Chapter 9 The Tight Binding Method

 regard a solid as a collection of weakly interacting neutral atoms.

Imagine assemble a group of sodium atoms into a bcc array with a lattice constant of the order of centimeters rather than angstroms. All electrons would be in atomic levels localized at lattice sites, bearing no resemblance to the linear combination of a few plane waves described in Nearly Free Electron Model.

If we shrink the artificially large lattice constant of the array of sodium atoms, at some point before the actual lattice constant of metallic sodium was reached we would have to modify our identification of electronic levels of the array with the atomic levels of isolated sodium atoms. This would become necessary for a particular atomic level, when the interatomic spacing become comparable to the spatial extent of its wave function, because an electron in that level would then feel the presence of the neighboring atoms.

The tight binding method deals with the case in which the overlap of atomic wave function is enough to require corrections to the picture of isolated atoms, but not so much as to render the atomic description completely irrelevant.
When \( \alpha \) is large, \( \Psi(y) \) does not feel the presence of \( \Psi(y-R) \) or \( U(y-R) \), \( R=\pm n\alpha \).

When \( \alpha \) is small, \( \Psi(y) \) starts to feel the presence of \( \Psi(y-R) \) and \( U(y-R) \), the potential energy from neighboring ions.

The eigenstates of the periodic potential can be approximated by linear combinations of atomic orbitals at each lattice site.
Start with atomic Hamiltonian $\hat{H}$ and well localized orbitals $\Psi_n$. $\hat{H} \Psi_n = E_n \Psi_n$

The full crystal Hamiltonion $H = \hat{H} + \Delta U(\vec{r})$

$U(\vec{r}) \leftrightarrow H$

$\Delta U = H - \hat{H}$
If \( \Delta U(\vec{r}) \to 0 \) when \( \psi_n(\vec{r}) \) is substantial, \( \psi_n(\vec{r}) \) will also be an eigenstate of the crystal Hamiltonian \( H = H_0 + \Delta U(\vec{r}) \).

Then each atomic level \( \psi_n(\vec{r}) \) would yield \( N \) degenerate levels in periodic potential, with wave function \( \psi_n(\vec{r} - \vec{R}) \), for each of the \( N \) sites \( \vec{R} \) in the lattice.

To satisfy the Bloch theorem \( \psi(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi(\vec{r}) \), linear combinations of these degenerate levels have to be found:

\[
\psi_n^{\vec{R}} = \sum_{\vec{R}'} e^{i\vec{k} \cdot \vec{R}'} \psi_n(\vec{r} - \vec{R}),
\]

where \( \vec{R} \) ranges through the \( N \) values in the first Brillouin zone consistent with the Born-von Karman periodic condition.

So,

\[
\psi_n^{\vec{R}}(\vec{r} + \vec{R}) = \sum_{\vec{R}'} e^{i\vec{k} \cdot (\vec{r} + \vec{R} - \vec{R}')} \\
= e^{i\vec{k} \cdot \vec{R}} \sum_{\vec{R}'} e^{i\vec{k} \cdot (\vec{r} - \vec{R}')} \psi_n(\vec{r} + \vec{R} - (\vec{R}' - \vec{R})) \\
= e^{i\vec{k} \cdot \vec{R}} \sum_{\vec{R}''} e^{i\vec{k} \cdot \vec{R}''} \psi_n(\vec{r} - \vec{R}'') \\
= e^{i\vec{k} \cdot \vec{R}} \psi_n(\vec{r}).
\]

- Bloch theorem satisfied.

At this point, the energy band has little structure, with \( E_n(\vec{k}) = E_n \), regardless of the value of \( \vec{k} \).
A more realistic assumption is that \( \Psi_n(\vec{r}) \) becomes small, but not precisely zero, when \( \Delta U(\vec{r}) \) becomes appreciable.

\[
\Psi(\vec{r}) = \sum_{\vec{R}} e^{i \vec{k} \cdot \vec{R}} \phi(\vec{r} - \vec{R})
\]

\[
\phi(\vec{r}) = \sum_n b_n \Psi_n(\vec{r}).
\]

Instead of an exact atomic stationary-state wave function, \( \phi(\vec{r}) \) is taken to be a linear combination of atomic wave functions \( \Psi_n(\vec{r}) \) and other wave functions with which \( \Psi_n(\vec{r}) \) is degenerate.

