

$\Rightarrow$ 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 $\frac{1}{2} \frac{\hbar^2 k^2}{m^*} \sim \tilde{\gamma} k^2 a^2$

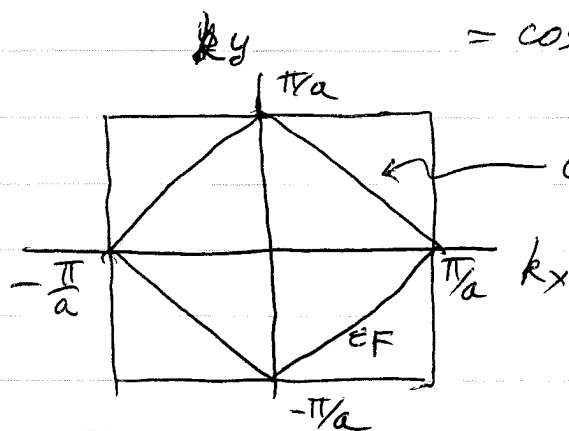
$\Rightarrow m^* \approx \frac{\hbar^2}{2 \tilde{\gamma} a^2}$

But at higher k

in 2D $E_k = E_0 - \beta - 2\tilde{\gamma} (\cos k_x a + \cos k_y a)$

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

$\cos k_x a + \cos(\pm \pi \pm k_x a)$
 $= \cos k_x a + \cos(\pi \pm k_x a) = 0$



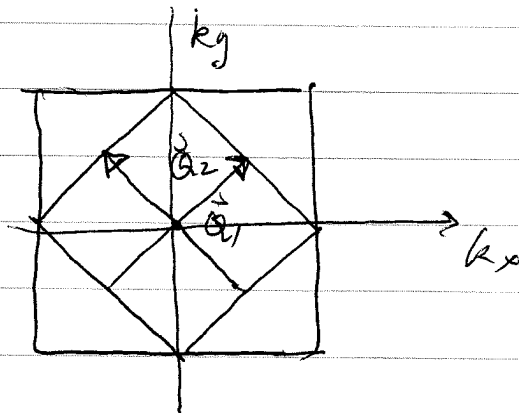
const energy surface
 enclosing $\frac{1}{2}$ area of
 1st BZ

$\nearrow$
 1st BZ (nested
 Fermi surface)

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



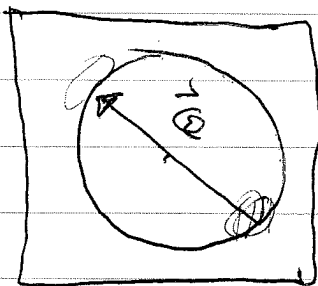
$\vec{G}$ maps a section of the Fermi surface onto another section.

← In the example, $\vec{G}_1$ takes $\frac{1}{4}$ Fermi surface onto opposite surface

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

system has strong susceptibility with respect to fluctuations at wavevector $\vec{G}$.

This does not happen for spherical Fermi surfaces



For a fixed wavevector $\vec{G}$ 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 BZ

$$\vec{k} = \vec{s k} + \vec{k}_0$$

$$E_k = E_0 - \beta - 2\tilde{\gamma} (\cos(\pm\pi + s k_x a) + \cos(\pm\pi + s k_y a))$$

$$= E_0 - \beta + 2\tilde{\gamma} (\cos s k_x a + \cos s k_y a)$$

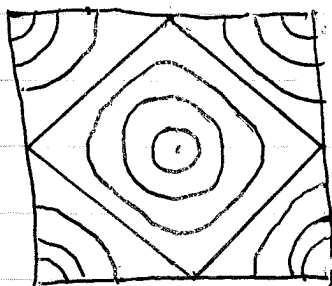
↑ sign is now "+"

$$\approx E_0 - \beta + 2\tilde{\gamma} (1 - \frac{1}{2}(s k_x a)^2 + 1 - \frac{1}{2}(s k_y a)^2)$$

