Day 10: Friday – 50 minutes

**Band Structure of the (Nearly) Infinite Chain**

In the lab you have explored the evolution of the energy levels and wave functions for one-dimensional chains of finite-depth square wells. You observed that as more and more atoms (wells) are added to the chain, bands of allowed energies develop around the energy levels of the bound states of the single atom (square well). There was one band for each of the original levels and there were as many states within each band as there were atoms in the chain.

To extend these ideas to real crystals, we have to consider very long chains since the number of atoms is huge (of order $10^{22}$ atoms per cubic centimeter in a real three-dimensional crystal). For simplicity, we will consider only one-dimensional “solids” since most of the important physics can be seen without the geometric complexity of the more realistic three-dimensional case.

There are two general approaches that theoretical physicists use to find the energy eigenvalues for a solid. The first approach is to assume a potential that is periodic in space and solve the Schrödinger equation for this potential. If the assumed potential consists of a one-dimensional string of square wells, we have the so-called Kronig-Penny model. This is simply an extension of the models of chains of a few square wells that we have been considering. Again, it is not possible to obtain closed form algebraic expressions for the energies – the eigenvalues are solutions of transcendental equations and have to be obtained numerically. When this is done, the result is, as expected, that the allowed energies fall into bands separated by “gaps,” i.e. ranges of energy in which there are no energy eigenvalues.

We are not going to analyze the Kronig-Penny model in detail. Instead, we will follow the second approach, one that incorporates the idea that the elements of the chain are actually atoms about which we already have quite a bit of information. The method
emphasizes the interactions between neighboring atoms rather than the periodicity of the structure, but we will see that we come out with the same general picture of the electronic structure of a solid. We will use some of the tools of the “bra” and “ket” language that was used in PH425.

Let's start with the Schrödinger equation for a particle subject to the periodic potential \( V(x) \) of the chain:

\[
\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = E \psi(x)
\]

The bracket on the left-hand side is the Hamiltonian (energy) operator and the Schrödinger equation is just the eigenvalue equation for the energy: \( H\psi(x) = E\psi(x) \). If we insert a string of square wells for \( V(x) \) and solve for \( E \), we are just doing the Kronig-Penny model. Now, however, we prefer to represent the state of the system by a state vector ket \( |\psi\rangle \), and the Schrödinger equation is, as we saw in PH425, \( H|\psi\rangle = E|\psi\rangle \).

But what is the basis in which we represent the state vector \( |\psi\rangle \)? This is where the central idea of this approach comes in. Let's assume that our chain consists of \( N \) hydrogen atoms and take into consideration that, at least in principle, we have already solved the Schrödinger equation for the isolated atoms. The eigenstates would be the states we usually call 1s, 2s, 2p, etc. (The method will apply to atoms of any element, but to keep it simple, let's think about hydrogen.) The (1s) ground state of the \( n^{th} \) atom in the chain can be represented by a state vector \( |1s,n\rangle \). For the time being, we will restrict our consideration to just the ground state, so we might as well use the simpler notation for the state vector of the atom, \( |n\rangle \). The idea is to use the atomic state vectors as the basis vectors for a representation of the whole chain, i.e.

\[
|\psi\rangle = \sum_{n=1}^{N} c_n |n\rangle.
\]

This will work because (i) the atomic state vectors are normalized \( \langle n|n\rangle = 1 \) and (ii) state vectors associated with different atoms are, to a very good approximation,
orthogonal \( \langle n | m \rangle = 0 \) if \( n \neq m \). The physical explanation of this that there is almost no overlap of the atomic orbitals associated with different atoms. Thus we can use the atomic state vectors as an orthonormal basis set. (Recall how we used the orthonormal set \( |+\rangle \) and \( |-\rangle \) to represent the state vector of a spin-1/2 particle in a magnetic field: \( |\psi\rangle = c_+ |+\rangle + c_- |_-\rangle \).) This representation of the electronic state of a solid is called the "Linear Combination of Atomic Orbitals" (LCAO) by theoretical physicists and chemists.

Substitute the state vector into the Schrödinger equation \( H|\psi\rangle = E|\psi\rangle \):

\[
H \sum_{n=1}^{N} c_n |n\rangle = E \sum_{n=1}^{N} c_n |n\rangle \quad \Rightarrow \quad \sum_{n=1}^{N} c_n H |n\rangle = \sum_{n=1}^{N} c_n E |n\rangle .
\]

Now, the trick is to project the Schrödinger equation onto a particular atomic state vector, say that for atom \( p \) using the bra \( \langle p | \):

\[
\sum_{n=1}^{N} c_n \langle p | H |n\rangle = E \sum_{n=1}^{N} c_n \langle p | |n\rangle = E c_p .
\]

The bracket in the left-hand term is a matrix element of the Hamiltonian \( H \) and that in the second term is an inner product that vanishes unless \( p = n \). It will be convenient to make the definitions:

\[
\alpha = \langle n | H |n\rangle \quad \text{for any} \quad n . \quad \text{(These will all be equal since the atoms are identical.)}
\]

\[
\beta = \langle n | H |m\rangle \quad \text{for} \quad n \neq m . \quad \text{We will make the nearest-neighbor approximation and assume that} \quad \beta = 0 \quad \text{unless} \quad m = n \pm 1 .
\]

