Electrons in a periodic potential

How electrons move in a periodic potential, like that of a semiconductor?

A semiconductor, like Si, consists of a regular array of atoms arranged in a crystal lattice. An essential property of a crystal is that it has *translational invariance*. This means that if we picked up the crystal and moved it by one lattice constant, it would look exactly the same as before we moved it. We can express this property mathematically,

$$U(x + a) = U(x)$$

where a is the *lattice constant* of a one-dimensional lattice.

If the potential is invariant under a translation, then the physical properties of any wave function that is a solution to the the Schroedinger equation must share the same properties. In particular, the probability density must be invariant:

$$\psi^*(x + a)\,\psi(x + a) = \psi^*(x)\,\psi(x)$$

$$P(x + a) = P(x)$$

The invariance of the probability density implies that the wave functions be of the general form

$$\psi(x + a) = \exp(i\gamma)\psi(x)$$

where is γ some constant. We can re-write γ as *ka*, where a is the lattice constant and k has the form of a wave number.
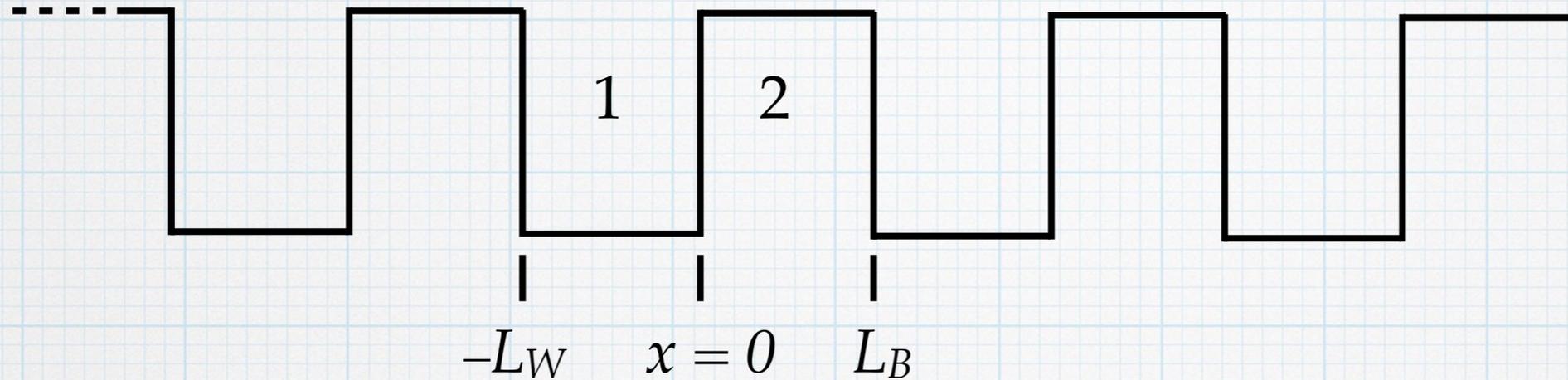
$$\psi(x + a) = \exp(ika)\psi(x)$$

This is known as *Bloch's theorem*. (This can be proven formally.)

The Bloch theorem can be put into an alternative form by defining a *Bloch lattice function, $u_k(x)$*, such that

$$\psi(x) = \exp(ikx)u_k(x)$$

The Bloch lattice functions are periodic with lattice constant *a*, $u_k(x+a)=u_k(x)$. You can see that this form of the wave function also satisfies the invariance requirement for the probability density.

One-dimensional crystal (Kronig-Penney problem)

1: free electron

$$\psi_1(x) = Ae^{i\beta x} + Be^{-i\beta x}$$

$$\beta = \sqrt{\frac{2mE}{\hbar^2}}$$

2: electron inside
   a barrier

$$\psi_2(x) = Ce^{\alpha x} + Be^{-\alpha x}$$

$$\alpha = \sqrt{\frac{2m(U_o - E)}{\hbar^2}}$$

Using connection rules at $x = 0$:

$$A + B = C + D$$

$$i\beta A - i\beta B = \alpha C - \alpha D$$

This give us two equations in four unknowns. To get more relationship, we make use of Bloch's theorem, which says that in a periodic potential

$$\psi(x + a) = \exp(ika)\,\psi(x)$$

Applying this at $x = L_B$ and $x = -L_w$ (which differ by one lattice constant)

$$\psi_2(L_B) = e^{ika}\psi_1(-L_W)$$

$$Ce^{\alpha L_B} + De^{-\alpha L_B} = e^{ika}\left(Ae^{-i\beta L_W} + Be^{i\beta L_W}\right)$$

Now we have three equations in the three unknowns. To get a fourth relationship, we note that the Bloch relationship should also apply to the derivative of the wave function.

$$\frac{\partial \psi_2}{\partial x}\bigg|_{x=L_B} = e^{ika} \frac{\partial \psi_1}{\partial x}\bigg|_{x=-L_W}$$

$$\alpha C e^{\alpha L_B} - \alpha D e^{-\alpha L_B} = e^{ika} \left(i\beta A e^{-i\beta L_W} - i\beta B e^{i\beta L_W} \right)$$

