## Lecture 27 Highlights Phys 402

## Electrons in a Periodic Potential: The Kronig-Penney Model

There is a big difference between metals and insulators, as illustrated <u>here</u>. What accounts for this difference? We can understand the difference by considering the solution to the one-dimensional Schrodinger equation for a "free" electron in a metal that is perturbed by the periodic attraction to the ion lattice.

A metal is made up of atoms that give up one or more electrons that become itinerant, meaning that they can roam all over the crystal. The resulting positive ions remain fixed in place (except for small oscillations about their equilibrium positions), and the electrons are free to roam the metal in plane-wave-like eigenstates:  $\exp[\pm i\vec{k} \cdot \vec{r}]$ . Electrons in a free-electron metal have extended states that cover the entire crystal. One can think of the periodic attractive interaction between the electrons and the ion cores as a perturbative interaction to the free-electron model. We shall set up and solve a model for the periodic potential and see what new physics results.



The Kronig-Penney model replaces the Coulomb attractive potential between a single electron and the regular array of positive ionic cores with a periodic square-well potential. We will work in one dimension since it is simple and illustrates the new physics just as well as the 3D case. We take the ions to have a periodic spacing a and the widths of their negative potential wells to be b < a. The Kronig-Penney model potential is:

$$V(x) = \begin{cases} 0, & \text{for } 0 < x < a - b \\ -V_0, & \text{for } a - b < x < a \\ V(x + a) \end{cases}$$

This last line is the periodicity constraint, the potential is identical when translated forward or backward by the repeat distance a, or any integer multiple of that distance.

The Schrodinger equation can be solved in the two segments of the unit cell as;

$$\psi(x) = Ae^{i\alpha x} + Be^{-i\alpha x}, \text{ for } 0 < x < a - b, \text{ where } \alpha = \sqrt{\frac{2mE}{\hbar^2}}, \text{ and}$$
$$\psi(x) = Ce^{i\beta x} + De^{-i\beta x}, \text{ for } a - b < x < a, \text{ where } \beta = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$$

where we are using "running wave" solutions (E > 0) for later use in enforcing periodic boundary conditions. We now need to find the constants A, B, C, D. First we can impose

continuity of the wavefunction and its first derivative with respect to x at the interface point x = 0. This yields two equations:

A + B = C + D,

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

For the other two equations we can use the periodicity constraint imposed by the potential: V(x + a) = V(x). Naively we would like to say that  $\psi(x + a) = \psi(x)$ , reflecting the periodicity of the potential. However, this is incorrect, and only captures a small fraction of the possible solutions to the TISE with a periodic potential.

