\[ \text{surfaces of constant energy } \sim k^2 \]
so are spherical, just like free electrons
(or in weak potential approx if \( k \) not near any Bragg plane)

\[ \text{effective mass } \frac{1}{2} \frac{21^2}{m^*} \sim \gamma \frac{k^2}{a^2} \]

\[ \Rightarrow m^* \sim \frac{6}{2\gamma a^2} \]

But at higher \( k \)

in 2D \[ \varepsilon_k = E_0 - \beta - 2\gamma (\cos k_x a + \cos k_y a) \]

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

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

\[ = \cos k_x a + \cos (\pi \pm k_x) = 0 \]

const energy surface

\[ \text{enclosing } \frac{1}{2} \text{ area of } 1\text{st BZ} \]

This will be Fermi surface

for \( Z = 1 \) \( \Rightarrow \) 1 electron per BL site, so 1st BZ

is half filled.

So Fermi surface need not be close to spherical!
Nested Fermi surface: when a common wavevector $k_x$ maps a section of the Fermi surface onto another section.

Example: $k_x < \vec{Q}$, takes a Fermi surface onto opposite surface.

⇒ Many electrons at Fermi surface can scatter by $\vec{Q}$ with little cost in energy.

⇒ System has strong susceptibility with respect to fluctuations at wavevector $\vec{Q}$.

This does not happen for spherical Fermi surfaces.

For a fixed wavevector $\vec{Q}$, 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 BZ:

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

\[
E_k = E_0 - \beta - 2 \delta \left( \cos (\pi + \vec{s} \cdot \vec{a}) + \cos (\pi + \vec{s} \cdot \vec{a}) \right)
\]

\[
= E_0 - \beta + 2 \delta \left( \cos \vec{s} \cdot \vec{a} + \cos \vec{s} \cdot \vec{a} \right)
\]

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

\[
= E_0 - \beta + 2 \delta \left( 1 - \frac{1}{2} (\vec{s} \cdot \vec{a})^2 + 1 - \frac{1}{2} (\vec{s} \cdot \vec{a})^2 \right)
\]

\[
= E_0 - \beta + 4 \delta - 8 \delta \frac{1}{8} \vec{s} \cdot \vec{a}^2
\]

\[
\uparrow \text{ depends only on } \vec{s} \vec{k}^2
\]

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

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

minimum energy of band is at origin \( \vec{k}_0 = 0 \)

maximum energy of band is at corners \( \vec{k}_0 = \pm \frac{\pi}{a} \hat{x} \pm \frac{\pi}{a} \hat{y} \)
Tight Binding Density of States

Here are plots of densities of states for the tight-binding Hamiltonian for "cubic" lattices in several dimensions. In three dimensions the energy is given by

$$\epsilon(k) = t[6 - 2(\cos k_x a + \cos k_y a + \cos k_z a)],$$

with analogous expressions for other dimensions. Note the Van Hove singularities.
What happens in our tight binding model if each con contributes 2 electrons, i.e., Z = 2?

If the width of the s-band ~ \( \frac{1}{2} \) is sufficiently small so that the maximum energy of the s-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 s-band, leaving the higher p-band empty. The \( \tilde{k} \) of the 1st BZ of the s-band are all filled and the Fermi surface (the points in \( \tilde{k} \)-space that have the most energetic electrons) will be the discrete points

\[
\tilde{k}_0 = \pm \frac{\pi}{a} \hat{x} \pm \frac{\pi}{a} \hat{y} \pm \frac{\pi}{a} \hat{z} \quad \text{(for s.c.-BL)}
\]

at the corners of the 1st BZ - these are the \( \tilde{k} \) that gives the largest \( E(\tilde{k}) \) for the s-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

$$\Psi(\mathbf{r}) = \sum_{n} \sum_{\mathbf{k}} b_{n} \Phi_{n}(\mathbf{r-R})$$

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

$$\langle \Phi_{n'}(\mathbf{r}) | H | \Phi_{k}(\mathbf{r}) \rangle = E_{k} \langle \Phi_{n'}(\mathbf{r}) | \Phi_{k}(\mathbf{r}) \rangle$$

