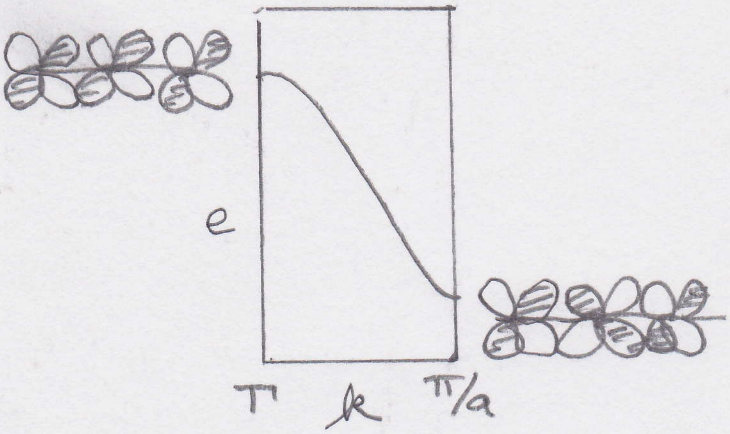
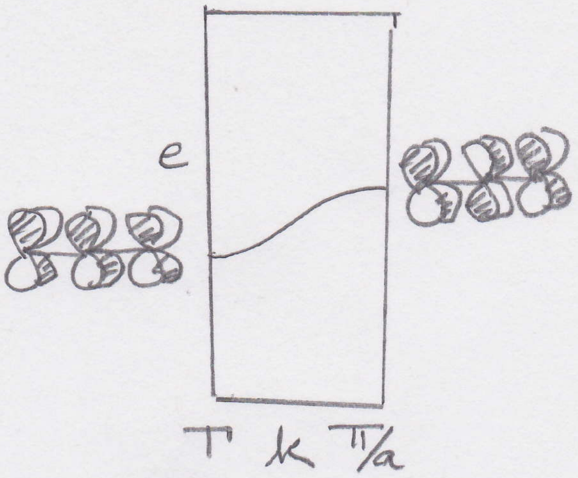
Answers - Chapter 13

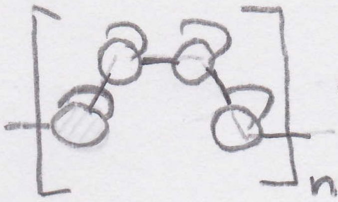
1.



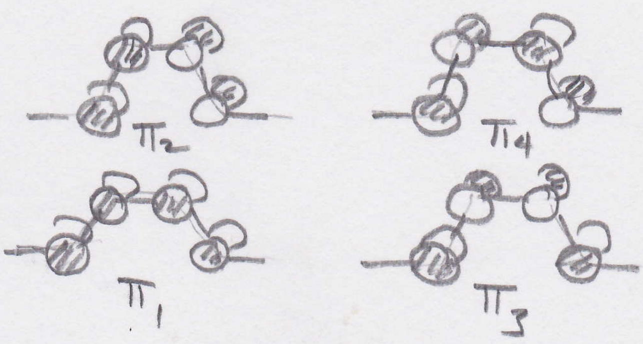


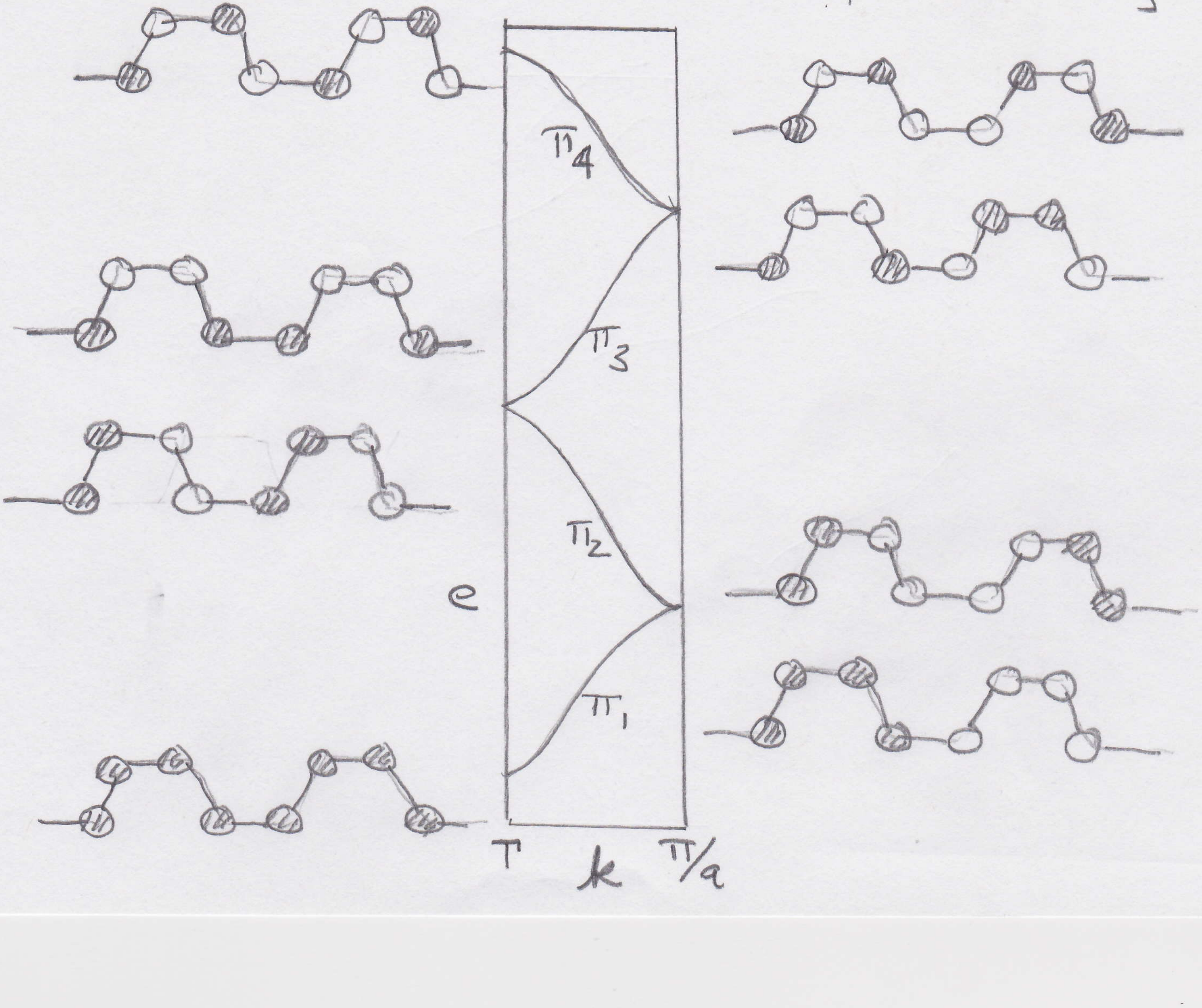
2. The unit cell is:

a)

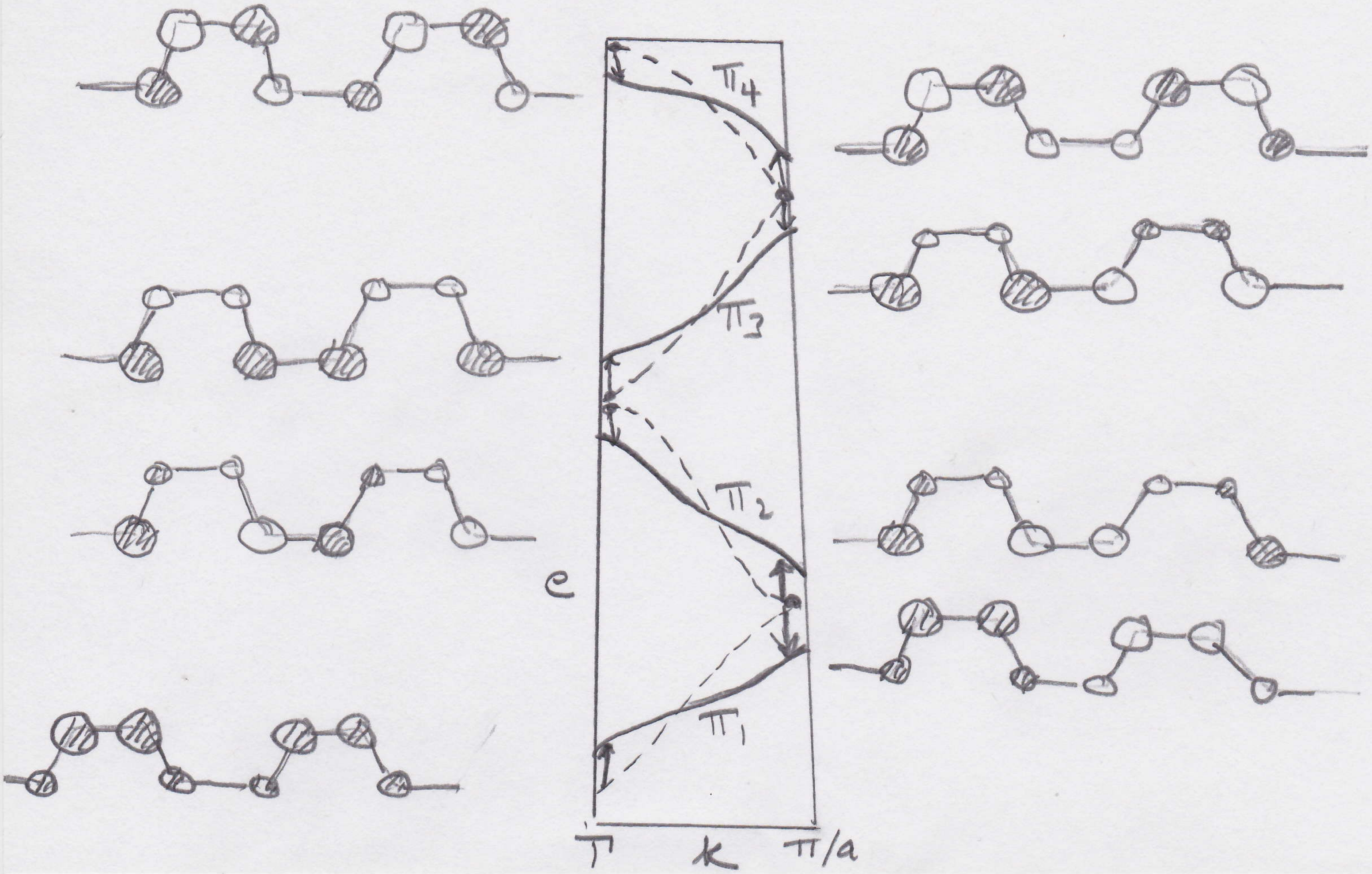


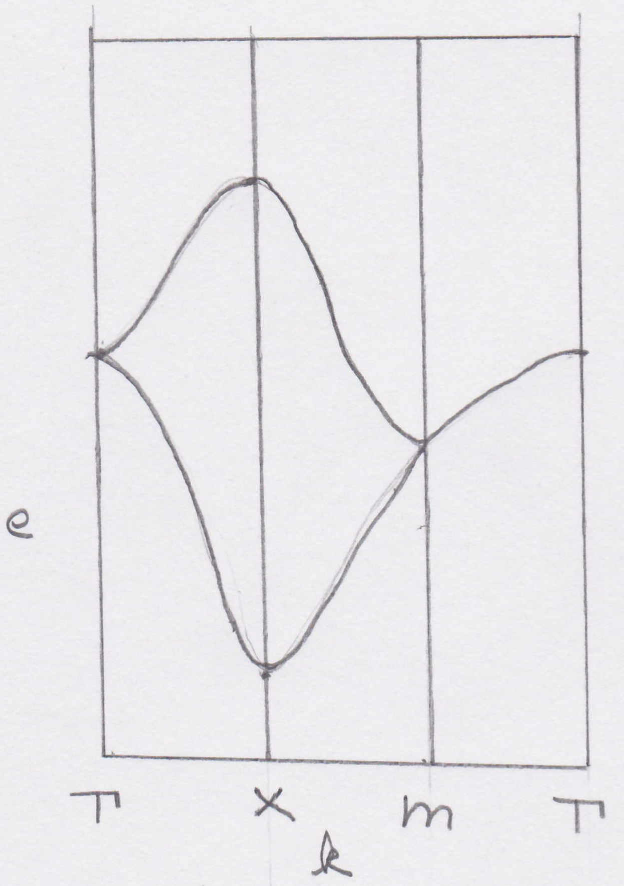
so there are 4π orbitals

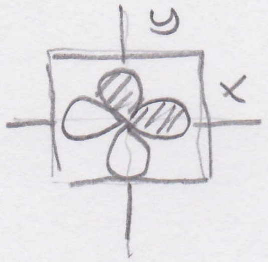




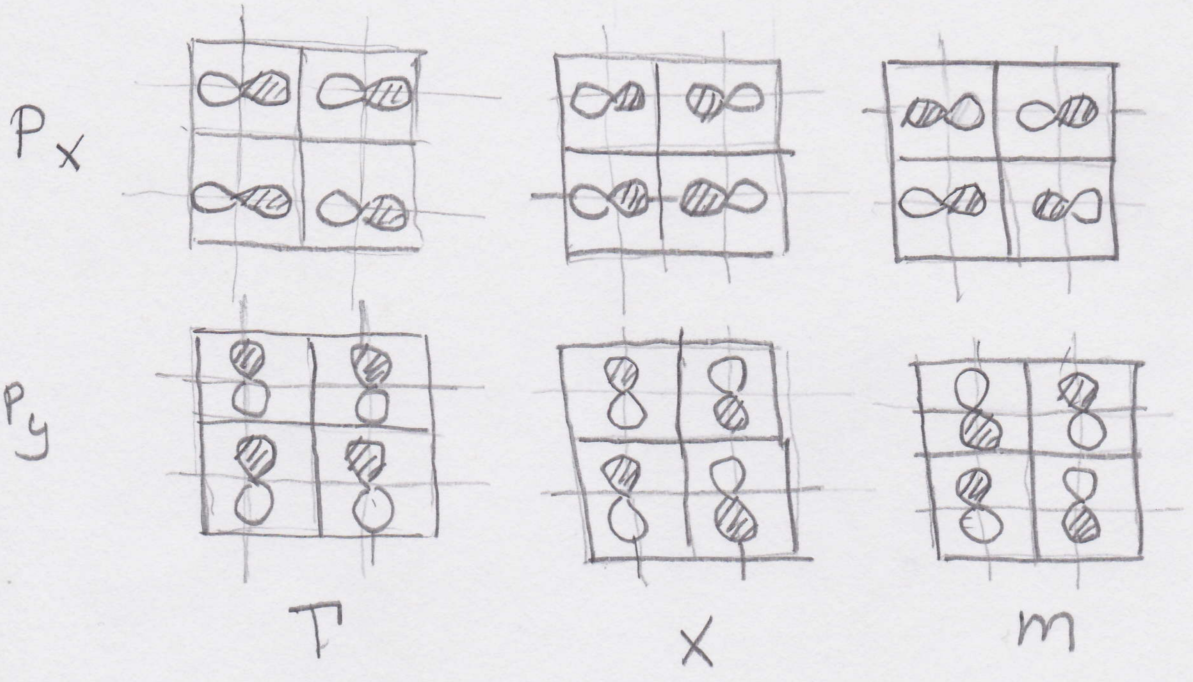
b) Examination of the crystal orbitals at Γ & π/a will tell whether a band goes up or down at this k point, i.e. if there is bonding between orbitals at the edge of the unit cell, then the band will be destabilized. Alternatively if there is antibonding, then the band is stabilized (note: this is for lengthening the distance between unit cells). Furthermore, when all C–C bond lengths are equal, then the coefficients are all equal within the unit cell to preserve mirror planes perpendicular to the propagation axis, as well as, glide planes. When every fourth bond is lengthed, then the crystal orbitals can mix. Another way to look at this is that if the l bonds are very long, then one has the π orbitals of butadiene. So



