the electrons will have the Fermi free-electron form "phasor" form
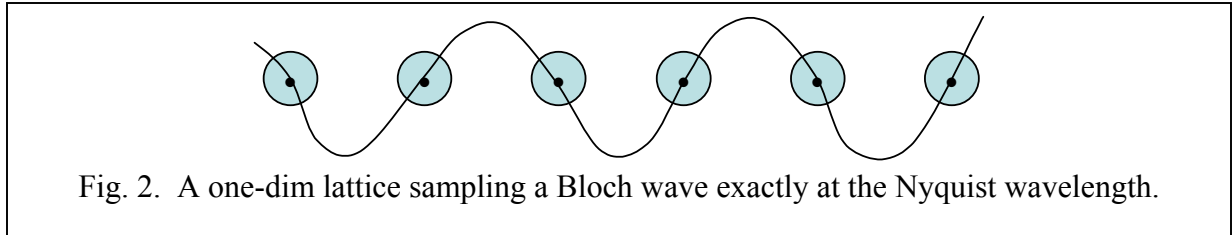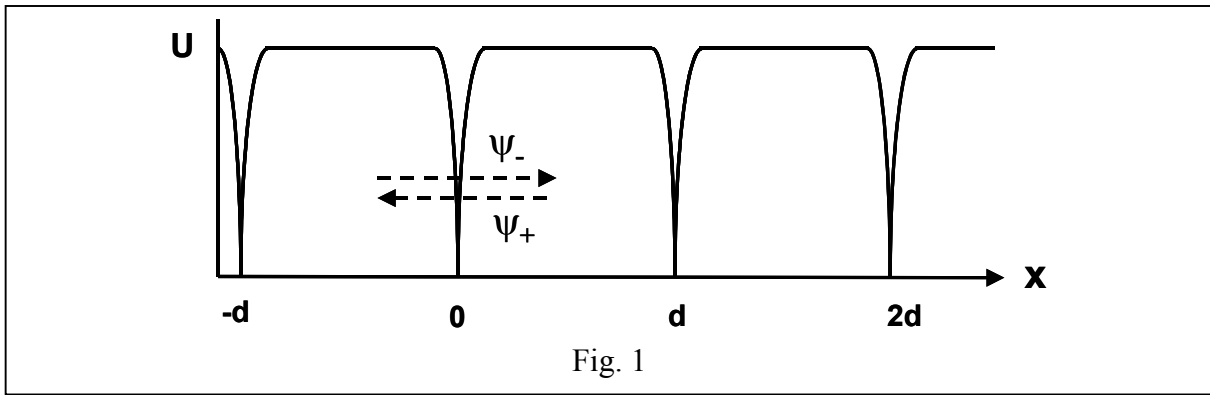
$$\psi = Ae^{+jkx} \text{ or } Ae^{-jkx} . \tag{4}$$

where the + sign in the argument denotes a wave function traveling to smaller x and the − sign denotes one traveling to greater x.[1] Given these "partial solutions", we can deduce the kinematics and energetics of the possible solutions to (1) and (3) as follows.

(1) Nyquist sampling and Kinematics.

As in lattice waves, the minimum value of k can be derived from the fact that the "partial solution" of (4) display the wave translational property $\psi(x + x') = \psi(x)e^{\pm jkx'}$. Assuming the solid is confined to a sample with boundaries at x = 0 and x = L, we get $\psi(L) = \psi(0)e^{\pm jkL}$. Is it still reasonable to expect that the two boundaries of the solid will be physically identical, so that $\psi(L) = \psi(0)$,

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[1] This assumes a time dependence of exp(jωt)

Fig. 1

Fig. 2. A one-dim lattice sampling a Bloch wave exactly at the Nyquist wavelength.

which $\Rightarrow e^{\pm jkL} = 1$?   This is a more difficult to argue in the case of electronic wavefunctions than it was for lattice waves. However, we can argue that the total wavefunction, no matter what the periodic potential is, should satisfy translational symmetry at the period of the potential, $\psi(x+nd) = \psi(x)e^{\pm jknd}$ where n is any integer, positive or negative. By choosing the right n so that nd is equal to L, the length of the sample, we arrive at the same discretization $k = 2n\pi/L$ as with lattice waves.

   The maximum k for the Bloch electrons is a different story. With lattice waves, the maximum k was π/d with d being the atomic interplanar separation. This value is just the Nyquist wave vector for the lattice waves being sampled in space at the lattice sites as shown in Fig. 2. But in the Bloch model we have a new effect – sampling of the Bloch electrons at the lattice sites. And at least for the delta-function lattice and its associated partial wavefunctions of (4), the k can exceed π/d. Physically, it just means that the kinetic energy of the electron, $(\hbar k)^2 / 2m$ is so large that the de-Broglie wavelength is much less than the Nyquist value – i.e., less than twice the interatomic separation.

(2) Bragg scattering and Energetics

   A spectacular result of the Bloch model is the collective scattering by the lattice of a single electron wavefunction, similar to the effect of a three-dimensional diffraction grating on electromagnetic radiation. This is called Bragg scattering and, like the electromagnetic case, can be either constructive or destructive in nature. For the one-dim delta-function case, we can model this scattering effect with an amplitude reflection coefficient r. If a given electron is described by a wave function propagating toward increasing x, then it is reasonable to assume that the collective reflection must create a significant component of the opposite-traveling wave. In terms of the partial solutions of (4) we have

$$\psi = Ae^{+jkx} + Be^{-jkx} .$$ (5)

where A and B are complex coefficients. We can determine a relation them by invoking the continuity of probability density $\rho = \psi\psi*$ at all points in space,

$$\psi\psi* = |A|^2 + |B|^2 + AB*e^{2jkx} + BA*e^{-2jkx} \tag{6}$$

And we apply the continuity at the $x = 0$ delta well in Fig. 1 such that for the limit as $\varepsilon \rightarrow 0$, $\psi\psi*(\varepsilon) = \psi\psi*(-\varepsilon)$. Mathematically, this is

$$|A|^2 + |B|^2 + AB*e^{2jk\varepsilon} + BA*e^{-2jk\varepsilon} = |A|^2 + |B|^2 + AB*e^{-2jk\varepsilon} + BA*e^{2jk\varepsilon}$$

or

$$AB*[2j\sin(2k\varepsilon)] = BA*[2j\sin(2k\varepsilon)]$$

or

$$AB* = BA* \tag{7}$$

Writing out $A \equiv A_0 e^{j\alpha}$ and $B \equiv B_0 e^{j\beta}$, (7) becomes

$$A^2/|A|^2 = B^2/|B|^2 \quad \text{or} \quad e^{j2\alpha} = e^{j2\beta} \quad \text{or} \quad \beta - \alpha = 0 \text{ or } \pi$$

Substitution back into (6) yields two possibilities:

$$\psi\psi*_0 = (A_0)^2 + (B_0)^2 + A_0 B_0 e^{2jkx} + A_0 B_0 e^{-2jkx} = (A_0)^2 + (B_0)^2 + 2A_0 B_0 \cos(2kx) \quad \text{for} \quad \beta - \alpha = 0$$

$$\psi\psi*_\pi = (A_0)^2 + (B_0)^2 - A_0 B_0 e^{2jkx} - A_0 B_0 e^{-2jkx} = (A_0)^2 + (B_0)^2 - 2A_0 B_0 \cos(2kx) \quad \text{for} \quad \beta - \alpha = \pi$$

The first solution has a maximum at $x = 0$ and a minimum at $2kx = \pi$ or $x = \pm d/2$ when $k = \pi/d$,
The second solution has a minimum at $x = 0$ and a maximum at $x = \pm d/2$ when $k = \pi/d$.
Like any pdf in probability theory, we can take the expectation value of the potential energy using the Dirac comb (3):

$$E\{V\} \equiv <V> = \frac{1}{N}\int_0^L \psi\psi*V(x)dx = \frac{1}{N}\int_0^L \psi\psi*\sum_0^{N_c}-V_0\delta(x\pm nd)$$

where N is the normalization constant. At $k = \pi/d$ this results in

$$<V> = -V_0[(A_0)^2 + (B_0)^2 + 2A_0 B_0]/N \text{ for } \psi\psi*_0$$

and

$$<V> = -V_0[(A_0)^2 + (B_0)^2 - 2A_0 B_0]/N \quad \text{for} \quad \psi\psi*_\pi$$

Note that in the special case that $B_0 = A_0$, we have $<V> = -4V_0$ for $\psi\psi*_0$ and $<V> = 0$ for $\psi\psi*_\pi$. In either case there is a gap in $<V>$ at $k = \pi/d$ *since both solutions were obtained for the same k* and, therefore, for the same kinetic energy, $\hbar^2 k^2/2m$.

