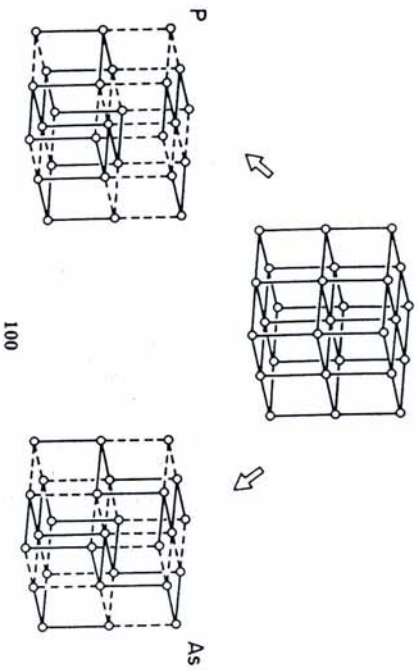


leads to the formation of a real band gap, i.e., to an insulator or a semiconductor. In other cases, a deformation is effective in producing bonds, thereby pulling some states down from the Fermi level region. But because of the three-dimensional linkage it may not be possible to remove all the states from the Fermi level region. Some DOS remains there; the material may still be a conductor.



One final comment that is relevant to the ThC_2Si_2 structure. The reader will note that we did not use a Peierls distortion argument in the resolution of the P-P pairing problem in that common structural type when we discussed it earlier. We could have done so, somewhat artificially, by choosing a structure in which the interlayer P...P separation was so large that the P-P σ and σ^* DOS came right at the Fermi level. Then a pairing distortion could have been invoked, yielding the observed bond. That, however, would have been a somewhat artificial approach. Peierls distortions are ubiquitous and important, but they're not the only way to approach bonds in the solid.

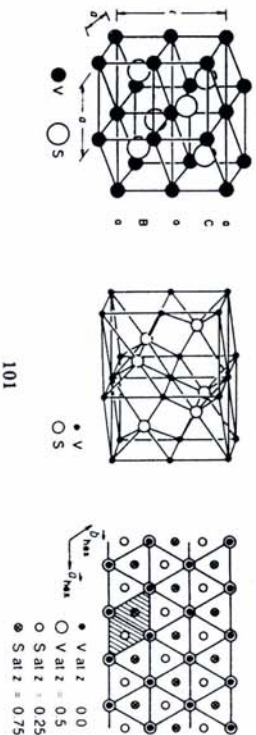
A BRIEF EXCURSION INTO THE THIRD DIMENSION

The applications discussed in the previous section make it clear that one must know, at least approximately, the band structure (and the consequent DOS) of two- and three-dimensional materials before one can make sense of their marvelous geometric richness. The band structures that we have discussed in detail have been mostly one- and two-dimensional.

Now let's look more carefully at what happens as we increase dimensionality.

Three dimensions really introduces little that is new, except for the complexities of drawing and the wonders of group theory in the 230 space groups. The s, p, d bands of a cubic lattice, or of face-centered or body-centered close-packed structures, are particularly easy to construct.^{9,40}

Let's look at a three-dimensional case of some complexity, the NiAs \rightarrow MnP \rightarrow NiP distortion.⁷⁵ The NiAs structure is one of the most common AB structures, with over a hundred well-characterized materials crystallizing in this type. The structure, shown in three different ways in 101, consists of hexagonal close-packed layers that alternate metal and nonmetal atoms. To be specific, let's discuss the VS representative. The structure contains a hexagonal layer of vanadium atoms at $z = 0$, then a layer of sulfur atoms at $z = 1/4$, then a second layer of metal atoms at $z = 1/2$, superimposable on the one at $z = 0$, and, finally, a second layer of main group atoms at $z = 3/4$. The pattern is repeated along the c direction to generate a three-dimensional stacking of the type AbAcAbAc. It should not be imagined, however, that this is a layered compound; it is a tightly connected three-dimensional array. The axial V-V separation is 2.94 Å; the V-V contacts within the hexagonal net are longer, 3.33 Å.⁷⁵