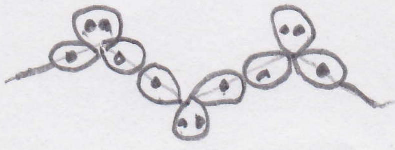




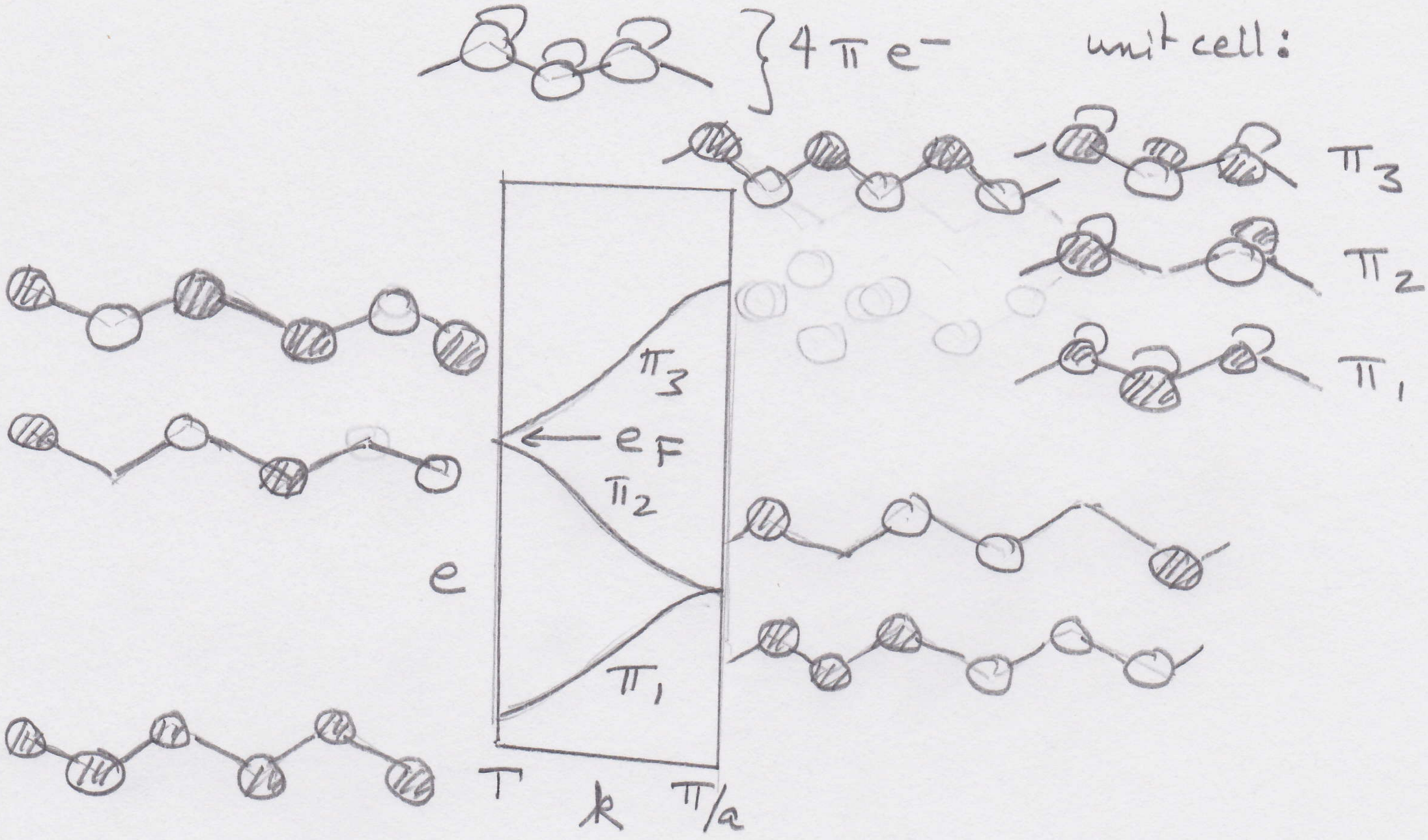
remember -
overlap: σ > π



4. $SrCa_2In_2Ge = In_2Ge^{6-} = 16e^-$ - for the structure one should have $2e^-$ In-In & In-Ge σ bonds and in-plane lone pairs:

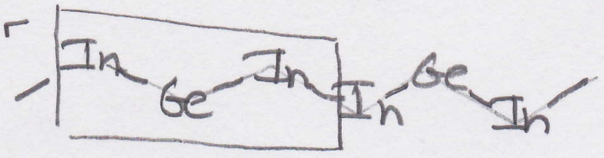


∴ $12e^-$ so there are $4e^-$ in the π system

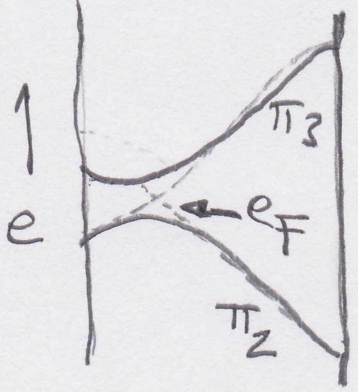


Notice that there has been a little "sleight of hand" here. Going from one unit cell to the next involves translation & then reflection along the propagation axis.

