An electron in a 1-D lattice

\[ \alpha \]

\[ n-2 \quad n-1 \quad ( \quad n+1 \quad n+2 \quad \ldots \]

\[ \text{\textit{n-th atom}} \]

\[ |n\rangle \]

The electron somehow "is associated with" or "belongs to" the \textit{n-th} atom.

\[ N\text{-state system, } N \rightarrow \infty. \quad \langle m | n \rangle = \delta_{mn} \]

There is always some probability for the electron to hop from the \textit{n-th} atom to the \textit{m-th} atom, i.e. \( H_{mn} \neq 0 \)

\[ \frac{dC_m}{dt} = -\frac{i}{\hbar} \sum_n H_{mn} C_n(t) \]

For simplicity, we assume \( H_{mn} = 0 \) except
$H_{nn} = E_0 \quad \& \quad H_{n,n-1} = H_{n-1,n} = -A$

Energy of "isolated" atom state.

Nearest neighbor hopping.

In $H_2^+$, we learned $H_{12} = H_{21} < 0$
if we choose $|1\rangle \& |2\rangle$ to be in-phase.
Now, we just define $H_{n,n-1} = H_{n-1,n} = -A$
with $A > 0$.

The Hamiltonian is

$$
\begin{pmatrix}
H_{n-2,n-1} & H_{n-1,n-1} & H_{n,n-1} & 0 \\
0 & H_{n-1,n} & H_{nn} & H_{n,n+1} & 0 \\
0 & H_{n,n+1} & H_{n+1,n+1} & H_{n+1,n+2} & 0 \\
\end{pmatrix}
= \begin{pmatrix}
E_0-A & 0 & 0 & 0 \\
-A & E_0-A & 0 & 0 \\
0 & -A & E_0 & -A \\
0 & 0 & -A & E_0
\end{pmatrix}
$$

$N \to \infty$ How do we find the eigenvalues & eigenvectors of this Hamiltonian??!!
well, $|\Psi> = \sum_n c_n |n>$, and we are looking for stationary states.

Let $c_n(x) = c_n(0) e^{-i \frac{E}{\hbar} t}$

$c_n(0) = f(n)$: some kind of discrete function

\[ \frac{i}{\hbar} \frac{dc_n}{dt} = \sum_m H_{nm} c_m(x) \]

\[ = -A c_{n-1}(x) + E_0 c_n(x) - A c_{n+1}(x) \]

\[ \therefore \frac{i}{\hbar} f(n) (-i \frac{E}{\hbar}) e^{-i \frac{E}{\hbar} t} = \left[ -A f(n-1) + E_0 f(n) - A f(n+1) \right] e^{-i \frac{E}{\hbar} t} \]

\[ (E - E_0) f(n) = -A \left[ f(n-1) + f(n+1) \right] \]

A discrete difference equation

Take a guess: $f(n) = c_n(0) e^{ikna}$

The 0th atom does not have to be the starting one.
\[(E-E_0)e^{ika} = -A(e^{-ika}e^{ika} + e^{ika}e^{ika})\]

\[E-E_0 = -A(e^{-ika} + e^{ika}) = -2A\cos(ka)\]

\[\therefore E = E_0 - 2A\cos(ka)\]

There are \(N \rightarrow \infty\) \(k\)'s, 
\[-\frac{\pi}{a} < k \leq \frac{\pi}{a}\]

The 1st Brillouin zone (BZ), width: \(2\pi/a\).

\(k \& k + \frac{2\pi}{a}\) are equivalent:

\[\cos((k + \frac{2\pi}{a})a) = \cos(-ka + 2\pi) = \cos(ka)\]

\[C_n(t) = C_0(0)e^{ika}e^{-\frac{E}{\hbar}t}\]

\[e^{i(k + \frac{2\pi}{a})na} = e^{i(k-na + i2\pi n)} = e^{i\hbar na}\]

— The same math as "aliasing" in sampling.
A plane wave $e^{ikx}$ sampled by the atomic chain.
The picture of a plane wave sampled by the periodic atomic chain: Bloch Theorem (in the 1-D form)

The eigenstates of the one-electron Hamiltonian in a periodic potential can be chosen to have the form

\[ \psi(x) = e^{ikx} u(x) \]

where \( u(x + na) = u(x) \).

Equivalently,

\[ \psi(x + na) = e^{i k n a} \psi(x) \]
Let's check whether our results follow the Bloch theorem.

Our results: 

$$|\Psi\rangle = \sum_n c_n(x) |n\rangle, \quad c_n(x) = c_0(x) e^{ikna} e^{-\frac{E_n}{\hbar} x}$$

Define $|\alpha\rangle = \phi(x)$, the $|n\rangle = \phi(x-na)$

$$\psi(x) = \sum_n e^{ikna} \phi(x-na)$$

Compare this to the figure on the last page. See the difference? Did we violate Bloch Theorem??