$$= E_0 - \beta + 4\tilde{\gamma} - \tilde{\gamma} |\vec{s k}|^2 a^2$$

↑ depends only on $|\vec{s k}|^2$

So constant energy curves are circular about $\vec{k}_0$



← constant energy surfaces

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

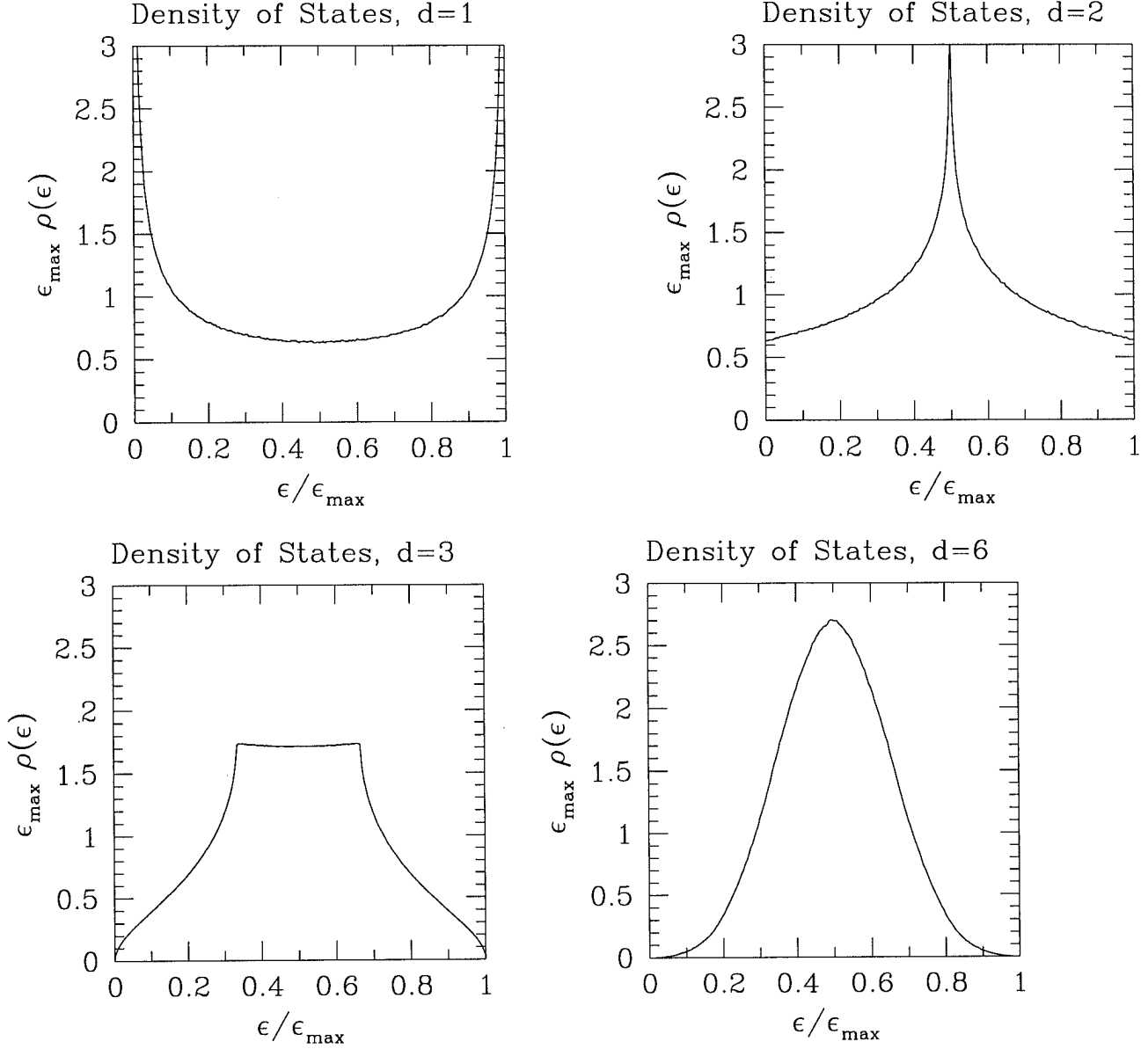
maximum energy of band is at corners $\vec{k}_0 = \pm \frac{\pi}{a} \hat{x} \pm \frac{\pi}{a} \hat{y}$