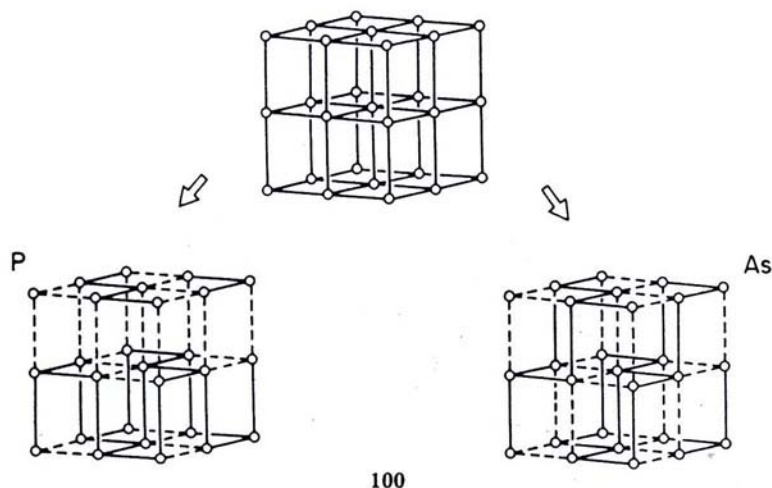


In terms of local coordination, each sulfur sits at the center of a trigonal prism of vanadiums, which in turn are octahedrally coordinated by six sulfurs. The V-S distances are typical of coordination compounds and, while there is no S-S bonding, the sulfurs are in contact with each other.

This is the structure of stoichiometric VS at high temperatures ($> 550^\circ\text{C}$). At room temperature, the structure is a lower symmetry, orthorhombic MnP one. The same structural transition is triggered by a subtle change in stoichiometry in VS_x, by lowering x from 1 at room temperature.⁷⁶

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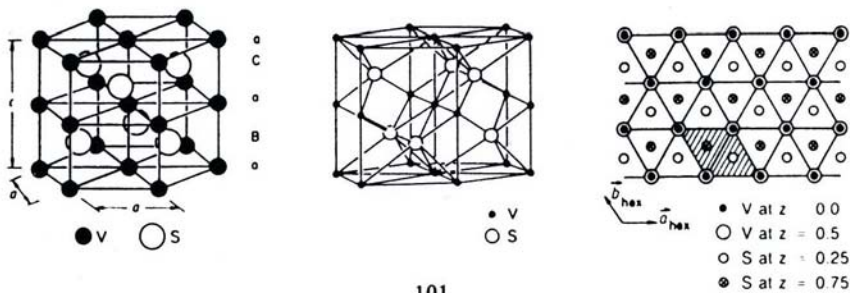
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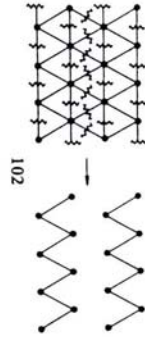


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type. Most (but not all) of the motion takes place in the plane perpendicular to the hexagonal axis. The net effect in each hexagonal net is to break it up into zig-zag chains, as in 102. The isolation of the chains is exaggerated: the short V-V contact emphasized in 102 changes from 3.33 to 2.76, but the V-V distance perpendicular to the plane (not indicated in 102) is not much longer (2.94 Å).



Still further distortions can take place. In NiP, the chains of Ni and P atoms describable in the MnP structure break up into Ni₂ and P₂ pairs. For phosphides, it is experimentally clear that the number of available electrons tunes the transition from one structural type to another. Nine or 10 valence electrons favor the NiAs structure (for phosphides), 11-14 the MnP, and a greater number of electrons the NiP alternative. For the arsenides this trend is less clear.

The details of these fascinating transformations are given elsewhere.⁷³ It is clear that any discussion must begin with the band structure of the aristotype, NiAs (here computed for VS). This is presented in Fig. 37, which is a veritable spaghetti diagram, and seemingly beyond the powers of comprehension of any human being. Why not abdicate understanding, just let the computer spew these bands out and accept (or distrust) them? No, that's too easy a way out. We can understand much of this diagram. First, the general aspect. The hexagonal unit cell is shown in 103. It contains two formula units V₂S₂. That tells us immediately that we should expect 4 × 2 = 8 sulfur bands, two 3s separated from six 3p. And 9 × 2 = 18 vanadium bands, of which 10, the 3d block, should be lowest.