Let's do the math.
\[ \psi(x) = \sum_n e^{i k n a} \phi(x-na) \]

\[ \psi(x+ma) = \sum_n e^{i k n a} \phi(x-(n-m)a) = e^{i k m a} \sum_n e^{i k (n-m)a} \phi(x-(n-m)a) = e^{i k m a} \psi(x) \]

We did NOT violate Bloch theorem!

Another way to look at this:

\[ \psi(x) = e^{i k x} \sum_n e^{-i k (x-na)} \phi(x-na) \]

This is the \( u(x) \) in the Bloch form of the wavefunction.
For a rigorous discussion on the tight binding model in 3D, see Ashcroft & Mermin. Solid State Physics Ch. 10.

Our discussion here will help you to understand the discussion there pp. 178-179 about Eq. (10.5).

\[
\psi(x) = \sum_{n} e^{ik_n x} \phi(x-na) \quad \text{3D equivalence} \quad \psi(R) = \sum_{\sqrt{R}} e^{iR \cdot \mathbf{R}} \phi(\mathbf{R} - \mathbf{R})
\]

We can already get quite some fundamental things of solid state physics from this simple discussion.

1. N atoms, each in the F\textsubscript{0} state if isolated.
   \[\rightarrow N \text{ states in one band} \quad (\text{Compare with H}_{\text{2}+}, 2\text{-state})\]

2. Bloch

3. Semiclassical
   Bloch wave \(e^{ik \cdot x} u(x)\) is equivalent to the plane wave \(e^{ik \cdot x}\) in free space.
A good description of the electron in the (1-D) solid is the wave packet.

\[ \text{Re } \psi(x) \]

The wave packet moves at the group velocity

\[ v = \frac{dw}{dk} = \frac{1}{\hbar} \frac{dE}{dk} \]

---

Digression: Group velocity & wave packet

The wave packet is the superposition of a continuum of different wavelengths.

Only at one point, all the wavelengths constructively interfere with each other — the peak of the packet envelope, where \( \frac{d\phi}{dk} = 0 \) phase of each wave

\[ i.e. \frac{d}{dk} (kx - wt) = 0 \]
\[ x - (\frac{dw}{dk}) t = 0 \]

\[ \Rightarrow \frac{dx}{dt} = v = \frac{dw}{dk} \]

\[ E = E_0 - 2A \cos(ka) \]

\[ \approx E_0 - 2A \left[ 1 - \frac{a^2 k^2}{2} \right] = (E_0 - 2A) + 4a^2 k^2 \]

Set to reference zero

\[ v = \frac{1}{\hbar} \frac{dE}{dk} = \frac{2Aa^2}{\hbar} k \]

Let \[ E = \frac{1}{2} m^* v^2 = \frac{1}{2} m^* \left( \frac{2Aa^2}{\hbar} k^2 \right) = A a^2 k^2 \]

\[ \therefore m^* = \frac{\hbar^2}{2Aa^2} \]

\[ m^* v = \frac{\hbar^2}{2Aa^2} \cdot \frac{2Aa^2}{\hbar} k = \hbar k \]
Now, let's consider a chain made of two types of atoms.

\[ |\psi\rangle = \sum_n \left[ C_{nA}(t) |n_A\rangle + C_{nB}(t) |n_B\rangle \right] \]

\[
\begin{align*}
\frac{i}{\hbar} \frac{dC_{nA}}{dt} &= -A_1 C_{(n-1)B} + E_{0A} C_{nA} - A_2 C_{nB} \quad (1) \\
\frac{i}{\hbar} \frac{dC_{nB}}{dt} &= -A_2 C_{nA} + E_{0B} C_{nB} - A_1 C_{(n+1)A} \quad (2)
\end{align*}
\]

Let
\[
\begin{align*}
C_{nA} &= C_{OA}(0) e^{ik_n a} e^{-\frac{E}{\hbar} t} \\
C_{nB} &= C_{OB}(0) e^{ik_n a} e^{-\frac{E}{\hbar} t}
\end{align*}
\]

(1) \Rightarrow \frac{i}{\hbar} C_{OA}(0) e^{ik_n a} \left( -i \frac{E}{\hbar} \right) e^{-\frac{E}{\hbar} t} = \left[ -A_1 C_{OB}(0) e^{-ik_n a} + E_{0A} C_{OA}(0) - A_2 C_{OB}(0) \right] e^{ik_n a} e^{-\frac{E}{\hbar} t}

\Rightarrow \left( E - E_{OA} \right) C_{OA}(0) + \left( A_1 e^{-ik_n a} + A_2 \right) C_{OB}(0) = 0 \quad (3)
\[(2) \Rightarrow i\hbar c_0 (0) e^{\text{i}ka} (-i \frac{E}{\hbar}) e^{-i\frac{E}{\hbar}t} = \left[-A_2 c_{0A}(0) + E_0 c_{0B}(0) - A_1 e^{\text{i}ka} c_{0A}(0)\right] e^{\text{i}ka} e^{-i\frac{E}{\hbar}t}\]

\[\Rightarrow (A_1 e^{\text{i}ka} + A_2) c_{0A} + (E - E_0) c_{0B}(0) = 0 \quad (4)\]