We will try to calculate \( \langle \Psi_m(\vec{r}) | H | \Psi(\vec{r}) \rangle \)

\[
H \Psi(\vec{r}) = (H_{\text{at}} + \Delta U(\vec{r})) \Psi(\vec{r}) = E(\vec{k}) \Psi(\vec{r}).
\]

\[
\langle \Psi_m | H_{\text{at}} | \Psi \rangle = \int \Psi_m^{*}(\vec{r}) H_{\text{at}} \Psi(\vec{r}) d\vec{r}.
\]

\[
= \int (\hat{H}_{\text{at}} \Psi_m)^{*} \Psi(\vec{r}) d\vec{r} = E_m \int \Psi_m^{*}(\vec{r}) \Psi(\vec{r}) d\vec{r}.
\]

\[
\langle \Psi_m | H | \Psi \rangle = \langle \Psi_m | H_{\text{at}} | \Psi \rangle + \langle \Psi_m | \Delta U | \Psi \rangle = E(\vec{k}) \langle \Psi_m | \Psi \rangle
\]

\[
= E_m \langle \Psi_m | \Psi \rangle + \langle \Psi_m | \Delta U | \Psi \rangle = E(\vec{k}) \langle \Psi_m | \Psi \rangle - E_m \langle \Psi_m | \Psi \rangle = \langle \Psi_m | \Delta U | \Psi \rangle.
\]

\[
(\epsilon - E_m) \sum_{\vec{R}} e^{i \vec{k} \cdot \vec{R}} \sum_n b_n \langle \Psi_m(\vec{r}) | \Psi_n(\vec{r} - \vec{R}) \rangle = \sum_{\vec{R}} e^{i \vec{k} \cdot \vec{R}} \sum_n b_n \langle \Psi_m(\vec{r}) | \Delta U | \Psi_n(\vec{r}) \rangle.
\]
separate terms for $\vec{r} = 0$ and $\vec{r} \neq 0$

$$(\varepsilon - E_m) \sum_n b_n \langle \psi_m | \psi_n \rangle + \sum_{\vec{r} \neq 0} \sum_n e^{i \frac{\vec{k} \cdot \vec{r}}{\hbar}} b_n \langle \psi_m(\vec{r}) | \psi_n(\vec{r} - \vec{R}) \rangle \cdot (\varepsilon - E_m)$$

$$= \sum_n b_n \langle \psi_m | \Delta V | \psi_n \rangle + \sum_{\vec{r} \neq 0} \sum_n e^{i \frac{\vec{k} \cdot \vec{r}}{\hbar}} b_n \langle \psi_m(\vec{r}) | \Delta V | \psi_n(\vec{r} - \vec{R}) \rangle$$

Note $\langle \psi_m | \psi_n \rangle = \delta_{mn}$

$$(\varepsilon - E_m) b_m = - (\varepsilon - E_m) \sum_{\vec{r} \neq 0} e^{i \frac{\vec{k} \cdot \vec{r}}{\hbar}} b_n \langle \psi_m(\vec{r}) | \psi_n(\vec{r} - \vec{R}) \rangle$$

$$+ \sum_n b_n \langle \psi_m | \Delta V | \psi_n \rangle + \sum_{\vec{r} \neq 0} e^{i \frac{\vec{k} \cdot \vec{r}}{\hbar}} b_n \langle \psi_m(\vec{r}) | \Delta V | \psi_n(\vec{r} - \vec{R}) \rangle$$

$$(\varepsilon(\vec{k}) - E_m) b_m = - (\varepsilon(\vec{k}) - E_m) \sum_n \left( \sum_{\vec{r} \neq 0} e^{i \frac{\vec{k} \cdot \vec{r}}{\hbar}} \int \psi_m^{*}(\vec{r}) \psi_n(\vec{r} - \vec{R}) d\vec{r} \right) b_n$$

$$+ \sum_n \left( \int \psi_m^{*}(\vec{r}) \Delta V(\vec{r}) \psi_n(\vec{r} - \vec{R}) d\vec{r} \right) b_n$$

$$+ \sum_n \left( \sum_{\vec{r} \neq 0} e^{i \frac{\vec{k} \cdot \vec{r}}{\hbar}} \int \psi_m^{*}(\vec{r}) \Delta V(\vec{r}) \psi_n(\vec{r} - \vec{R}) d\vec{r} \right) b_n$$

This is an eigenvalue equation.

If we have a total of $i$ degenerate states $\langle \psi_n \rangle$, we will have a total of $i$ equations with a total of $i$ variables $b_n$.

A set of homogeneous linear equations for $b_n$.

Let the determinant be zero, and solve $\varepsilon(\vec{k})$. 


All three terms on the right side of the equation are small.
So, \((E(\mathbf{k}) - E_m) b_n\) is always small.

\(E(\mathbf{k}) - E_m\) is small whenever \(b_n\) is not, vice versa.

Only those states close to \(E(\mathbf{k})\) contribute substantially to the linear combination \(\phi(\mathbf{r}) = \sum b_n \psi_n(\mathbf{r})\).

* Application to an s-band arising from a single atomic s-level.