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

$$\epsilon(k) = t[6 - 2(\cos k_x a + \cos k_y a + \cos k_z a)], \quad (1)$$

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 $\sim \tilde{\gamma}$ 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 $\vec{k}$ of the 1st BZ of the s-band are all filled and the Fermi surface (the points in $\vec{k}$ -space that have the most energetic electrons) will be the discrete points

$$\vec{k}_0 = \pm \frac{\pi}{a} \hat{x} \pm \frac{\pi}{a} \hat{y} \pm \frac{\pi}{a} \hat{z} \quad (\text{for s.c. BL})$$

at the corners of the 1st BZ - these are the $\vec{k}$ that gives the largest $E(\vec{k})$ 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 wavefunction ψ_k should take this into account, we therefore take

$$\psi_k(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \sum_n b_n \phi_n(\vec{r} - \vec{R})$$

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

One then considers the matrix elements

$$\begin{aligned} \langle \phi_{n'}(\vec{r}) | H | \psi_k(\vec{r}) \rangle &= E_k \langle \phi_{n'}(\vec{r}) | \psi_k(\vec{r}) \rangle \\ &= \langle \phi_{n'}(\vec{r}) | H_{at} + \Delta U | \psi_k(\vec{r}) \rangle \\ &= E_{n'} \langle \phi_{n'}(\vec{r}) | \psi_k(\vec{r}) \rangle + \langle \phi_{n'}(\vec{r}) | \Delta U | \psi_k(\vec{r}) \rangle \end{aligned}$$

One then gets:

$$0 = (E_{n'} - E_k) \langle \varphi_{n'}(\vec{r}) | \psi_k(\vec{r}) \rangle + \langle \varphi_{n'}(\vec{r}) | \Delta U(\vec{r}) | \psi_k(\vec{r}) \rangle$$

$$0 = (E_{n'} - E_k) \sum_n \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \int d^3r \varphi_{n'}^*(\vec{r}) \varphi_n(\vec{r} - \vec{R}) b_n \\ + \sum_n \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \int d^3r \varphi_{n'}^*(\vec{r}) \Delta U(\vec{r}) \varphi_n(\vec{r} - \vec{R}) b_n$$

$$0 = \sum_n \left[\sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \left\{ (E_{n'} - E_k) \int d^3r \varphi_{n'}^*(\vec{r}) \varphi_n(\vec{r} - \vec{R}) \right. \right. \\ \left. \left. + \int d^3r \varphi_{n'}^*(\vec{r}) \Delta U(\vec{r}) \varphi_n(\vec{r} - \vec{R}) \right\} \right] b_n$$

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

We can rewrite the above in matrix form

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

$$\text{where } M_{n'n} = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \left\{ (E_{n'} - E_k) \int d^3r \varphi_{n'}^*(\vec{r}) \varphi_n(\vec{r} - \vec{R}) \right. \\ \left. + \int d^3r \varphi_{n'}^*(\vec{r}) \Delta U(\vec{r}) \varphi_n(\vec{r} - \vec{R}) \right\}$$

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 $\det M = 0$, where M 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 this polynomial then determines n_0 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 $\vec{k}$ for the n_0 bands that arise from the n_0 atomic orbitals. — for each value of $\vec{k}$ there will be n_0 energies $E_n(\vec{k})$, $n=1, \dots, n_0$.

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 wavefunction of the Bloch electron state Ψ_{nk} , giving the amount that each atomic orbital ϕ_n mixes into the state Ψ_{nk} .

We can rewrite $M_{n'n}$ by separating out the $\vec{R}=0$ term from the rest.

$$M_{n'n} = (E_{n'} - E_k) \int d^3r \phi_{n'}^*(\vec{r}) \phi_n(\vec{r}) + \int d^3r \phi_{n'}^*(\vec{r}) \Delta U(\vec{r}) \phi_n(\vec{r}) \\ + \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \left\{ (E_{n'} - E_k) \int d^3r \phi_{n'}^*(\vec{r}) \phi_n(\vec{r} - \vec{R}) + \int d^3r \phi_{n'}^*(\vec{r}) \Delta U(\vec{r}) \phi_n(\vec{r} - \vec{R}) \right\}$$

Now $\int d^3r \phi_{n'}^*(\vec{r}) \phi_n(\vec{r}) = \delta_{n'n}$ as the atomic orbitals are normalized.