What should U vs. k look like ? From symmetry considerations alone it is straightforward to see that at $k = 0$ and at $k = \pi/d$, the slope of $<V>$ vs k goes to zero (more on this later).

(3) General Solution: Floquet's and Bloch's theorem

The exact solution to (1) and (2) for the Bloch wavefunction and the associated eigenvalues is much more complicated than one-dim delta-comb potential suggests. But the solution is guided by another one-dim result called Floquet's theorem, which pertains to the solution of any wave equation in which there is a potential-energy term having exact periodicity.
In free space the solution to a linear wave equation has the translational property.

$$f(x + x') = f(x)e^{jkx'}$$

When a periodic term is added to the wave equation that modulates f with period d, then we get the Floquet result

$$f(x + nd) = f(x)e^{jknd}$$

where n is any integer.

Applied to the Bloch model for the Schrodinger equation in crystals, Floquet's theorem generalizes to the three-dim result:

$$\psi(\vec{r} + \vec{R}) = e^{j\vec{k}\cdot\vec{R}}\psi(\vec{r}) \tag{8}$$

where $\vec{R}$ is any crystal lattice vector, and $\vec{k}$ is the crystal wave vector. In between lattice points, we expect a phase evolution factor $e^{j\vec{k}\cdot\vec{r}}$, as in the delta-function model.   So another plausible solution is

$$\psi(\vec{r}) = e^{j\vec{k}\cdot\vec{r}}\varphi_k(\vec{r}) \tag{9}$$

where $e^{j\vec{k}\cdot\vec{r}}$ is the "envelope" function, and ϕ_k is the "cell-periodic" function, which has the same translational symmetry as V(r)

$$\phi_k(\vec{r}) = \phi_k(\vec{r}+\vec{R})$$

As we shall soon see, the more general Bloch solution is:

$$\psi_{n,k}(\vec{r}) = e^{j\vec{k}\cdot\vec{r}}\phi_{n,k}(\vec{r}) \tag{10}$$

where n is the band index.   The self-consistency between (9) and (8) is evident in the following:

$$\psi(\vec{r}+\vec{R}) = e^{j\vec{k}\cdot(\vec{r}+\vec{R})}\phi_k(\vec{r}+\vec{R}) = e^{j\vec{k}\cdot\vec{R}}e^{j\vec{k}\cdot\vec{r}}\phi(\vec{r}) = e^{j\vec{k}\cdot\vec{R}}\psi(\vec{r}) \tag{11}$$

In fact, this is an alternative statement of Bloch's theorem and equivalent physically to Eqn (9).

Many books dwell on the proof of (10) because of its elegance and obvious importance to crystal physics.   Here we will focus more on its application and its impact on the energy spectrum of electrons in a crystal.   Up front, it is important to realize that the Bloch model is most useful in describing electrons that are "nearly free", i.e., electrons that maintain their plane-wave like character of "free" electrons while displaying a periodicity indicative of the crystal lattice. Electrons that are bound to a particular atom – the so-called "core" electrons – are better described via solutions to a Schrodinger equation that includes the electrostatic potential of other "core" electrons.   In applying Bloch's theorem to electronic materials, it is somewhat surprising how many important properties there are, so we discuss several next.

(4) Important aspects of Bloch's Theorem

(1) Probability density. Consistent with probability theory, the quantity $\rho(x) = \psi(x)\psi(x)^*$ is the probability density function (pdf) for finding the electron a given point x over an ensemble of measurements of its position. When calculated for a Bloch electron, we get

$$\rho(\vec{r}) = \psi\psi^* = e^{-j\vec{k}\cdot\vec{r}}\phi_{n,k}(\vec{r})e^{j\vec{k}\cdot\vec{r}}\phi_{n,k}^*(\vec{r}) = \phi_{n,k}(\vec{r})\phi_{n,k}^*(\vec{r})$$

That is, the envelope function drops out, leaving the pdf significant only at lattice sites.

(2) $\hbar\vec{k}$ *is not* the momentum eigenvalue as in free space. To see this, we operate with the momentum operator

$$\vec{p}\psi_{nk} = \frac{\hbar}{j}\vec{\nabla}\psi_{nk} = \frac{\hbar}{j}\vec{\nabla}\left[e^{j\vec{k}\cdot\vec{r}}\phi_{nk}(\vec{r})\right] = \hbar\vec{k}\psi_{n,k} + e^{j\vec{k}\cdot\vec{r}}\frac{\hbar}{j}\vec{\nabla}\phi_{n,k}(\vec{r})$$

The last term is distinctly nonzero in a crystal but vanishes in free space. So $\hbar\vec{k}$ has special meaning as "crystal momentum", which is why $\vec{k}$ is called the crystal wave vector.

(3) A crystal wave vector $\vec{k}'$ outside the 1st Brillouin zone can always be translated to inside the 1st zone by the addition of a suitable reciprocal lattice vector $\vec{G}$, i.e., $\vec{k}' = \vec{k} + \vec{G}$ with no physically essential change to the Bloch wave function To see this we apply Eqn (11) above to $\vec{k}' = \vec{k} + \vec{G}$

$$\psi_{k'}\left(\vec{r} + \vec{R}\right) = e^{j\vec{k}'\cdot\vec{R}}\psi_{k'}\left(\vec{r}\right) = e^{j\left(\vec{k}+\vec{G}\right)\cdot\vec{R}}\psi_{k'}\left(\vec{r}\right) = e^{j\vec{k}\cdot\vec{R}}\psi_{k'}\left(\vec{r}\right)$$

since $e^{j\vec{K}\cdot\vec{R}} = 1$ by definition.

We also have $\psi_k\left(\vec{r} + \vec{R}\right) = e^{j\vec{k}\cdot\vec{R}}\psi_k\left(\vec{r}\right)$. The ratio of these two Bloch wavefunctions is

$$\frac{\psi_{k'}\left(\vec{r} + \vec{R}\right)}{\psi_k\left(\vec{r} + \vec{R}\right)} = \frac{\psi_{k'}\left(\vec{r}\right)}{\psi_k\left(\vec{r}\right)}$$

This can only be true of $\psi_{k'}\left(\vec{r}\right) = C\psi_k\left(\vec{r}\right)$ where C is a complex constant of unit magnitude. And we know from elementary quantum mechanics that multiplying a wave function by a constant does not change the essential physics.

