

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 ion 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  $\psi_k$  should take this into account, we therefore take

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

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

One then considers the matrix elements

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

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  $n_0^{\text{th}}$  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  $\Psi_{n\vec{k}}$ , giving the amount that each atomic orbital  $\varphi_n$  mixes into the state  $\Psi_{n\vec{k}}$ .

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

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

Now  $\int d^3r \varphi_{n'}^*(\vec{r}) \varphi_n(\vec{r}) = \delta_{n'n}$  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  $\Delta U$  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  $\varphi_n$  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  $l_z = \pm 1, 0$ . So our trial Bloch wavefunction would be

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

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  $E_n(\vec{k})$  we will find that the lowest band  $E_1(\vec{k})$  is like the  $s$ -band we found when we <sup>first</sup> 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

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

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

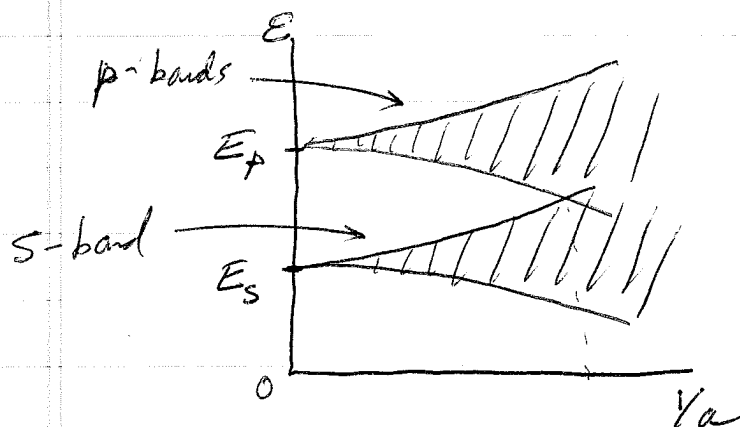
As the ion spacing  $a$  decreases, however, the  $s$  band will start to overlap the  $p$ -bands. It is now necessary to compute the 4 bands in a combined calculation using

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

and one will find that for values  $\mathbf{k}$  where the bands overlap, one may have Bloch wavefunctions  $\Psi_{\mathbf{k}}$  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  $\psi_s$  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  $n^{\text{th}}$  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  $E_n(\vec{k})$ , can also be viewed as arising from a variational calculation.

If one takes 
$$\psi_k = \sum_{\vec{r}} e^{i\vec{k} \cdot \vec{r}} \sum_n b_n \psi_n(\vec{r} - \vec{r}_0)$$

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

$$\sum_n M_{n'n} b_n = 0 \quad \text{that we derived earlier!}$$



## 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

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

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

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

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

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

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

let  $\vec{R} - \vec{R}' \rightarrow \vec{R}$  in sum

Now minimize  $E$  with respect to the  $b_n$

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

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

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

So

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

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

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  $H = H_{at} + \Delta U$

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

So we get

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

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

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

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

$+ \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \left\{ (E_{n'} - E) \alpha_{n'n}(\vec{R}) - \gamma_{n'n}(\vec{R}) \right\}$   
same as we found before, only here we call  $\epsilon_{\vec{k}} \equiv E$  !