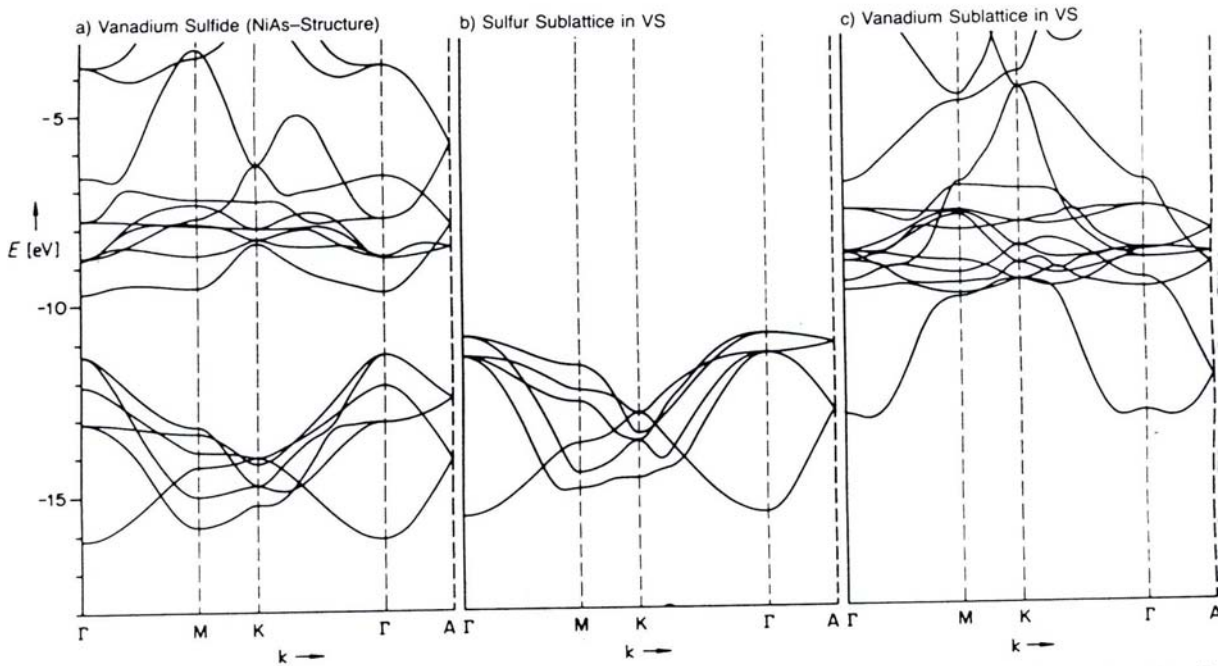
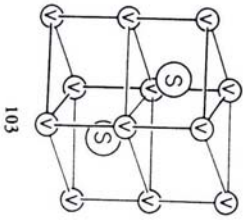
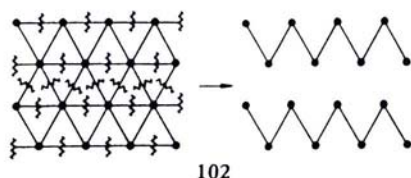


Figure 37 The band structure for VS in the NiAs structure (left), together with the band structures of its S (middle) and V (right) sublattices.