(4) The Bloch wave functions must be associated with a "band index" n because for any given $\vec{k}$ there are an infinite number of possible energy eigenvalues to Schrödinger's equation. To see this, we simply substitute (9) into (1) and (2)

$$\psi\left(\vec{r}\right) = e^{j\vec{k}\cdot\vec{r}}\varphi_k\left(\vec{r}\right) \quad\rightarrow\quad \frac{-\hbar^2}{2m}\nabla^2\psi\left(\vec{r}\right) + V\left(\vec{r}\right)\psi\left(\vec{r}\right) = U\left(\vec{r}\right)$$

$$\Rightarrow \frac{-\hbar^2}{2m}\vec{\nabla}\left(j\vec{k}\,e^{j\vec{k}\cdot\vec{r}}\phi_k\left(\vec{r}\right) + e^{j\vec{k}\cdot\vec{r}}\vec{\nabla}\phi_k\left(\vec{r}\right)\right) + V\left(\vec{r}\right)\psi = U\psi\left(\vec{r}\right)$$

$$\Rightarrow \frac{-\hbar^2}{2m}\left[-k^2 e^{j\vec{k}\cdot\vec{r}}\phi_k\left(\vec{r}\right) + \vec{\nabla}\phi_k\,2jk\,e^{j\vec{k}\cdot\vec{r}} + e^{j\vec{k}\cdot\vec{r}}\vec{\nabla}^2\phi_k\left(\vec{r}\right)\right] + V\left(\vec{r}\right)\psi_k = U_k\psi_k$$

Now divide both sides by $e^{j\vec{k}\cdot\vec{r}}$.

Get $\dfrac{-\hbar^2}{2m}\left[\left(-k^2 + 2jk\vec{\nabla}\right)\phi\left(\vec{r}\right) + \vec{\nabla}^2\phi\left(\vec{r}\right)\right] + V\left(\vec{r}\right)\phi\left(\vec{r}\right) = U\phi\left(\vec{r}\right)$

This is a classic eigenvalue problem for $\phi\left(\vec{r}\right)$. So for a given k and the periodic boundary condition $\phi\left(\vec{r}\right) = \phi\left(\vec{r} + \vec{R}\right)$, there will be an infinite number discrete eigenvalues for each k. We must label these both by k and the "quantum number" n

$$\phi\left(\vec{r}\right) \rightarrow \phi_{nk}\left(\vec{r}\right) \text{ where } \phi_{nk}\left(\vec{r}\right) = \phi_{nk}\left(\vec{r} + \vec{R}\right)$$

and $$U \rightarrow U_{n,k}.$$

where $U_{n,k}$ is called the nth energy "band" at wave vector k.

And the most general form of Bloch's theorem becomes $\psi_{n,k} = e^{j\vec{k}\cdot\vec{r}}\phi_{n,k}\left(\vec{r}\right)$

(5) In addition to the cell-periodic function, the energy eigenvalues are also periodic in k for each n.
$$U_{n,\vec{k}+\vec{G}} = U_{n,\vec{k}}$$

This leads to the concept of the "band structure" as the collection of the curves $U_{n,\vec{k}}$ vs $\vec{k}$ for all possible n values, each curve confined to the 1st *Brillouin zone*.

(6) It can be shown, in general, that the group velocity of an electron confined to band n is:

$$\vec{v}_n(\vec{k}) = \frac{1}{\hbar}\vec{\nabla}_k U_{n,k}(\vec{k})$$

where $\vec{\nabla}_k$ denotes the gradient operator in k space. This implies that an electron in energy state $U_n(\vec{k})$ moves at a *uniform* velocity $\vec{v}_n(\vec{k})$ *even in the presence of collective scattering from the lattice*. And if the scattering is elastic, the velocity will be maintained forever.

(5) Effective Mass Theorem

Suppose that we look at a *minimax* point of one of the bands $U_n(\vec{K})$, i.e., a point where $\vec{\nabla}_k = 0$ with either $\vec{\nabla}_k^2 > 0$ (minimum) or $\vec{\nabla}_k^2 < 0$ (maximum). For simplicity we look at the form of $U_{n,k}(\vec{k})$ along one direction of $\vec{k}$, say k_j

$$U_n(k_j) = U_n(k_{j0}) + \left.\frac{\partial U_n}{\partial k_j}\right|_{k_{jo}}(k_j - k_{j0}) + \frac{1}{2}\frac{\partial^2 U_n}{\partial k_j^2}(k_j - k_{j0})^2 \tag{20}$$

Using the definition for $v_n(\vec{K})$ given above, we can now find equations of motion for an electron in lattice. We consider an operation with units of acceleration:

$$\frac{dv_g}{dt} = \frac{1}{\hbar}\frac{d}{dt}\frac{\partial U_n}{\partial k_j} = \frac{1}{\hbar}\frac{\partial}{\partial k_j}\frac{dU_n}{dt}$$

$$= \frac{1}{\hbar}\frac{\partial}{\partial k_j}\left(\frac{\partial U_n}{\partial k_j}\right)\left(\frac{dK_j}{dt}\right) = \frac{1}{\hbar^2}\frac{\partial^2 U}{\partial k_j^2}\frac{d(\hbar k)}{dt} \tag{21}$$

On the other hand, over a short period of time dt, an external force *F* will accelerate the electron and do work (energy increase)

$$dW_e = Fdx = Fv_g dt = \frac{F}{\hbar}\frac{\partial U}{\partial k}dt \quad.$$

But from calculus $dW_e \equiv dU = \frac{\partial U}{\partial K}dK$ as well. Equating these two, we get

$$F_j = \hbar\frac{dk_j}{dt} = \frac{d(\hbar k_j)}{dt}$$

Substituting this into (21) and applying Netwon's law $\vec{F} = m\vec{a}$, we get

$$\frac{dv_g}{dt} \equiv a = \frac{1}{\hbar^2}\frac{\partial^2 U}{\partial k_j^2}\cdot F \equiv \frac{F}{m^*}$$

where a is the acceleration and m* is the effective mass defined by

$$m^* = \hbar^2\left(\frac{\partial^2 U}{\partial k_j^2}\right)^{-1} \tag{22}$$

This is one of the most profound results in solid-state physics.
The effective mass theorem can be generalized to three dimensions by

$$U\left(\vec{k}\right) = U\left(\vec{k_0}\right) + \frac{1}{2}\sum_{i,j=1}^{3}\left(k_i - k_{0i}\right)\frac{\partial^2 U\left(\vec{k_0}\right)}{\partial k_i \partial k_j}\left(k_j - k_{0j}\right)$$

In this case $\dfrac{\partial^2 U\left(\vec{k_0}\right)}{\partial k_i \partial k_j}$ defines a 3×3 matrix called the reciprocal effective-mass tensor.

(6) Implications of Effective-Mass Theorem

The expression for the effective mass (22) is one of the most profound results of the Bloch model, and also extremely important from a technologic standpoint.   It implies that at a local minimum of the band structure, m* must have a positive value. But it does not constrain the magnitude. In other words m* could be greater than m_e, the electron mass in vacuum, or it could be less than m_e.   And since a = F/m*, m* < m_e means that the electron will respond to an external force (e.g., a uniform electric field) more quickly than it would in vacuum, at least for short times.

By the same token, at a local maximum of the band structure, m* must have a negative value. This means that the electron will respond to an external force in the opposite direction as expected. For example, an electrostatic force pointing in the positive x direction will create an acceleration of the negative-m* electron in the negative x direction – at least for short times. These amazing predictions are, of course, a reality for the electrons occupying the "conduction" and "valence" band of practically all of the common semiconductors in use today. And they are often taken for granted, particularly in semiconductor device courses. But for many students they are rather counterintuitive, and raise many important questions. For example, how can an electron in a dense crystal accelerate more quickly than in vacuum when it has so many atoms "in its way" ?   This was one of the issues that motivated F. Bloch in his seminal work,[2] and is an obligation of any good course on solid-state to explain in simple physical terms.