b) For

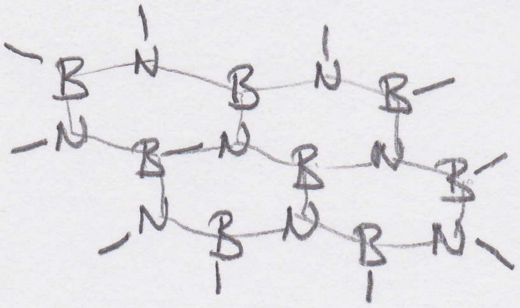


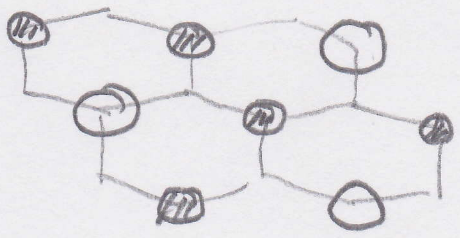
the above bands with coefficients on Ge will be stabilized, hence π_1 and π_3 will be stabilized and π_2 will be unperturbed. There will be mixing near the Γ point so:

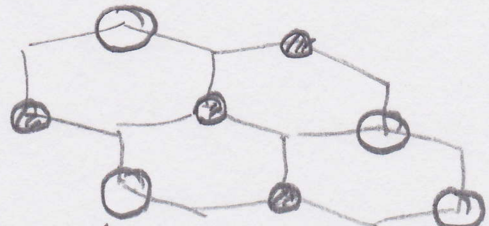


a small gap should open

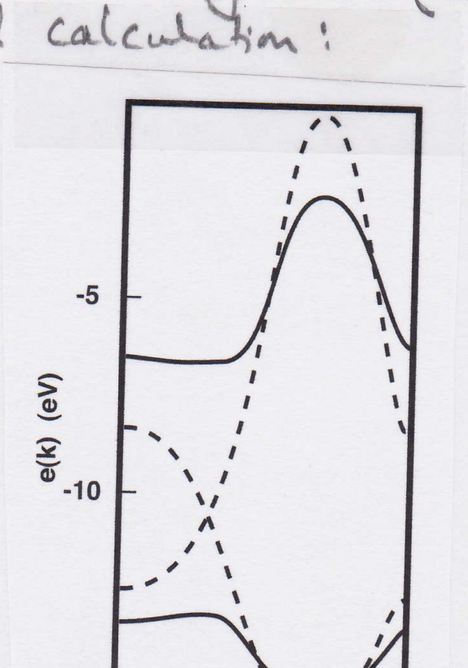
5. At Γ, X & M the coefficients at the 2 carbons are equal, so if $|\delta\alpha_N| \approx |\delta\alpha_C|$ then the band position at this point will not be changed. However this is *not* the case at the K point. Here if one takes ± combinations of the degenerate set one gets:




(+) comb,


(−) comb,

so at K the (+) combination is exclusively on B and so it is destabilized ($e^{(1)} = (+)$) and the (−) combination is stabilized being exclusively on N ($e^{(1)} = (-)$). Here is an Extended Hückel calculation:

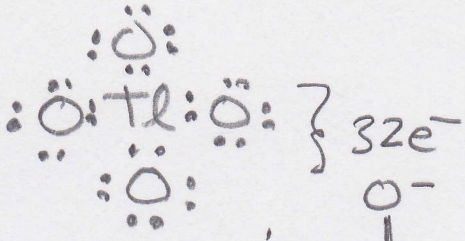


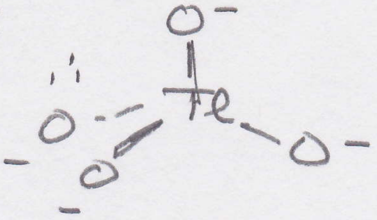
Here the dashed lines are the two π orbitals in C_2

There are changes in the two π bands for BN at Γ and M but clearly the largest are at the K point. While C_2 is a semi-metal, B-N is an insulator!

6. a) $K_5TlO_4 = TlO_4^{5-} =$

$5+3+4(6)=32e^-$





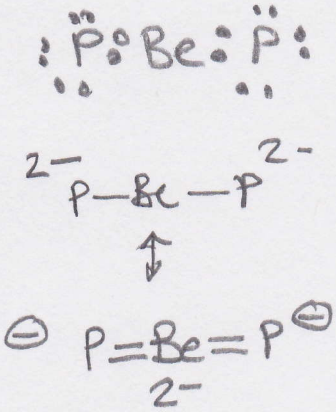
b) $BaHgO_4 = HgO_4^{2-} = 2+4+24 =$ $32e^-$