We then went on a "subroutine" to derive the nature of the solution for  $\psi(x)$  that correctly captures the effect of the periodic potential. This is a derivation of Bloch's theorem. First we discussed the translation operator  $\hat{T}$ . It has the effect of translating a wavefunction forward in x by a specified amount:  $\hat{T}(a)\psi(x) = \psi(x-a)$ . We showed that it can be written in terms of the momentum operator as  $\hat{T}(a) = e^{-ia\hat{p}/\hbar}$ . Linear momentum is said to be the generator of translations.  $\hat{T}$  is a unitary operator satisfying  $\hat{T}(a)^{\dagger}\hat{T}(a) = 1$ , so that the inverse is equal to the adjoint:  $\hat{T}(a)^{-1} = \hat{T}(-a) = \hat{T}(a)^{\dagger}$ . Operators  $\hat{O}$  are defined to transform under translation as:  $\hat{O}' = \hat{T}^{\dagger} \hat{O} \hat{T}$ . The effect of translation on the position operator is  $\hat{T}(a)^{\dagger}\hat{x}\hat{T}(a) = \hat{x} + a$ , and on the momentum operator  $\hat{T}(a)^{\dagger}\hat{p}\hat{T}(a) = \hat{p}$ . Hence for any operator:  $\hat{T}(a)^{\dagger}\hat{Q}(\hat{x},\hat{p})\hat{T}(a) = \hat{Q}(\hat{x}+a,\hat{p})$ . A Hamiltonian operator is said to be translationally invariant if it satisfies  $\hat{T}(a)^{\dagger}\hat{\mathcal{H}}(\hat{x},\hat{p})\hat{T}(a) = \hat{\mathcal{H}}(\hat{x}+a,\hat{p}) = \hat{\mathcal{H}}(\hat{x},\hat{p})$ . This is the case for the Kronig-Penney model because V(x + a) = V(x). Thus, using the unitary property of the translation operator, the Kronig-Penney Hamiltonian satisfies  $\widehat{\mathcal{H}}(\hat{x}, \hat{p})\widehat{T}(a) = \widehat{T}(a)\widehat{\mathcal{H}}(\hat{x}, \hat{p})$ , or in other words, the Hamiltonian and translation operator commute:  $[\hat{\mathcal{H}}(\hat{x}, \hat{p}), \hat{T}(a)] = 0$ . If this is so, then there exist a complete set of simultaneous eigenfunctions for these two operators, and call the simultaneous eigenfunctions  $\psi(x)$ . The eigenvalue equations are  $\widehat{\mathcal{H}}(\widehat{x},\widehat{p})\psi(x) = E\psi(x)$  (which is the TISE that we are trying to solve), and  $\widehat{T}(a)\psi(x) = \widehat{\mathcal{H}}(\widehat{x},\widehat{p})\psi(x)$  $\lambda \psi(x)$ , where  $\lambda$  is the eigenvalue of the translation operator. Because  $\hat{T}(a)$  is a unitary operator, its eigenvalues are of unit modulus, and can be written as  $\lambda = e^{i\phi}$ , where  $\phi$  is real. We shall choose  $\phi = -qa$ , where q is called the crystal momentum, and will be determined later. Hence we have  $\hat{T}(a)\psi(x) = e^{-iqa}\psi(x) = \psi(x-a)$ .

Now we can finally propose Bloch's theorem. Write the wavefunction  $\psi(x)$  in the following odd form:  $\psi(x) \equiv e^{iqx} u(x)$ , where u(x) is an unknown function, for now. Now substitute this ansatz for  $\psi(x)$  into the above equation:  $e^{-iqa} \psi(x) = \psi(x - a)$ . The result is that u(x + a) = u(x). Hence the function u(x) must have the same periodicity as the potential. In other words, Bloch's theorem states that the solutions to the TISE are  $\psi(x) \equiv e^{iqx} u(x)$ , which is a free-particle eigenstate multiplied by a periodic function in x, with period a. Note that this is very different from the (incomplete) naïve statement that  $\psi(x + a) = \psi(x)$ .

Here is a very brief alternative statement. For differential equations that have periodic coefficients like the Schrodinger equation for the electron in this periodic potential, one can make a specific ansatz for the solution. The Bloch theorem states that the solution to the Schrodinger equation can be written in the form  $\psi(x) = e^{iqx}u(x)$ , where q is a real number and the function u(x) has the same periodicity as the potential, in this case u(x + a) = u(x). Bloch's theorem (proven in these notes) is a special case of Floquet's theorem. Note that both q and u(x) are unknown at this time.

Now back to the solution of the Kronig-Penney model. Writing the solution to the Schrodinger equation in the Bloch form, we can solve for the periodic function as  $u(x) = e^{-iqx}\psi(x)$ , which becomes:

$$u(x) = \begin{cases} Ae^{i(\alpha-q)x} + Be^{-i(\alpha+q)x} & \text{for } 0 < x < a - b \\ Ce^{i(\beta-q)x} + De^{-i(\beta+q)x} & \text{for } a - b < x < a \end{cases}$$

We then impose the periodicity constraint on u(x) by insisting that this function and its first derivative are periodic on either end of the unit cell, namely:

$$u(-b) = u(a - b), \text{ and}$$
$$\frac{du}{dx}|_{x=-b} = \frac{du}{dx}|_{x=a-b}.$$

