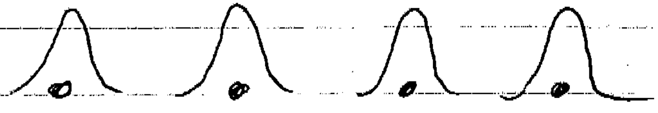
Tight Binding Method

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 eigenstate 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" ~~shell~~ orbital electron. This atomic state is non-degenerate. Let its wave function be $\varphi_0(\vec r)$ for ion centered at origin.

We can construct a Bloch electron state out of the individual atomic states $\varphi_0(\vec r-\vec R)$ by

$$\psi_k(\vec r) = \sum_i e^{i\vec k\cdot\vec R_i}\varphi_0(\vec r-\vec R_i)$$

Counting: We go from N atomic wavefunction $\varphi_0(\vec r-\vec R_i)$, N values of $\vec R_i$, to N Bloch wavefunctions $\psi_k(\vec r)$, N values of $\vec k$ in 1st BZ.

(only mix atomic wavefunctions $\varphi_0(\vec r-\vec R_i)$ where electron has same spin value)

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

H is Hamiltonian of entrire system
Hat is Hamiltonian of atom at origin
ΔU is potential from all atoms <u>except</u> the one at the origin

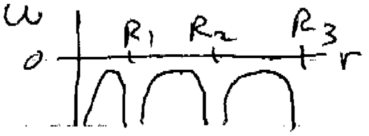
ie if total potential is $U(\vec{r}) = \sum_{R_i} v(\vec{r}-\vec{R}_i)$ ↖ atomic potential

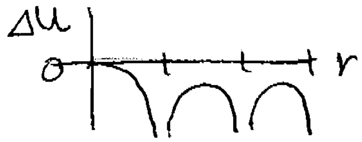
$$H = \frac{p^2}{2m} + U(\vec{r})$$

$$H_{at} = \frac{p^2}{2m} + v(\vec{r})$$

$$\Delta U = \sum_{R_i \neq 0} v(\vec{r}-\vec{R}_i) = U(\vec{r}) - v(\vec{r})$$

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





<u>Now consider:</u>

$$\langle \varphi_0 | H | \psi_k \rangle = \langle \varphi_0 | H_{at} + \Delta U | \psi_k \rangle$$

$$\underset{\substack{\nearrow \\ \text{energy of Bloch} \\ \text{state } \psi_k}}{\varepsilon_k} \langle \varphi_0 | \psi_k \rangle = \underset{\substack{\uparrow \\ \text{atomic energy} \\ \text{level of } \varphi_0}}{E_a} \langle \varphi_0 | \psi_k \rangle + \langle \varphi_0 | \Delta U | \psi_k \rangle$$

$$\varepsilon_k = E_a + \frac{\langle \varphi_0 | \Delta U | \psi_k \rangle}{\langle \varphi_0 | \psi_k \rangle}$$

$$\langle \varphi_0 | \psi_k \rangle = \sum_i e^{i\vec{k}\cdot\vec{R}_i} \int d^3r \; \varphi_0^*(\vec{r})\, \varphi_0(\vec{r}-\vec{R}_i)$$

$$= \underset{\substack{\uparrow \\ \text{from } \vec{R}_i = 0}}{1} + \sum_{R_i \neq 0} e^{i\vec{k}\cdot\vec{R}_i} \underbrace{\int d^3r \; \varphi_0^*(\vec{r})\, \varphi_0(\vec{r}-\vec{R}_i)}_{\text{overlap}}$$

If ions are far apart, overlap integrals are small. Only keep nearest neighbor terms, ie only sum over the smallest non-zero values of $\vec{R}$.

$$\langle \varphi_0 | \psi_k \rangle = 1 + \sum_{nn} e^{i\vec{k}\cdot\vec{R}_i} \underbrace{\int d^3r \; \varphi_0^*(\vec{r})\, \varphi_0(\vec{r}-\vec{R}_i)}_{\alpha(\vec{R}_i)}$$

$$\boxed{\langle \varphi_0 | \psi_k \rangle = 1 + \sum_{nn} e^{i\vec{k}\cdot\vec{R}_i}\, \alpha(\vec{R}_i)} \qquad \alpha \text{ is small}$$

$$\langle \varphi_0 | \Delta U | \psi_k \rangle = \sum_i e^{i\vec{k}\cdot\vec{R}_i} \int d^3r \; \varphi_0^*(\vec{r})\, \Delta U(\vec{r})\, \varphi(\vec{r}-\vec{R}_i)$$

$$= \int d^3r \; \varphi_0^*(\vec{r})\, \Delta U(\vec{r})\, \varphi_0(\vec{r})$$

$$+ \sum_{R_i \neq 0} e^{i\vec{k}\cdot\vec{R}_i} \int d^3r \; \varphi_0^*(\vec{r})\, \Delta U(\vec{r})\, \varphi(\vec{r}-\vec{R})$$

again, keep only terms for nearest neighbor $\vec{R}_i$.