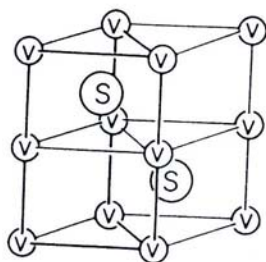
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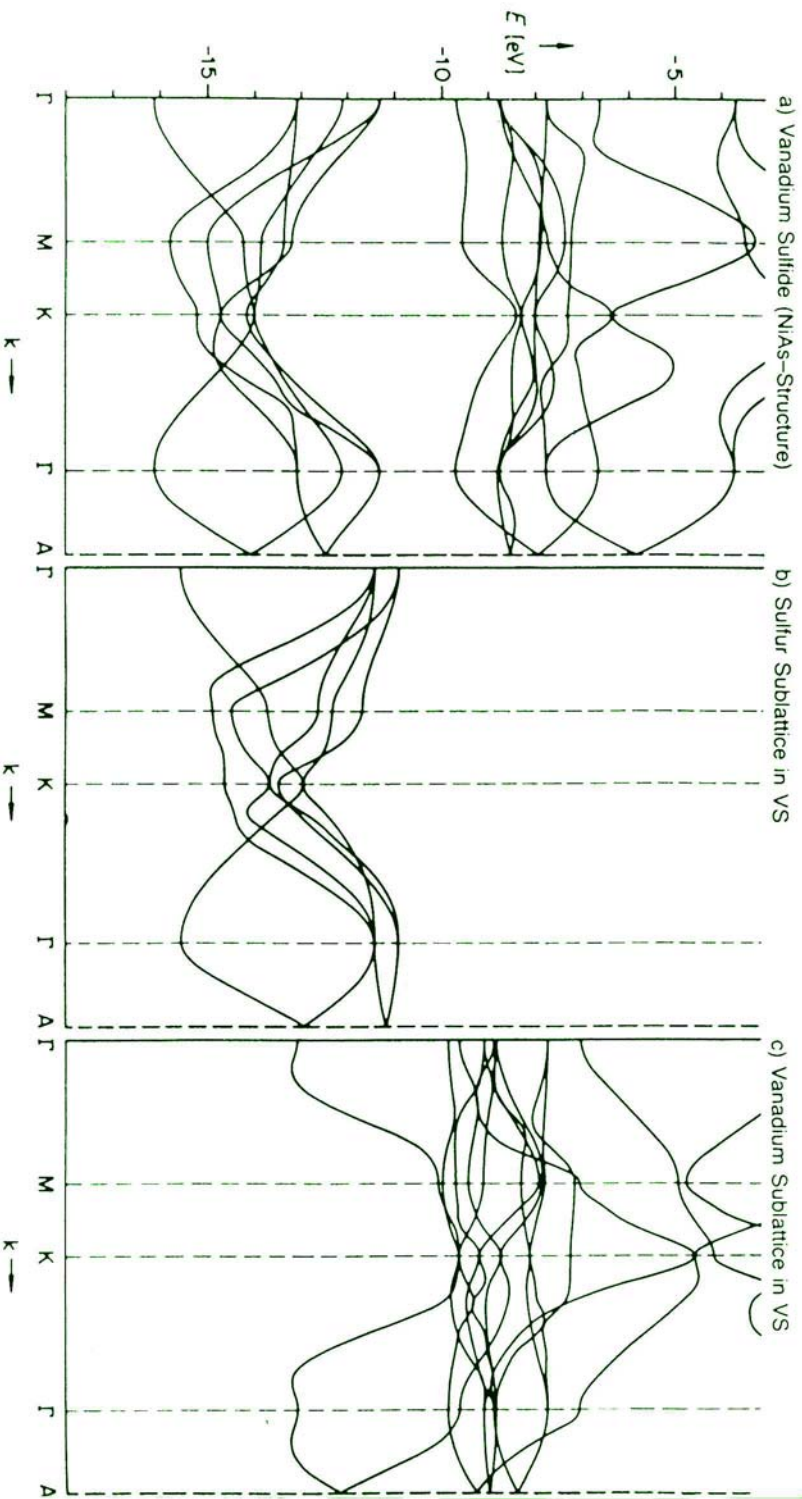
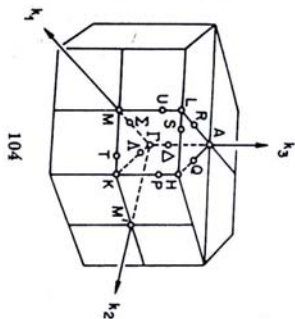


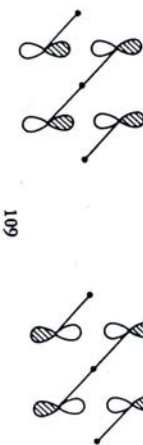
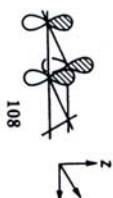
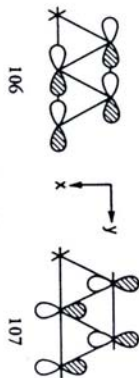
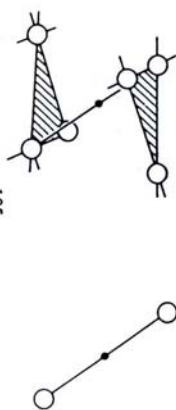
Figure 37 The band structure for VS in the NIAs structure (left), together with the band structures of its S (middle) and V (right) sublattices.