∴ again tetrahedral

c) $K_4P_2Be = P_2Be^{4-} =$

$4+2+10e^- = 16e^-$

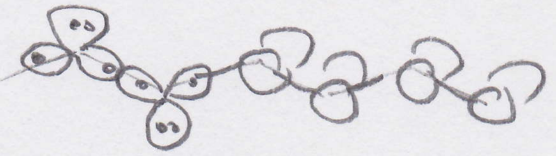
so



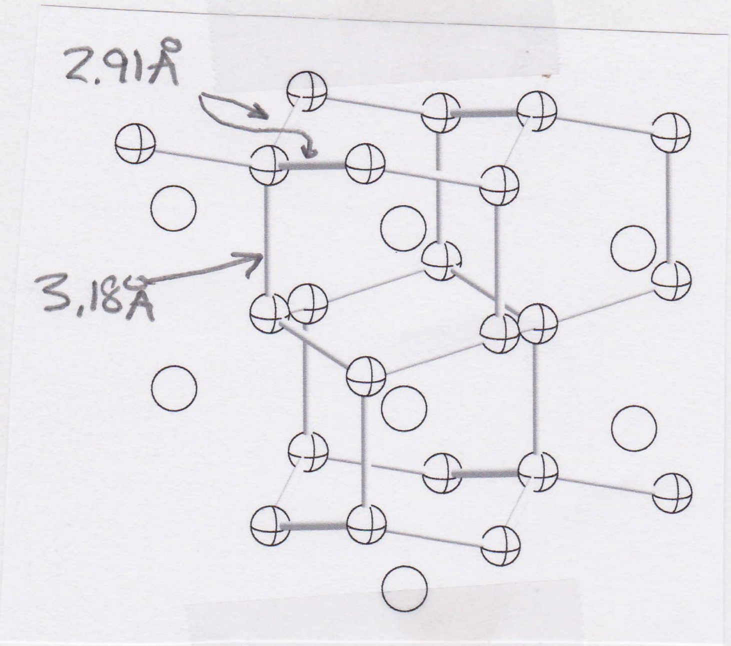
7. a) $Ba_2Ge_4 = Ge_4^{4-}$ each Ge^- has $5e^-$ ∴ 1 lone pair + 3 bonds

the structure of Ge_4^{4-} tetrahedra is consistent with the Z-K rules.

b) $CaIn_2 = In_2^{2-} = In^{-1}$ In^{-1} has $4e^-$. In the structure each In is 2-coordinate so with 2 σ bonds per In, this leaves 2 e^- – so the π system would be totally empty, i.e.

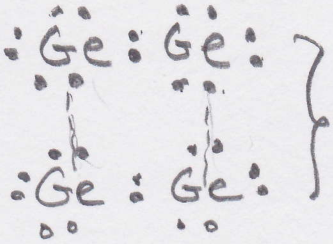


. This would not obey the Z-K formalism. On the other hand, connecting the chains gives:



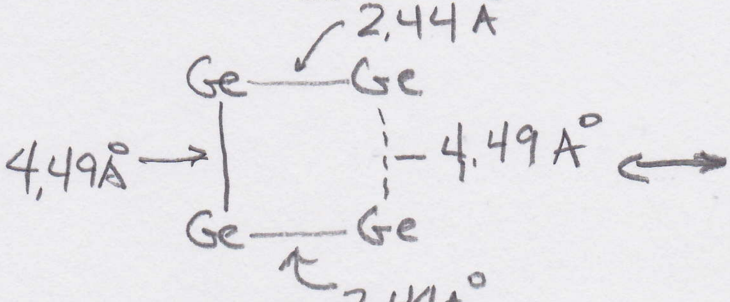
So each In^{-1} is now 4-coordinate. This is called a "stuffed" diamond ~~or~~ adamantane structure. Within each adamantane unit is a Ca^{2+} cation. Notice that there are two different In–In bonds with very different bond lengths.

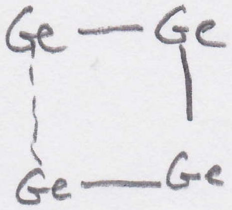
c) $Li_9Ge_4 = Ge_4^{9-} \rightarrow 25e^-$



28e⁻ – so 3 less e⁻

The distances are:



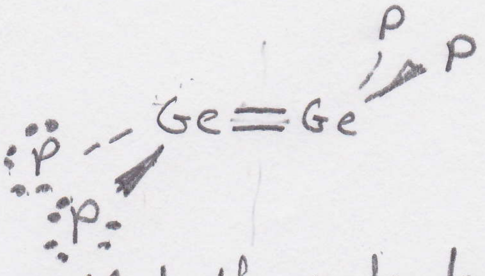


are 3e⁻
?bond delocalized
over 2 centers?

This structure does not apear to obey Z-K rules

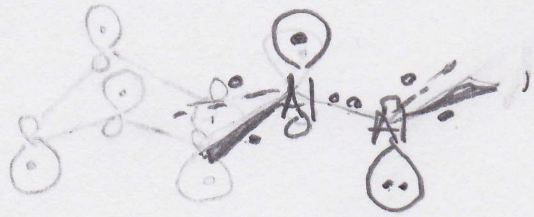
d) $Ba_2GeP_2 = GeP_2^{4-} =$

$4+4+10=18e^-$



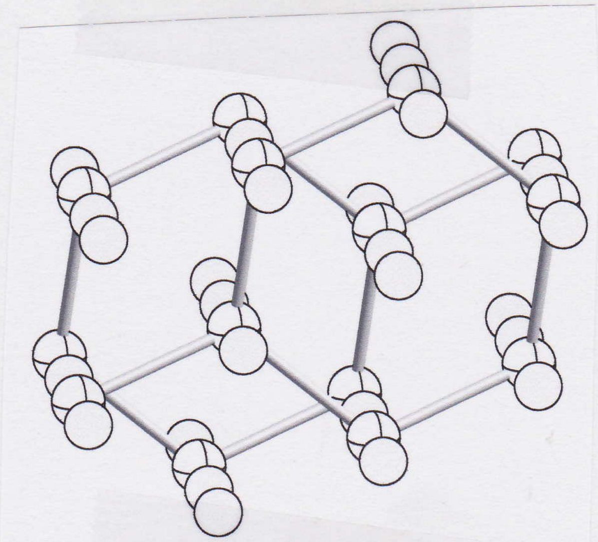
This obeys the Z-K rules. Notice that the molecule is distorted along the lines discussed in Chapter 10.3C.

