Tight Binding Method

If ions are spaced far apart on the length scale on which the atomic bound state wavefunction decays, then expect that atomic wavefunctions will give a good approximation to the Bloch electron eigenstates in the periodic potential of all ions.

However, the tails of the atomic wavefunctions will overlap allowing the electron to hop from ion to ion, behaving like a free Bloch electron.

For simplicity, assume the atomic valence electron is a single "s" orbital electron. This atomic state is non-degenerate. Let its wave function be \( \phi_0(\vec{r}) \) for ion centered at origin.

We can construct a Bloch electron state out of the individual atomic states \( \phi_0(\vec{r} + \vec{r}_0) \) by

\[
\psi_k(\vec{r}) = \sum_{\vec{r}_0} e^{i \frac{2\pi}{a} \vec{k} \cdot \vec{r}_0} \phi_0(\vec{r} + \vec{r}_0)
\]

Counting: We go from \( N \) atomic wavefunction \( \psi_0(\vec{r} + \vec{r}_0) \), \( N \) values of \( \vec{r}_0 \), to \( N \) Bloch wavefunctions \( \psi_k(\vec{r}) \), \( N \) values of \( \vec{k} \) in 1st BZ.

(only mix atomic wavefunctions \( \phi_0(\vec{r} - \vec{r}_0) \) where electron has same spin value)
Let \( H = H_{\text{at}} + \Delta U \)

\( H \) is Hamiltonian of entire system

\( H_{\text{at}} \) is Hamiltonian of atom at origin

\( \Delta U \) is potential from all atoms except the one at the origin

If total potential is \( U(\vec{r}) = \sum_{i \neq 0} \mathcal{V}(\vec{r} - \vec{r}_i) \), atomic potential

\[ H = \frac{\vec{p}^2}{2m} + U(\vec{r}) \]

\[ H_{\text{at}} = \frac{\vec{p}^2}{2m} + \mathcal{V}(\vec{r}) \]

\[ \Delta U = \sum_{i \neq 0} \mathcal{V}(\vec{r} - \vec{r}_i) = U(\vec{r}) - \mathcal{V}(\vec{r}) \]

Choose energy scale so that \( \Delta U(0) = 0 \).

Now consider:

\[
\begin{align*}
\langle \phi_0 | H | \psi_k \rangle &= \langle \phi_0 | H_{\text{at}} + \Delta U | \psi_k \rangle \\
\mathcal{E}_k \langle \phi_0 | \psi_k \rangle &= \mathcal{E}_a \langle \phi_0 | \psi_k \rangle + \langle \phi_0 | \Delta U | \psi_k \rangle \\
\end{align*}
\]

Energy of block + atomic energy level of \( \phi_0 \)

\[ \mathcal{E}_k = \mathcal{E}_a + \frac{\langle \phi_0 | \Delta U | \psi_k \rangle}{\langle \phi_0 | \psi_k \rangle} \]
\[
\langle \psi_0 | \psi_k \rangle = \sum_{n} e^{i \mathbf{k} \cdot \mathbf{R}_n} \int d^3 r \, \psi_0^*(r) \psi_0 (r - \mathbf{R}_n)
\]
\[
= 1 + \sum_{\mathbf{R}_n \neq 0} e^{i \mathbf{k} \cdot \mathbf{R}_n} \int d^3 r \, \psi_0^*(r) \psi_0 (r - \mathbf{R}_n) \tag{overlap}
\]

"If cons are far apart, overlap integrals are small. Only keep nearest neighbor terms, i.e. only sum over the smallest non-zero values of \( \mathbf{R}_n \)."

\[
\langle \psi_0 | \psi_k \rangle = 1 + \sum_{n} e^{i \mathbf{k} \cdot \mathbf{R}_n} \int d^3 r \, \psi_0^*(r) \psi_0 (r - \mathbf{R}_n) \tag{\alpha(\mathbf{R}_n)}
\]

\[
\langle \psi_0 | \Delta U | \psi_k \rangle = \sum_{n} e^{i \mathbf{k} \cdot \mathbf{R}_n} \int d^3 r \, \psi_0^*(r) \Delta U(r) \psi_0 (r - \mathbf{R}_n)
\]
\[
= \int d^3 r \, \psi_0^*(r) \Delta U(r) \psi_0 (r)
\]
\[
+ \sum_{\mathbf{R}_n \neq 0} e^{i \mathbf{k} \cdot \mathbf{R}_n} \int d^3 r \, \psi_0^*(r) \Delta U(r) \psi_0 (r - \mathbf{R}_n) \tag{\alpha(\mathbf{R}_n)}
\]

"Again, keep only terms for nearest neighbor \( \mathbf{R}_n \)."

