

Topic 9-1: Bloch Theorem and the Central Equation
Kittel Pages: 167-174

Summary: We begin here by postulating Bloch's theorems which develop the form of the wavefunction in a periodic solid. We then show that the second postulate of Bloch's theorem can be derived from the first. As we continue to prove Bloch's first theorem we also derive the central equation as a result of the process this proof takes. Finally, we introduce the vanishing potential and a physical interpretation of Bloch's theorem.

- We started with the free electron model, which assumed an infinite square well potential
- However, in reality the bottom of the well isn't flat; the nuclei create potential wells that are *periodic* within the box
- Now we will consider a periodic solid through Bloch's theorem
 - **Bloch's theorem is just a way to describe the wavefunction for periodic solids**
 - Bloch's theorem constrains ψ and thus E for periodic solids
- Bloch's theorem contains two postulates
 - **1)** Because we have a solid that is periodic at the atomic scale, we get a traveling wave solution ($e^{i\vec{k}\cdot\vec{r}}$) for ψ that is *modulated* by the translational symmetry of the lattice ($u_{\vec{k}}$)
 - $\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}$ where $u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{T})$
 - Wavefunction reflects the symmetry of the lattice via $u_{\vec{k}}$
 - Traveling wave solution suggests that we must have invoked periodic boundary conditions for the macroscopic solid. Indeed we will when we prove Bloch-1.
 - **2)** Alternatively, we can describe the wavefunction a $\psi_{\vec{k}}(\vec{r} + \vec{T}) = c\psi_{\vec{k}}(\vec{r})$. Which is to say, in a slightly different way, the wavefunction at $r+T$ is very related to the wavefunction at r .
 - c is a modulation term, we'll explore in detail below

Proof that Bloch-2 falls out of Bloch-1: We're going to start with the Bloch-1 postulate above, and then....

- By replacing r with $r+T$, we can write the wavefunction as:

$$\psi_{\vec{k}}(\vec{r} + \vec{T}) = e^{i\vec{k}\cdot(\vec{r}+\vec{T})}u_{\vec{k}}(\vec{r} + \vec{T}) \quad [1]$$

- But we have defined $u_{\vec{k}}$ to be periodic in T : $u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{T})$

$$u_{\vec{k}}(\vec{r}) = \frac{\psi_{\vec{k}}(\vec{r})}{e^{i\vec{k}\cdot\vec{r}}} \quad [2]$$

- Combining these expressions together, we obtain:

$$\psi_{\vec{k}}(\vec{r} + \vec{T}) = e^{i\vec{k}\cdot(\vec{r}+\vec{T})} \frac{\psi_{\vec{k}}(\vec{r})}{e^{i\vec{k}\cdot\vec{r}}} \quad [3]$$

- Since some of the exponential terms cancel in the above we end up with

$$\psi_{\vec{k}}(\vec{r} + \vec{T}) = e^{i\vec{k}\cdot\vec{T}}\psi_{\vec{k}}(\vec{r}) \quad [4]$$

- But wait, this is Bloch-2! Cool, now we know what c must be. From cell to cell, the wavefunction varies by a phase shift given by $e^{i\vec{k}\cdot\vec{T}}$
- All Bloch's theorem does is connect the wavefunction of the solid to terms of the underlying translational symmetry

Proof of Bloch-1: Now let's prove that $\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}$

- To get this done, we're going to first have to convert the Schrodinger equation into a form suitable for periodic samples.

Development of Fourier series expressions for ψ and V

- The potential is periodic so we can write it as a Fourier series $V(\vec{r}) = \sum_{\vec{G}} v_G e^{i\vec{G}\cdot\vec{r}}$ where we sum over the reciprocal lattice since the periodicity of the potential is on the atomic scale
- As this is a proof, we're not going to assume that the wavefunction has a periodicity on the length scale of the unit cell.
- However, we will invoke periodic boundary conditions. As such, the wavefunction needs to repeat itself every length L , such that $\psi(x)=\psi(x+L)$
- Can write this as a Fourier series as well
- $\psi = \sum_{\vec{k}} c_k e^{i\vec{k}x}$ where $k = \frac{2\pi n}{L}$ and n is an integer
 - k needs to involve waves that are periodic with L not a (This is a critical and often overlooked subtlety)
- Remember we are working on two different length scales:

- Microscopic scale periodicity in the crystal – translational symmetry \vec{T}
- Periodicity at the macroscopic scale - periodic boundary conditions in L

Insertion of Fourier series expressions for ψ and V into TISE

- Take our Fourier series expansions for ψ and V and plug them into the time independent Schrodinger equation (TISE) to solve for energy
- Using the one electron approximation we get

$$\frac{1}{2m} (-i\hbar\nabla^2\psi) + \sum_{\vec{G}} v_G e^{i\vec{G}\cdot\vec{r}} \psi = E\psi \quad [5]$$

- After taking some derivatives we end up with

$$\sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} c_k e^{i\vec{k}\cdot\vec{r}} + \sum_{\vec{G}} \sum_{\vec{k}} c_k v_G e^{i(\vec{k}+\vec{G})\cdot\vec{r}} = E \sum_{\vec{k}} c_k e^{i\vec{k}\cdot\vec{r}} \quad [6]$$