This yields two more equations involving the coefficients A, B, C, D. We end up with 4 linear equations in 4 unknowns. The 4 equations can be summarized in matrix form as

$$\overline{\vec{M}}\vec{K} = \vec{0}$$
, where  $\vec{K} = \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix}$ . To get a non-trivial solution to this equation we have to insist

that the matrix  $\overline{\overline{M}}$  be non-invertible (otherwise the solution would be  $\vec{K} = \vec{0}$ ). This is guaranteed if the determinant of  $\overline{\overline{M}}$  is equal to zero. The result (after much algebra) is the following algebraic equation:

$$\frac{-\beta^2 - \alpha^2}{2\alpha\beta}\sin(\beta b)\sin[\alpha(a-b)] + \cos(\beta b)\cos[\alpha(a-b)] = \cos(qa)$$

We can simplify this equation by taking the limit of very deep and narrow square wells, in other words  $V_0 \rightarrow \infty$  and  $b \rightarrow 0$  such that  $V_0 b = constant$ , or in other words  $\beta^2 b = constant$ . In this limit  $\beta b$  becomes a small parameter such that  $\sin \beta b \cong \beta b$  and  $\cos \beta b \cong 1$ , and  $a - b \cong a$  and  $\beta^2 \gg \alpha^2$ . With this approximation, the equation becomes:  $\frac{-\beta^2 ba}{2} \frac{\sin(\alpha a)}{\alpha a} + \cos(\alpha a) = \cos(qa).$ Define  $P \equiv \frac{\beta^2 ba}{2}$  as the dimensionless strength of the potential. One then has the following

Define  $P \equiv \frac{\beta^2 ba}{2}$  as the dimensionless strength of the potential. One then has the following equation for the eigen-energies of the electrons in this periodic potential as a function of the crystal momentum q:  $-P \frac{\sin[\alpha a]}{\alpha a} + \cos(\alpha a) = \cos(qa)$ . (1)

But what are the values of the crystal momentum q? We can find them by also imposing periodic boundary conditions on the wavefunction (note that this is a distinctly different condition from the periodicity of the potential). In other words, we take the ion lattice to be a long string involving  $N \gg 1$  ions that wraps back on itself to become a large circle. (Note that this condition comes with the assumption made at the outset of the calculation that the solutions are of the form of travelling waves,  $\psi(x) \sim e^{i\alpha x}$ .) Under these circumstance we can demand that  $\psi(x + Na) = \psi(x)$ . Using the Block form for  $\psi(x) = e^{iqx}u(x)$ , and the periodicity of u(x), we conclude that  $e^{iqNa} = 1$ , or in other words  $q = \frac{2\pi n}{Na}$ , with n being any integer. Since N is so large, these values of q are very close together. Note that as n increases from 0 to N the value of  $\cos(qa)$  cycles from +1 to -1 and then back to +1. A further increase of n just finds the same solutions over again. Hence there are just N unique states described by the wavefunction satisfying periodic boundary conditions on an N-ion lattice. Now to solve Eq. (1). Recall that *P* is a measure of the strength of the periodic potential created by the positive ions. Note that if P = 0 (no periodic potential) one has  $\alpha a = qa$ , or that  $E = \frac{\hbar^2 q^2}{2m}$ , the properties of a free particle. If we take the case of P = 10 (a strong periodic potential), then the situation is as shown in the <u>figure</u> below.



Note that there are ranges of  $\alpha a$  (i.e. energy) for which there is NO solution to the equation! This means that there are broad ranges of energy in which there are no propagating wave solutions to the Schrödinger equation. These are called energy gaps, and they play a prominent role in determining whether a material is an insulator or metal.

From the periodic boundary condition we see that there are exactly N states in each band (2N when we include spin). Thus a metal with an odd valence (1, 3, 5, ...) will fill up half of a band with electrons. In this case there will be un-occupied states at energies infinitesmally higher than the Fermi energy, allowing the material to accept energy and create conduction. On the other hand materials with an even valance (2, 4, 6, ...) will exactly fill one or more bands, leading to a situation where the next available unoccupied energy state is very far above the Fermi energy (compared to the spacing between the states in an energy band). These materials will be insulators. Further discussion of even/odd valence in 3D materials is <u>posted</u> on the class web site.