Define \( \beta = -\int d^3 r \, \psi_0^*(r) \Delta U(r) \psi_0 (r) \)

\[
\gamma(\mathbf{R}) = -\int d^3 r \, \psi_0^*(r) \Delta U(r) \psi_0 (r - \mathbf{R})
\]

\[
\langle \psi_0 | \Delta U | \psi_k \rangle = -\beta - \sum_{n} e^{i \mathbf{k} \cdot \mathbf{R}_n} \gamma(\mathbf{R}_n)
\]
\[ \varepsilon_k = E_a - \beta \left(1 + \frac{\sum_{mn} e^{i k \cdot R_m} \gamma(R)}{1 + \sum_{mn} e^{-i k \cdot R_n} \alpha(R)} \right) \]

\[ \varepsilon_k = E_a - \beta - \sum_{mn} e^{i k \cdot R_m} (\gamma(R) - \beta \alpha(R)) \]

since \(\alpha\) small, \(\frac{1}{1+\alpha} \approx 1 - \alpha\)

Now \(\alpha(R) = \int d^3r \, \phi_0^*(r) \phi_0(r + R) = \int d^3r \, \phi_0^*(R + r) \phi_0(r) = \alpha^*(-R) \)

For s-orbital has real wave function \(\phi_0 \Rightarrow \alpha = \alpha^* \)
so \(\alpha(R) = \alpha(-R) \)

\[ \gamma(R) = -\int d^3r \, \phi_0^* (r) \Delta U(r) \phi_0 (r - R) \]

\[ = -\int d^3r \, \phi_0^* (-r) \Delta U(-r) \phi_0 (-r - R) \]

If crystal has inversion symmetry, ie \(\Delta U(-r) = \Delta U(r)\)
and since s-orbital is spherically symmetric, ie \(\phi_0 (r)\) dependent only on \(|r|\) so \(\phi_0 (r) = \phi_0 (-r)\), then

\[ = -\int d^3r \, \phi_0^* (r) \Delta U(r) \phi_0 (r + R) = \gamma(-R) \]

so \(\gamma(R) = \gamma(-R)\) and \(\alpha(R) = \alpha(-R)\)

\[ \varepsilon_k = E_a - \beta - \sum_{mn} \left[ \gamma(R) - \beta \alpha(R) \right] \cos k \cdot R_m \]
Moreover, if the crystal has cubic symmetry, then since \( \gamma_0 \) is rotationally symmetric, \( \varphi(r) \) and \( \varphi(2r) \) will be the same value for all \( nnR \).

\[
\varphi_0(r) \quad \varphi_0(2r)
\]

All will have cubic symmetry so \( \varphi(R) = \varphi(2R) \)

\[
\varphi(R) = \varphi(2R)
\]

\[
E_R = E_a - \beta - \bar{\gamma} \sum_{nn} \cos(k \cdot R) \quad \bar{\gamma} = \gamma - \beta \alpha
\]

See A+M for case of face lattice.