The explanation relies on two very important and distinct quantum mechanical effects for electrons occupying the higher energy bands of practically every crystal. The first is the collective scattering from all the atoms in the lattice – the same effect that manifestly requires the use of quantum mechanics for the Bloch model. The second and less obvious effect is tunneling through the atomic potential barriers. Tunneling is a strictly quantum-mechanical transport effect whereby electrons can transmit through "classically-forbidden" regions. By classically forbidden, we mean that the difference between their total energy and potential energy in these regions is negative – i.e., their *kinetic energy is negative*.

The combination of the tunneling-through and collective scattering from the atomic lattice of a crystal is sometimes called *resonant tunneling* – a fancy descriptor that occurs not only in crystals but can be engineered for useful device effects in semiconductor heterostructures. The canonical such heterostructure is the *superlattice*. The Bloch-electron model for superlattices will be discussed at the end of the chapter, and the transport theory will addressed later.

(7) Tunneling and Collective Scattering in Crystals

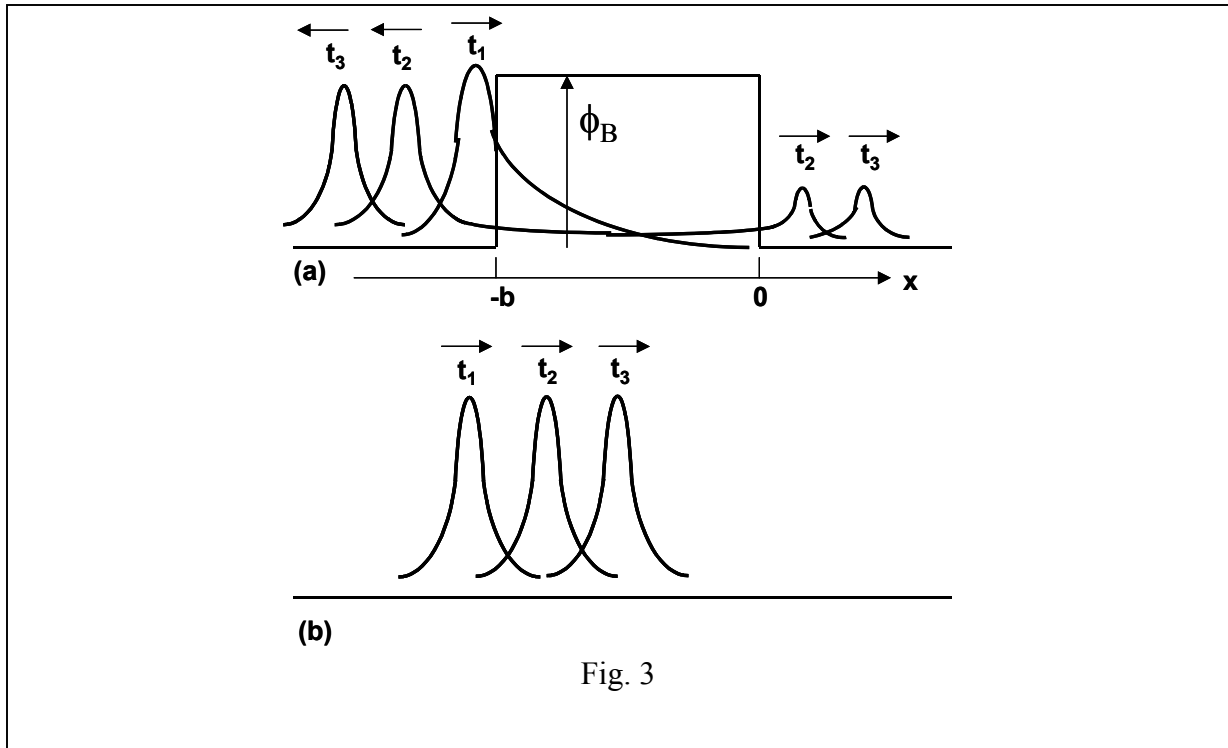[2] and led to his Nobel Prize in 1952.

Fig. 3

      The tunneling phenomenon is made clear by the one-dimensional square-barrier shown in Fig. 3(a) – a standard problem of elementary quantum mechanics. The barrier is assumed to exist in the region $0 < x < b$. A "free electron" is assumed to moving through the entire region (including the barrier) with the (phasor) wavefunction

$$\psi = Ae^{-jkx} + Be^{jkx} \text{ for } x < -b,$$
$$\psi = Ce^{-jkx} + De^{jkx} \text{ for } -b < x < 0, \tag{23}$$
and
$$\psi = Ee^{-jkx} + Fe^{jkx} \text{ for } x > 0.$$

Since the potential energy V is zero in the incident region, and final regions, the one-dim Schrodinger equation predicts that $k = \left(2mU_k / \hbar\right)^{1/2} \equiv \beta$ in both regions, where U_k is the total (and kinetic) energy. And thus

$$\psi = Ae^{-j\beta x} + Be^{j\beta x} . \qquad\qquad x < -b \tag{24}$$
$$\psi = Ee^{-j\beta x} + Fe^{j\beta x} \qquad\qquad x > 0 \tag{25}$$

      But inside the barrier where the potential energy is V_B and $V_B > U_k$, we get the prediction $k = [2m*(U_k - V_B)/\hbar^2]^{1/2} = j[2m*(V_B - U_k)/\hbar^2]^{1/2} \equiv j\alpha$ where α is a real number. Thus we get the result

$$\psi = Ce^{\alpha x} + De^{-\alpha x} \qquad\qquad -b < x < 0 \tag{26}$$

the sum of a growing and decaying exponential. For the single barrier problem, the decaying exponential generally dominates the wavefunction in the barrier and causes the amplitude of the forward traveling component Ee^{-jkx} in the final region to be very small. In other words, the particle probability density $\rho = \psi\psi*$ is much less for $x > b$ than for $x < a$. In the language of electromagnetic wave theory, the barrier is very reflective or "lossy."
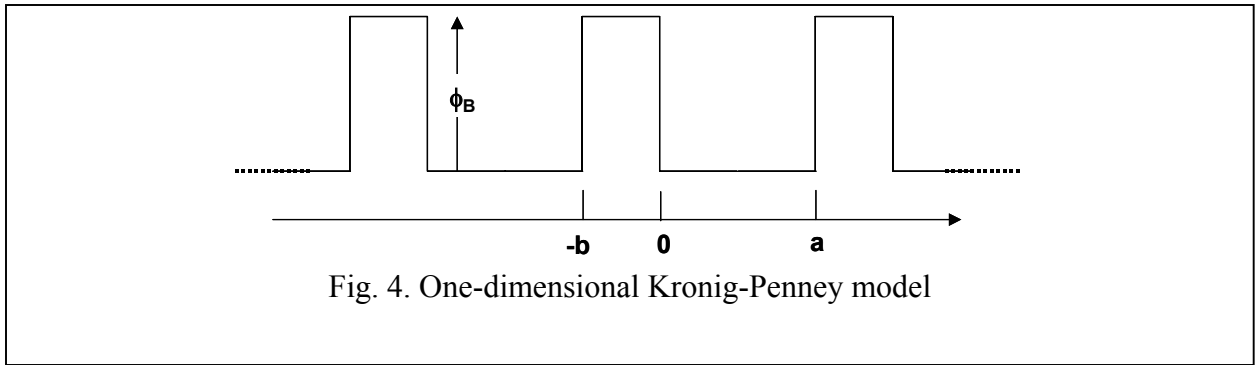
Fig. 4. One-dimensional Kronig-Penney model

Although lossy, the single-barrier tunneling process can be very fast. As will be derived later in the discussion of quantum transport theory, the motion of a particle in a solid is best simulated by forming an electronic wavepacket – i.e., a superposition of plane wavefunctions (23) often constructed by Fourier integration. Fig. 3(a) shows qualitatively the motion of such a wavepacket incident on the barrier versus the motion in free space. The contrast is made at three different times. Interestingly, the arrival of the wavepacket at $t = t_2$ quickly excites the decaying exponential in the barrier which, in turn, excites the corresponding wavepacket in the final region. Although the final-region wavepacket is greatly reduced in magnitude, it commences propagating in the final region before the same wavepacket would arrive there if propagating through vacuum. The qualitative behavior of the wavepacket in vacuum at the same three times is shown in Fig. 3(b). The passage of the electron is effectively "accelerated" by the tunneling through the barrier !