Since \( p \) could be any number between 1 and \( N \), the equation above leads to a set of \( N \) linear equations for the \( N \) coefficients \( c_n \). If \( N \) is huge, a "brute force" approach to this problems would require us to diagonalize a "huge x huge" matrix. Fortunately, life is made much simpler by the fact that in the nearest neighbor approximation, most of the possible terms in these equations are zero. A typical equation, valid anywhere except at the ends of the chain would be

\[
\beta c_{p-1} + \alpha c_p + \beta c_{p+1} = E c_p .
\]
\begin{align*}
\beta c_{p-1} + (\alpha - E)c_p + \beta c_{p+1} &= 0. & \quad \ast
\end{align*}

We have seen this sort of thing before. Recall the discussion of the monatomic linear chain of masses connected by spring constants \( \kappa \) for which we assumed wave functions of the form \( \psi_n = A_n e^{i\omega t} \). Substitution into Newton's second law gave us

\begin{align*}
m\dot{\psi}_n &= -m\omega^2 \psi_n = \kappa (\psi_{n-1} - 2\psi_n + \psi_{n+1}) \\
\kappa A_{n-1} - (2\kappa - m\omega^2)A_n + \kappa A_{n+1} &= 0. & \quad \ast\ast
\end{align*}

Note the similarity between the starred equations. We can take the same approach with the quantum problem as we did with the masses and springs, i.e. assume wave-like solutions of the form \( c_p = e^{i(\kappa a - \delta)} \) and substitute in equation (\ast) to get

\begin{align*}
\beta e^{i(\kappa (p-1)a - \delta)} + (\alpha - E)e^{i(\kappa pa - \delta)} + e^{i(\kappa (p+1)a - \delta)} &= 0 \\
\beta e^{-i\kappa a} + (\alpha - E) + \beta e^{i\kappa a} &= 0.
\end{align*}

Solve for \( E \) to get the band energy function \( E(k) \):

\[ E(k) = \alpha + 2\beta \cos(ka) \]

Recalling that for phonons, \( E(k) = \hbar \omega(k) \), we can see that the band function is essentially a dispersion relation for the electrons.
Notice that $E(k)$ is periodic in $k$-space with period $2\pi/a$ so that the first Brillouin zone extends from $-\pi/a$ to $+\pi/a$. The near-neighbor matrix element $\beta$ is usually negative giving a minimum energy at $k = 0$ and maxima at $k = \pm \pi/a$.

**Boundary conditions and allowed values of $k$**

The band function gives us the relation between energy and $k$, but we still have to apply the boundary conditions to determine what values of $k$ are allowed. For a solid containing a huge number of atoms, it is a better idea to use periodic boundary conditions than fixed. This allows for the possibility of propagating electron waves and tends to reduce the importance of the boundaries, that is, the surface of the crystal. The periodic boundary condition amounts to writing: $c_{n=0} = c_{n=N}$ or $e^{iNka} = 1$. This implies $Nka = q \frac{2\pi}{N}$ where $q$ is an integer. Thus the allowed values of the wave vector $k$ are $k_q = q \frac{2\pi}{Na}$ where $q$ runs from $-N/2$ to $+N/2$. This allows for running deBroglie waves in both directions along the chain. (Including the state $q = 0$, this would seem to add up to $N + 1$ states, but because of the periodicity of the band function, we have to remember that the state at $k = -\pi/a$ is the same as that at $k = +\pi/a$ so there are exactly $N$ distinct states for our $N$-atom chain.)

**Multiple Bands from Multiple Atomic Levels**

We derived a band function from a set of single levels assigned to each atom (presumed to be the 1s ground state). To include the effects of higher energy atomic states, state vectors representing these states would have to be included in the basis set. The basis would include kets like $|1s, n\rangle$ and $|2s, n\rangle$, for example, if we used two atomic levels per atom. The result of doing this would be the formation of additional energy bands with band functions (dispersion relations) similar to the one we calculated. The band widths could be different because the near-neighbor matrix elements ($\beta$) would, in general, be different for each band. As long as the $\beta$-values are not so large
that bands begin to overlap one another, the resulting band structure would be a series of branches of $E(k)$ curves defining bands of allowed energies, separated by gaps of forbidden energies. Here is an illustration for two atomic levels per atom at energies $\alpha = 0$ and 10:

![Energy band structure illustration](image)

The upper band has a $\beta$-value and corresponding width that is twice that of the lower band. The allowed $k$-values are the same as before, $k_q = q \frac{2\pi}{Na}$, but now there are two possible energy values (energy eigenvalues) for each value of $k$. (This is reminiscent of the acoustic and optical branches of the phonon dispersion relation for the diatomic chain – two frequencies per $k$-value.) In discussing the energy band structure of real materials, the bands are often labeled by the atomic states from which they are derived. One speaks of the “1s band,” the “3d band,” etc.