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 wave function 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:

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

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

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

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

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

We can rewrite the above in matrix form

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

where $M_{n'n} = \sum_R e^{i\vec{k}\cdot\vec{R}} \left\{ (E_{n'} - \varepsilon_k) \int d^3r \, \varphi_{n'}^*(\vec{r}) \varphi_n(\vec{r} - \vec{R}) \right.$

$$\left. + \int d^3r \, \varphi_{n'}^*(\vec{r}) \Delta U(\vec{r}) \varphi_n(\vec{r} - \vec{R}) \right\}$$

For the above set of homogeneous linear equation 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 $\det M = 0$, where M is an $n_0 \times n_0$ matrix, then gives an n_0^{th} order polynomial in the unknown ε_k. Finding the zeros of this polynomial then determines n_0 values of ε_k (since M is an Hermitian matrix, these ε_k are all real valued). The resulting ε_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 $\varepsilon_n(\vec{k})$, $n = 1, ..., n_0$.

For each $\varepsilon_n(\vec{k})$ 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 separating out the $\vec{R} = 0$ term from the rest.

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

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

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

$$M_{n'n} = (E_{n'}-\mathcal{E}_k)\,\delta_{n'n} - \beta_{n'n}$$

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

And the condition

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

Can be written as

$$(\mathcal{E}_k - E_{n'})\, b_{n'} = -\sum_n \beta_{n'n}\, b_n$$

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

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

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 $|\varphi_{n'}^*(r)\varphi_n(r)|$ 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 wave function would be

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

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

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 $\mathcal{E}_n(\vec{k})$ we will find that the lowest band $\mathcal{E}_1(\vec{k})$ is like the s-band we found when we first introduced the tight binding model. That is, as $\vec{k}$ varies, $\mathcal{E}_1(\vec{k})$ will sweep out a narrow range of energies about E_s with $\max_{\vec{k}} \mathcal{E}_1(\vec{k}) < E_p$, 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 $\mathcal{E}_2(\vec{k})$, $\mathcal{E}_3(\vec{k})$, $\mathcal{E}_4(\vec{k})$ will be nearly degenerate p-bands, with a narrow energy width about E_p and $\min_{\vec{k}} \mathcal{E}_j(\vec{k}) > E_s$ $j = 2,3,4$. 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, ie used
$$\psi_k = \sum_R e^{i\vec{k}\cdot\vec{R}} \, \varphi_s(\vec{r}-\vec{R}) \qquad \text{for the } s\text{-band}$$

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

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

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

and one will find that for values k where
the bands overlap, one may have Bloch
wave functions 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
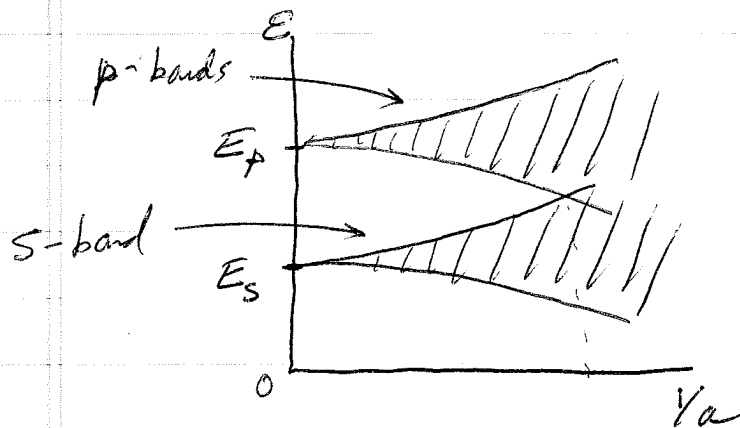
here the s and   here we have s-p hybridization
p bands have   Even if $Z=2$ the material will be
little mixing.   conducting with partially filled
If $Z=2$, material   s and p bands.
will be insulator — s band filled, p-bands empty

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 nth 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)

Note: 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 variational calculation.

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

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

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

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

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

we have

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

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

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

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

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

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

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

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

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

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

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 $E = \varepsilon_n(\vec{k})$ ⟵ ~~onegewaluaas~~

$\llcorner$ n solutions to det $M = 0$

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

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

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

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

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

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

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

So

$$\textcircled{0} = \sum_n \Bigg[(E_{n'} - E)\delta_{n'n} - \beta_{n'n}$$

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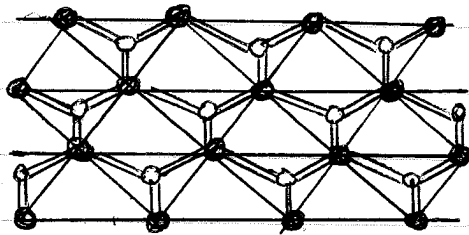
$$= \sum_n M_{n'n} b_n$$

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

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

Same as we found before, only here we call $\varepsilon_k \equiv E$!
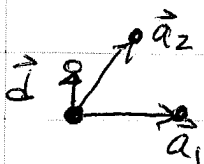
Band structure of Graphene