$$= \langle \Phi_{n'}(\mathbf{r}) | H_{\text{at}} + AU | \Phi_{k}(\mathbf{r}) \rangle$$

$$= E_{n'} \langle \Phi_{n'}(\mathbf{r}) | \Phi_{k}(\mathbf{r}) \rangle + \langle \Phi_{n'}(\mathbf{r}) | AU | \Phi_{k}(\mathbf{r}) \rangle$$
One then sets:

$$0 = (E_n' - E_k) \left< \Phi_n'(\vec{r}) | \Psi_k(\vec{r}) \right> + \left< \Phi_n'(\vec{r}) | \Delta U(\vec{r}) | \Psi_k(\vec{r}) \right>$$

$$0 = (E_n' - E_k) \sum_n \sum_R e^{i \vec{k} \cdot \vec{R}} \int d^3 r \phi_n^*(\vec{r}) \phi_n(\vec{r} - \vec{R}) b_n$$

$$+ \sum_n \sum_R e^{i \vec{k} \cdot \vec{R}} \int d^3 r \phi_n^*(\vec{r}) \Delta U(\vec{r}) \phi_n(\vec{r} - \vec{R}) b_n$$

$$0 = \sum_n \left[ \sum_R e^{i \vec{k} \cdot \vec{R}} \left\{ (E_n' - E_k) \int d^3 r \phi_n^*(\vec{r}) \phi_n(\vec{r} - \vec{R}) \right. \right.$$

$$+ \left. \int d^3 r \phi_n^*(\vec{r}) \Delta U(\vec{r}) \phi_n(\vec{r} - \vec{R}) \right\} \right] b_n$$

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 no possible values) in no unknowns - the $$b_n$$.

We can rewrite the above in matrix form

$$\sum_n M_{n'n} b_n = 0$$

where $$M_{n'n} = \sum_R e^{i \vec{k} \cdot \vec{R}} \left\{ (E_n' - E_k) \int d^3 r \phi_n^*(\vec{r}) \phi_n(\vec{r} - \vec{R}) \right. \right.$$

$$+ \left. \int d^3 r \phi_n^*(\vec{r}) \Delta U(\vec{r}) \phi_n(\vec{r} - \vec{R}) \right\}$$

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

For each $E_n(\vec{k})$ the corresponding solutions $b_n$ (the $b_n$'s will depend on both $\vec{k}$ and the band index $n$) determine the wave function of the Bloch electron state $\psi_{n_0 k}$ giving the amount that each atomic orbital $\phi_n$ mixes into the state $\psi_{n_0 k}$.

We can rewrite $M_{n n'}$ by separately cutting out the $\vec{k} = 0$ term from the rest:

$$M_{n n'} = (E_{n} - E_{n'}) \int d^3 r \phi_{n}^{\ast}(\vec{r}) \phi_{n'}(\vec{r}) + \int d^3 r \phi_{n}^{\ast}(\vec{r}) \Delta U(\vec{r}) \phi_{n'}(\vec{r})$$

$$+ \sum_{\vec{k} \neq 0} e^{i \vec{k} \cdot \vec{R}} \left\{ (E_{n} - E_{n'}) \int d^3 r \phi_{n}^{\ast}(\vec{r}) \phi_{n'}(\vec{r} - \vec{R}) \right.$$ 

$$+ \int d^3 r \phi_{n}^{\ast}(\vec{r}) \Delta U(\vec{r}) \phi_{n'}(\vec{r} - \vec{R}) \right\}$$

Now $\int d^3 r \phi_{n}^{\ast}(\vec{r}) \phi_{n}(\vec{r}) = \delta_{n n'}$ 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

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

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

And the condition

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

can be written as

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

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

\[ - \sum_{n} \left[ \sum_{R \neq 0} e^{i \vec{k} \cdot \vec{R}} \gamma_{n'n}(\vec{R}) \right] b_n \]