define $\beta \equiv -\int d^3r \; \varphi_0^*(\vec{r})\, \Delta U(\vec{r})\, \varphi_0(\vec{r})$

$$\gamma(\vec{R}) \equiv -\int d^3r \; \varphi_0^*(\vec{r})\, \Delta U(\vec{r})\, \varphi_0(\vec{r}-\vec{R}_i)$$

$$\boxed{\langle \varphi_0 | \Delta U | \psi_k \rangle = -\beta - \sum_{nn} e^{i\vec{k}\cdot\vec{R}_i}\, \gamma(\vec{R})}$$

$$\mathcal{E}_k \simeq E_a - \left[\frac{\beta + \sum_{nn} e^{i\vec{k}\cdot\vec{R}_i}\,\gamma(\vec{R})}{1+\sum_{nn} e^{i\vec{k}\cdot\vec{R}_i}\,\alpha(\vec{R})}\right]$$

$$\boxed{\mathcal{E}_k \simeq E_a - \beta - \sum_{nn} e^{i\vec{k}\cdot\vec{R}_i}\left(\gamma(\vec{R}) - \beta\alpha(\vec{R})\right)}$$

since α small, $\frac{1}{1+\alpha} \simeq 1-\alpha$

Now $\alpha(\vec{R}) = \int d^3r\; \varphi_0^*(\vec{r})\,\varphi_0(\vec{r}-\vec{R}) = \int d^3r\; \varphi_0^*(\vec{r}+\vec{R})\,\varphi_0(\vec{r})$
$= \alpha^*(-\vec{R})$

For s-orbital has real wave function $\varphi_0 \Rightarrow \alpha = \alpha^*$
so $\alpha(\vec{R}) = \alpha(-\vec{R})$

$$\gamma(\vec{R}) = -\int d^3r\,\varphi_0^*(\vec{r})\,\Delta U(\vec{r})\,\varphi_0(\vec{r}-\vec{R})$$

take $\vec{r} \to -\vec{r}$

$$= -\int d^3r\;\varphi_0^*(-\vec{r})\,\Delta U(-\vec{r})\,\varphi_0(-\vec{r}-\vec{R})$$

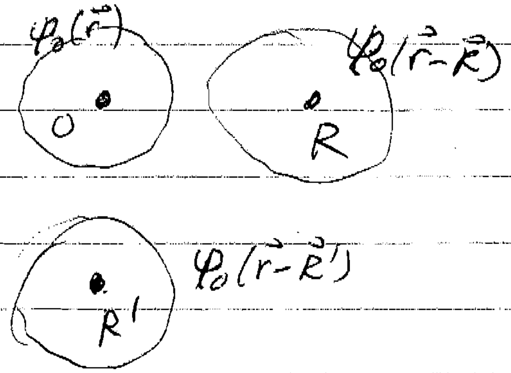
If crystal has inversion symmetry, ie $\Delta U(-\vec{r}) = \Delta U(\vec{r})$ and since s-orbital is spherically symmetric, ie $\varphi_0(\vec{r})$ depends only on $|\vec{r}|$ so $\varphi_0(\vec{r}) = \varphi_0(-\vec{r})$, then

$$= -\int d^3r\;\varphi_0^*(\vec{r})\,\Delta U(\vec{r})\,\varphi_0(\vec{r}+\vec{R}) = \gamma(-\vec{R})$$

So $\gamma(\vec{R}) = \gamma(-\vec{R})$ and $\alpha(\vec{R}) = \alpha(-\vec{R})$

$$\boxed{\mathcal{E}_k = E_a - \beta - \sum_{nn}\left[\gamma(\vec{R}) - \beta\alpha(\vec{R})\right]\cos \vec{k}\cdot\vec{R}}$$