e) $Li_3Al_2 = Al_2^{3-} = 9e^-$ The structure then would have:



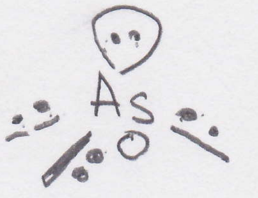
i.e. the bond with lone pair electrons would be half-full

This also is not an example of a "stuffed" cluster like $CaIn_2$. A view from the top shows that there is a layer of Li atoms directly above and below the Al sheets –



thus, this compound does not obey the Z-K formalism.

f) $K_3In_2As_3 = In_2As_3^{3-}$ let $As^{3-} =$



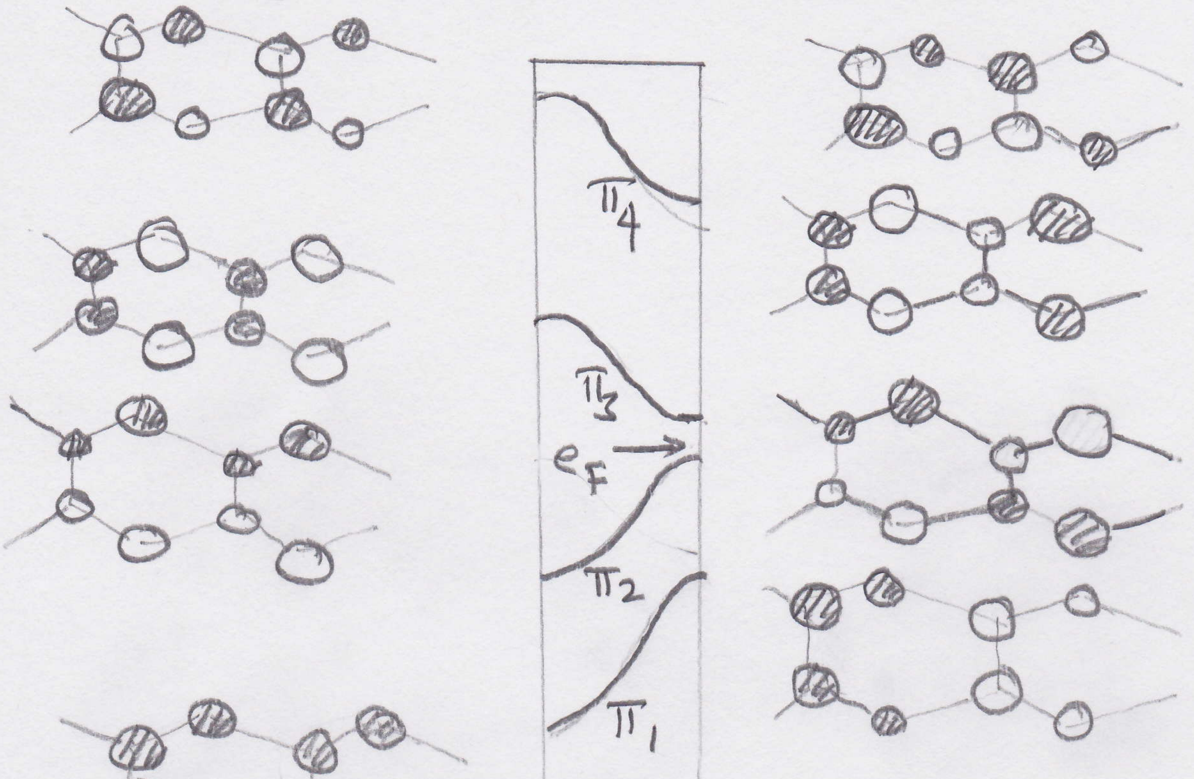
} 3-coordinate

$= 3+15+6 =$
$24e^-$ or $8e^-$ per As

} 4-coordinate

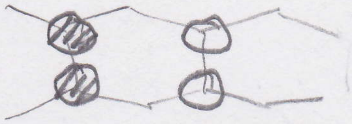
Obeys the Z-K rules.

8. a) The starting orbitals for the cisoid butadiene unit cell were given in 2a). The orbitals then are:

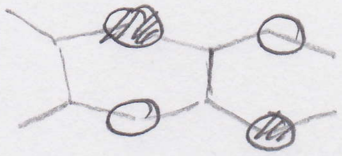


b) The crystal orbitals at $k = \Gamma$ are symmetric or antisymmetric with respect to the xy mirror planes when the two C–C long bond lengths in $\underset{\sim}{B}$ are shortened. This is not true for the $k = \pi/a$ solution.