Graphene is a single ^{2D} layer of graphite, consisting of carbon atoms arranged in a honeycomb structure.

honeycomb structure : underlying triangular BL
with two point basis

Denote $\begin{cases} \bullet & \text{as "A" sites} \\ \circ & \text{as "B" sites} \end{cases}$

A sites sit on the sites $\vec{R}$ of the underlying triangular lattice.
B sites sit at sites $\vec{R} + \vec{d}$

primitive vectors of the BL $\begin{cases} \vec{a}_1 = a\,\hat{x} \\ \vec{a}_2 = \frac{a}{2}\,\hat{x} + \frac{\sqrt{3}}{2}\,a\,\hat{y} \end{cases}$
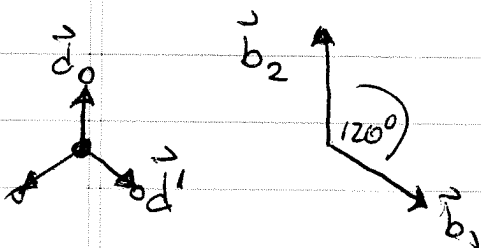

basis vectors $\begin{cases} \vec{0} \\ \vec{d} = \frac{1}{3}\left(\vec{a}_2 + (\vec{a}_2 - \vec{a}_1)\right) \\ \qquad = \frac{a}{\sqrt{3}}\,\hat{y} \end{cases}$
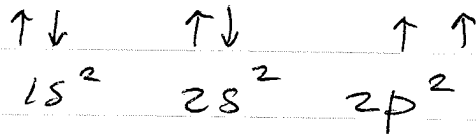
primitive vectors of R.L. $\begin{cases} \vec{b}_1 = \frac{2\pi}{a}\,\hat{x} - \frac{2\pi}{\sqrt{3}\,a}\,\hat{y} \\ \vec{b}_2 = \frac{4\pi}{\sqrt{3}\,a}\,\hat{y} \end{cases}$

nearest neighbors of A site are displaced from A by vectors
$$\vec{d}, \quad \vec{d}' = (\vec{a}_1 - \vec{a}_2) + \vec{d} = \frac{a}{2}\hat{x} - \frac{a}{2\sqrt{3}}\hat{y}, \quad \vec{d}'' = -\vec{a}_2 + \vec{d} = -\frac{a}{2}\hat{x} - \frac{a}{2\sqrt{3}}\hat{y}$$

<u>Atomic</u> Carbon has electron structure

    ↑↓   ↑↓   ↑ ↑

 $1s^2$ $2s^2$ $2p^2$ **6** electrons

                   4 electrons in outermost
                        $n=2$ shell.

The $1s^2$ electrons have significantly lower energy than the $n=2$ electrons. When C is in the honeycomb structure, they remain tightly bound to the C ion and do not participate in bonding or conduction. We thus forget about them!

The $2s^2$ and $2p^2$ electrons are very close in energy. When C is placed in the honeycomb structure, these atomic orbitals will mix ("hybridize").

The $n=2$ orbitals are
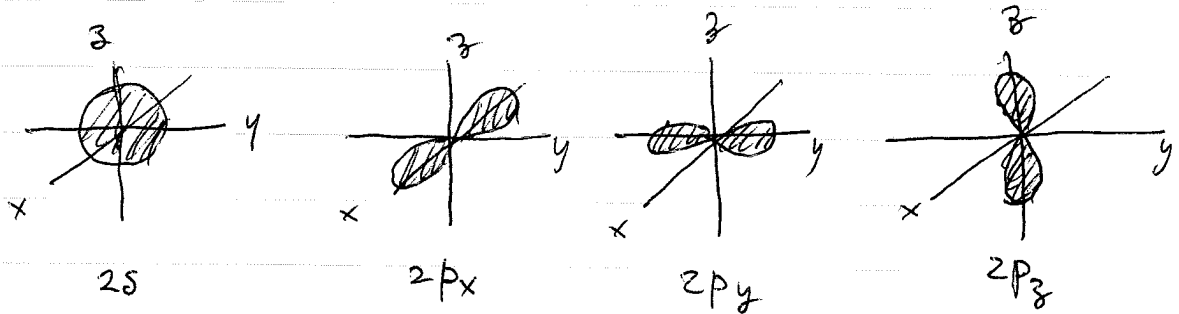
      2S $2p_x$ $2p_y$ $2p_z$

2s is spherically symmetric
2p has lobes oriented along $\hat{x}$, $\hat{y}$, and $\hat{z}$ axes

honeycomb structure we take to be in the xy plane

If one does a tight binding calculation of the band structure from the $n=2$ shell electrons, one should mix in all $2s$, $2p_x$, $2p_y$, $2p_z$ orbitals.