Moreover if the crystal has cubic symmetry, then since φ_0 is rotationally symmetric, $\gamma(\vec{R})$ and $\alpha(\vec{R})$ will be the same value for all nn $\vec{R}$



All will have cubic symmetry so $\gamma(\vec{R}) = \gamma(\vec{R}')$
$\alpha(\vec{R}) = \alpha(\vec{R}')$

$$\varepsilon_k = E_a - \beta - \tilde{\gamma} \sum_{nn} \cos(\vec{k}\cdot\vec{R}) \qquad \tilde{\gamma} = \gamma - \beta\alpha$$

See A+M for case of fcc lattice.
Here we consider the simpler sc lattice
nn $\vec{R}$ are $\pm a\hat{x}$, $\pm a\hat{y}$, $\pm a\hat{z}$

$\vec{k}\cdot\vec{R}$ are $\pm k_x a$, $\pm k_y a$, $\pm k_z a$

$$\varepsilon_k = E_a - \beta - 2\tilde{\gamma}(\cos k_x a + \cos k_y a + \cos k_z a)$$

band width $\varepsilon_k^{max} - \varepsilon_k^{min} = 12\tilde{\gamma}$

for small k, $\cos ka \simeq 1 - \frac{1}{2}k^2a^2$

$$\varepsilon_k \cong E_a - \beta - 2\tilde{\gamma}\left(3 - \tfrac{1}{2}k_x^2a^2 - \tfrac{1}{2}k_y^2a^2 - \tfrac{1}{2}k_z^2a^2\right)$$

$$\cong E_a - \beta - 6\tilde{\gamma} + \tilde{\gamma}k^2a^2$$

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

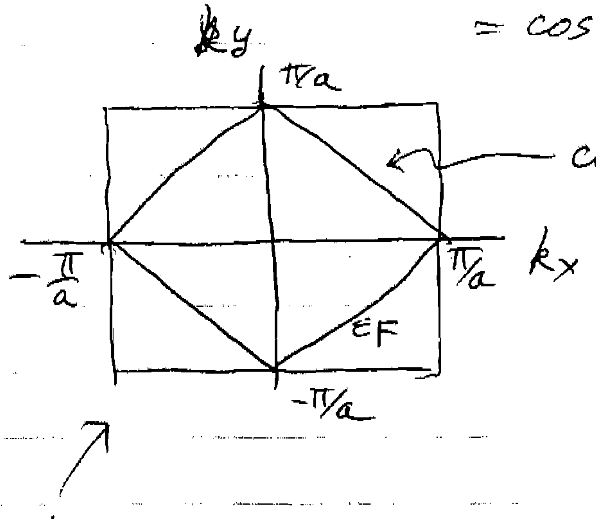
$$\Rightarrow \quad m^* \simeq \frac{\hbar^2}{2\tilde{\gamma} a^2}$$

But at higher k

in 2D $\quad \mathcal{E}_k = E_0 - \beta - 2\tilde{\gamma}\,(\cos k_x a + \cos k_y a)$

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

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



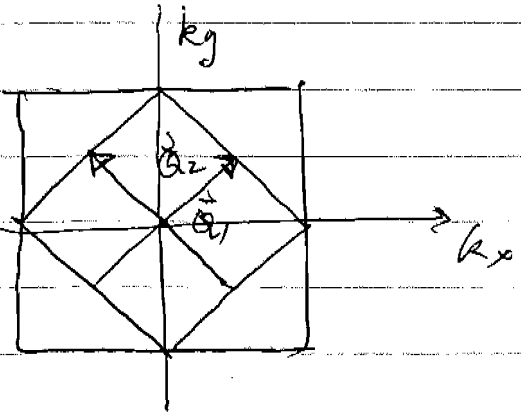
const energy surface enclosing $\frac{1}{2}$ area of 1st BZ

(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 wavevect $\vec{Q}$ maps a section of the fermi surface onto another section.