The Brillouin zone, 104, has some special points labeled in it. There are conventions for this labeling.^{9,13} The zone is, of course, three-dimensional. The band structure (Fig. 37) shows the evolution of the levels along several directions in the zone. Count the levels to confirm the presence of six low-lying bands (which a decomposition of the DOS shows to be mainly S 3p) and 10 V 3d bands. The two S 3s bands are below the energy window of the drawing. At some special points in the Brillouin zone there are degeneracies, so one should pick a general point to count bands.



A feeling that this structure is made up of simpler components can be pursued by decomposing it into V and S sublattices. This is what Fig. 37b and c does. Note the relatively narrow V d bands around -8 to -9 eV. There is metal-metal bonding in the V sublattice, as shown by the widths of the V s, p bands. There are also changes in the V d bands on entering the composite VS lattice. A chemist would look for the local $t_{2g}-e_g$ splitting characteristic of vanadium's octahedral environment.

Each of these component band structures could be understood in further detail.⁷⁷ Take the S 3p substructure at Γ . The unit cell contains two S atoms, redrawn in a two-dimensional slice of the lattice in 105 to emphasize the inversion symmetry. Diagrams 106–108 are representative x, y, and z combinations of one S two-dimensional hexagonal layer at Γ . Obviously, x and y are degenerate, and the x, y combination should be above z—the former is locally σ antibonding, the latter π bonding. Now combine two layers. The x, y layer Bloch functions will interact less (π overlap) than the z functions (σ antibonding for the Γ point, 109). These qualitative considerations (x, y above z, the z bands split more than the x, y bands) are clearly visible in the positioning of bands 3–8 in Fig. 37a and b.

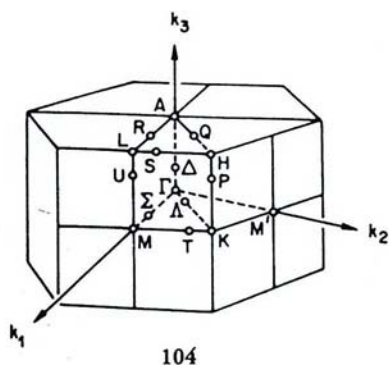


With more, admittedly tedious, work, every aspect of these spaghetti diagrams can be understood. And, much more interestingly, so can the electronic tuning of the NiAs \rightarrow MnP \rightarrow NiP displacive transition.⁷⁵ Now let's return to some simpler matters, concerning surfaces:

QUALITATIVE REASONING ABOUT ORBITAL INTERACTIONS ON SURFACES

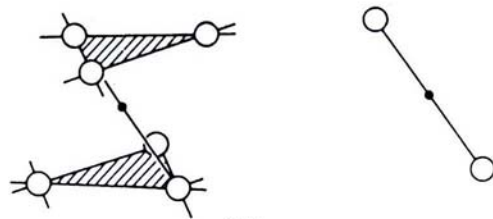
The previous sections have shown that one can work back from band structures and densities of states to local chemical actions—electron transfer and bond formation. It may still seem that the qualitative construction of surface-adsorbate or sublattice-sublattice orbital interaction diagrams in the forward direction is difficult. There are all these orbitals. How to estimate their relative interaction?

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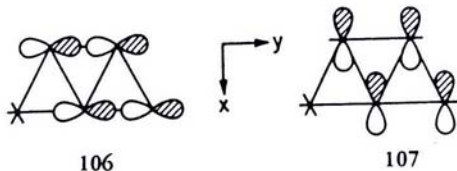


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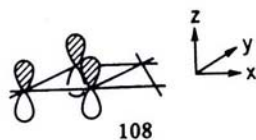


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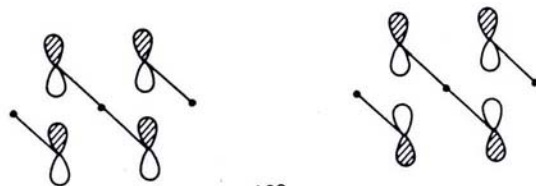


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109

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Symmetry and perturbation theory make such a forward construction relatively simple, as they do for molecules. First, in extended systems the wave vector k is also a symmetry label, classifying different irreducible representations of the translation group. In molecules, only levels belonging to the same irreducible representation interact. Similarly, in the solid only levels of the same k can mix with each other.^{9,15}