Here we consider the simpler so lattice \( nnR \) are \( \pm a \hat{x}, \pm a \hat{y}, \pm a \hat{z} \)

\( k \cdot R \) are \( \pm k \hat{x}a, \pm k \hat{y}a, \pm k \hat{z}a \)

\[
E_R = E_a - \beta - 2\bar{\gamma} \left( \cos k_x a + \cos k_y a + \cos k_z a \right)
\]

\[
\text{band width} \quad \varepsilon_k - \varepsilon_{\mu} = 12 \bar{\gamma}
\]

for small \( k \), \( \cos k a \approx 1 - \frac{1}{2} k^2 a^2 \)

\[
E_R \approx E_a - \beta - 2\bar{\gamma} \left( 3 - \frac{1}{2} k_x^2 a^2 - \frac{1}{2} k_y^2 a^2 - \frac{1}{2} k_z^2 a^2 \right)
\]

\[
\approx E_a - \beta - 6\bar{\gamma} + \bar{\gamma} k^2 a^2
\]
surfaces of constant energy \( \sim k^2 \)
so are spherical, just like free electrons
(or in weak potential approx if \( k \) is not near any Bragg plane)

effective mass \( \frac{1}{2} \frac{\hbar^2}{m^*} \sim \gamma k^2 \)

\[ m^* \sim \frac{\hbar^2}{\gamma a^2} \]

But at higher \( k \)

in 2D \( E_k = E_0 - \beta - 2\delta (\cos k_x a + \cos k_y a) \)

the curves \( k_y = \pm \frac{\pi}{a} \pm k_x \) have constant energy

\( \cos k_x a + \cos (\pi \pm k_x) \)

\( k_y \)

\[ \text{const energy surface} \]

\[ \text{enclosing} \frac{1}{4} \text{ area of} \]

\( 1^{st} \text{ BZ} \)

\[ \text{This will be Fermi surface} \]

\[ \text{for } Z=1 \Rightarrow \text{ 1 electron per BZ site, so } 1^{st} \text{ BZ} \]

\( \text{is half filled.} \)

So Fermi surface need not be close to spherical!
Nested Fermi surface

where a common wavevector $\overrightarrow{K}$ maps a section of the Fermi surface onto another section.

In the example, $\overrightarrow{K}$ takes 1/4 Fermi surface onto opposite surface.

Many electrons at Fermi surface can scatter by $\overrightarrow{G}$ with little cost in energy.

System has strong susceptibility with respect to fluctuations at wavevector $\overrightarrow{G}$.

This does not happen for gapped Fermi surfaces.

For a fixed wave vector $\overrightarrow{G}$, as shown, only a small fraction of Fermi surface can scatter at little energy cost.
For \( \vec{k} \) near \( \vec{k}_0 = \pm \frac{\pi}{a} \hat{x} \pm \frac{\pi}{a} \hat{y} \) corner of B.Z.

\[
\vec{k} = \vec{sk} + \vec{k}_0
\]

\[
\varepsilon_k = E_0 - \beta - 2\bar{\gamma} (\cos (\pm \pi + sk_\lambda a) + \cos (\pm \pi + sk_\gamma a))
\]

\[
= E_0 - \beta + 2\bar{\gamma} (\cos sk_\lambda a + \cos sk_\gamma a)
\]

\[
\uparrow \text{ sign is now } +
\]

\[
= E_0 - \beta + 2\bar{\gamma} (1 - \frac{1}{2} (sk_\lambda a)^2 + 1 - \frac{1}{2} (sk_\gamma a)^2)
\]

\[
= E_0 - \beta + 4\bar{\gamma} - \bar{\gamma} sk^2 \frac{a^2}{18k^2}
\]

\[\uparrow \text{ depends only on } \vec{k}\]

so constant energy curves are circular about \( \vec{k}_0 \)

\[\leftarrow \text{ constant energy surfaces}\]

minimum energy of band is at origin \( \vec{k} = 0 \)

maximum energy of band is at corners \( \vec{k}_0 = \pm \frac{\pi}{a} \hat{x} \pm \frac{\pi}{a} \hat{y} \)
What happens in our tight binding model if each con contributes 2 electrons, i.e. \( z = 2 \)?

If the width of the 5-band \( \approx \delta \) is sufficiently small so that the maximum energy of the 5-band is well below the energy of the atomic p-orbital (actually it needs to be below the lowest energy of the p-band computed from the p-orbitals), then the \( 2N \) electrons will completely fill the \( 2N \) states of the 5-band, leaving the higher p-band empty. The \( \mathbf{k} \) of the 1st \( BZ \) of the 5-band are all filled and the Fermi surface (the points in \( \mathbf{k} \)-space that have the most energetic electrons) will be the discrete points
\[
\mathbf{k}_0 = \pm \frac{\pi}{a} \hat{x} \pm \frac{\pi}{a} \hat{y} \pm \frac{\pi}{a} \hat{z} \quad (\text{for } s.c.-BZ)
\]
at the corners of the 1st \( BZ \) -- these are the \( \mathbf{k} \) that gives the largest \( E(\mathbf{k}) \) for the 5-band.