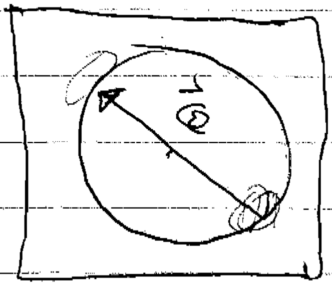


← In this example, $\vec{Q}_1$ takes $\frac{1}{4}$ fermi surface onto opposite surface

⇒ 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 wave vector $\vec{Q}$ 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

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

$$\varepsilon_k = E_a - \beta - 2\tilde{\gamma}\left(\cos(\pm\pi + \delta k_x a) + \cos(\pm\pi + \delta k_y a)\right)$$

$$= E_a - \beta + 2\tilde{\gamma}\left(\cos \delta k_x a + \cos \delta k_y a\right)$$

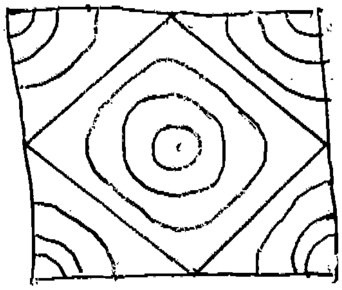
↑ sign is now "+"

$$\simeq E_a - \beta + 2\tilde{\gamma}\left(1 - \tfrac{1}{2}(\delta k_x a)^2 + 1 - \tfrac{1}{2}(\delta k_x a^2)\right)$$

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

↑ depends only on $|\delta\vec{k}|^2$

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 $\vec{k}_0 = \pm\frac{\pi}{a}\hat{x} \pm \frac{\pi}{a}\hat{y}$

What happens in our tight binding model if each ion contributes 2 electrons, ie $Z=2$?

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

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

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

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

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

$$\langle \varphi_{n'}(\vec{r}) | H | \psi_k(\vec{r}) \rangle = \varepsilon_k \langle \varphi_{n'}(\vec{r}) | \psi_k(\vec{r}) \rangle$$

$$= \langle \varphi_{n'}(\vec{r}) | H_{at} + \Delta U | \psi_k(\vec{r}) \rangle$$

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

One then gets:

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

$$0 = (E_{n'} - \mathcal{E}_k) \sum_n \sum_R e^{i\vec{k}\cdot R} \int d^3r\, \varphi^*_{n'}(\vec{r})\, \varphi_n(\vec{r}-\vec{R})\ b_n$$

$$+ \sum_n \sum_R e^{i\vec{k}\cdot R} \int d^3r\, \varphi^*_{n'}(\vec{r})\, \Delta U(\vec{r})\, \varphi_n(\vec{r}-\vec{R})\ b_n$$

$$\boxed{0 = \sum_n \left[\sum_R e^{i\vec{k}\cdot\vec{R}} \left\{ (E_{n'} - \mathcal{E}_k) \int d^3r\, \varphi^*_{n'}(\vec{r})\, \varphi_n(\vec{r}-\vec{R}) + \int d^3r\, \varphi^*_{n'}(\vec{r})\, \Delta U(\vec{r})\, \varphi_n(\vec{r}-\vec{R}) \right\} \right] b_n}$$

If there are n_0 atomic orbitals used in the approximation for $\psi_k(\vec{r})$, then the above is a set of n_0 linear equation (as n' takes all n_0 possible values) in n_0 unknowns - the b_n.

We can rewrite the above in matrix form

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

$$\text{where } M_{n'n} = \sum_R e^{i\vec{k}\cdot\vec{R}} \left\{ (E_{n'} - \mathcal{E}_k) \int d^3r\, \varphi^*_{n'}(\vec{r})\, \varphi_n(\vec{r}-\vec{R}) + \int d^3r\, \varphi^*_{n'}(\vec{r})\, \Delta U(\vec{r})\, \varphi_n(\vec{r}-\vec{R}) \right\}$$

For the above set of homogeneous linear equations to have an non-trivial solution (ie not all $b_n = 0$) it is necessary that the determinant of the matrix $M_{n'n}$ vanish.

The condition $\det \mathbb{M} = 0$, where $\mathbb{M}$ is an $n_0 \times n_0$ matrix, then gives an n_0^{th} order polynomial in the unknown $\mathcal{E}_k$. Finding the zeros of this polynomial then determines n_0 values of $\mathcal{E}_k$ (since $\mathbb{M}$ is an Hermitian matrix, these $\mathcal{E}_k$ are all real valued). The resulting $\mathcal{E}_k$ are the 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 $\mathcal{E}_n(\vec{k})$, $n = 1, \ldots, n_0$.
For each $\mathcal{E}_n(\vec{k})$ 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 $\varphi_{n'}$ mixes into the state ψ_{nk}.