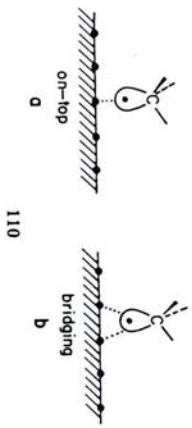
Second, the strength of any interaction is measured by the same expression as for molecules:

$$\Delta E = \frac{|H_{ij}|^2}{E_i^0 - E_j^0}$$

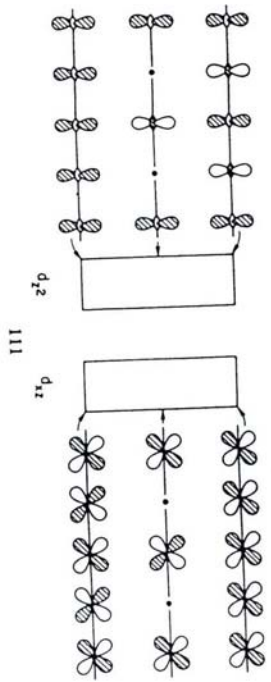
Overlap and separation in energy matter, and can be estimated.^{6,8,11}

There are some complicating consequences of there being a multitude of levels, to be sure. Instead of just saying that "this level does (or does not) interact with another one," we may have to say that "this level interacts more (or less) effectively with such and such part of a band." Let me illustrate this with some examples.

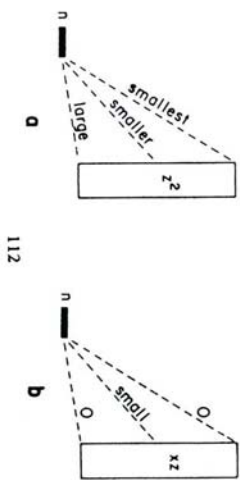
Consider the interaction of methyl, CH_3 , with a surface, in on-top and bridging sites, 110.⁷⁸ Let's assume low coverage. The important methyl orbital is obviously its nonbonding or radical orbital n , a hybrid pointing away from the CH_3 group. It will have the greatest overlap with any surface orbitals. The position of the n orbital in energy is probably just below the bottom of the metal d band. How to analyze the interactions of metal and methyl?



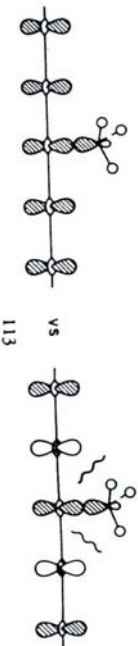
It's useful to take things apart and consider the metal levels one by one. Diagram 111 illustrates schematically some representative orbitals in the z^2 and xz bands. The orbitals at the bottom of a band are metal-metal bonding, those in the middle nonbonding, at the top antibonding. Although things are assuredly more complicated in three dimensions, these one-dimensional pictures are indicative of what transpires.



The methyl radical orbital (it's really a band, but the band is narrow for low coverage) interacts with the entire z^2 and xz bands of the metal, except at a few special symmetry-determined points where the overlap is zero. But it's easy to rank the magnitude of the overlaps, as I've done in 112 for on-top adsorption.



n interacts with the entire z^2 band but, because of the better energy match, more strongly so with the bottom of the band, as 113 shows. For interaction with xz , the overlap is zero at the top and bottom of the band, and never very efficient elsewhere, 114. For adsorption in the bridge, as in 110b, we would estimate the overlaps to go as 115. There is nothing mysterious in these constructions. The use of the perturbation theoretical apparatus and specifically the role of k in delimiting interactions on surfaces goes back to the work of Grimley⁴⁵ and Gadzuk,⁴⁴ and has been consistently stressed by Salem.⁴⁷