Now we have two eq's about two unknowns, \(c_{0A}(0)\) & \(c_{0B}(0)\):

\[
\begin{align*}
(E - E_{0A}) c_{0A}(0) + (A_1 e^{\text{i}ka} + A_2) c_{0B}(0) &= 0 \quad (3) \\
(A_1 e^{\text{i}ka} + A_2) c_{0A}(0) + (E - E_{0B}) c_{0B}(0) &= 0 \quad (4)
\end{align*}
\]

\[
\begin{vmatrix}
E_{0A} - E & -(A_1 e^{\text{i}ka} + A_2) \\
(A_1 e^{\text{i}ka} + A_2) & E_{0B} - E
\end{vmatrix} = 0 \quad (5)
\]

Hmm... this looks like the secular equations we solve to find the eigenvalues.

We'll talk about this later.

\[(E - E_{0A})(E - E_{0B}) - (A_1 e^{\text{i}ka} + A_2)(A_1 e^{\text{i}ka} + A_2) = 0\]

Math Digression

Two eq's about two unknowns

\[
\begin{align*}
\alpha x + \beta y &= 0 \\
\gamma x + \delta y &= 0
\end{align*}
\]

You will have either one solution \(x = y = 0\) (not very interesting) or the two lines overlap each other.

\[
\begin{align*}
\alpha \gamma x + \beta \delta y &= 0 \\
\alpha \gamma x + \alpha \delta y &= 0
\end{align*}
\]

The two lines overlap if \(ad = bc\), i.e. \[\begin{vmatrix} a & b \\ c & d \end{vmatrix} = 0\]

Now you recall why we find the eigenvalues the way we do it!
\[ E^2 - (E_0_A + E_0_B)E + \left[ E_0_A E_0_B - (A_1^2 + A_2^2 + 2A_1A_2 \cos(k\alpha)) \right] = 0 \]

\[ E = \frac{(E_0_A + E_0_B) \pm \sqrt{(E_0_A + E_0_B)^2 - 4E_0_A E_0_B + 4(A_1^2 + A_2^2 + 2A_1A_2 \cos(k\alpha))}}{2} \]

\[ = \frac{E_0_A + E_0_B}{2} \pm \frac{1}{2} \sqrt{(E_0_A - E_0_B)^2 + 4(A_1^2 + A_2^2 + 2A_1A_2 \cos(k\alpha))} \]

\( \alpha = 0 \): \[ E = \frac{E_0_A + E_0_B}{2} \pm \frac{1}{2} \sqrt{(E_0_A - E_0_B)^2 + 4(A_1^2 + A_2^2)^2} \]

\( \alpha = \pi \): \[ E = \frac{E_0_A + E_0_B}{2} \pm \frac{1}{2} \sqrt{(E_0_A - E_0_B)^2 + 4(A_1 - A_2)^2} \]

There's a gap if A \times B types of atoms are different.
What if $A$ & $B$ are identical, i.e.,

$E_{\text{c}} = E_{\text{c}}' = E_0$ & $A_1 = A_2 = A$ ?

($b = \frac{a}{2}$)

$E_0 = E_0 \pm \sqrt{2A^2 + 2A^2 \cos (ka)} = E_0 \pm A \sqrt{2 \left[ 1 + \cos (ka) \right]}$

$= E_0 \pm 2A \left| \cos \frac{ka}{2} \right|$
Now, let's have another look at Eq's (3) & (4)

\[
\begin{align*}
(E - E_{0A}) C_{0A}(0) + (A_1 e^{-i k a} + A_2) C_{0B}(0) &= 0 \\
(A_1 e^{i k a} + A_2) C_{0A}(0) + (E - E_{0B}) C_{0B}(0) &= 0
\end{align*}
\]

(3) (4)

Let's re-write them as:

\[
\begin{align*}
E_{0A} C_{0A}(0) - (A_1 e^{-i k a} + A_2) C_{0B}(0) &= E C_{0A}(0) \\
-(A_1 e^{i k a} + A_2) C_{0A}(0) + E_{0B} C_{0B}(0) &= E C_{0B}(0)
\end{align*}
\]

Or, in the matrix form:

\[
\begin{pmatrix}
E_{0A} & -(A_1 e^{-i k a} + A_2) \\
-(A_1 e^{i k a} + A_2) & E_{0B}
\end{pmatrix}
\begin{pmatrix}
C_{0A}(0) \\
C_{0B}(0)
\end{pmatrix}
= E
\begin{pmatrix}
C_{0A}(0) \\
C_{0B}(0)
\end{pmatrix}
\]

It seems that we are trying to find the eigenvalues for a 2-state system.

Yes, we are. For each given \(k\), \(\begin{pmatrix} C_{0A}(0) \\ C_{0B}(0) \end{pmatrix}\) gives us the "amplitudes" of the electron "associated" with lattice A or lattice B.