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

$$M_{n'n} = (E_{n'} - \mathcal{E}_k) \int d^3r\, \varphi_{n'}^*(\vec{r})\, \varphi_n(\vec{r}) + \int d^3r\, \varphi_{n'}^*(\vec{r})\, \Delta U(\vec{r})\, \varphi_n(\vec{r})$$

$$+ \sum_{\vec{R}\neq 0} e^{i\vec{k}\cdot\vec{R}} \Big\{ (E_{n'} - \mathcal{E}_k) \int d^3r\, \varphi_{n'}^*(\vec{r})\, \varphi_n(\vec{r}-\vec{R}) + \int d^3r\, \varphi_{n'}^*(\vec{r})\, \Delta U(\vec{r})\, \varphi_n(\vec{r}-\vec{R}) \Big\}$$

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

$$M_{n'n} = (E_{n'}-\mathcal{E}_k)\,\delta_{n'n} - \beta_{n'n}$$
$$+\sum_{R\neq 0} e^{i\vec{k}\cdot\vec{R}}\left\{(E_{n'}-\mathcal{E}_k)\,\alpha_{n'n}(\vec{R}) - \gamma_{n'n}(\vec{R})\right\}$$

And the condition

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

Can be written as

$$(\mathcal{E}_k - E_{n'})\,b_{n'} = -\sum_n \beta_{n'n}\,b_n$$
$$+\sum_n \Big[(E_{n'}-\mathcal{E}_k)\sum_{R\neq 0} e^{i\vec{k}\cdot\vec{R}}\,\alpha_{n'n}(\vec{R})\Big]\,b_n$$
$$-\sum_n \Big[\sum_{R\neq 0} e^{i\vec{k}\cdot\vec{R}}\,\gamma_{n'n}(\vec{R})\Big]\,b_n$$

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 $(\mathcal{E}_k - E_{n'})\, b_{n'}$ is small

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

or $(\mathcal{E}_k - E_{n'})$ large and $b_{n'}$ small

Hence only those atomic orbitals φ_n where the atomic energy E_n is close to the band energy $\mathcal{E}_k$ (so $\mathcal{E}_k - E_n$ is small) will mix appreciably into the Bloch state ψ_k, ie have $b_n \sim O(1)$. Those orbitals φ_n not close to the band energy ($|\mathcal{E}_k - E_n|$ large) will not mix appreciably, ie 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

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

$$\left. + b_{p_y} \varphi_{p_y}(r-R) + b_{p_z} \varphi_{p_z}(\vec{r}-\vec{R}) \right\}$$

The resulting matrix M will be 4×4

Let E_s ad E_p be the atomic energy levels of the s ad p orbitals. We have $E_s < E_p$

If the ion spacing a is large, over-laps are small, ad we expect narrow bands. When we solve $\det M = 0$ to get the 4 values of $\varepsilon_n(\vec{k})$ we will find that the lowest band $\varepsilon_1(\vec{k})$ is like the s-band we found when we first introduced the tight binding model. That is, as $\vec{k}$ varies, $\varepsilon_1(\vec{k})$ will sweep out a narrow range of energies about E_s with $\max_{\vec{k}} \varepsilon_1(\vec{k}) < E_p$, and we will have Bloch states with $b_s \sim 1$ ad $b_{p_x} \sim b_{p_y} \sim b_{p_z}$ very small.

The bands $\varepsilon_2(\vec{k})$, $\varepsilon_3(\vec{k})$, $\varepsilon_4(\vec{k})$ will be nearly degenerate p-bands, with a narrow energy width about E_p and $\min_{\vec{k}} \varepsilon_j(\vec{k}) > E_s$ $j=2,3,4$. 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 ad the p-bands separately, ie used

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

and

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

for the 3 p-bands

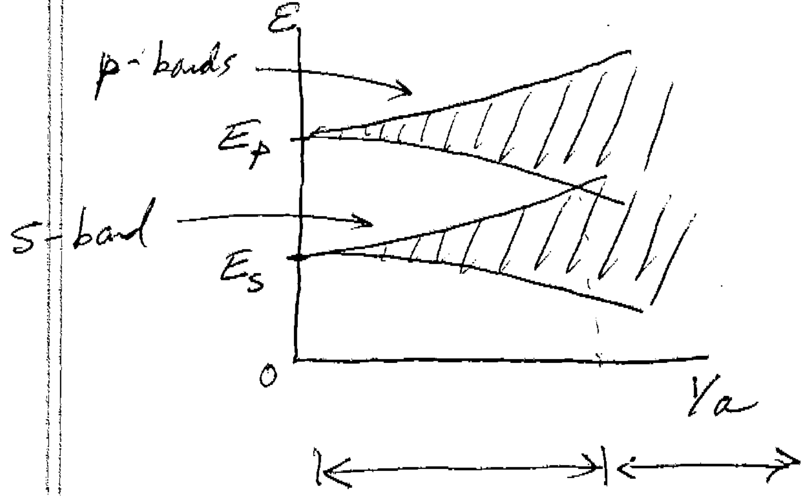
As the ion spacing a decreases, however, the s band will start to overlap the p-bands. It is now necessary to compute the 4 bands in a combined calculation using