If we define:

$$\beta_{n'n} \equiv - \int d^3r \varphi_{n'}^*(\vec{r}) \Delta U(\vec{r}) \varphi_n(\vec{r})$$

$$\alpha_{n'n}(\vec{R}) \equiv \int d^3r \varphi_{n'}^*(\vec{r}) \varphi_n(\vec{r} - \vec{R})$$

$$\gamma_{n'n}(\vec{R}) \equiv - \int d^3r \varphi_{n'}^*(\vec{r}) \Delta U(\vec{r}) \varphi_n(\vec{r} - \vec{R})$$

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

$\Rightarrow \alpha_{n'n}, \gamma_{n'n}$ are all small

Also, $\beta_{n'n}$ is small since $|\varphi_{n'}^*(r) \varphi_n(r)|$ is large only at $r \approx 0$ where ΔU is small

So all terms on right hand side of above equation are small

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

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

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

Hence only those atomic orbitals ϕ_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 ψ_k , i.e. have $b_n \sim O(1)$.

Those orbitals ϕ_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 $l_z = \pm 1, 0$. So our trial Bloch wavefunction would be

$$\psi_k = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \left\{ b_s \phi_s(\vec{r} - \vec{R}) + b_{p_x} \phi_{p_x}(\vec{r} - \vec{R}) + b_{p_y} \phi_{p_y}(\vec{r} - \vec{R}) + b_{p_z} \phi_{p_z}(\vec{r} - \vec{R}) \right\}$$

The resulting matrix M will be 4×4

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 $E_n(\vec{k})$ we will find that the lowest band $E_1(\vec{k})$ is like the s -band we found when we ^{first} introduced the tight binding model. That is, as $\vec{k}$ varies, $E_1(\vec{k})$ will sweep out a narrow range of energies about E_s with $\max_{\vec{k}} E_1(\vec{k}) < E_p$, and we will have Bloch states with $b_s \sim 1$ and $b_{p_x} \sim b_{p_y} \sim b_{p_z}$ 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 $\min_{\vec{k}} E_j(\vec{k}) > E_s$ $j=2,3,4$. The Bloch state will have b_s very small while some of the b_{p_x} , b_{p_y} , b_{p_z} 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, i.e. used

$$\psi_{\vec{k}} = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \phi_s(\vec{r} - \vec{R}) \quad \text{for the } s\text{-band}$$

$$\text{and } \psi_{\vec{k}} = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \{ b_{p_x} \phi_{p_x}(\vec{r} - \vec{R}) + b_{p_y} \phi_{p_y}(\vec{r} - \vec{R}) + b_{p_z} \phi_{p_z}(\vec{r} - \vec{R}) \} \\ \text{for the 3 } p\text{-bands}$$

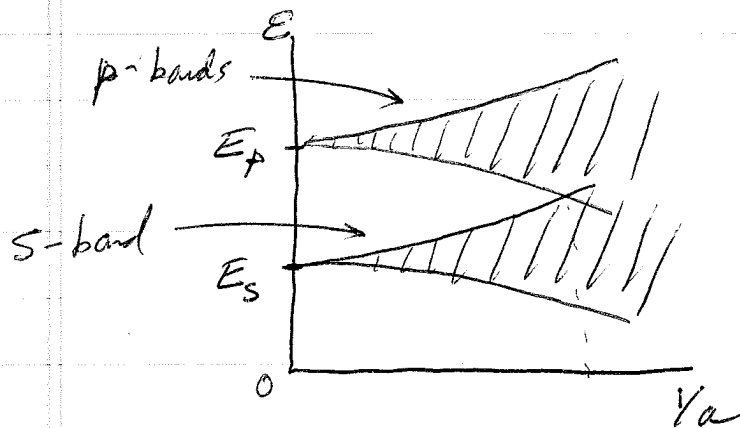
As the ion spacing a decreases, lower, the s band will start to overlap the p -bands. It is now necessary to compute the 4 bands in a combined calculation using

$$\Psi_k = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \left\{ b_s \varphi_s(\vec{r}-\vec{R}) + b_{p_x} \varphi_{p_x}(\vec{r}-\vec{R}) + b_{p_y} \varphi_{p_y}(\vec{r}-\vec{R}) + b_{p_z} \varphi_{p_z}(\vec{r}-\vec{R}) \right\}$$

and one will find that for values k where the bands overlap, one may have Bloch wavefunctions Ψ_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



here the s and p bands have little mixing. If $Z=2$, material will be insulator - s band filled, p -bands empty

here we have s-p hybridization. Even if $Z=2$ the material will be conducting with partially filled s and p bands.