The details of this fascinating effect will be derived later using tunneling-time techniques (both group-delay and Larmor-clock). For now, we only need to justify the profound implications of the effective-mass theorem, so resort to a plausibility argument. Although not forbidden quantum mechanically, the barrier is not a region where the electron is likely to be located from a probabilistic standpoint. This is evident in the dominant decaying exponential solution to the wavefunction. The greater the decay constant α, the less the electron "wants" to be in the barrier. Hence, the more rapidly it will "get out" once it is forced to "get in". [3]

(8) Kronig-Penney Model
Qualitative Behavior

Now we consider not just one barrier but a sequence of barriers as shown in Fig. 4 . If the physical separation of the barriers is just right, the collective reflection from all of them will tend to destructively interfere in the incident region, reducing the net reflected wavefunction. And as in electromagnetic wave theory, this reduction in reflection is always accompanied by an increase in transmission.[4] In electromagnetic terms, the multiple barrier structure is acting like a distributed Bragg reflector (DBR) – a very common structure in optical mirrors and semiconductor lasers.

But at the same time, the wavepacket picture would suggest that the passage of the electron through the entire structure could still occur faster than the passage through the same distance in vacuum. The electrons still do not "want" to be in the barriers. But because the "wells" between the barriers are now classically allowed, the transmission time through them

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[3] The human analogy is working for a demanding boss. Once a job is started, the employee is more likely to finish quickly. But there is usually lower probability of success at the final stage.
[4] This assumes that the barrier region is not absorptive, i.e., does not annihilate electronic probability in some way.

must also be considered. As will be shown below in an example, the transmission time through the wells can easily be longer than through the equivalent length of free space, so one must be careful. Fortunate to the field of electronics, many semiconductors provide a short enough transmission time through the "wells" that the fast barrier tunneling dominates the overall structural traversal time, and the overall transport is faster than in vacuum, leading to $|m^*| < m_e$.

In summary, crystals can and do exhibit two effects that profoundly affect the electronic behavior in solids for electrons occupying the higher energy bands for which the Bloch model works well. The collection of potential barriers created by the atoms requires that the electron exercise the tunneling phenomenon to get through. Tunneling occurs very quickly but with low transmission probability for a single barrier. But under special conditions, the transmission probability can be restored to high values through the collective Bragg scattering from the entire atomic lattice, and the fast tunneling can still accelerate the transport through the entire crystal compared to the transport through the same distance of vacuum.

Quantitative Behavior

The mathematics of the Kronig-Penney model is a great exercise in quantum mechanics and the application of the Bloch theorem. We use the same wave functions (24) - (26) except now we apply continuity of the wavefunction and probability current at the barrier interfaces, and periodicity through the Bloch theorem. The continuity of the wavefunction at $x = -b$ and $x = 0$ implies

$$Ae^{j\beta b} + Be^{-j\beta b} = Ce^{-\alpha b} + De^{+\alpha b} \tag{27}$$
$$C + D = E + F \tag{28}$$

The continuity of probability current implies that $(1/m)\,\partial\psi/\partial x$ is continuous across each interface,[5] so that at $x = -b$ and $x = 0$ we have

$$-Aj\beta e^{j\beta b} + Bj\beta e^{-j\beta b} = C\alpha e^{-\alpha b} - D\alpha e^{+\alpha b} \tag{29}$$
$$C\alpha - D\alpha = -Ej\beta + Fj\beta \tag{30}$$

And finally we apply Bloch's theorem in the form $\psi(x+X) = \psi(x)e^{jkX}$ twice with X being the lattice period. The first application is between $x = -(b+a)$ and $x = 0$, yielding

$$\psi(x=0) = E + F = C + D = e^{jk(a+b)}\,\psi(x = -a-b) = e^{jk(a+b)}[Ae^{j\beta(a+b)} + Be^{-j\beta(a+b)}] \tag{31}$$
$$\psi = Ce^{\alpha x} + De^{-\alpha x}$$

The second application is between $x = -b$ and $x = a$, yielding

$$\psi(x=a) = Ee^{j\beta(a)} + Fe^{-j\beta(a)}] \ = e^{jk(a+b)}\,\psi(x = -b) = e^{jk(a+b)}[Ae^{j\beta(b)} + Be^{-j\beta(b)}] \tag{32}$$

At this point it is very important to recognize the following facts. (1) The set of equations (27) – (32) constitutes six equations and six unknowns, A, B, C, D, E, and F (in Kittel there are apparently only four unknowns, but two are solved for implicity through a few skipped steps). (2) The six equations can be written in square matrix form, which when multiplied times the

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[5] The mass is identical in all regions for this version of the model. But when applying the Kronig-Penney model to so-called superlattice structures, m will no longer be continuous.

column vector formed by A-thru-F equals zero; the determinant of the matrix must equal zero, which yields a polynomial equation for k in terms of α, β, a, b, and fundamental constants. (3) the k appearing and (31) and (32) is the *crystal wave vector*, not generally equal to β or α in equations (27) through (30) ! In other words, β and α are just "local" wave vectors specific to the "well" and "barrier" regions, and k is the crystal wave-vector to be treated as an input parameter in the problem.

The solution to (27)-to-(32) is indeed tedious and left to a homework problem. Fortunately the answer is well known an given in Kittel Chap. 7 (21a).

$$\frac{\alpha^2 - \beta^2}{2\alpha\beta}\sinh\alpha b\sin\beta a + \cosh\alpha b\cos\beta a = \cos k(a+b)$$

This equation is a great exercise in practially all aspects of the Bloch theorem, particularly the group velocity theorem and the effective mass theorem. And it is easily solved on a computer just by inverting the right side using the $\cos^{-1}$ function (see HW#7).

(9) Bloch Model in Wave Vector Space

A fundamental complication of the Bloch model is the different requirements on discretization of the kinetic and potential energy terms.

$$KE = \frac{\hbar^2 k^2}{2m} \Rightarrow \Delta k = \frac{2\pi}{L}$$

$$PE = V(\vec{r}) = V(\vec{r} + \vec{R}) \Rightarrow \Delta k = \frac{2\pi n}{d}$$