The system is then an insulator, with a finite energy gap between states at the Fermi surface and the lowest unoccupied electron states (in the p-band).
If, however, the s-band gets too wide, and starts to overlap the p-band, we need to go back and reconsider our initial approximation of assuming that the conduction electron at each con was only in the s-orbital. If the electron energy is large enough, the electron can get excited to the p-orbital or even higher, so our initial guess for the Bloch wave function \( \psi \) should take this into account. We therefore take

\[
\psi^k(\mathbf{r}) = \sum_{\mathbf{R}} \psi^k(\mathbf{r}) = \sum_{n} b_n \Phi_n(\mathbf{r} - \mathbf{R})
\]

where the \( \Phi_n \) are atomic wave functions with energy \( E_n \), and \( b_n \) are coefficients to be determined. One should take all \( \Phi_n \) whose energy \( E_n \) is expected to be close to the energy of the band(s), one is computing — determining which \( \Phi_n \) to include is a self-consistent procedure — more on this later.

One then considers the matrix elements

\[
\langle \Phi_{n'}(\mathbf{r}) | H | \psi_k(\mathbf{r}) \rangle = E_k \langle \Phi_{n'}(\mathbf{r}) | \psi_k(\mathbf{r}) \rangle
\]

\[
= \langle \Phi_{n'}(\mathbf{r}) | H + \Delta U | \psi_k(\mathbf{r}) \rangle
\]

\[
= E_{n'} \langle \Phi_{n'}(\mathbf{r}) | \psi_k(\mathbf{r}) \rangle + \langle \Phi_{n'}(\mathbf{r}) | \Delta U | \psi_k(\mathbf{r}) \rangle
\]
One then gets:

\[ 0 = (E_{n'} - E_k) \langle \Psi_{n'}(\vec{r}) | \Psi_k(\vec{r}) \rangle + \langle \Psi_{n'}(\vec{r}) | \delta U(\vec{r}) | \Psi_k(\vec{r}) \rangle \]

\[ 0 = (E_{n'} - E_k) \sum \int d^3 \vec{r} \, \varphi_{n'}^*(\vec{r}) \varphi_k(\vec{r} - \vec{R}) b_n \]

\[ + \sum \int d^3 \vec{r} \, \varphi_{n'}^*(\vec{r}) \delta U(\vec{r}) \varphi_k(\vec{r} - \vec{R}) b_n \]

\[ 0 = \sum \left( \sum \int d^3 \vec{r} \, \varphi_{n'}^*(\vec{r}) \delta U(\vec{r}) \varphi_k(\vec{r} - \vec{R}) \right)^2 \int b_n \]

If there are no atomic orbitals used in the approximation for \( \Psi_k(\vec{r}) \), then the above is a set of no linear equation (as \( n' \) takes all possible values) in no unknowns - the \( b_n \).

We can rewrite the above in matrix form

\[ \sum M_{n' n} b_n = 0 \]

where \( M_{n' n} = \sum \int d^3 \vec{r} \, \varphi_{n'}^*(\vec{r}) (E_{n'} - E_k) \varphi_k(\vec{r}) \varphi_k(\vec{r} - \vec{R}) \)

\[ + \int d^3 \vec{r} \, \varphi_{n'}^*(\vec{r}) \delta U(\vec{r}) \varphi_k(\vec{r} - \vec{R}) \]

For the above set of homogeneous linear equation to have a non-trivial solution (i.e., not all \( b_n = 0 \)) it is necessary that the determinant of the matrix \( M_{n' n} \) vanish.
The condition \( \det M = 0 \), where \( M \) is an \( n \times n \) matrix, then gives an \( n \)-th order polynomial in the unknown \( E_k \). Finding the zeros of this polynomial then determines no values of \( E_k \) (since \( M \) is an Hermitian matrix, these \( E_k \) are all real valued). The resulting \( E_k \) are the Bloch energies of the Bloch electrons at crystal momentum \( \bar{k} \) for the \( n \) bands that arise from the \( n \) atomic orbitals, — for each value of \( \bar{k} \) there will be \( n \) energies \( E_n^k(\bar{k}) \), \( n = 1, \ldots, n_0 \).