Trickery to simplify the periodic version of the TISE

- Can take advantage of the orthogonality of the wave vectors
 - Generally, $\int_0^L dx e^{-ik'x} e^{ikx} = L\delta_{k,k'}$ where k and k' are different wave vectors
 - Only for $k = k'$ do we get a nonzero value for this integral
 - If we multiply our TISE by $e^{-ik'\cdot\vec{r}}$ and then take the integral with respect to r the sums drop out due to the aforementioned orthogonality

$$\int [\sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} c_k e^{i\vec{k}\cdot\vec{r}} e^{-ik'\cdot\vec{r}} + \sum_{\vec{G}} \sum_{\vec{k}} c_k v_G e^{i(\vec{k}+\vec{G})\cdot\vec{r}} e^{-ik'\cdot\vec{r}}] d\vec{r} = \int E \sum_{\vec{k}} c_k e^{i\vec{k}\cdot\vec{r}} e^{-ik'\cdot\vec{r}} d\vec{r} \quad [7]$$

- From evaluating this we get:

$$\frac{\hbar^2 k^2}{2m} c_k + \sum_{\vec{G}} v_G c_{k-G} = E c_k \quad [8]$$

- Drop the prime on the k because we are no longer summing in k
- This is the **central equation**. Very nice. Now we're doing the science.
- *Central equation is the TISE expressed in Fourier series form for a periodic structure.* It may not look like the TISE, since the ψ is no longer obviously present. However, remember that ψ is now defined in terms of c_k terms: $\psi = \sum_{\vec{k}} c_k e^{i\vec{k}\cdot\vec{r}}$, which are in there!

Extracting out the wave function's form from the central equation in a rather delicate way:

- For a particular k and c_k to solve for the energy the only other coefficients we need to know are those shifted by \vec{G} : the other c_{k-G} within the $\sum_{\vec{G}} v_G c_{k-G}$
 - So in essence we only care about our original k point and the k points shifted by g_1 or $-g_1$ (for a 1D crystal)

- Don't care about any k points between these important points
- The utility of the central equation is that it takes a set of N points, each with its own Fourier coefficient, and knocks the sum down to only a handful of points that are needed to solve for the energy of our system
 - Doesn't matter which original k point we choose
 - Can develop N independent equations, one for each k point in the first Brillouin zone
 - For a 1D sample 1 cm long that gives 10^7 independent solutions!
 - Eventually we will figure out which c_{k-G} are nonzero and will throw out the rest
- Can take $\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{k}} c_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$ and rewrite it so that it is periodic on the atomic scale

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G})\cdot\vec{r}} \quad (\text{delicate, yes?})$$
- Now we are building $\psi_{\vec{k}}(\vec{r})$ from waves that satisfy periodicity in the sample as well as the atomic scale

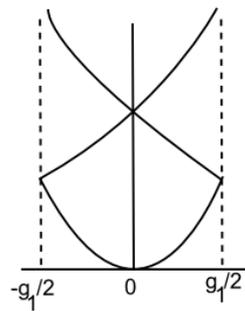
Now back to Bloch's theorem: Recall we wanted to prove: $\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}$

- We can solve for modulation term u by separating out the $e^{i\vec{k}\cdot\vec{r}}$ term
 - $\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{\vec{k}-\vec{G}} e^{-i\vec{G}\cdot\vec{r}} e^{i\vec{k}\cdot\vec{r}}$
 - Therefore, $u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{\vec{k}-\vec{G}} e^{i\vec{G}\cdot\vec{r}}$ which is periodic at the atomic scale!
- Can show that $\psi_{\vec{k}}(\vec{r}) = \psi_{\vec{k}+\vec{G}}(\vec{r})$ and by extension $E_{\vec{k}} = E_{\vec{k}+\vec{G}}$

First implementation of Bloch: The vanishing potential

- If the potential is periodic, but so **weak** that it is vanishing, we can estimate our potential as a flat box and our dispersion will basically be parabolic like the free electron model
- But since we still have periodic boundary conditions, $\psi_{\vec{k}}(\vec{r}) = \psi_{\vec{k}+\vec{G}}(\vec{r})$ and we thus repeat our parabolas at $k+g$, $k-g$, $k+2g$ and so on for the dispersion
- **Definition:** Call one parabola centered at $k=0$ the *extended zone scheme*
- **Definition:** Call multiple parabolas the *periodic zone scheme*
- These schemes contain the same information since $\psi_{\vec{k}}(\vec{r}) = \psi_{\vec{k}+\vec{G}}(\vec{r})$

- **Definition:** Usually plot the *reduced zone scheme*, the dispersion within just the first Brillouin zone



1st brillouin zone is
between the dotted
lines

Physical interpretation of Bloch's theorem:

- Wavefunction is periodic at two length scales:
 - u is periodic in T (the atomic scale, lattice spacing a)
 - $e^{i\vec{k}\cdot\vec{r}}$ is periodic in L (sample scale)
- Multiplying $Re[u] \cdot Re[e^{i\vec{k}\cdot\vec{r}}]$ we get how the real part of ψ is modulated