In other words, the kinetic energy, as in the Fermi model, is periodic only relative to the entire sample. But the potential energy is periodic in the lattice constant.
So the interesting question is, for which periodicity should the total energy (eigenvalues) comply.
To address this important question, we consider the atomic lattice as interacting with the electron wave in a discrete sense. The collective interaction effect, as expressed through quantum-mechanical scattering, is a form of discrete spatial sampling. But when k >> π/d (certainly possible for the electrons), the lattice is *under-sampling* the Bloch wave. From fundamental digital sampling theory, this means that *aliasing* can occur. Aliasing means that Fourier components at frequencies above the Nyquist value (half the sampling rate) will display the same effects through the interaction as frequencies below the Nyquist frequency. Stated in terms of crystal kinematics, aliasing means that to accurately describe an arbitrary Bloch wavefunction at a given k, we will need to include the Bloch waves at k + G = k + 2πn/d, where G is the generic reciprocal lattice vector.
Strictly speaking the interaction process is not exactly the same for the aliased k values as for the fundamental ones because aliased ks have higher kinetic energy and, therefore, a different scattering cross section from the atoms. But the phase-dependent part of the scattering and its strong collective effect *is* correctly described by the aliasing. And one of the key aspects of the aliasing principle is that the fundamental plus all aliased components of an arbitrary function can perfectly represent the waveform at a given Fourier component. So if we know (or guess) these components, we can perfectly reconstruct the effect of $V(\vec{r})$ on ψ.
We can develop these important effects quantitatively by re-writing the Schrodinger equation in momentum space. We begin by decomposing the wavefunction and the potential energy in the appropriate Fourier series, starting in one dimension for simplicity:

$$\psi(x) = \sum_k C_k e^{jkx} \tag{41}$$

$$V(x) = \sum_G V_G e^{jGx} \tag{42}$$

By substitution into the Schrodinger equation, we get

$$\frac{+\hbar^2}{2m} \sum_k C_k k^2 e^{jkx} + \sum_G \sum_k V_G C_k e^{j(k+G)x} = U \sum_k C_k e^{jkx} \tag{43}$$

Now we seek to utilize the orthogonality property of complex exponentials by multiplying both sides of (43) by $e^{-jk'x}$ and integrating over the entire crystal.

Recall: $\displaystyle\int_{crystal} e^{j(k-k')x} dx = \delta_{k,k'}$ $\displaystyle\int_{crystal} e^{j(k-k'+G)x} dx = \delta_{k,k'-G}$

$$\Rightarrow C_{k'}\left[\frac{\hbar^2}{2m}(k')^2 - U\right] + \sum_G V_G C_{k'-G} = 0$$

or because k' is a dummy wave vector $\Rightarrow C_k\left[\frac{\hbar^2}{2m}k^2 - U\right] + \sum_G V_G C_{k-G} = 0$ (44)

$$C_k = \frac{\sum_G V_G C_{k-G}}{\frac{\hbar^2}{2m}k^2 - U}$$

The key point is that C_k depends only on C_k values at k + G. So we can deduce for a given n

$$\psi_k(x) = \sum_G C_{k-G} e^{j(k-G)x} \tag{45}$$

This is an impressive simplification of (41) – the Bloch wavefunction has been transformed from a Fourier series in k space to a Fourier series in G space. At first this might seem impossible, but a re-write justifies the simplification:

$$\psi_k(x) = \sum_G C_{k-G} e^{-jGx} e^{jkx} \equiv \phi_k(x) e^{jkx}$$

We have arrived back at one form of Bloch's theorem, now with a specific definition for the cell-periodic function $\phi_k(x)$ as a Fourier series. So (45) does make sense – it is just a plane-wave (Fermi) function modulated by a (atomic) cell-periodic function. Stated differently, the under-sampling of the electronic wave function by the atomic lattice sites introduces a contribution to ψ_k from other (higher) frequencies k + G in the Fourier representation. This is just the aliasing concept of digital signal processing applied to x and k instead of time and frequency.

Generalizing this to 3-dim we get

$$\psi_{\vec{k}}(\vec{r}) = \sum_G C_{\vec{k}-\vec{G}} e^{j(\vec{k}-\vec{G})\cdot\vec{r}}$$

And the re-write becomes

$$\psi_{\vec{k}}(\vec{r}) = \sum_G C_{\vec{k}-\vec{G}} e^{-j\vec{G}\cdot\vec{r}} e^{j\vec{k}\cdot\vec{r}} \equiv \phi_{n,\vec{k}}(\vec{r}) e^{j\vec{k}\cdot\vec{r}} \tag{46}$$

This leads to another realization about the Bloch wave function: namely that there is a correlation between the $\vec{G}$ vectors and the band index, n. In other words, for each term $C_{\vec{k}-\vec{G}} e^{-j\vec{G}\cdot\vec{r}}$, we get a unique contribution to $\phi_{\vec{k}}(\vec{r})$ that we call $\phi_{n,\vec{k}}(\vec{r})$. In mathematical terms, the band index n is in "one-to-one correspondence" with the reciprocal lattice vectors !

The three-dim analogue to (44) is written

$$\Rightarrow C_{\vec{k}}\left[\frac{\hbar^2 |\vec{k}|^2}{2m} - U\right] + \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k}-\vec{G}} = 0 \tag{47}$$

In solid-state physics this is usually called the "central" equation. Its use requires some special considerations. First, the term $V_{\vec{G}}$ for $\vec{G} = 0$ is not interesting from a physical standpoint because it corresponds to a uniform potential energy throughout the crystal so can not scatter

electrons. It corresponds to the "dc term" in Fourier analysis of voltage (or current) waveforms in electrical circuit analysis. Hence, it can be set to zero.

Second, and related is the fact that in using (47) for a given $\vec{k}$, the summation will contribute C coefficients only at other values of $\vec{k}$ removed from the chosen one by a nonzero $\vec{G}$. Third, since the C_k are really the coefficients in the expansion of ϕ, and since aliasing is occurring, $C_{\vec{k}}$ in the first term of (47) is to be varied parametrically over all the possible values of $\vec{k} + \vec{G}$ and the contribution from the summation term is evaluated accordingly. *But the eigenvalue term U is fixed in this process since it is just a constant.*

This reasoning allows us to represent (47) in an elegant matrix form that is very handy in applying it to problems. In doing so, it is useful to define the following quantities:

$$U_0(\vec{k} + \vec{G}) = \frac{\hbar^2 \left|\vec{k} + \vec{G}\right|^2}{2m} \qquad \text{for any nonzero } \vec{G}$$

$$W_{k+G} = \frac{\hbar^2 |\vec{k}+\vec{G}|^2}{2m_e} - U = U_0 - U \quad \text{for any nonzero } \vec{G}$$

Each $C_{k\text{-}G}$ coefficient in (46) can be associated with an element of a column vector. The first five vector elements and the associated 5x5 matrix are shown below. Of course, the matrix has as many dimensions as rows in the column vector, and the column vector has as many rows as needed to accurately describe the Bloch function.

$$\begin{pmatrix} W_{\vec{k}-\vec{G}_2} & V_{\vec{G}_1} & V_{\vec{G}_2} & V_{\vec{G}_3} & V_{\vec{G}_4} \\ V_{-\vec{G}_1} & W_{\vec{k}-\vec{G}_1} & V_{\vec{G}_1} & V_{\vec{G}_2} & V_{\vec{G}_3} \\ V_{-\vec{G}_2} & V_{-\vec{G}_1} & W_{\vec{k}} & V_{\vec{G}_1} & V_{\vec{G}_2} \\ V_{-\vec{G}_3} & V_{-\vec{G}_2} & V_{-\vec{G}_1} & W_{\vec{k}+\vec{G}_1} & V_{-\vec{G}_2} \\ V_{-\vec{G}_4} & V_{-\vec{G}_3} & V_{-\vec{G}_2} & V_{-\vec{G}_1} & W_{\vec{k}+\vec{G}_2} \end{pmatrix} \begin{bmatrix} C_{\vec{k}-\vec{G}_2} \\ C_{\vec{k}-\vec{G}_1} \\ C_{\vec{k}} \\ C_{\vec{k}+\vec{G}_1} \\ C_{\vec{k}+\vec{G}_2} \end{bmatrix} \qquad (48)$$

This matrix one very special property. We know that V(r) is a real function so that from the Fourier series of (42) and the use of the Euler identity we require that $V_{\vec{G}_1} = V_{-\vec{G}_1}$. In other words, the matrix is (48) is *symmetric*.