For well separated bands one needs only

- the single ϕ_s orbital to get the s-band
- the three p orbitals ($l=1, m_z=0, \pm 1$) to get the 3 p-bands
- the five d orbitals ($l=2, m_z=0, \pm 1, \pm 2$) to get the 5 d-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 ψ_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 $E_n(\vec{k})$, can also be viewed as arising from a variational calculation.

If one takes
$$\psi_k = \sum_{\vec{r}} e^{i\vec{k} \cdot \vec{r}} \sum_n b_n \phi_n(\vec{r} - \vec{r})$$

as a trial variational wavefunction 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 $\sum_n M_{nn} b_n = 0$ that we derived earlier!

Tight Binding as Variational Calculation

$$\text{let } \psi_k = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \sum_n b_n \varphi_n(\vec{r} - \vec{R})$$

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

$$E = \frac{\langle \psi_k | H | \psi_k \rangle}{\langle \psi_k | \psi_k \rangle} = \frac{\int d^3r \psi_k^*(\vec{r}) H(\vec{r}) \psi_k(\vec{r})}{\int d^3r \psi_k^*(\vec{r}) \psi_k(\vec{r})}$$

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

we have

$$\begin{aligned} \langle \psi_k | \psi_k \rangle &= \sum_{\vec{R}\vec{R}'} \sum_{nn'} e^{i\vec{k} \cdot (\vec{R} - \vec{R}')} b_{n'}^* b_n \int d^3r \varphi_{n'}^*(\vec{r} - \vec{R}') \varphi_n(\vec{r} - \vec{R}) \\ &\quad \text{let } \vec{r} - \vec{R}' \rightarrow \vec{r} \text{ in integral} \\ &= \sum_{\vec{R}\vec{R}'} \sum_{nn'} e^{i\vec{k} \cdot (\vec{R} - \vec{R}')} b_{n'}^* b_n \int d^3r \varphi_{n'}^*(\vec{r}) \varphi_n(\vec{r} - \vec{R} + \vec{R}') \end{aligned}$$

$$\text{Define } \alpha_{n'n}(\vec{R}) \equiv \int d^3r \varphi_{n'}^*(\vec{r}) \varphi_n(\vec{r} - \vec{R}) \quad \text{then}$$

$$\begin{aligned} \langle \psi_k | \psi_k \rangle &= \sum_{\vec{R}\vec{R}'} \sum_{nn'} e^{i\vec{k} \cdot (\vec{R} - \vec{R}')} b_{n'}^* b_n \alpha_{n'n}(\vec{R} - \vec{R}') \\ &\quad \text{let } \vec{R} - \vec{R}' \rightarrow \vec{R} \text{ in sum} \\ &= N \sum_{\vec{R}} \sum_{nn'} e^{i\vec{k} \cdot \vec{R}} b_{n'}^* b_n \alpha_{nn}(\vec{R}) \end{aligned}$$

Similarly

$$\begin{aligned} \langle \psi_k | H | \psi_k \rangle &= \sum_{\vec{R}\vec{R}'} \sum_{nn'} e^{i\vec{k} \cdot (\vec{R} - \vec{R}')} b_{n'}^* b_n \int d^3r \varphi_{n'}^*(\vec{r} - \vec{R}') H(\vec{r}) \varphi_n(\vec{r} - \vec{R}) \\ &\quad \text{let } \vec{r} - \vec{R}' \rightarrow \vec{r} \text{ in integral} \\ &= \sum_{\vec{R}\vec{R}'} \sum_{nn'} e^{i\vec{k} \cdot (\vec{R} - \vec{R}')} b_{n'}^* b_n \int d^3r \varphi_{n'}^*(\vec{r}) H(\vec{r} + \vec{R}') \varphi_n(\vec{r} - \vec{R} + \vec{R}') \end{aligned}$$