For each \( E_n^k(\bar{k}) \) the corresponding solutions \( b_n^k \) (the \( b_n^k \)'s will depend on both \( \bar{k} \) and the band index \( n \)) determine the wave function of the Bloch electron state \( \Psi_n^k \), giving the amount that each atomic orbital \( \phi_n \) mixes into the state \( \Psi_n^k \).

We can rewrite \( M_{n' n} \) by separating out the \( \bar{k} = 0 \) term from the rest,

\[
M_{n' n} = (E_n^k - E_k) \int d^3r \phi_{n'}^* (\bar{r}) \phi_n (\bar{r}) + \int d^3r \phi_{n'}^* (\bar{r}) \mathcal{H} (\bar{r}) \phi_n (\bar{r})
\]

\[
+ \sum_{\bar{k} \neq 0} e^{i \bar{k} \cdot \bar{r}} \left\{ (E_n^k - E_k) \int d^3r \phi_{n'}^* (\bar{r}) \phi_n (\bar{r} - \bar{k}) + \int d^3r \phi_{n'}^* (\bar{r}) \mathcal{H} (\bar{r}) \phi_n (\bar{r} - \bar{k}) \right\}
\]

Now \( \int d^3r \phi_n^* (\bar{r}) \phi_n (\bar{r}) = \delta_{n n} \) as the atomic orbitals are normalized.
If we define:

\[ \beta_{n'n} = -\int d^3r \: \Phi_{n'}^* (\vec{r}) \Delta U(\vec{r}) \Phi_n (\vec{r}) \]

\[ \alpha_{n'n}(\vec{r}) = \int d^3r \: \Phi_{n'}^* (\vec{r}) \Phi_n (\vec{r}-\vec{r}) \]

\[ \gamma_{n'n}(\vec{r}) = -\int d^3r \: \Phi_{n'}^* (\vec{r}) \Delta U(\vec{r}) \Phi_n (\vec{r}-\vec{r}) \]

Then:

\[ M_{n'n} = (E_{n'} - E_k) \delta_{n'n} - \beta_{n'n} \]

\[ + \sum_{\vec{r} \neq 0} e^{ik \cdot \vec{r}} \left\{ (E_{n'} - E_k) \alpha_{n'n}(\vec{r}) - \gamma_{n'n}(\vec{r}) \right\} \]

And the condition:

\[ \sum_n M_{n'n} b_n = 0 \]

Can be written as:

\[ (E_k - E_{n'}) b_{n'} = -\sum_n \beta_{n'n} b_n \]

\[ + \sum_n \left[ (E_{n'} - E_k) \sum_{\vec{r} \neq 0} e^{ik \cdot \vec{r}} \alpha_{n'n}(\vec{r}) \right] b_n \]

\[ - \sum_n \left[ \sum_{\vec{r} \neq 0} e^{ik \cdot \vec{r}} \gamma_{n'n}(\vec{r}) \right] b_n \]

Now if tight binding is to be a good approx, we expect overlap integrals will be small

\[ \Rightarrow \alpha_{n'n}, \gamma_{n'n} \text{ are all small} \]

Also, \( \beta_{n'n} \) is small since \( |\Phi_{n'}^* (\vec{r}) \Phi_n (\vec{r})| \)

is large only at \( r \approx 0 \) where \( \Delta U \) is small.
So all terms on right hand side of above equation are small

\[ \Rightarrow \text{left hand side } (E_k - E_n') b_n' \text{ is small} \]

\[ \Rightarrow (E_k - E_n') \text{ small ad } b_n' \sim O(1) \]

or \((E_k - E_n') \text{ large ad } b_n' \text{ small}\)

Hence only those atomic orbitals \( \phi_n \) where
the atomic energy \( E_n \) is close to the band energy \( E_k \)
(so \( E_k - E_n \) is small) will mix appreciably into
the Bloch state \( \psi_k \), i.e., have \( b_n \sim O(1) \).
These orbitals \( \phi_n \) not close to the band energy
\((|E_k - E_n| \text{ large})\) will not mix appreciably, i.e.,
we will have \( b_n \text{ small} \).