As in the analysis of lattice waves, the physical stipulation that non-trivial solutions for the column matrix exist requires, in turn, that the matrix be non-invertible or, equivalently, that the determinant of the matrix must vanish. Since U is in every diagonal component of (48), the determinant operation will always lead to a polynomial equation in U that will have one solution for each order of the polynomial. And the order of the polynomial equals the dimension of the matrix, which also equals the number of G vectors included in the column matrix (including G = 0 for the "central" element).   So each of the solutions for U is in one-to-correspondence to the G vectors, as we deduced before !

(10) Nearly Free Electron Approximation (NFEA)

One might wonder about the utility of the above analysis when we still have not specified the most fundamental parameter of the Bloch model – the crystal wave vector. The answer lies in the fact that the electrons occupying the highest few bands in many crystalline materials,

particularly metals and semiconductors, are well suited to the Bloch model in that they are essentially free to move about the crystal. So a reasonable starting point is to assume that k is the "free" electron wave vector – the same as for the Fermi-gas model. We then apply (47) with the thought that there are a limited number of C_k and V_G components needed to describe the Bloch wave function, and include only those in the calculation. In essence, we are assume the electron is "nearly free" , and then we "turn on" the atomic potential energy as a small *perturbation*. Clearly the NFEA should fail for tightly-bound or, so-called, "core" electrons. This raises the need for other methods such as *tight binding* which are outside the scope of this text.[6]

Free-Electron Kinematics

A subtle aspect of the NFEA is that it starts by assuming the electrons are "free" *energetically*, but not *kinematically*.   In other words, the effect of the crystal potential on the energy eigenvalues is ignored, but its qualitative effect of aliasing the Bloch wavefunction is not. Another way to say it is that we set up the problem with the correct discretization of k but leave out the potential energy in the first pass.   Stated mathematically, we have

$$U = U_0(\vec{k} + \vec{G}) = \frac{\hbar^2 \left| \vec{k} + \vec{G} \right|^2}{2m} \quad .$$

The kinematics is simply to include all possible reciprocal lattice vectors in this expression, including $\vec{G} = 0$.

As with other subtle concepts in science and engineering, it is often best to explain by example. We start with a 1-dim lattice having period d, such that $\vec{G} \equiv G = 2\pi m / d$. By letting m be all possible integers including zero, we get the "band structure" shown in Fig. 5(a). The free electron curve is shown as the continuous parabola assuming d = 4 Ang. *To account for the crystal kinematics, we simply apply the Nyquist sampling criterion for sampling of the free electron by the lattice points.* Any wave of a given amplitude in the range $–k_N < k < k_N$ will be indistinguishable (i.e., ambiguous) by digital sampling from waves of the same amplitude at frequencies $k = 2mk_N$ where m is any integer. This is called the "aliasing" effect in the signal-processing field of electrical engineering[7]

Motivated by the aliasing effect, we divide up k space in Fig. 5(a) into sections of width $2k_N$ – called "Brillouin zones (BZs)". And to acknowledge the ambiguity effect, we translate each portion of the free-electron U-vs-k curve in a particular BZ back to the 1st BZ as shown schematically by the horizontal arrows. Once translated back, we need only displayed the U-vs-k curves in the 1st BZ as shown in the expanded view of Fig. 5(b).   In solid-state physics, this is called the "reduced-Brillouin-zone" scheme, or simply the "reduced zone scheme".

To emphasize how powerful the concept of "aliasing", we show in Fig. 6 how it works with electromagnetic waves being sampled in space by a lattice of scatterers. This was, in fact, the type of problem that L. Brillouin and others were working on originally, largely to explain the rich behavior of electromagnetic scattering by crystals of very high frequency electromagnetic waves called X-rays. Interestingly, this field has been rejuvenated in recent years with the advent of *photonic crystals* – Bravais-based three-dimensional lattices of

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[6] For a good reference on the tight-binding and other methods to solve Schrodinger equation for core electrons, see N. Ashcroft and D. Mermin, "Solid State Physics," (Hold, Rinehart, and Winston, New York, 1976).
[7] For a good review of digital sampling theory in electrical engineering, go to www.answers.com and type in "aliasing".

electromagnetic scatterers. Fig. 6 would be the kinematic starting point for the electromagnetic analog to the NFEA – the "nearly free photon" approximation.

Nearly-Free-Electron Energetics: Quantitative Analysis of the "Band Gap"

As with the kinematics, we demonstrate the energy solution in the NFEA with an example. Suppose we have a 1-dim lattice with only one significant potential-energy Fourier coefficient, $V_{\vec{G}_1} = V_{-\vec{G}_1} \equiv V_G$. Let's also suppose that the only two Ck coefficients are important in the Bloch wavefunction $C_{\vec{k}}$ and $C_{\vec{k}-\vec{G}_1}$. We expect this to be an accurate representation for k near the Nyquist value π/d, i..e., $C_{\vec{k}=\pi/d}$. This is because Bragg reflection will be strong at this point, creating a backward traveling component $C_{\vec{k}=\pi/d-2\pi/d}$.   In this case, we can consider only $C_{\vec{k}}$ and $C_{\vec{k}-\vec{G}_1}$ (which correspond to n = 1 and n = 2, respectively) and write (48) as

$$\begin{pmatrix} W_{\vec{k}\text{-}\vec{G}_1} & V_G \\ V_G & W_{\vec{k}} \end{pmatrix} \begin{bmatrix} C_{\vec{k}\text{-}\vec{G}_1} \\ C_{\vec{k}} \end{bmatrix} = 0$$

The vanishing of the determinant operation along with the definitions given before (48) lead to

$$\det \begin{Bmatrix} U_0(k\text{-}G_1) - U & V_G \\ V_G & U_0(k) - U \end{Bmatrix} = 0$$

Which leads to the second-order polynomial equation

$$U^2 - U[U_0(k) + U_0(k\text{-}G_1)] + U_0(k)U_0(k\text{-}G_1) - V_G^2 = 0 \tag{49}$$

Eqn (49) immediately soluble by the quadratic formula, yielding

$$U = (1/2)\left\{ U_0(k) + U_0(k\text{-}G_1) \pm \sqrt{\left[U_0(k) + U_0(k\text{-}G_1)\right]^2 - 4\left[U_0(k)U_0(k\text{-}G_1) - V_G^2\right]} \right\}$$

This fascinating expression is plotted in Fig. 7 for d = 4 Angstrom, $G_1 = 2\pi/d$, and V_G = 1.0 eV along with the two free-electron curves for V_G = 0. As before, the two bands are designated by n = 1 and n = 2. The n = 1 and n = 2 free-electron bands cross over as before. But in the presence of the V_G potential, they split equal-and-opposite about the cross-over point at k = k_N. This creates an energy "band gap" defined by

for k = π/d, n = 1: $U_k = U_{\pi/d} = U_0(k) - V_G$
and for k = π/d, n = 2: $U_{k\text{-}G1} = U_{-\pi/d} = U_0(k\text{-}G_1) + V_G$