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

and one will find that for values $\vec{k}$ 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 <u>well separated bands</u> 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 ($l=2, m_z=0, \pm1, \pm2$) 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 ~~plus~~ all six of these orbitals (ie the 5 $(n-1)$d orbitals and the single ns orbital)

<u>Note:</u> Our equation $\det M = 0$, that determines the tight binding band structure energies $\varepsilon_n(\vec{k})$, can also be viewed as arising from a <u>variational calculation</u>.

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

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 $\sum_{n} M_{n'n} b_n = 0$ that we derived earlier!

Tight Binding as Variational Calculation

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

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

$$\langle\psi_k|\psi_k\rangle = \sum_{RR'}\sum_{nn'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\, b_{n'}^* b_n \int d^3r\, \varphi_{n'}(\vec{r}-\vec{R}')\, \varphi_n(\vec{r}-\vec{R})$$

let $\vec{r}-\vec{R}' \to \vec{r}$ in integral

$$= \sum_{RR'}\sum_{nn'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\, b_{n'}^* b_n \int d^3r\, \varphi_{n'}^*(\vec{r})\, \varphi_n(\vec{r}-\vec{R}+\vec{R}')$$

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

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

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

$$= N \sum_{R}\sum_{nn'} e^{i\vec{k}\cdot\vec{R}}\, b_{n'}^* b_n\, \alpha_{n'n}(\vec{R})$$

Similarly

$$\langle\psi_k|H|\psi_k\rangle = \sum_{RR'}\sum_{nn'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\, b_{n'}^* b_n \int d^3r\, \varphi_{n'}^*(\vec{r}-\vec{R}')\, H(\vec{r})\, \varphi_n(\vec{r}-\vec{R})$$

let $\vec{r}-\vec{R}' \to \vec{r}$ in integral

$$= \sum_{RR'}\sum_{nn'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\, b_{n'}^* b_n \int d^3r\, \varphi_{n'}^*(\vec{r})\, H(\vec{r}+\vec{R}')\, \varphi_n(\vec{r}-\vec{R}+\vec{R}')$$

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

and define

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

$$\langle \psi_k | H | \psi_k \rangle = -\sum_{RR'} \sum_{nn'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} b^*_{n'} b_n \tilde{\gamma}_{n'n}(\vec{R}-\vec{R}')$$

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

$$= -N \sum_{R} \sum_{nn'} e^{i\vec{k}\cdot\vec{R}} b^*_{n'} b_n \tilde{\gamma}_{n'n}(\vec{R})$$

Now minimize E with respect to the b_n

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

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

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

So

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

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

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

$E = \varepsilon_n(\vec{k})$ ← [illegible]

n solutions to $\det M = 0$

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

$$\tilde{\gamma}_{nn'}(\vec{R}) = -\int d^3r\, \varphi^*_{n'}(\vec{r})\left[H_{at} + \Delta U(\vec{r})\right]\varphi_n(\vec{r}-\vec{R})$$

$$= -E_{n'}\int d^3r\, \varphi^*_{n'}(\vec{r})\,\varphi_n(\vec{r}-\vec{R})$$

$$\underbrace{-\int d^3r\, \varphi^*_{n'}(\vec{r})\,\Delta U(\vec{r})\,\varphi_n(\vec{r}-\vec{R})}$$

$$= -E_{n'}\,\alpha_{n'n}(\vec{R}) + \gamma_{n'n}(\vec{R})$$

$\uparrow$ same as defined in earlier discussion

So we get

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

Note $\alpha_{n'n}(0) = \delta_{n'n}$ by orthogonality of the φ_n

and $\gamma_{n'n}(0) \equiv -\beta_{n'n}$ as defined in our earlier discussion

So

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

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

with

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

same as we found before, only here we call $\mathcal{E}_k \equiv E$!