As an example, consider the possible mixing of
5 and p orbitals. There is one s-orbital and
three p-orbitals, \( p_x, p_y, p_z \), corresponding to
angular momenta \( l = \pm 1, 0 \). So our trial
Bloch wavefunction would be

\[ \psi_k = \sum_{\vec{R}} e^{i \vec{k} \cdot \vec{R}} \left\{ b_s \phi_s (\vec{r} - \vec{R}) + b_{px} \phi_{px} (\vec{r} - \vec{R}) \right. \]

\[ + b_{py} \phi_{py} (\vec{r} - \vec{R}) + b_{pz} \phi_{pz} (\vec{r} - \vec{R}) \left. \right\} \]

The resulting matrix \( M \) will be \( 4 \times 4 \).
Let $E_s$ and $E_p$ be the atomic energy levels of the $s$ and $p$ orbitals. We have $E_s < E_p$.

If the ion spacing $a$ is large, overlaps are small, and we expect narrow bands. When we solve $\det H = 0$ to get the 4 values of $E_j(\vec{k})$, we will find that the lowest band $E_j(\vec{k})$ is like the $s$-band we found when we introduced the tight binding model, that is, as $\vec{k}$ varies, $E_j(\vec{k})$ well sweep out a narrow range of energies about $E_s$ with $\max E_j(\vec{k}) < E_p$, and we will have Bloch states with $b_s \sim 1$ and $b_p \sim b_p \sim b_p^3$ very small.

The bands $E_2(\vec{k})$, $E_3(\vec{k})$, $E_4(\vec{k})$ will be nearly degenerate $p$-bands, with a narrow energy width about $E_p$ and $\min E_j(\vec{k}) > E_s$ $j=2,3,4$. The Bloch state will have $b_s$ very small while some of the $b_p$, $b_p$ are $\sim O(1)$.

In this case the results we get will be essentially the same as if we had computed the $s$-band and the $p$-bands separately. We used

$$\psi_k = \sum_{\vec{p}} e^{i \vec{k} \cdot \vec{p}} \phi_s(\vec{r}-\vec{p})$$

for the $s$-band

and

$$\psi_k = \sum_{\vec{p}} e^{i \vec{k} \cdot \vec{p}} \left[ b_{px} \phi_{px}(\vec{r}-\vec{p}) + b_{py} \phi_{py}(\vec{r}-\vec{p}) + b_{pz} \phi_{pz}(\vec{r}-\vec{p}) \right]$$

for the 3 $p$-bands.
As the ion spacing $a$ decreases, however, the $s$ bands will start to overlap the $p$-bands. It is now necessary to compute the 4 bands in a combined calculation using
\[
\Psi_k = \sum_{k} \alpha e^{i k \cdot R} \left[ b_s \varphi_s (r-R) + b_p \varphi_p (r-R) \right]
\]
and one will find that for values $k$ where the bands overlap, one may have Bloch wave functions $\Psi_k$ in which both $b_s$ and some $b_p$ are large.

When this happens it is called "$s$-$p$ mixing" or "$s$-$p$ hybridization".

We can sketch the situation schematically as follows:

\[\begin{align*}
E_p & \quad p\text{-bands} \\
E_s & \quad s\text{-band} \\
0 & \quad \text{Ya}
\end{align*}\]

Here the $s$ and $p$ bands have little mixing.

If $Z = 2$, material will be insulator - $s$ band filled, $p$-bands empty.