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 \( \left| \Phi_n^*(\vec{r}) \Phi_n(\vec{r}) \right| \) is large only at \( r = 0 \) where \( \Delta U \) is small.
So all terms on right hand side of above equation are small

⇒ left hand side \((E_k - E_{n'}) b_{n'}\) is small

⇒ \((E_k - E_{n'})\) small and \(b_{n'} \sim O(1)\)

or \((E_k - E_{n'})\) large and \(b_{n'}\) small

Hence only those atomic orbitals \(\varphi_n\) 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 \(b_n \sim O(1)\).
Those orbitals \(\varphi_n\) not close to the band energy
\((|E_k - E_{n'}|\) large\) will not mix appreciably, i.e.,
we will have \(b_n\) small.

As an example, consider the possible mixing of
S and p orbitals. There is one s-orbital and
three p-orbitals \(p_x, p_y, p_z\), corresponding to
angular momenta \(l_2 = \pm 1, 0\). So our trial
Bloch wavefunction would be

\[
\psi_k = \sum_R e^{i \mathbf{k} \cdot \mathbf{R}} \left\{ b_S \varphi_S (\mathbf{r} - \mathbf{R}) + b_{p_x} \varphi_{p_x} (\mathbf{r} - \mathbf{R}) \\
+ b_{p_z} \varphi_{p_z} (\mathbf{r} - \mathbf{R}) \right\}
\]

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 $det M = 0$ to get the 4 values of $E_i(\mathbf{k})$, we will find that the lowest band $E_1(\mathbf{k})$ is like the $s$-band we found when we introduced the tight binding model. That is, as $\mathbf{k}$ varies, $E_1(\mathbf{k})$ will sweep out a narrow range of energies about $E_s$ with $\max_{\mathbf{k}} E_1(\mathbf{k}) < E_p$, and we will have Bloch states with $b_s \approx 0$ and $b_{p_x} \approx b_{p_y} \approx b_{p_z}$ very small.

The bands $E_2(\mathbf{k})$, $E_3(\mathbf{k})$, $E_4(\mathbf{k})$ will be nearly degenerate $p$-bands, with a narrow energy width about $E_p$ and $\min_{\mathbf{k}} E_j(\mathbf{k}) > E_s$ for $j = 2, 3, 4$. The Bloch state will have $b_s$ very small while some of the $b_{p_x}$, $b_{p_y}$, $b_{p_z}$ are $\approx 0(1)$.

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

$$\psi_1 = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \phi_s (\mathbf{r} - \mathbf{R})$$

for the $s$-band and

$$\psi_1 = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \left[ b_{p_x} \phi_{p_x} (\mathbf{r} - \mathbf{R}) + b_{p_y} \phi_{p_y} (\mathbf{r} - \mathbf{R}) + b_{p_z} \phi_{p_z} (\mathbf{r} - \mathbf{R}) \right]$$

for the 3 $p$-bands.
As the ion spacing decreases, however, the s-bands will start to overlap the p-bands. It is now necessary to compute the 4 bands via a combined calculation using

$$\Psi_k = \sum_i \frac{e^{i\mathbf{k} \cdot \mathbf{R}_i}}{R} (b_s c_{\text{s}}(\mathbf{R} - \mathbf{R}_i) + b_{px} c_{px}(\mathbf{R} - \mathbf{R}_i) + b_{py} c_{py}(\mathbf{R} - \mathbf{R}_i) + b_{pz} c_{pz}(\mathbf{R} - \mathbf{R}_i))$$

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 $b_{p_x}$, $b_{p_y}$ or $b_{p_z}$ are large.