use $H(\vec{r}) = H(\vec{r} + \vec{R})$ is periodic on the BL

and define

$$\tilde{\gamma}_{nn'}(\vec{R}) \equiv - \int d^3r \varphi_{n'}^*(\vec{r}) H(\vec{r}) \varphi_n(\vec{r} - \vec{R})$$

$$\begin{aligned}
 \langle \psi_k | H | \psi_k \rangle &= - \sum_{R R'} \sum_{n n'} e^{i \vec{k} \cdot (\vec{R} - \vec{R}')} b_{n'}^* b_n \tilde{\gamma}_{n'n}(\vec{R} - \vec{R}') \\
 &= -N \sum_R \sum_{n n'} e^{i \vec{k} \cdot \vec{R}} b_{n'}^* b_n \tilde{\gamma}_{n'n}(\vec{R}) \quad \text{let } \vec{R} - \vec{R}' \rightarrow \vec{R} \text{ in sum}
 \end{aligned}$$

Now minimize E with respect to the b_n

$$\frac{\partial E}{\partial b_{n'}^*} = \frac{\frac{\partial}{\partial b_{n'}^*} \langle \psi_k | H | \psi_k \rangle}{\langle \psi_k | \psi_k \rangle} - \frac{\langle \psi_k | H | \psi_k \rangle}{\langle \psi_k | \psi_k \rangle^2} \frac{\partial \langle \psi_k | \psi_k \rangle}{\partial b_{n'}^*} = 0$$

multiply all terms by $\langle \psi_k | \psi_k \rangle$

$$\frac{\partial}{\partial b_{n'}^*} \langle \psi_k | H | \psi_k \rangle - \underbrace{\frac{\langle \psi_k | H | \psi_k \rangle}{\langle \psi_k | \psi_k \rangle}}_{= E} \frac{\partial \langle \psi_k | \psi_k \rangle}{\partial b_{n'}^*} = 0$$

So

$$\frac{\partial}{\partial b_{n'}^*} \langle \psi_k | H | \psi_k \rangle - E \frac{\partial}{\partial b_{n'}^*} \langle \psi_k | \psi_k \rangle = 0$$

$$- \sum_R \sum_n e^{i \vec{k} \cdot \vec{R}} \tilde{\gamma}_{n'n}(\vec{R}) b_n - E \sum_R \sum_n e^{i \vec{k} \cdot \vec{R}} \alpha_{n'n}(\vec{R}) b_n = 0$$

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

$$E = \varepsilon_n(\vec{k}) \quad \leftarrow \begin{array}{l} \text{reorganized} \\ n \text{ solutions to } \det M = 0 \end{array}$$

We can further write $H = H_{at} + \Delta U$

$$\begin{aligned}\tilde{\gamma}_{nn'}(\vec{R}) &= - \int d^3r \varphi_{n'}^*(\vec{r}) [H_{at} + \Delta U(\vec{r})] \varphi_n(\vec{r}-\vec{R}) \\ &= -E_{n'} \int d^3r \varphi_{n'}^*(\vec{r}) \varphi_n(\vec{r}-\vec{R}) \\ &\quad - \underbrace{\int d^3r \varphi_{n'}^*(\vec{r}) \Delta U(\vec{r}) \varphi_n(\vec{r}-\vec{R})}_{\substack{\uparrow \text{ same as defined} \\ \text{in earlier discussion}}} \\ &= -E_{n'} \alpha_{n'n}(\vec{R}) + \gamma_{n'n}(\vec{R})\end{aligned}$$

So we get

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

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

$$\begin{aligned}0 &\stackrel{S_0}{=} \sum_n \left[(E_{n'} - E) \delta_{n'n} - \beta_{n'n} \right. \\ &\quad \left. + \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \{ (E_{n'} - E) \alpha_{n'n}(\vec{R}) - \gamma_{n'n}(\vec{R}) \} \right] b_n \\ &= \sum_n M_{n'n} b_n\end{aligned}$$

with $M_{n'n} = (E_{n'} - E) \delta_{n'n} - \beta_{n'n}$

$$+ \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \{ (E_{n'} - E) \alpha_{n'n}(\vec{R}) - \gamma_{n'n}(\vec{R}) \}$$

same as we found before, only here we call $\epsilon_k \equiv E$!