In order to preserve the xy mirror plane, one must mix π_3 into π_1 and π_4 into π_2, at $k = \pi/a$ giving

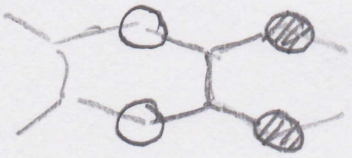


π_1

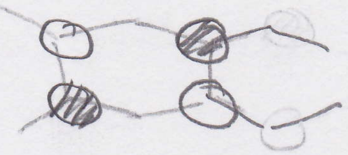


π_2

and mixing π_1 into π_3 and π_2 in π_4 with the reverse phases:

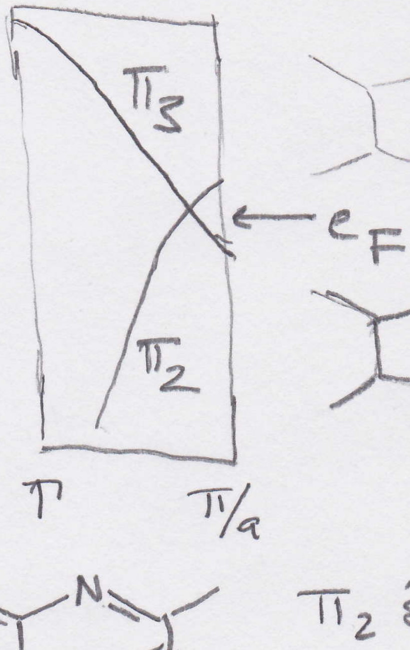


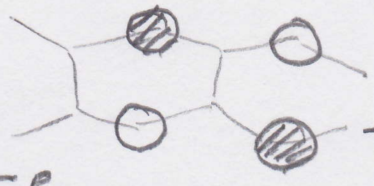
π_3



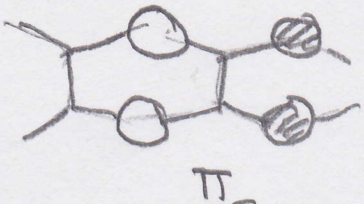
π_4

The major difference here is that π_2 & π_3 are very close in energy an, in fact π_2 lies higher than π_3 if non-nearest neighbors are taken into account:

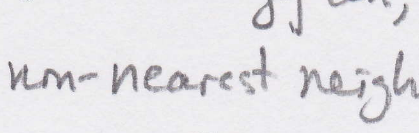




π_2



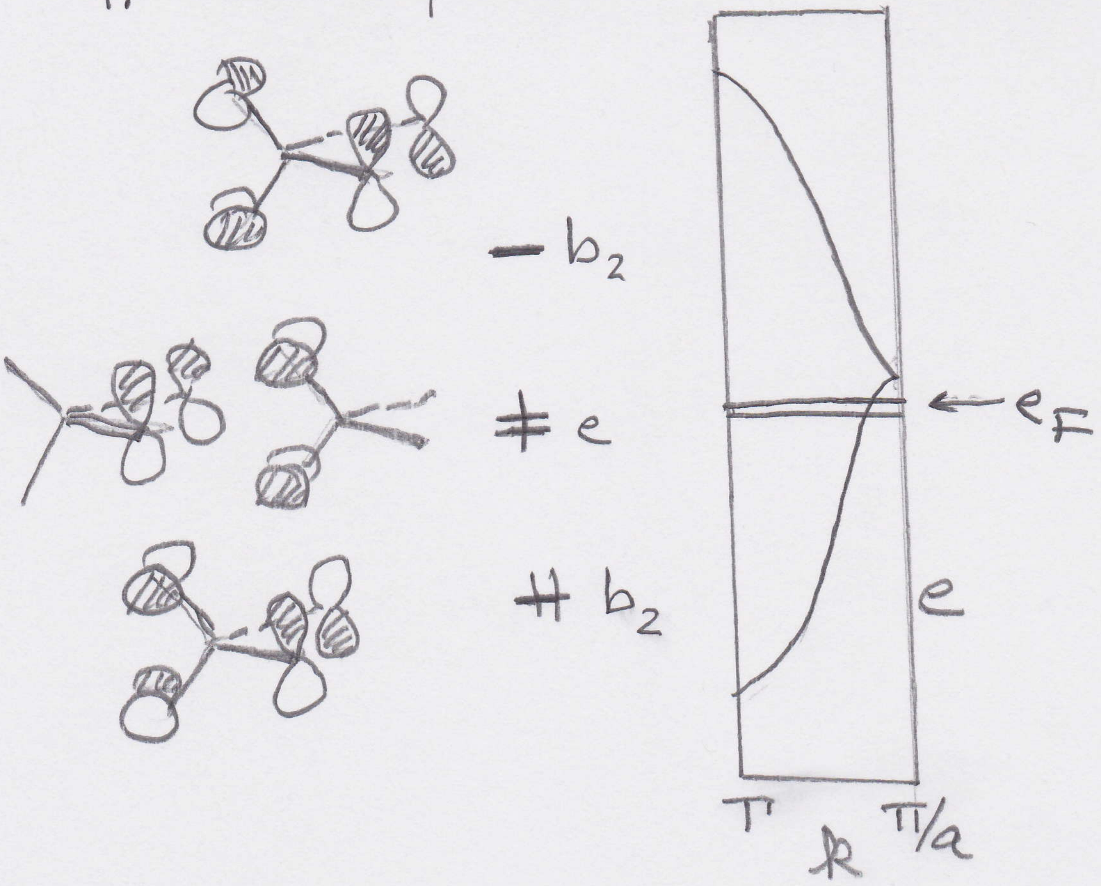
π_3

c) For  π_2 & π_3 will be greatly stabilized at the $k = \pi/a$ point.

But  will stabilize π_1 and π_4 (which is empty) at $k = \pi/a$

π_1 & π_2 will be stabilized at $k = \Gamma$ for both structures. Therefore,  should be more stabile.

9. The four p AOs combine in the following way



You should draw the crystal orbitals to ascertain the band dispersions! Notice that e_F occurs in a region that have a very high spin density.