* Non-degenerate

Eigenvalue equation becomes

\[
E(\mathbf{k}) - E_s = -(E(\mathbf{k}) - E_s) \sum_{R=0}^{\infty} \int \psi_s^*(\mathbf{r}) \psi_s(\mathbf{r}-\mathbf{R}) d\mathbf{r} \mathbf{e}^{i \mathbf{k} \cdot \mathbf{R}} 
+ \int \psi_s^*(\mathbf{r}) \Delta U(\mathbf{r}) \psi_s(\mathbf{r}) d\mathbf{r} 
+ \sum_{R=0}^{\infty} \int \psi_s^*(\mathbf{r}) \Delta U(\mathbf{r}) \psi_s(\mathbf{r}-\mathbf{R}) d\mathbf{r} \mathbf{e}^{i \mathbf{k} \cdot \mathbf{R}}
\]

\(\lambda(\mathbf{R}) = \int d\mathbf{r} \psi_s^*(\mathbf{r}) \psi_s(\mathbf{r}-\mathbf{R})\).

\(\beta = -\int d\mathbf{r} \psi_s^*(\mathbf{r}) \Delta U(\mathbf{r}) \psi_s(\mathbf{r})\).

\(\gamma(\mathbf{R}) = -\int d\mathbf{r} \psi_s^*(\mathbf{r}) \Delta U(\mathbf{r}) \psi_s(\mathbf{r}-\mathbf{R})\).

\(E - E_s = -(E - E_s) \sum \lambda(\mathbf{R}) \mathbf{e}^{i \mathbf{k} \cdot \mathbf{R}}\)

\(\epsilon = \beta - \frac{\hbar \gamma(\mathbf{R})}{\hbar} \mathbf{e}^{i \mathbf{k} \cdot \mathbf{R}}\).
\[ \epsilon(\mathbf{\bar{r}}) = E_s - \frac{\beta \Xi + \sum \psi(\mathbf{\bar{r}}) e^{i\mathbf{\bar{k}} \cdot \mathbf{\bar{R}}}}{1 + \sum \alpha(\mathbf{\bar{r}}) e^{i\mathbf{\bar{k}} \cdot \mathbf{\bar{R}}}} \]

\( \alpha(\mathbf{\bar{r}}) \) is a small quantity in the denominator. Can be ignored.

\[ \therefore \epsilon(\mathbf{\bar{r}}) = E_s - \beta - \sum \psi(\mathbf{\bar{r}}) e^{i\mathbf{\bar{k}} \cdot \mathbf{\bar{R}}} \]

Also assume only nearest neighbor separations give appreciable overlap integral \( \psi(\mathbf{\bar{r}}) \)

\[ \therefore \epsilon(\mathbf{\bar{r}}) = E_s - \beta - \sum \psi_{\text{nn}}(\mathbf{\bar{r}}) e^{i\mathbf{\bar{k}} \cdot \mathbf{\bar{R}}} \]

For face-centered cubic crystal (fcc), the 12 nearest neighbors of the origin are at

\[ \mathbf{\bar{R}} = \frac{a}{2} (\pm 1, \pm 1, 0), \quad \frac{a}{2} (\pm 1, 0, \pm 1), \quad \frac{a}{2} (0, \pm 1, \pm 1) \]

\[ \mathbf{\bar{k}} = (k_x, k_y, k_z) \]

\[ \mathbf{\bar{k}} \cdot \mathbf{\bar{R}} = \frac{a}{2} (\pm k_x, k_j) \quad i, j = x, y, z \]

\( \Delta U(\mathbf{\bar{r}}) \) has the full cubic symmetry, and is therefore unchanged by permutations of its arguments or changes in their signs.

In addition, s-level wave function \( \psi_s(\mathbf{\bar{r}}) \) depends only on the magnitude \( |\mathbf{\bar{r}}| \).

\[ \therefore \psi(\mathbf{\bar{r}}) \] is the same constant \( \psi \) for all 12 nearest neighbors.
\[ \varepsilon(k) = E_0 - \beta - 4\gamma \left( \cos \frac{1}{2} k_x a \cos \frac{1}{2} k_y a + \cos \frac{1}{2} k_y a \cos \frac{1}{2} k_x a \right) + \cos \frac{1}{2} k_y a \cos \frac{1}{2} k_x a \right) \]

\[ \gamma = - \int d^2 \Psi_s^*(x,y) \Delta U(x,y) \Psi_s(x-\frac{1}{2} a, y-\frac{1}{2} a, f) \]

bandwidth proportional to \( \gamma \).

The smaller the overlap, the narrower the band.

\[ V(r) \]

\[ \text{Energy level} \]

\[ \text{(spacing)}^{-1} \]

\[ \text{band} \]

\[ \begin{align*}
V = 0 & \quad n=1 \\
V = 3 & \quad n=2 \\
V = 6 & \quad n=3
\end{align*} \]

\[ \begin{align*}
\text{Application to } p- \text{levels} \\
p- \text{level triply degenerate}
\end{align*} \]

\[ 3 \times 3 \text{ determinant } = 0 \]

\[ d-\text{level } 5 \times 5 \text{ secular problem} \]

transition metal, \( s \)-level and \( d \)-level close.

\[ 6 \times 6 \text{ secular problem (s-d hybridization)} \]