Even if $Z = 2$, the material will be conducting with partially filled $s$ and $p$-bands.
For well-separated bands, one needs only

1. the single $4s$ orbital to get the $s$-band
2. the three $p$-orbitals ($l=1, m_l=0, \pm 1$) to get the $3p$-bands
3. the five $d$-orbitals ($l=2, m_l=0, \pm 1, \pm 2$) to get the $5d$-bands

In transition metals with valence electron in the
$s$-orbital of the $n$th shell, the $(n-1)d$ orbitals
are often close in energy to the $ns$ orbital.

We therefore expect possible "$s-d$ hybridization"
and to compute the tight binding band structure,
we should use a Bloch state $\Psi_k$ that mixes
in $\Psi_k$ all six of these orbitals (i.e. the
5 $(n-1)d$ orbitals and the single $ns$ orbital)

Note: Our equation det $M = 0$, that
determines the tight binding band structure
energies $E_n(k)$, can also be viewed as
arising from a variational calculation.

If one takes $\Psi_k = \sum \frac{e^{i \mathbf{k} \cdot \mathbf{R}}}{\mathbf{R}} \sum b_n \phi_n (\mathbf{R}-\mathbf{R})$
as a trial variational wave function
with the $b_n$ as free parameters, then
computes

$$E = \frac{\langle \Psi_k | H | \Psi_k \rangle}{\langle \Psi_k | \Psi_k \rangle}$$

then choosing the $b_n$ to minimize $E$ can be
shown to result in exactly the same equation

$$\sum b_n = 0$$

that we derived earlier!
Tight Binding as Variational Calculation

Let \( \psi_k = \sum_n \frac{e^{i R \cdot r}}{R} b_n \phi_n(r) \)

be a variational Bloch wave function, and \( E \) the expected value of its energy

\[
E = \frac{\langle \psi_k | H | \psi_k \rangle}{\langle \psi_k | \psi_k \rangle} = \frac{\int d^3 r \, \psi_k^\ast \, H(r) \, \psi_k(r)}{\int d^3 r \, \psi_k^\ast \, \psi_k(r)}
\]

We then will minimize \( E \) with respect to the parameters \( b_n \).

We have

\[
\langle \psi_k | \psi_k \rangle = \sum_{R R'} \sum_{n n'} e^{i R \cdot (R' - R)} b_n^\ast b_n \int d^3 r \, \phi_n^\ast (r-R') \phi_n (r-R')
\]

let \( R-R' \rightarrow R \) with integral

\[
= \sum_{R R'} \sum_{n n'} e^{i \vec{R} \cdot (\vec{R'} - \vec{R})} b_n^\ast b_n \int d^3 r \, \phi_n^\ast (r) \phi_n (r-R+R')
\]

Define \( \alpha_{n n'} (\vec{R}) = \int d^3 r \, \phi_n^\ast (r) \phi_n (r-R) \) then

\[
\langle \psi_k | \psi_k \rangle = \sum_{R R'} \sum_{n n'} e^{i \vec{R} \cdot (\vec{R'} - \vec{R})} b_n^\ast b_n \alpha_{n n'} (\vec{R} - \vec{R}')
\]

let \( \vec{R} - \vec{R}' \rightarrow \vec{R} \) in sum

\[
= N \sum_{R n n'} e^{i \vec{R} \cdot \vec{R'}} b_n^\ast b_n \alpha_{n n'} (\vec{R})
\]

Similarly

\[
\langle \psi_k | H | \psi_k \rangle = \sum_{R R'} \sum_{n n'} e^{i \vec{R} \cdot (\vec{R'} - \vec{R})} b_n^\ast b_n \int d^3 r \, \phi_n^\ast (r-R') H(r) \phi_n (r-R)
\]

let \( R-R' \rightarrow R \) with integral

\[
= \sum_{R R'} \sum_{n n'} e^{i \vec{R} \cdot (\vec{R'} - \vec{R})} b_n^\ast b_n \int d^3 r \, \phi_n^\ast (r) H(r+R') \phi_n (r-R+R')
\]

use \( H(r) = H(r+R') \) is periodic on \( R \) and define

\[
\tilde{\phi}_{n n'} (\vec{R}) = - \int d^3 r \, \phi_n^\ast (r) H(r) \phi_n (r-R)
\]
\[ \langle \psi_k | H | \psi_k \rangle = -\sum \sum e^{i \mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} b_{n'}^* b_n \tilde{\gamma}_{nn'}(\mathbf{R} - \mathbf{R}') \]