In other words, the band-gap formed at k_N is exactly twice the perturbation V_G.
This is identical to solution of the well-known coupled-mode problem of classical mechanics, or to the degenerate-state perturbation problem of quantum mechanics.
Physically, the key point to remember is that the perturbation has its maximum effect at k = k_N, and creates a "band gap" that scales with the magnitude of the potential energy Fourier coefficient V_G. This makes sense intuitively – the stronger the potential energy, the greater the Bragg scattering !
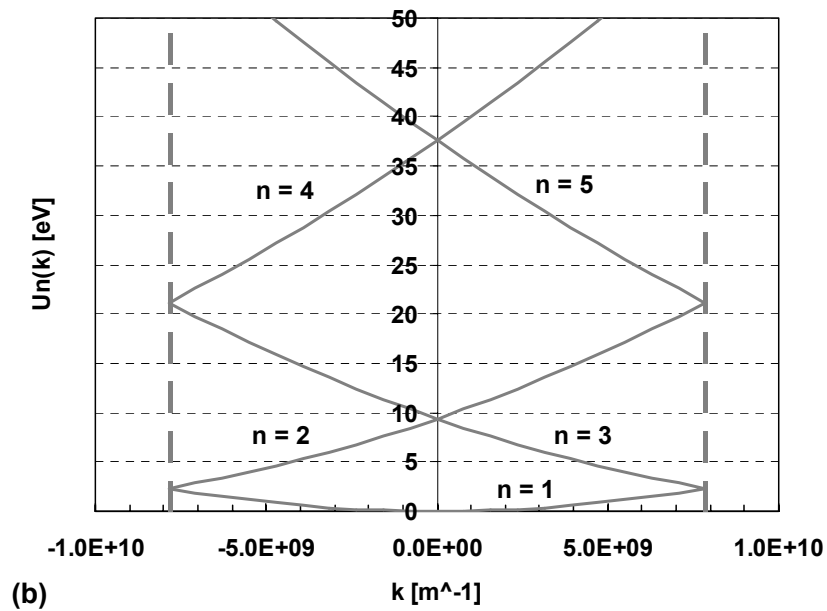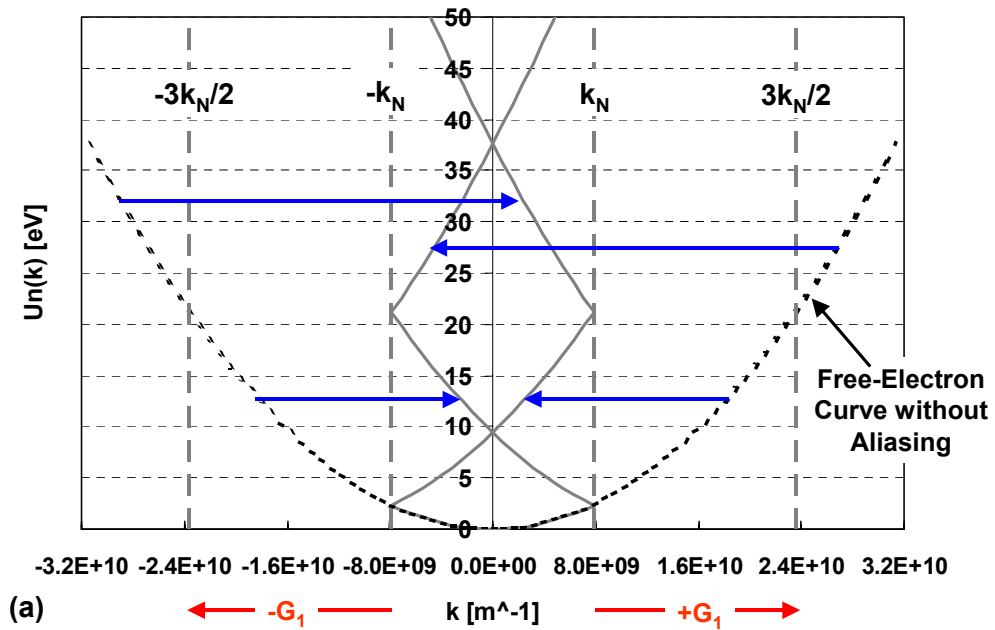
Fig. 5. Expansion of (a) in the 1st Brillouin zone (i.e., reduced zone scheme)
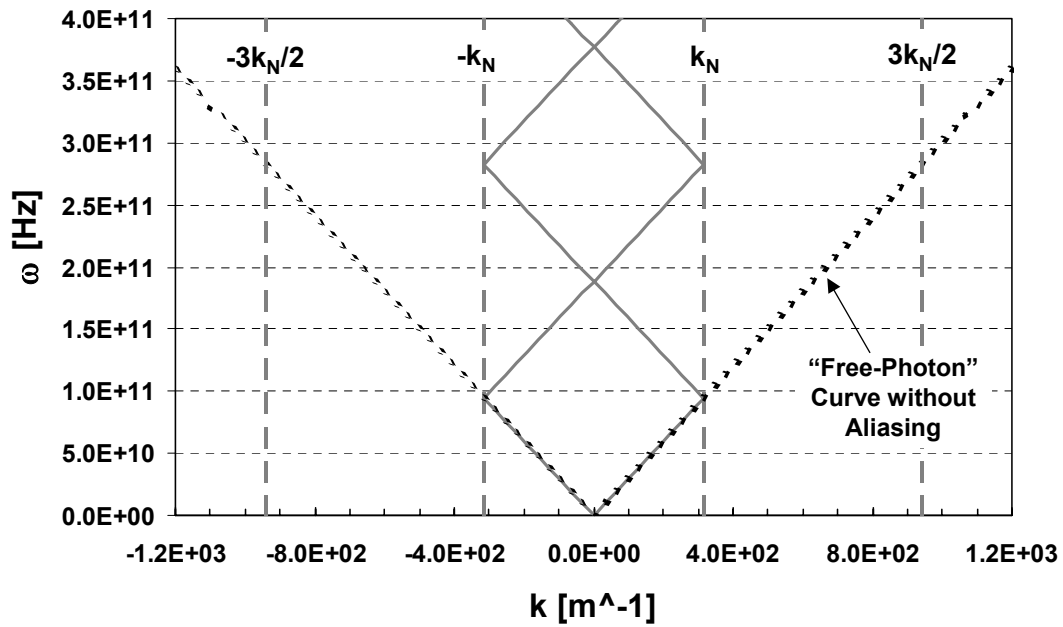
Fig. 6. Analogous plot to Fig. 5(a) for "free" electromagnetic waves being sampled in free space by an array of scatterers (or detectors) of period $d = 1$ cm, such that $k_N = \pi/d = 314$ m^{-1}. The free space "dispersion curve" is $\omega = |k|c$ where c is the speed of light in vacuum.
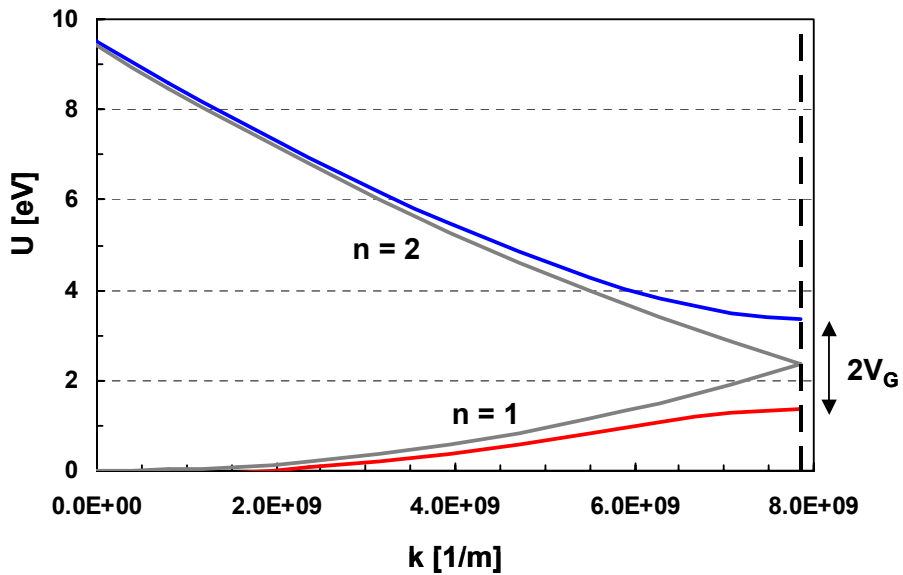

Fig.7. Energetics of NFEA in one-dimensional crystal around $k = k_N$