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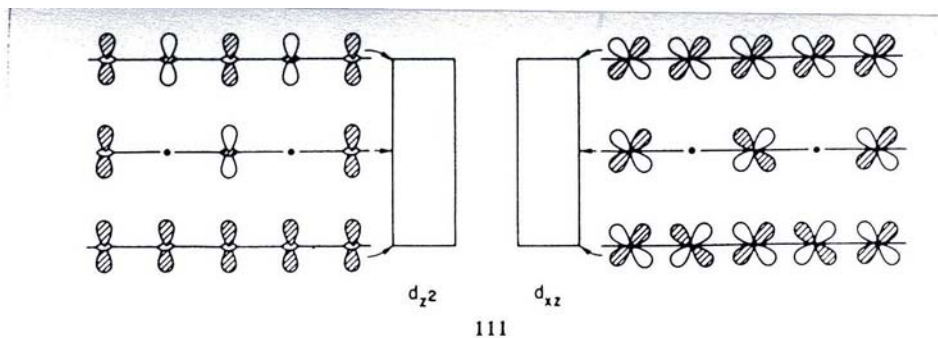
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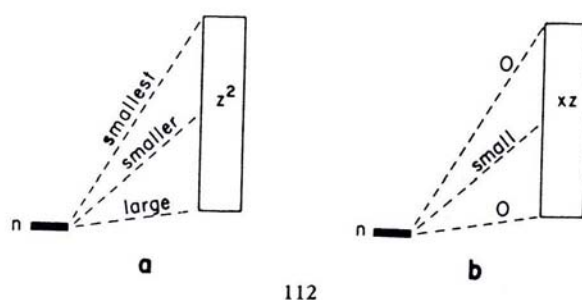


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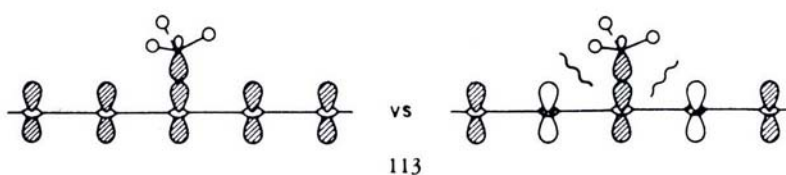
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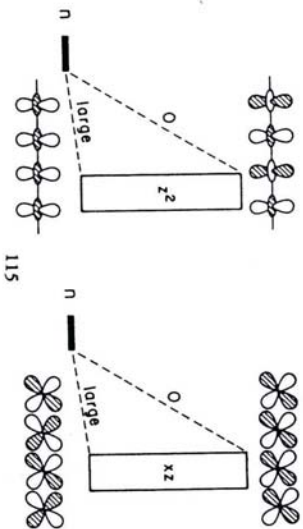
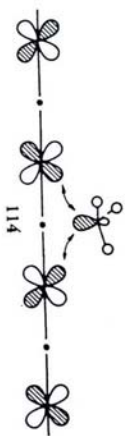


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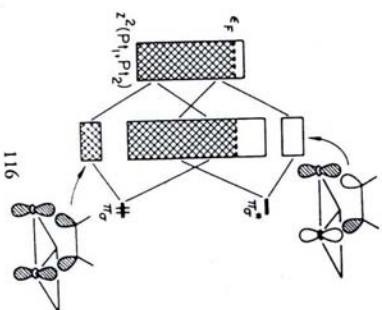


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For a second example, let's return to acetylene on Pt(111), specifically in the twofold and fourfold geometries.²⁹ In the twofold geometry, we saw earlier (from the decomposition of the DOS) that the most important acetylene orbitals were π_o and π_o^* . These point toward the surface. Not surprisingly, their major interaction is with the surface z^2 band. But π_o and π_o^* interact preferentially with different parts of the band, picking out those metal surface orbitals which have nodal patterns similar to those of the adsorbate. Diagram 116 shows this: in the twofold geometry at hand the π_o^* orbital interacts better with the bottom of the surface z^2 band and the π_o orbital with the top of that band.



Note the "restructuring" of the z^2 band that results: in that band some metal-metal bonding levels that were at the bottom of the band are pushed up, while some of the metal-metal antibonding levels are pushed down. Here, very clearly, is part of the reason for weakening of metal-metal bonding on chemisorption.

We pointed out earlier that fourfold site chemisorption was particularly effective in weakening the surface bonding, and transferring electrons into π_o^* as well as π_o , thus also weakening C-C bonding. The interaction responsible was drawn out in 61. Note that it involves the overlap of π_o^* specifically with the top of the xz band. Two formally empty orbitals interact strongly, and their bonding component (which is antibonding within the metal and within the molecule) is occupied.

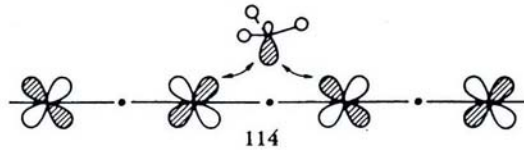
In general, it is possible to carry over frontier orbital arguments, the language of one-electron perturbation theory, to the analysis of surfaces.