Since there are __two atoms__ per primitive cell of the BL (since it is BL with two-point basis) and there are __four atomic orbitals__ to consider, the Bloch wavefunction is a mixture of __8 terms__:

$$\psi_{\vec{k}} = \sum_R e^{i\vec{k}\cdot\vec{R}} \{ b_{AS}\, \varphi_{AS} + b_{AP_x}\, \varphi_{AP_x} + b_{AP_y}\, \varphi_{AP_y} + b_{AP_z}\, \varphi_{AP_z}$$
$$+ b_{BS}\, \varphi_{BS} + b_{BP_x}\, \varphi_{BP_x} + b_{BP_y}\, \varphi_{BP_y} + b_{BP_z}\, \varphi_{BP_z} \}$$

where φ_{AS}, φ_{AP_x} etc are the s, p_x, etc atomic orbital wavefunctions centered at sites "A", and φ_{BS}, φ_{BP_x} etc are the s, p_x, etc atomic orbital wavefunctions centered at sites "B".

For each value $\vec{k}$ in 1st BZ one then get __eight__ energies $E_n(\vec{k})$, i.e 8 bands.

<u>Digression</u>: For C in a <u>3D diamond structure</u> (fcc with 2-point basis) one finds that the s, p_x, p_y, and p_z orbitals all mix together roughly equally — this is called "sp^3" hybridization since one s mixes with three p orbitals. The 8 bands separate into two distinct groups: the lowest four bands are called "σ-bonding" bands. Here the

wavefunctions from the A and B sites add roughly symmetrically so that the electron probability density is concentrated midway between A and B atoms. These four σ-bonding bands give Bloch electron wavefunctions where the electron density is concentrated on the nearest neighbor bonds of the diamond structure. These are the covalent bonds that hold the diamond structure together. The higher four bands are called "σ^*-antibonding" bands. Here the A and B site wavefunctions add roughly antisymmetrically so that the electron probability vanishes midway between A and B. The σ^*-antibonding bands lie higher in energy than the σ-bonding bands and do not overlap them. In the ground state, each ~~ion~~ of the two ions in a primitive cell of the BL give 4 electrons, for a total of 8 electrons per BL cell. These 8 electrons fill up the 4 σ-bonding bands (each band can hold 2 electrons per ion — since each k can have spin $\uparrow$ and spin $\downarrow$) Hence the 4 σ-bonding bands are completely filled and the 4 σ^*-antibonding bands are completely empty. There is a finite energy gap between the σ and σ^* bands $\Rightarrow$ diamond is an insulator
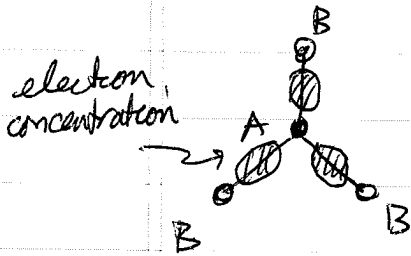

election
concentration $\rightarrow$
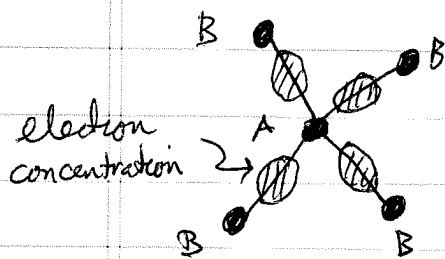
the 4 nearest neighbors of an A site are
the equidistant B sites that lie at
the vertices of a regular tetrahedron.
The σ-bonding states concentrate electron
density along bonds connecting nearest neighbors

Graphene : For C in a 2D honeycomb structure one finds that the s, p_x, and p_y orbitals all mix together roughly equally (these are the orbitals which have significant electron probability in the xy plane) — while the p_z orbital remains separated. The s-p_x-p_y mixed states are called "sp^2" hybridization as one s mixes with two p orbitals.

The sp^2 states give rise to 3 σ-bonding bands and 3 σ^*-antibonding bands. The p_z states give rise to two bands - the π-band and the π^*-band. (so we have a total of 8 bands)

The σ-bonding bands give wavefunctions with electron concentration along the three nearest neighbor bonds between A and B sites in the xy plane. These are the covalent bonds that hold the honeycomb structure together.

electron concentration →

The σ-bonding bands have the lowest energy and all lie ~~below~~ below the Fermi energy. In the ground state they are completely filled taking 6 of the 8 electrons per BZ cell. Since these bands are filled, they play no role in electric conduction in graphene.

The σ^*-antibonding bands all lie above the Fermi energy. In the ground state they are completely empty, hence we ignore them. (There is a finite energy gap between the min energy of the σ^* bands and the Fermi energy)

All the interesting effects concerning conduction therefore lie with the π and π^* bands. These lie essentially between the σ and σ^* bands (though actually the σ band near its max overlaps some with the min of the π band, and the max of the π^* band overlaps somewhat with the min of the σ^* band. But these overlapping regions lie well below or well above, respectively, the Fermi energy and so play no role in conduction — conduction is determined by electrons in close vicinity of the Fermi energy only!)

We will soon see that the π and π^* bands do <u>not</u> overlap. Therefore in the ground state, with 8 electrons per BL cell, 6 electrons go to completely filling the 3 σ bands, and 2 electrons go to completely filling the π band. The π^* and σ^* bands are completely empty. This would be an insulator except—
We will see that the π and $\overline{\pi^*}$ bands