\text{Let } \mathbf{R} - \mathbf{R}' \rightarrow \mathbf{R} \text{ in sum}

\[ = -N \sum \sum e^{i \mathbf{k} \cdot \mathbf{R}} b_{n'}^* b_n \tilde{\gamma}_{nn'}(\mathbf{R}) \]

Now minimize \( E \) with respect to the \( b_n \)

\[ \frac{\partial E}{\partial b_n^*} = \frac{\partial}{\partial b_n^*} \langle \psi_k | H | \psi_k \rangle - \frac{\partial}{\partial b_n^*} \langle \psi_k | \psi_k \rangle \frac{2}{\langle \psi_k | \psi_k \rangle} \langle \psi_k | \psi_k \rangle = 0 \]

multiply all terms by \( \langle \psi_k | \psi_k \rangle \)

\[ \frac{\partial}{\partial b_n^*} \langle \psi_k | H | \psi_k \rangle - \frac{\partial}{\partial b_n^*} \langle \psi_k | \psi_k \rangle \frac{2}{\langle \psi_k | \psi_k \rangle} \langle \psi_k | \psi_k \rangle = 0 \]

\[ \Rightarrow \frac{\partial}{\partial b_n^*} \langle \psi_k | H | \psi_k \rangle = E \frac{\partial}{\partial b_n^*} \langle \psi_k | \psi_k \rangle = 0 \]

\[ \Rightarrow -\sum \sum e^{i \mathbf{k} \cdot \mathbf{R}} \tilde{\gamma}_{nn'}(\mathbf{R}) b_n = E \sum \sum e^{i \mathbf{k} \cdot \mathbf{R}} \tilde{\gamma}_{nn'}(\mathbf{R}) b_n = 0 \]

Above is just a set of linear equations to solve for the \( b_n \). A non-trivial solution requires that the determinant of the matrix of the linear system will vanish. This determines the Bloch energies \( E = \varepsilon_n(\mathbf{k}) \in \mathbb{R} \) are eigenvalues.

\[ \text{In solutions to } \det M = 0 \]
We can further write \( H = H_0 + \Delta U \)

\[
\delta_{nn'}(\vec{r}) = -\int d^3\vec{r} \phi_{n'}^*(\vec{r}) \left[ H_0 + \Delta U(\vec{r}) \right] \phi_n(\vec{r} - \vec{r})
\]

\[
= -E_n' \int d^3\vec{r} \phi_{n'}^*(\vec{r}) \phi_n(\vec{r} - \vec{r})
- \int d^3\vec{r} \phi_{n'}^*(\vec{r}) \Delta U(\vec{r}) \phi_n(\vec{r} - \vec{r})
\]

\[
= -E_n' \delta_{nn'}(\vec{r}) + \gamma_{nn'}(\vec{r})
\]

So we get

\[
\sum_n \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \left[ (E_{n'} - E) \delta_{nn'}(\vec{R}) - \gamma_{nn'}(\vec{R}) \right] b_n = 0
\]

Note \( \delta_{nn'}(0) = \delta_{nn'} \) by orthogonality of the \( \phi_n \)

and \( \gamma_{nn'}(0) = -\beta_{nn'} \) as defined in our earlier discussion.

So

\[
\Theta = \sum_n \left[ (E_{n'} - E) \delta_{nn'} - \beta_{nn'}
+ \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \left\{ (E_{n'} - E) \delta_{nn'}(\vec{R}) - \gamma_{nn'}(\vec{R}) \right\} \right] b_n
\]

\[
= \sum_n M_{nn'} b_n
\]

with

\[
M_{nn'} = (E_{n'} - E) \delta_{nn'} - \beta_{nn'}
+ \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \left\{ (E_{n'} - E) \delta_{nn'}(\vec{R}) - \gamma_{nn'}(\vec{R}) \right\}
\]

Same as we found before, only here we call \( E\_k = E \).