THE FERMI LEVEL MATTERS

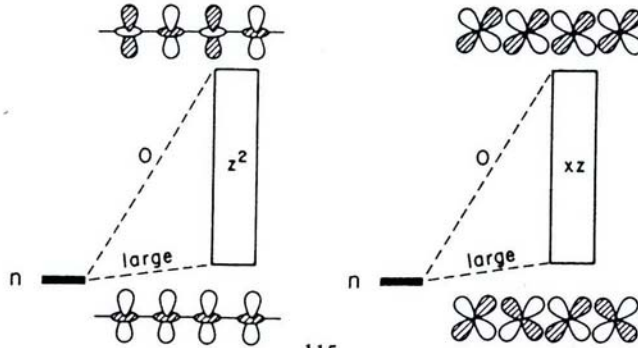
Ultimately one wants to understand the catalytic reactivity of metal surfaces. What we have learned experimentally is that reactivity depends in interesting ways on the metal, on the surface exposed, on the impurities or coadsorbates on that surface, on defects, and on the coverage of the surface. Theory is quite far behind in making sense of these determining factors of surface reactivity, but some pieces of understanding emerge. One such factor is the role of the Fermi level.

The Fermi level in all transition series falls in the d band—if there is a total of x electrons in the $(n)d$ and $(n + 1)s$ levels, then a not-bad approximation to the configuration or effective valence state of any metal is d^{x-s} . The filling of the d band increases as one goes to the right in the transition series. But what about the position of the Fermi level?

What actually happens is shown schematically in 117 (a repeat of 48), perhaps the most important diagram of metal physics. For a detailed discussion of the band structure, the reader is directed to the definitive work of O. K. Andersen.⁴⁰ Roughly, what transpires is that the center of gravity of the d band falls as one moves to the right in the transition series. This is a consequence of the ineffective shielding of the nucleus for one d electron by all the other d electrons. The magnitude of the ionization potential of a single d electron increases to the right. The orbitals also become more contracted, resulting in a less dispersed band as one moves to the right. At the same time, the band filling increases. The position of the band center of gravity and the filling compete, the former wins out. Thus the Fermi level

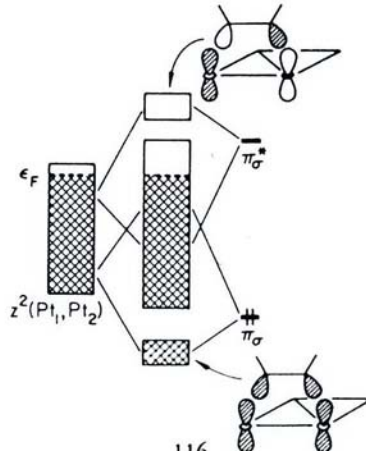


114



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For a second example, let's return to acetylene on Pt(111), specifically in the twofold and fourfold geometries.²⁹ In the twofold geometry, we saw earlier (from the decomposition of the DOS) that the most important acetylene orbitals were π_σ and π_σ^* . These point toward the surface. Not surprisingly, their major interaction is with the surface z^2 band. But π_σ and π_σ^* interact preferentially with different parts of the band, picking out those metal surface orbitals which have nodal patterns similar to those of the adsorbate. Diagram 116 shows this; in the twofold geometry at hand the π_σ orbital interacts better with the bottom of the surface z^2 band and the π_σ^* with the top of that band.



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Note the "restructuring" of the z^2 band that results: in that band some metal-metal bonding levels that were at the bottom of the band are pushed up, while some of the metal-metal antibonding levels are pushed down. Here, very clearly, is part of the reason for weakening of metal-metal bonding on chemisorption.

We pointed out earlier that fourfold site chemisorption was particularly effective in weakening the surface bonding, and transferring electrons into π^* as well as π_σ^* , thus also weakening C-C bonding. The interaction responsible was drawn out in 61. Note that it involves the overlap of π^* specifically with the top of the xz band. Two formally empty orbitals interact strongly, and their bonding component (which is antibonding within the metal and within the molecule) is occupied.

In general, it is possible to carry over frontier orbital arguments, the language of one-electron perturbation theory, to the analysis of surfaces.