This give us four equations in the four unknown coefficients. Writing these in matrix form:

$$\begin{bmatrix} 1 & 1 & -1 & -1 \\ i\beta & -i\beta & -\alpha & \alpha \\ e^{-i\beta L_W} e^{ika} & e^{i\beta L_W} e^{ika} & -e^{\alpha L_B} & e^{-\alpha L_B} \\ i\beta e^{-i\beta L_W} e^{ika} & -i\beta e^{i\beta L_W} e^{ika} & -\alpha e^{\alpha L_B} & \alpha e^{-\alpha L_B} \end{bmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = 0$$
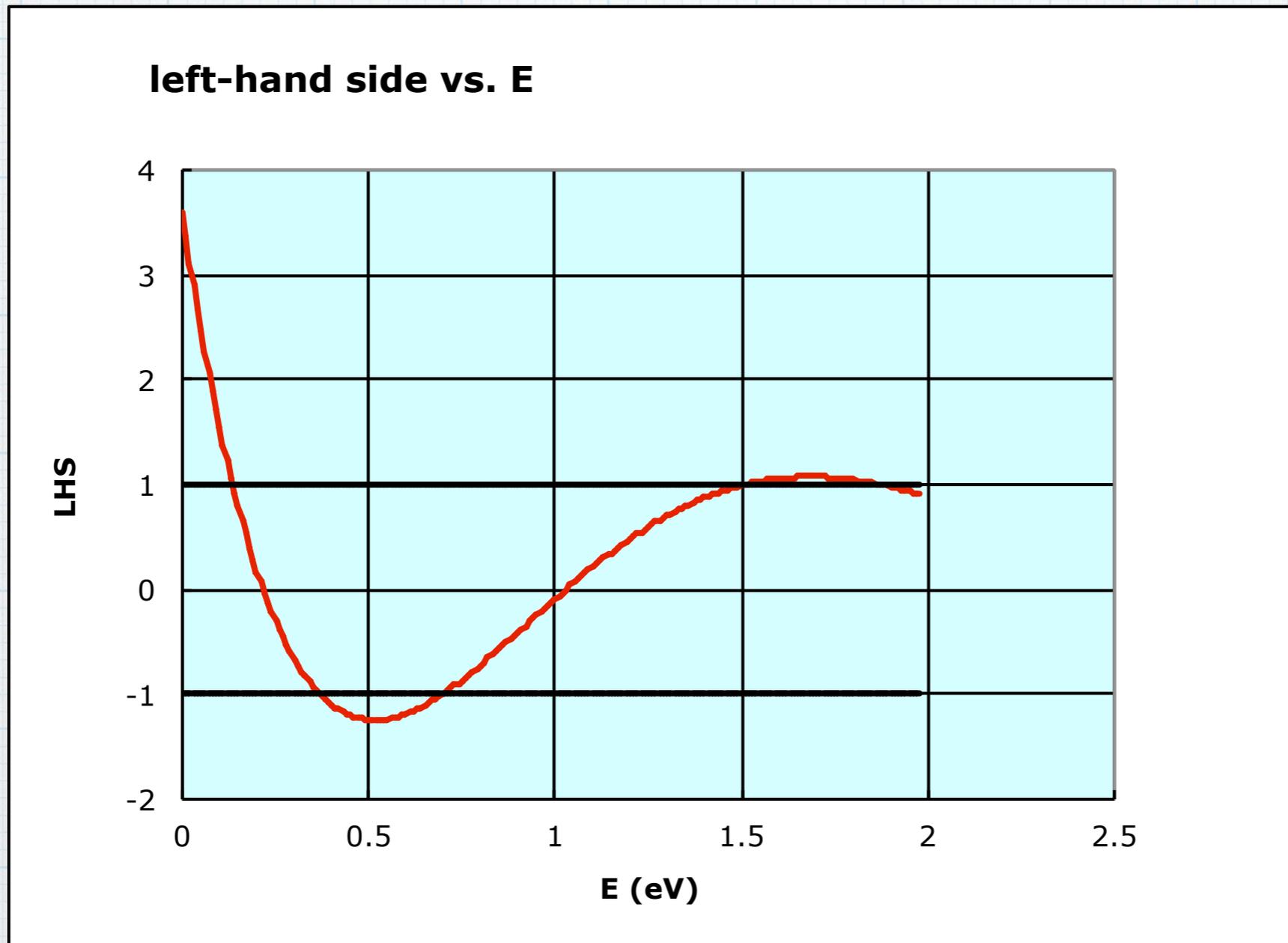
We see that the four equations form a homogeneous set. The only way in which a unique solution can be obtained is if the determinant of the matrix is zero, a process that leads to a characteristic equation that can be solved to find the relationship between the crystal wave number k and the energy of the electron. Generally, this information is of more value than the form of the actual wave functions.

Grunting through algebra needed to compute the determinant and set it to zero leads to the *characteristic equation*

$$\frac{\alpha^2 - \beta^2}{2\alpha\beta} \sinh \alpha L_B \sin \beta L_W - \cosh \alpha L_B \cos \beta L_W = \cos ka$$

Everything on the left depends on energy (through α and β). The right side depends on k - crystal wave number. This is, in a sense, and E-k relationship – albeit an awkward one.

Below is a plot of the LHS versus E for an electron in a periodic potential with U_o = 2 eV, L_w = 0.9 nm and L_B = 0.1 (a = 1 nm).

left-hand side vs. E

In looking at the plot, we see that $|f| > 1$ in some regions. This means that there are ranges of k where there are no solutions!

So we have *bands* of regions of where there are solutions and bands where there are no solutions (forbidden bands). This is the origin of the energy bands that show up in crystal structures.

One way to visualize this is to make a plot of E vs. k, which can be compared to the free-electron case.

$$E = \frac{\hbar^2 \beta^2}{2m}$$

To make the E-k diagram, you might imagine picking a value of k and then computing the corresponding value of E using the characteristics equation. However, it works better to go the other way: go through the various values of E and then compute the corresponding k.

$$k = \pm\frac{1}{a} \arccos\left[f\left(E\right)\right]$$

Below is a plot of E versus k for an electron in a periodic potential with $U_o = 2$ eV, $L_w = 0.9$ nm and $L_B = 0.1$ ($a = 1$ nm).

Band diagram