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

We can sketch the situation schematically as follows:

```
\begin{aligned}
&\text{p-bands} \\
&\text{s-bands}
\end{aligned}
```

- Here we have s-p hybridization.
- Even if $Z = 2$, the material will be conducting with partially filled s and p bands.
- If $Z = 2$, material will be insulator - s bands filled, p-bands empty.
For well separated bands, one needs only
- the single $s$ orbital to get the $s$-band
- the three $p$ orbitals ($l=1, m_l=0, \pm 1$) to get the $3p$-bands
- 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 these 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 $\Psi_k = \sum_n b_n \Psi_n(R-R) = \sum_n \sum_k b_n \phi_n(R-R)$
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
$$\sum_n b_n n = 0$$
that we derived earlier!
Let \( \psi_k = \frac{1}{R} \sum e^{i \mathbf{k} \cdot \mathbf{r}} \sum b_n \phi_n(1 - \mathbf{r}) \)

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

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

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

we have

\[
\langle \psi_k | \psi_k \rangle = \sum_{RR'} \sum_{nn'} e^{-i \mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} b_n^* b_{n'} \int d^3r \, \phi_n^*(\mathbf{r}) \phi_{n'}(\mathbf{r} - \mathbf{R})
\]

\[
= \sum_{RR'} \sum_{nn'} e^{-i \mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} b_n^* b_{n'} \int d^3r \, \phi_{n'}^*(\mathbf{r}) \phi_n(\mathbf{r} - \mathbf{R} + \mathbf{R}')
\]

Define \( \alpha_{nn'}(\mathbf{r}) = \int d^3r \, \phi_{n'}^*(\mathbf{r}) \phi_n(\mathbf{r} - \mathbf{R}) \) then

\[
\langle \psi_k | \psi_k \rangle = \sum_{RR'} \sum_{nn'} e^{-i \mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} b_n^* b_{n'} \alpha_{nn'}(\mathbf{R} - \mathbf{R}')
\]

\[
= N \sum_{RR'} \sum_{nn'} e^{-i \mathbf{k} \cdot \mathbf{R}} b_n^* b_{n'} \alpha_{nn'}(\mathbf{R})
\]

Similarly

\[
\langle \psi_k | H | \psi_k \rangle = \sum_{RR'} \sum_{nn'} e^{-i \mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} b_n^* b_{n'} \int d^3r \, \phi_n^*(\mathbf{r} - \mathbf{R}') H(\mathbf{r}) \phi_n(\mathbf{r} - \mathbf{R})
\]

\[
= \sum_{RR'} \sum_{nn'} e^{-i \mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} b_n^* b_{n'} \int d^3r \, \phi_n^*(\mathbf{r}) H(\mathbf{r} + \mathbf{R}') \phi_n(\mathbf{r} - \mathbf{R} + \mathbf{R}')
\]

use \( H(\mathbf{r}) = H(\mathbf{r} + \mathbf{R}) \) to periodic on the BL

and define

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

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

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

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

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

So

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

\[- \sum_{R} \sum_{n} e^{i \overline{k} \cdot \overline{r}} \tilde{\gamma}_{nn}(\overline{R}) b_n - E \sum_{R} \sum_{n} e^{i \overline{k} \cdot \overline{r}} \alpha_{nn}(\overline{R}) b_n = 0\]

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 \( E = \varepsilon_n(\overline{k}) \). There are \( n \) solutions to \( \det M = 0 \).
We can further write \( H = H_0 + \Delta H \)

\[
\hat{\Sigma}_{nn'}(\vec{R}) = - \int d^3 r \, \phi_n^*(\vec{r}) \left[ H_0 + \Delta H(\vec{R}) \right] \phi_n(\vec{R} - \vec{r})
\]

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

\[
= -E_n \alpha_{n'n}(\vec{R}) + \gamma_{n'n}(\vec{R})
\]

Same as defined in earlier discussion

So we get

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

Note \( \alpha_{n'n}(0) = S_{n'n} \) by orthogonality of the \( \phi_n \)
and \( \gamma_{n'n}(0) = -\beta_{n'n} \) as defined in our earlier discussion

So

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

\[
= \sum_n \left[ (E_{n'} - E) \alpha_{n'n} - \beta_{n'n} \right] b_n
\]

with \( \sum_n \left[ (E_{n'} - E) \alpha_{n'n} - \beta_{n'n} \right] b_n = 0 \)

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

Same as we found before, only here we call \( \varepsilon_\vec{R} = E \).